The Development of An Integrated Multistaged Fluid-Bed Retorting Process

**Final Report
September 1990 - August 1994**

S.D. Carter
D.N. Taulbee
J.L. Stehn
A. Vego
T.L. Robl

February 1995

Work Performed Under Contract No.: DE-FC21-90MC27286

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Kentucky
Lexington, Kentucky

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ACKNOWLEDGMENTS

The work described herein was performed at the University of Kentucky Center for Applied Energy Research (CAER) under Cooperative Agreement DE-FC21-90MC27286 with the Laramie Project Office of the Morgantown Energy Technology Center (METC), U.S. Department of Energy. Such funding does not constitute an endorsement by DOE of the views expressed in this document.

The authors gratefully acknowledge the work of numerous persons at the CAER who participated in this work. J. Hower and T. Salter characterized the mining site geology and coordinated the raw shale mining and preparation efforts. U. Graham did the SEM/EDX analyses of the oil shale clinkers. The authors thank B. Farmer and A. Howard for machining work, G. Morgan, D. Smith, and M. Scarbowski for operating and engineering support, G. Thomas, M. Grider, B. Schram, M. Stewart, and B. Rathbone for sample analysis, D. McLean, and M. Yewell for raw shale acquisition and preparation, B. Adkins for data acquisition programming, O. Vanlandingham, J. Herrington, D. Lanter for facility modifications, and G. Tremoulet for clerical assistance.

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1. EXECUTIVE SUMMARY

1.1 ABSTRACT

This report summarizes the development of an integrated multistage fluidized bed retorting process (KENTORT II) during the period of September 28, 1990 through September 30, 1994 under Cooperative Agreement No. DE-FC21-90MC27286 with the Morgantown Energy Technology Center, U.S. Department of Energy. The KENTORT II process includes integral fluidized bed zones for pyrolysis, gasification, and combustion of the oil shale. The purpose of this program was to design and test the KENTORT II process at the 50-lb/hr scale. The program included bench-scale studies of coking and cracking reactions of shale oil vapors over processed shale particles to address the issues of scale up associated with solid-recycle retorting. The most significant finding from the bench-scale studies was that higher amounts of carbon coverage were found to reduce the rate of subsequent carbon deposition by shale oil vapors onto processed shale particles. However, carbon-covered materials were also found to be active in terms of cracking and coking.

The main focus of the program was the design, construction, and operation of the 50-lb/hr KENTORT II PDU. Extensive cold-flow modeling and shakedown procedures were performed before the PDU was made ready for operation. Seven mass-balanced, steady-state runs were completed which were within the window of design operating conditions. All goals for the system were achieved in terms of shale feedrate (50 lb/hr), run duration (10 hours), shale recirculation rates (4:1 to pyrolyzer and 10:1 to combustor), bed temperatures (pyrolyzer: 530°C, gasifier: 750°C, and combustor: 830°C), and general operating stability. The highest oil yields (up to 109% of Fischer assay) were achieved for those runs which lasted for approximately 10 hours or more. The relatively high carbon content of the solids used for heat transfer to the pyrolysis zone was determined to contribute to the enhanced oil yield that was achieved at this scale of operation. The prospects for maintaining enhanced oil yield following further scale up of this technology were determined to be favorable because of the buffering capacity of the gasification zone. A major recommendation from the study was that the lower value products such as heavy oil or gas be used to coke the recycled shale to selectively improve the product slate, while maintaining or even increasing the oil yield.

1.2 INTRODUCTION AND BACKGROUND

It is now well accepted that fluidized bed pyrolysis of oil shale at near-zero hydrogen partial pressure will generate higher than Fischer assay oil yields. The amount of enhancement varies according to shale type, but for most shales, it can be significant. It has been shown that fluidized bed pyrolysis of eastern and western U.S. oil shales can enhance oil yields by 50%^{1,2,3,4,5} and 10%^{6,7} above Fischer assay, respectively. In addition, fluidized bed technology offers the advantages of rapid pyrolysis kinetics, total use of mined shale, and thermal efficiency. The Center for Applied Energy Research (CAER) has developed a commercial retorting concept, KENTORT II, which is based on fluidized bed technology. This process has been successfully demonstrated in a 3-inch diameter, 5-lb/hr system at the CAER using eastern U.S. oil shale.⁸ The objective of the current program is to scale the KENTORT II process to a 6-inch diameter, 50-lb/hr reactor.

Approximately 40% of the original carbon remains in the spent shale following fluidized bed pyrolysis of Eastern shale. This is more carbon than is required to provide process heat, so an intermediate gasification stage was included in the KENTORT II design to convert this excess carbon to synthesis gas. The gasification section is also important because it permits steam/iron sulfide reactions to go nearly to completion. These reactions remove the majority of the sulfur from the shale as H_2S in the case of eastern shale because approximately 90% of its sulfur is present as iron sulfides. The removal of sulfur from the shale as H_2S prior to combustion creates a relatively concentrated stream of H_2S which is easier to scrub than a dilute stream of SO_2 from combustion. The H_2S serves as feedstock for elemental sulfur production which improves process economics because of the by-product credit. For shales which do not contain large amounts of residual carbon and/or iron sulfides following pyrolysis, the gasification step is not plausible.

Following gasification, the carbon remaining in the shale is combusted to provide process heat. The heat of combustion is transferred to the gasification and pyrolysis zones via recirculation of the processed shale because sufficient heat cannot be transferred using gases alone. Following combustion, essentially all of the carbon and sulfur in the shale have been removed. This has important environmental implications because the potential for acid drainage by the disposed spent shale is significantly reduced when the sulfur content is low.^{9,10}

Operation of the KENTORT II process was shown to be viable at the 5-lb/hr scale during the previous cooperative agreement, and questions relative to scale-up then became the focus for subsequent research. The most critical issue to be addressed was the effect of scale-up on oil yield and the overall product composition. The work performed under the current cooperative agreement dealt almost exclusively with scale-up issues. While the construction and operation of the 50-lb/hr PDU was the focal point of this work, substantial efforts were also devoted to the investigation of the chemistry involved with shale-induced coking and cracking reactions. By more fully understanding the coking and cracking reactions, the interpretation of the PDU results was facilitated and future scale-up made less uncertain.

1.3 OBJECTIVES AND APPROACH

The primary objective of this program was to perform the research necessary to design, construct, test, and optimize the KENTORT II process at the 50-lb/hr scale. The tasks for the program are listed below:

Task 1 - Design and Construction of the KENTORT II PDU

- 1.1 - Cold-Flow Modeling of the PDU
- 1.2 - Bench-Scale Coking and Cracking Chemistry Studies Related to Solid-Recycle Retorting
- 1.3 - Final Design and Construction of the KENTORT II PDU

Task 2 - Operation of the KENTORT II PDU

- 2.1 - PDU Shakedown
- 2.2 - PDU Test Matrix

Task 3 - Shale Acquisition and Product/By-Product Characterization

- 3.1 - Collection and Characterization of the Oil Shale Feedstock
- 3.2 - Characterization of the KENTORT II Products
- 3.3 - Economic Evaluation

The development and operation of the PDU proceeded concurrently with the bench-scale coking and cracking studies. The bench-scale studies were intended to provide information for the design and operating parameters of the PDU, but the results were more useful in interpreting the results from the PDU because nothing was discovered during the bench-scale work that changed the rationale about the initial design of the PDU. This report is basically organized according to the task list above. A separate chapter represents each of the subtasks with the exception that subtasks 1.1 and 1.3 are described in a single chapter entitled "KENTORT II PDU Development and Design" and Task 2 is represented by a single chapter entitled "KENTORT II PDU Test Results."

1.4 RESULTS

1.4.1 Oil Shale Mining. Oil shale from the Cleveland Member of the Ohio Shale was selected for use in the KENTORT II study based upon the judgment that it represented one of the shale types in the eastern U.S. that has the highest probability for initial commercial development. Mining of the shale was conducted in Montgomery County, Kentucky. Because there are no open oil shale mines in the area, a road-construction contractor was selected to prepare a mine site, do the excavation, perform the mining, and reclaim the site. The contractor also crushed the shale to 8 x 0 mesh at its facility and delivered 85 55-gal barrels of oil shale to the CAER. The shale was further screened at the CAER as required for the various tests in the cold-flow model and the 50-lb/hr KENTORT II PDU. The average carbon, hydrogen, nitrogen, and sulfur content of the shale was 11.7, 1.2, 0.8, and 1.9 wt%, respectively. The master shale sample used for the bench-scale studies was from the previous cooperative agreement because the shale for the PDU was not prepared in time for those studies.

1.4.2 Bench-Scale Coking and Cracking Studies. Solids-induced coking and cracking reactions of shale oil vapors are significant in the KENTORT II process because hot processed shale is mixed with raw shale to provide the heat for pyrolysis. Studies were conducted in three different experimental systems aimed at obtaining information concerning the effects of processed shales on coking and cracking reactions. Master batches of pyrolyzed, partially gasified, and combusted shales were prepared for use as coking/cracking substrates in all parts of the studies. In the first system, coking kinetics and cracking chemistry studies were conducted in a fluidized bed apparatus in which nascent shale oil vapors were generated and subsequently contacted with the various coking/cracking substrates. In the second system, model compound studies in a fixed bed apparatus were conducted to determine how the major hydrocarbon types were affected by contact with the coking/cracking substrates. In the third system, studies were conducted in a two-stage fixed-bed reactor to investigate the effects of high pressure (nitrogen and hydrogen) on coking and cracking reactions.

1a) Fluidized Bed Studies-Coking Kinetics. This phase of the fluidized bed work was dedicated to measuring the coking kinetics of nascent shale oil vapors in contact with the coking substrates (processed shales and other related shale minerals). A unique apparatus was developed which allowed the deposition of carbon on the solids to be monitored in real time. This study showed that carbon deposition was rapid over bare mineral surfaces, but that the rate slowed down significantly when the particle surfaces became covered with carbonaceous material. The coking reactions were determined to adhere well to first-order kinetics and the rapid period of carbon deposition was almost completely insensitive to temperature in the range of 530 to 600°C. No real catalytic activity was observed for the processed shales and related shale minerals that were studied. Pore diffusion limitations were not found to be significant for the particle sizes studied. The relative coke forming tendency for the processed shales (descending coke-forming tendency) were ranked in order of ascending carbon content:

combusted > gasified > pyrolyzed shale. Among low-carbon substrates that were tested, the materials with the highest surface area (as measure by Hg porosimetry) also had the highest coking activity.

1b) Fluidized Bed Studies-Cracking Chemistry. The second phase of the fluidized bed study was designed to identify the volatile products of vapor-solid contact. Only products characteristic of free radical reactions (i.e. 1-n-alkenes and high percentage of CH₄ and C₂'s) were observed as a result of pyrolysis and secondary contact with solids. The vapor-phase residence time of the shale oil vapors resulted in a change of the hydrocarbon gas composition suggesting more extensive cracking. Vapor-solid contact was responsible for increased gas production, but it did not change the composition of the gases which suggests that the coking/cracking substrates did not change the reaction mechanism. Like the coking kinetics study, the combusted shale converted more oil vapors to gaseous and solid products than the gasified or pyrolyzed shales. The conclusion from both phases of the fluidized bed study was that shale oil contact with the processed shales promoted the extent of coking and cracking reactions (in proportion to the non-carbon-covered surface area), but the reactions were not catalytic in nature and resembled free-radical thermal cracking reactions.

2) Fixed-Bed Hydrocarbon Cracking Study. A novel means of measuring the adsorption and cracking of hydrocarbons over solid particles at short vapor-phase residence times (0.2-0.5 s) was developed. Compared to the aforementioned fluidized bed studies, the activity of the processed shales was found to be different in this study for the model hydrocarbon compounds that were studied (n-hexane, ethylbenzene, 1-decene, 1-hexene, cyclohexane, cyclohexene, butylbenzene, n-heptane, benzene, toluene, and n-decane). The general order of cracking and adsorptive activity was: gasified > pyrolyzed > combusted shale. It is believed that the lighter hydrocarbons examined in this study tended to interact more strongly with surface carbon in the pyrolyzed and gasified shales. This resulted in a longer retention time and more extensive reactions. In the fluidized bed coking study, however, there was a great affinity for the large, high-boiling, aromatic oil vapors to be irreversibly adsorbed onto the bare shale surfaces. The reactions of hydrocarbons over substantially carbon-covered surfaces in both studies were consistent with free radical reactions. The cracking rates for the hydrocarbons were ordered as follows: cyclic olefins > cyclic aliphatics > α -olefins > n-alkanes. Aromatics were found to be resistant to cracking except for alkyl chains attached to the ring.

3) High-Pressure Coking and Cracking Study in a High-Pressure, Fixed-Bed Reactor. A two-stage fixed-bed reactor capable of operating at pressures up to 15 MPa was used for this test series. In addition to providing more information concerning the effects of oil vapor partial pressure on the coking mechanisms of shale oil vapors, the study was also applicable to elucidating the coking reactions that may be expected during the catalytic hydrotreating of shale oils. The effect of combusted oil shale in the second stage was to significantly lower the molecular weight and increase the

aromaticity of the shale oil under both thermal pyrolysis and hydrolypyrolysis conditions. High pressure hydrogen (15 MPa) essentially eliminated carbon deposition on the combusted shale, which suggests that a free radical mechanism is important for coking unto combusted shale. A significant amount of carbon was deposited on the hydrotreating catalyst under both thermal pyrolysis and hydrolypyrolysis conditions, illustrating a significant difference between the surface activities of the combusted shale and the hydrotreating catalyst.

1.4.3 KENTORT II PDU Development and Design. Cold-flow studies in a clear-plastic, scale model of the PDU were conducted to ensure that the PDU would operate stably and that the required solid recirculation rates would be achieved. Three particle size ranges were tested in the cold-flow model (20x60, 8x20, and 8x60 mesh). The 20x60 mesh range exhibited the smoothest fluidization qualities. Some trial-and-error adjustments to the diplegs for the incoming solids to the gasification zone were required, but otherwise, there were no major modifications necessary. Once the needed changes were made, the required solid-recycle rates to the pyrolyzer (4:1) and the combustor (10:1) were met with comfortable margins, and all aspects of the cold-flow system worked flawlessly.

The material selected for the PDU was 316H SS because of its good high temperature properties. To prevent sulfide corrosion in the gasification and combustion zones, the reactor was aluminized inside and outside. This type of treatment was found to work well for the high-temperature zones of the 3-inch diameter KENTORT II system. The main reactor sections consisted of 6-inch Schedule 40 pipe joined by 150-lb ANSI flanges which were sealed with spring-energized Inconel C-rings. The gasification section was made of 8-inch pipe to compensate for the higher gas velocity due to the higher temperature. Perforated plates sandwiched between the flanges served as gas distributors for the fluidized beds. The entire retort was covered with 6 inches of alumina-silicate insulation. Electrical heat-tapes beneath the insulation were used to compensate for heat losses from the pyrolysis and cooling zones. The main sources of start-up heat for the reactor were a propane gas burner located upstream of the combustor plenum chamber and an electric tube furnace which preheated the fluidizing gas for the cooling, gasification, and pyrolysis zones. The oil collection system consisted of an insulated cyclone to remove fine solids, an air-cooled heat exchanger, a two-stage electrostatic precipitator (ESP) to collect oil, a water-cooled condenser for steam and oil vapor, and mist coalescers at the end.

The feed hopper was designed to hold approximately 300 lb of shale and a screwfeeder was designed to supply shale at a rate of 50 lb/hr to the pyrolysis zone. Shale could be added to the hopper during a run so that the run duration was not limited by the hopper capacity. The spent shale receiver had a capacity of approximately 500lb, but it was not possible to safely extract hot processed shale during operation. Thus, the practical operating duration of the reactor was limited to 500 lb.

1.4.4 KENTORT II PDU Test Results. A fairly extensive shakedown period was required to make the PDU completely operational. Most of the problems were associated

with heat losses. Low temperature in the gasification section was found to be a problem during the initial hot-flow tests, so efforts were made to further increase the temperature of the system by raising the temperature of the combustor. To do so, more heat input by the propane burner was applied, but this eventually caused the plenum-chamber materials to fail. Subsequently, the orientation of the burner was changed so that the flame did not impinge directly on a metal surface and the interior of the plenum chamber was lined with a ceramic casting to protect it from the high temperatures. This redesign was successful in raising the temperature range of the combustor, but it also made it possible to sinter the alumina-silicates in the shale minerals if the plenum temperature were allowed to go too high. Having found a safe operating temperature for the combustor plenum, the gasification temperature could then be gradually raised to an acceptable level during the preheating period. Once the heat-up procedure was established, the test matrix for the PDU was initiated.

Seven mass-balanced, steady-state runs were performed which ranged in duration from 3.25 to 10.25 hours. The reason for premature run termination in nearly all cases was the operation of the ESP. Short-circuiting of the charge on the plates by condensed steam and by the build up of fines-laden heavy oil caused failure of the ESP in many cases. Improved heat tracing and a baffle arrangement at the inlet of the ESP reduced these problems so that its operating capacity was effectively lengthened to match that of the spent shale collection bin (10 hours).

The gasification temperatures that were attained during the test series were at the lower end of the targeted temperature range (ca. 750°C) due to heat losses from the system. Therefore, it was not possible to adjust the gasification and combustion temperatures so that a range of solid-recycle rates among the zones could be tested. As a result, the runs during the test series had substantially the same operating conditions. The temperatures averaged 527°C in the pyrolyzer, 741°C in the gasifier, and 821°C in the combustor. The average shale feedrate was 51 lb/hr, and the average run duration was 7.1 hours. In order to generate and distribute the maximum amount of heat for the system, the maximum solid-recycle rates of 4:1 and 10:1 to the pyrolysis and combustion zones, respectively, were utilized.

Run duration was identified as the most influential parameter affecting oil yield because of the time required to displace the shale in the reactor at the start of each run. During the preheating period, recirculating shale was utilized to transfer heat to the rest of the system. This recirculating shale had become essentially devoid of carbon prior to the start of each run because the shale had made multiple passes through the combustor. As indicated from the coking kinetics study, coking proceeds quickly onto solid particles that are not carbon covered. Carbon deposition onto the recirculating shale in the pyrolyzer was rapid until the inventory of carbon in the retort gradually increased. The highest oil yields (up to 109% of Fischer assay) were attained for the runs with the longest run duration.

Compared to the 3-inch diameter KENTORT II system,⁸ the higher solid-recycle ratio to the combustion zone of the PDU (10:1) resulted in much greater combustion of the residual carbon in the shale. Autothermal operation of the PDU was nearly achieved even though

thermal losses were rather large. The propane burner was only used to preheat the fluidizing air to combustion temperature once raw shale was being fed to the retort. Therefore, the carbon in the shale was supplying all of the heat for the system with the exception of the preheated fluidizing gases. In a commercial system the fluidizing gases would be largely preheated by recovering the heat from the hot gases leaving the retort. Organic carbon utilization ranged from 90.5 to 93 %, but if the carbon on the fines recovered in the pyrolysis cyclone had been used as fuel to generate additional heat in the combustor, the carbon utilization would have been 95 to 96.5%. Overall sulfur removal from the shale ranged from 43 to 68%, and H_2S was the primary sulfur-bearing specie generated. The production of SO_2 was higher than in the 3-inch diameter KENTORT system,⁸ but the level was still much lower than H_2S , and the ratio of the yields (approx. 2:1) was appropriate for the direct application of the Claus reaction for elemental sulfur production.

1.4.5 Product Characterization. Complete analyses of the oil, water, and gas produced from each of the steady-state runs were performed. The separate oil fractions that were collected as a result of the stepwise trapping of oil were analyzed individually and were proportionally combined into composite samples for more extensive testing, including physical tests. Because the run conditions were not substantially varied from run to run and the oil properties did not change significantly, no attempt was made to correlate run conditions with oil properties. The average composite oil properties were as follows: H/C ratio 1.35, N 0.9 wt%, S 2.7 wt%, ash 12 wt%, water 2.9 wt%, heating value 15200 Btu/lb, density 1.068 g/mL, pour point -27°F, viscosity 222 cP@25°C and 99 cP@40°C, Conradson carbon 21%, aromatic carbon 44%, avg. mol. wt. 303 amu, As 48 ppm, V 16 ppm, Fe 340 ppm, and Ni 56 ppm. In general, the oil properties from the PDU were not substantially different from the oil produced by the 3-inch diameter bench-scale KENTORT II system.⁸ However, the PDU oils were somewhat lower in viscosity, pour point, and average molecular weight and higher in aromatic content which suggests that cracking reactions were more prevalent in the PDU as would be expected. It should be noted that the differences in the shales used in the two studies could have influenced the oil properties also.

The condensed water from the PDU had an average pH of 3.2 compared to the basic pH (8.5) found for the 3-inch diameter system. In addition, the content of dissolved and suspended solids from the PDU was higher than for the 3-inch system. Both of these results have been attributed to greater disruption of the mineral matrix, caused by more extensive combustion, resulting in greater particle attrition and greater removal of inorganics in the vapor phase. The trace metals content for the water from the PDU was equal to or slightly greater than that of the 3-inch system, and no particularly high concentrations were observed.

Due to the stacked design of the KENTORT II system, the gases produced in the gasification and pyrolysis zones were combined into one stream. An average of 10.1% of the carbon in the raw shale was measured as gases from these zones. On a N_2 - O_2 -free basis, this gas stream contained an average of 25.65 vol% hydrocarbons, 32.0 vol% H_2 , 10.3 vol% CO , 16.0 vol% CO_2 , and 16.0 vol% H_2S . Of the hydrocarbons, methane and ethane were the most

predominant. Larger n-alkanes and 1-alkenes were also prevalent, and the gas composition was comparable with previous retorting results with this type of shale.

Samples of ESP oil from the 3-inch diameter system and composite oils from the PDU were evaluated for their potential use as an asphalt cement or modifier. A preliminary analysis of samples from the 3-inch unit was performed first. The screening studies showed that the most promising applications for the ESP oil were as an asphalt modifier or an asphalt-recycling agent. The results also showed that aging or hardening was an area of concern for this material. In an effort to resolve this problem, a 4.3-kg sample of composite oil from run# KT940518 of the PDU was thermally treated in an inert atmosphere to accelerate the aging process. The sample appeared to be reasonably stable following this treatment. The sample was then sent to the Western Research Institute (WRI) for evaluation as an asphalt modifier and rejuvenating agent. This work was not complete at the time of this writing, but a subsequent report from WRI is expected. While no conclusions concerning the applicability of KENTORT II oil for asphalt applications can be made at this time, the fact that the oil can be stabilized is encouraging.

1.4.6 Economic Evaluation. The development of any synthetic fuel industry is not currently feasible because of the low-priced and plentiful reserves of petroleum around the world. Rather than evaluate the economics of the KENTORT II process on the basis of a 50,000 bbl/day commercial plant to produce primarily transportation fuels, scenarios were studied where specialty products from a small-scale KENTORT II plant (7,500 ton/day) could make a foothold in a market or markets so that an oil shale industry could be developed in the short term. For reference, Foster Wheeler performed the economics for a grass-roots 50,000-bbl/day retort for eastern U.S. oil shale using fluidized bed technology and selling sulfuric acid and electrical power as by-products.¹¹ The cost of the syncrude was found to be \$35/bbl which was lower than any other processing scenario that they studied for eastern or western U.S. oil shales or for coal liquefaction. The important factor in this analysis was the large by-product credit for electricity and sulfuric acid.

In the current study, both established and potential markets for trace elements, sulfur, cement, asphalt, bricks, fixed gases, specialty fibers, adsorbent carbons, chemicals, and chemical feedstocks were examined. Though a more detailed evaluation would be needed, there appears to be a significant potential to improve retorting economics by the sale of one or more of the following by-products: Al, Fe, K, Co, Cr, Ni, V, H₂, BTX, alpha olefins, asphalt modifiers, specialty carbon fibers, chemicals (components containing N, S, and O), adsorbent carbons, and cement. The latter three appear to have the most potential to impact commercial development. Market size is an important consideration for many of these value-added products because even a small-scale commercial retort has the potential to saturate regional markets and drive prices down considerably.

1.5 CONCLUSIONS AND RECOMMENDATIONS

The scale up of the KENTORT II technology to a 50-lb/hr, 6-inch diameter PDU was successfully completed. In general, there were no detrimental effects as a result of the scale up. Carbon utilization of up to 96.5% was shown to be feasible if the carbon-rich fines from the pyrolysis cyclone were reinjected to the system to be combusted. The operation of the retort was shown to be stable throughout the test matrix, and premature termination of runs was always due to malfunction of ancillary equipment. On average, a small decrease in oil yield compared to the 3-inch diameter KENTORT II system was observed, but the highest oil yield from the PDU was still as high as 109% of Fischer assay. Such high yields are excellent for a solid-recycle retort of this size. This enhanced oil yield is due to the presence of the gasification stage in the KENTORT II system. The gasification zone consists of solids that have been processed in the system to various extents which results in a relatively high carbon content of the solids due to mixing. Less coking occurs in the pyrolyzer because of the elevated carbon content of these heat-carrying solids. In retorts that recirculate solids directly to the pyrolyzer from the combustor, the recycle solids have higher coking activity because the average carbon content is relatively low. Therefore, the potential to maintain enhanced oil yield in further scale up of the KENTORT II appears promising.

Further development of the KENTORT II and other oil shale processes is highly recommended because of the tremendous oil shale resources that are available in the U.S. In particular, the following recommendations for furthering the development of the KENTORT II and other solid-recycle retorts are made:

- o All oil shale processes generate some liquid products that are of relatively low commercial value. By coking these materials onto the recycle solids, the coking potential of the solids is greatly reduced and the coking then becomes selective rather than general. This approach will not necessarily increase oil yield, but it will allow the selective improvement of the product suite. It is suggested that coke formation studies of heavy oils and gases onto processed shales be a major focus of subsequent study. If gases are used for coking, however, the oil yield would increase.
- o The study of value-added products from oil shale should be continued. In almost all cases, commercially successful oil shale ventures have sold by-products in addition to shale oil as a liquid fuel. Applications in asphalt paving and specialty carbon fibers continue to look encouraging.
- o Collection of oil, especially heavy oil, is not a trivial problem. Optimization of the operation and design of electrostatic precipitators (ESP) for oil collection should be emphasized during subsequent process development efforts.

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2. MINING AND CHARACTERIZATION OF OIL SHALE SAMPLE

Oil shale from the Cleveland Member of the Ohio Shale was selected for use in the KENTORT II study based upon the judgment that it represented one of the shale types in the eastern U.S. that has the highest probability for initial commercial development. Mining of the shale was conducted in Montgomery County, Kentucky, during this quarter. The contractor cleared the hillside and, in the course of site preparation, removed about 5 tons of the Mississippian Sunbury Shale and 5 tons of the Cleveland Shale, placed the shale in bags, and transported the bags to the CAER. Site preparation continued with the development of a 30 x 30 foot bench on the top of the Cleveland. Thirty-two eight-foot holes on approximately four-foot centers were drilled, loaded, and detonated. An estimated 100 tons of shale was loosened by the blast. The shale was excavated and transported to the contractor's crushing facility where it was crushed, double-screened, and loaded into 85 55-gal barrels. The barrels, containing a total of 25-30 tons of shale, were then transported to the CAER.

The sample was reduced in size using a crushing train at a limestone quarry, and a small amount of contamination was present, as expected. The limestone pieces were large and were easily screened out. The sample was mined and prepared during a period of extremely wet weather, so it was dried before further processing.

The target size range for the samples was 8 x 0 mesh, with as much near 8 mesh materials as possible. The particle size distribution of an air-dried aliquot was classified by screening (Figure 2-1, Table 1-1). In general, the shale was found to be close to the targeted size distribution. There was, however, a significant percentage of oversize material which was in the 4 x 8 mesh (~2.4 x 4.8 mm) size range. This is likely due to differences in the crushing behavior of the shale compared to the limestone.

One particular concern in preparing the sample was excessive fines generation, especially in the very fine size range (i.e. -60 mesh or -0.25 mm). This component of the shale was only 11% of the total, which, based upon previous research, is well within acceptable limits.¹

Each size fraction was analyzed for total carbon, hydrogen and nitrogen which averaged 11.7%, 1.2% and 0.8%, respectively. This compares very well with the total carbon for the defined resource zone from Montgomery County where cores D-5 and D-6 averaged 11.5% and 12.0%, respectively.² There may be a slight trend toward lower carbon values with decreasing size (Table 2-1). However, the standard deviation for the carbon was 0.4 or

Figure 2-1. Cumulative size distribution of KENTORT II run of mine feedstock.

Table 2-1. KENTORT II feedstock, run of mine, air-dried. Elemental data is in weight percent (as-received basis).

	Size in mm		Weight%	C	H	N	S	Ash
	Plus	Minus						
+1/4	6.35							
1/4x4	4.75	6.35	3.0%	12.6	1.4	0.8	2.0	80.9
4x8	2.36	4.75	37.3%	11.7	1.2	0.8	2.0	81.7
8x12	1.70	2.36	14.0%	11.5	1.2	0.8	2.1	81.7
12x16	1.18	1.70	11.3%	11.8	1.2	0.8	2.0	81.8
16x18	1.00	1.18	5.5%	11.8	1.2	0.8	2.1	80.6
18x20	0.85	1.00	2.3%	11.7	1.2	0.7	2.1	81.0
20x30	0.60	0.85	5.5%	11.4	1.1	0.7	1.6	82.6
30x60	0.25	0.60	9.9%	11.3	1.1	0.8	1.8	82.8
60x100	0.15	0.25	3.1%	11.3	1.1	0.8	1.8	82.1
-100		0.15	8.0%	11.3	1.3	0.7	1.8	81.8

approximately 3% of the mean. This is comparable to an analytic uncertainty of approximately 2% for this determination. Thus any variation in carbon with particle size may not be of significance.

The sample was air dried and screened of the +8 mesh and -60 mesh material. The fine fraction was stored separately and was available for blending with the 8x60 mesh materials (2.4 x 0.25 mm). This approach allowed fines content of the feedstock to be treated as a variable in the experimental design of the runs.

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3. BENCH-SCALE CRACKING AND COKING STUDIES

3.1 APPROACH

In oil shale processes where the pyrolysis zone is heated by recirculating solids, adsorption of oil vapor and subsequent coking and cracking onto these solids can lead to significant oil yield reduction. It has been shown that the type of solid heat carrier can have a large effect on the magnitude of oil loss.^{1,2,3,4} The focus of interest for this study has been the coking and cracking tendencies of materials used for heat transfer in the KENTORT II process. Since shale is recirculated among pyrolysis, gasification, and combustion zones to transfer heat in the KENTORT II process, the solids that are recycled to the pyrolysis zone from the gasification zone are composed of a mixture of shale particles which have been gasified and combusted to various degrees. By determining the coking kinetics of these materials and their deactivation with time, oil coking can be predicted as a function of solid recycle rate and temperature. In doing so, operating regimes may be identified which limit oil loss, or conversely, coking and cracking conditions may be chosen which improve oil quality by selective removal of undesirable components.

Three different techniques were utilized to further the understanding of the chemistry and kinetics associated with solids-recycle retorting. One was a fixed bed reactor system to study the coking and cracking characteristics of model compounds (section 3.2). A fixed bed apparatus was necessary because the conversion of model compounds was too low in the fluidized bed apparatus that is described. This work permitted the study of cracking products in real time. The work described in this section (3.2) was part of a Ph.D. dissertation by Taulbee.⁵

Another system that was used was a dual fluidized bed reactor in which one of the beds of solids was contacted with shale oil vapors that were produced simultaneously in the other bed, a pyrolyzer (section 3.3). This technique allowed a wide range of solid-recycle ratios to be simulated and permitted the accurate control of the exposure time and temperature of the solids. Gasified and combusted shales were the primary substrates of interest, but other materials such as naturally occurring minerals were also tested. The reactor had two modes of operation. One was a kinetic mode in which the rate of carbon deposition was determined under a range of temperatures and space velocities. The other mode of operation was designed to characterize the products of cracking, both liquid and gaseous, under simulated solid-recycle conditions (section 3.4). These two modes of operation in the fluidized bed reactor will be referred to as coking kinetics and cracking chemistry studies.

The third portion of the cracking and coking studies utilized a two-stage hydropyrolysis reactor at the University of Strathclyde, Glasgow, Scotland (section 3.5). This reactor enabled the examination of secondary reactions under high pressure conditions (up to 15 MPa) which were unattainable in existing equipment at the CAER. By examining coking and cracking under a wide range of pressures, more information about the basic rate controlling phenomena was made available. In addition, hydrotreating catalysts could be used

in the second stage to enable a precursory examination of the upgradability of the shale oils. The work described in sections 3.3-3.6 and Appendix A was part of a Ph.D. dissertation by Carter.⁶

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3.2 THE ADSORPTION AND CRACKING OF HYDROCARBONS OVER PROCESSED OIL SHALES.

Because of the complexity of the product oil and the organic-inorganic interactions that transpire within the retort, direct fundamental investigation of the process chemistry is a formidable task. Most such studies have, therefore, tended to focus on simple measurement of the amount of carbon deposited onto the oil-shale substrates rather than focusing on the nature of the cracking reactions themselves. That is, prior studies have generally entailed exposing an oil stream to a hot substrate then measuring the increase in the substrate carbon content. This approach is both more straightforward and, at least from an engineering stance, more meaningful since the primary objective of retorting is generally to recover as much oil as possible regardless of the relationship between product yield and product quality.

Numerous studies aimed at measuring the relative coke inducing tendencies of oil shale substrates, such as discussed earlier in this chapter, have been attempted. Most of these studies have relied on measuring carbon deposition onto the coking substrates via elemental analysis with a lesser number attempting to monitor coking losses by collection and measurement of oil yields. Although significant experimental problems were encountered when measuring oil losses to coke by either of these approaches, reliably differentiating between solids-induced cracking and solids-induced coking reactions has proven to be substantially more difficult. For this reason, previous investigations of the magnitude of cracking reactions induced by interaction with oil-shale particles have often been confined to collecting and measuring the volatility of the hydrocarbon product following exposure. This is obviously a crude approach but still has some merit since more extensive cracking generally yields a more volatile product. One such study was that by Wallman et al.¹ who reported cracking kinetics based on increased gas production. Unfortunately, this is an ambiguous measurement. In many instances, gas components have undergone multiple reactions prior to exiting the reactor and continuing gas evolution from surface coke deposits undoubtedly contribute to the volume of gas produced.

In one of the more in-depth studies of solids-induced cracking, Levy et al. injected Fischer Assay oil through a fixed-bed reactor packed with sand or combusted shale.² They reported a significant level of coke deposition onto the shale ash, depletion of the high-boiling fractions, increased methane production attributed to coking reactions, and a higher oil aromaticity. An interesting detail from this study was a reported H/C molar ratio of 0.6 at 500 °C and 0.3 at 600 °C for the coke deposited onto the combusted shale ash. Such variation in surface carbon deposits implies that the coke structure is not fixed. As will be discussed, a variable coke structure has implications for the current investigation because it implies that substrate carbon is evolved during the cracking experiment. In addition, the differences reported in H/C ratios at different exposure temperatures implies that some of the evolved carbon likely originated from coke deposited during the exposure as opposed to inherent carbon in the shale substrate.

The only prior studies to include gasified shale as one of the study substrates were those by Rubel et al.³ and Carter et al.^{4,5} With the exception of one portion of the study by Rubel which found gasified shale to be the more active substrate, these studies concluded that the

relative order of coking of shale oil over the processed-shale substrates was combusted > gasified > pyrolyzed. Additional discussion of the results from these and other studies, in the context of the current investigation, will be deferred to the Results and Discussion section.

Notwithstanding the substantial effort that has been directed at measuring the relative coke-inducing tendencies of processed oil-shale substrates, fundamental knowledge of solids-induced reactions during retorting of oil shale is sparse. Questions abound as to the relative role the heat-carrying shales play in regulating product yield and composition. One of the primary obstacles to addressing these questions is the lack of an approach that can examine the relevant cracking reactions in a meaningful manner. That is, there is no approach currently in use that is simple enough to provide results that can be understood but that are relevant to the reactions that occur in an oil-shale retort utilizing solids heat transfer. Such an understanding is of added importance for the KENTORT II unit, since, within limits, the detrimental effect of recycling hot solids can be minimized by varying the relative proportion of gasified versus combusted particles or by selecting the optimum combination of recycle rate and particle temperature.

Accordingly, a primary objective of this study was to develop and evaluate a technique that could determine the relative losses of hydrocarbons during exposure to processed oil-shale substrates at elevated temperature. A second objective was to use this technique to obtain a better qualitative understanding of the interactions between hydrocarbons and oil shale substrates. This includes determining the effects of exposure time and temperature on substrate activity, measuring the relative lability of different hydrocarbon types, and examining the initial high-activity interval for evidence of a reaction mechanism that differs from the mechanism which controls the latter portions of the hydrocarbon exposure interval.

The kinetics of shale-oil coking losses over processed oil shales was the focus of the study described in the first part of this chapter. In a similar fashion, the current study will focus on adsorption and cracking of hydrocarbons. However, in lieu of utilizing freshly generated shale oil, measurement of adsorption and coking/cracking losses in the apparatus described here dictated the use of model compounds.

For the sake of clarity, *cracking* reactions will be defined as those reactions in which carbon-carbon bonds are broken with little or no carbon deposition on the shale substrate particles. *Coking* reactions will refer to those reactions that result in a portion of the hydrocarbon being deposited on the cracking substrate. In a more rigid definition, cracking and coking are part of the same process and cannot be completely isolated. However, different hydrocarbons exhibit different rates of coke formation for a given cracking substrate while different cracking substrates exhibit different rates of coke formation for a given hydrocarbon.

The following sections represent a condensed version of a dissertation presented to and accepted by the University of Kentucky in partial fulfillment of the requirements for a Ph.D. degree in Chemistry.⁶

3.2.1. THE CRACKING REACTOR.

3.2.1.1. General description.

A reactor system was designed and constructed specifically for this study. An overview of the system along with details on the less significant components is presented here. More detailed descriptions of the major system components, run procedures, analytical techniques, and data management protocols are given in subsequent sections.

A schematic of the system is shown in Figure 3-1. High purity nitrogen, delivered at 100 psi, was split into parallel carrier lines, routed through a pair of metering valves, and introduced to a heated valve oven. The nitrogen-carrier gas was metered at 150 cm³/min ambient temperature into one of these lines, termed the *bypass*, and at a variable rate to the other, *hydrocarbon-carrier* line. All carrier/transfer lines were constructed of 1/16 x 0.03 inch 304 stainless steel. Stainless-steel connectors were used throughout the system.

The bypass carrier line was routed through an 8-port valve, an 18 inch transfer line maintained at 275 °C, a 48 inch preheat loop, and into one of the parallel tube reactors positioned in a Lindberg tube furnace. In the initial switching-valve position, this line was connected to the reactor tube that was packed with the cracking substrate, i.e., the *substrate reactor*.

High-purity Ar was also introduced at 100 psi and metered at either 50 or 60 cm³/min (ambient) to the hydrocarbon-carrier line downstream from the N₂ metering valve. A liquid-chromatography pump was used to dispense the model hydrocarbons being investigated. The hydrocarbon passed through a restriction coil and into the valve oven via a 75-cm, downward-spiraling, volatilization-surge suppressor coil before connecting to the hydrocarbon carrier line inside the valve oven. The restriction coil served to maintain back pressure to the pump and thereby provided a more constant delivery rate of the hydrocarbon during pump-piston switchover. The volatilization-surge suppressor coil served to provide a more uniform rate of vaporization of the hydrocarbon, thereby suppressing flash-vaporization spikes during a run. The hydrocarbon-carrier line was then routed to the switching valve and paralleled the bypass line to the reactor furnace. In the initial switching-valve position, this stream was routed to the tube reactor which was packed with sand (the *bypass reactor*).

The tube reactors were constructed of 9 x 3/8 o.d. x 1/4 inch i.d. 316 stainless steel. One of the reactors, the bypass, was packed with 6.0 ± 0.05 g of sand for all runs, while the second, the substrate reactor, was packed with 4.0 ± 0.05 g of one of the substrates under investigation: pyrolyzed, gasified, or combusted shale, or with sand (6 g) for the control runs. The substrates were centered in each reactor tube between quartz wool plugs with an approximate 2.5-inch length void on each end. The substrates were loaded to the appropriate reactor with a type K, subminiature thermocouple positioned in each reactor (4 inches from the entry to the substrate tube and 2.5 inches from the entry to the bypass tube). Thermocouple readings from the substrate reactor were used to monitor the reaction temperature.

After passing through the reactors, the carrier lines were combined into a 1/8 inch o.d. ss exit tube. The exit stream was continuously sampled just inside the reactor furnace with a heated-capillary tube which was connected to the inlet of a quadrupole mass spectrometer (QMS).

Figure 3-1. Schematic diagram of the cracking reactor.

3.2.1.2. Major system components.

3.2.1.2.1. Hydrocarbon delivery system. A Waters model 6000A dual-reciprocating liquid chromatography (LC) pump was used to dispense the liquid hydrocarbons for all experiments. Due to condensation problems at higher flow rates, only the lowest settings of 0.1, 0.2, and 0.3 mL/min could be used. However, at such low settings, back-pressure to the pump was inadequate to force consistent closure of the pump checkvalves, resulting in fluctuations in the delivery rate. Also, at low back pressures, there were periodic oscillations in the hydrocarbon flow during pump piston switchover. To alleviate these problems, a 50-m x 0.25-mm restriction coil along with an additional 3-m x 0.1-mm coil were placed in series between the LC pump and the valve oven to increase back pressure to the pump. This configuration provided a consistent flow of hydrocarbon to the valve oven without measurable fluctuations during piston switchover.

3.2.1.2.2. Switching-valve oven. The switching valve used to direct carrier flows to either the bypass or substrate bed was a high temperature (300 °C), high pressure (300 psi) model N-60, 8-port valve manufactured by Valco, inc. The valve was bolted to an actuator/base plate inside a Chemical Data Systems model 820GS valve oven and remotely switched by an air actuator. A set of temperature controller units supplied with the valve oven was connected to a resistive thermal detector (RTD) and used to maintain a preset valve-oven temperature of 275 ± 5 °C for all runs. A second RTD was positioned about midway between the valve oven and the reactor furnace and in contact with the parallel carrier lines. These lines along with the RTD were wrapped with asbestos tape, followed by resistance-heating tape then enclosed with a second layer of asbestos tape. The transfer-line temperature was monitored and maintained at 280 ± 10 °C with a second controller unit on the CDS valve oven.

3.2.1.2.3. Reactor furnace and reactor-temperature profile. The tube furnace used for all experiments was a Lyndberg model Sola Basic. A Lyndberg model 59344 controller supplied electrical power to a Lyndberg furnace rated at 1300 W at 240 V. The furnace was equipped with a temperature-readout dial. However, power input to the furnace was manually adjusted to maintain the targeted reaction temperature using the thermocouple readout from the substrate bed (4 inches from the entrance to the substrate reactor).

Numerous precautions were taken to minimize variations in temperature across the reactor including centering the reactor so that each end was at least one inch inside the furnace, using preheater loops to assist in elevating the carrier streams to reaction temperature, and machining 4-cm thick fire brick to provide a crude seal around the reactor ends in an effort to reduce heat loss. The temperature profile across the reactor tube is shown in Figure 3-2. Data for these plots were obtained by centering 6-g of sand between quartz-wool plugs in both tube reactors, then inserting a thermocouple 4 inches into the bypass reactor and a second ~8 inches into the substrate reactor. The furnace temperature was then adjusted to either 500 or to 600 °C using the bypass thermocouple and substrate temperature readings taken at one-inch intervals as the thermocouple was withdrawn from the substrate reactor. Except for the readings nearest the entry and exit, repeat tests diverged by less than 5 °C at equivalent points across the reactor.

As can be seen, there remains a significant temperature variation across the reactors, particularly at the reactor entry, in spite of the precautions taken to minimize such variation. In an effort to ascertain if inadequate carrier preheating was responsible for the temperature variation, the reactor temperature profile is also shown as measured without carrier-gas flow. Although somewhat improved on the front end, the temperature profile without carrier flow was very similar to that with carrier flow. This indicates that the temperature variation across the reactor was due primarily to either inhomogeneous heating by the reactor furnace or to conductive heat losses at the reactor ends, not to preheating problems.

It should be noted that, as measured from the reactor entry, a 4-g load of processed shale spanned the region from about 6.5 cm to 17.0-18.5 cm (depending on the substrate) of the reactor tube. Thus, at a nominal setting of 500 °C, the temperature ranged from approximately 475 to 515 °C over this length of the reactor. Similarly, at 600 °C, the temperature of the substrate would be expected to range from about 585 to 620 °C. Using the plots in Figure 3-2, an average temperature of 503 and 605 °C was calculated across the substrate bed for the 500 and 600 °C settings, respectively.

Figure 3-2. Temperature profile across the cracking reactor.

3.2.1.2.4. Quadrupole mass spectrometer (QMS) system. The quadrupole mass spectrometer, along with all vacuum pumps, transfer capillary, and control units were part of the VG/Fisons model Sensorlab 300D package. The Sensorlab unit was controlled from a personal computer loaded with Thermosoft™ software (VG/Fisons). The mass range of the Sensorlab system was 1-300 amu with 1-amu resolution.

The combined reactor-effluent stream was continuously sampled approximately 5-cm inside the reactor furnace by a 1.8-m x 0.32-mm i.d. fused-silica capillary tube encased in a stainless-steel capillary sheath. The other end of the capillary tube was attached to the inlet of the QMS. The stainless-steel sheath was heated to approximately 175 °C.

The inlet to the QMS, along with one end of the heated capillary, was maintained at a pressure of $\sim 10^{-4}$ torr with a mechanical vacuum pump. The pressure drop across the capillary

resulted in a flow rate of about 12 cm³/min through the tube under ambient conditions. This provided a transit time through the tube of less than 0.5 s. The precise residence time within the capillary was not determined because flow rates tended to vary as a function of the hydrocarbon being studied (changing gas viscosity) and with daily changes in the capillary condition. The QMS end of the transfer capillary was positioned to the interior of a Metricel LeakTM which served to separate the spectrometer inlet from the ion source. Both the capillary and Metricel LeaksTM were replaced several times over the course of this study due to frequent clogging. The ion source was maintained between 10⁻⁶ and 10⁻⁹ torr with a turbomolecular pump.

The average time required for effluents to travel from the substrate bed to the QMS detector was conservatively estimated to be on the order of one second. Details on operation of the mass spectrometer are described later in the section on Data Collection.

Due to the manner in which hydrocarbon cracking losses were measured, the linearity of the QMS was not considered to be a problem. This was because the concentration of the model hydrocarbons generally varied by no more than 20-30% during a given run and the manufacturer claimed linear response over several orders of magnitude. Nonetheless, a check of the QMS response was conducted to insure against potential non-linearity.

Linearity tests were conducted at ambient temperature using argon and nitrogen flow only. The carrier gas delivery pressures were the same as those used throughout the study (100 psi). Nitrogen flow was maintained at 100 mL/min ambient as argon flow was varied from 8.7 to 145 mL/min. Following data collection, ratios of argon to nitrogen molecular-ion intensities were plotted as a function of the argon flow rate. These ratios are shown in Figure 3-3 along with a linear least squares line. As can be seen, there was no significant deviation in linearity over the range investigated. As this tested response range is substantially greater than the range over which the hydrocarbon concentration varied during the experiments conducted in this study, the linearity of the mass spectrometer was judged to be acceptable.

3.2.1.3. *Substrates examined.*

The three processed oil shale substrates examined in this study (Table 3-1) originated from an in-house master sample (CLE-003) of the Cleveland Member of the Ohio shale from Fleming County, Kentucky. These substrates were splits of the processed-shale samples used in the fluidized-bed coking study described earlier in this Chapter. The processed shales selected for study represent the three types of solids to which vapor-phase shale oil is exposed in the pyrolysis section of the KENTORT reactor. All three substrates were prepared in a fluidized-bed reactor using N₂, steam, or air as the fluidizing medium under the conditions listed in Table 3-1. The substrates were thoroughly blended, then coned, quartered, and stored in one-L plastic containers. The oil-shale substrates were screened and processed as 20 x 60 mesh particles. The Ottawa sand was screened to 20 x 30 mesh before use.

The mineralogy of the Cleveland Member shale is reasonably consistent, with four minerals generally accounting for over 95% of the inorganic matrix: silicates (primarily illites), quartz, chlorite, and kaolinite in the approximate ratio of 13:4:2:1.^{7,8} Additional information on substrate analyses is given later.

Figure 3-3. Test of the mass spectrometer linearity.

3.2.1.4. Model hydrocarbons.

The model hydrocarbons investigated in this study are listed in Table 3-2, along with information on the runs in which each was examined and on purity and boiling point. The listed purities are those specified by the manufacturer. All were purchased from the Aldrich Chemical Company except for *n*-heptane and benzene, which were manufactured by the Mallinckrodt Chemical Company.

With the exception of tetralin, the hydrocarbons selected for study represent components that are produced in relatively high abundance during pyrolysis of Eastern U.S. shale oils, and in particular, when pyrolysis is conducted with a KENTORT II reactor. Further, all the hydrocarbon types that are produced at significant levels (about 1% or greater) are represented by the model hydrocarbons selected for this study: *n*-alkanes are represented by hexane, heptane, and decane; α -olefins are represented by 1-hexene and 1-decene; aromatics and alkylated aromatics by benzene, toluene, ethylbenzene, and butylbenzene; a cyclic aliphatic by cyclohexane; and a cyclic olefin by cyclohexene.

All the non-cyclic alkanes and olefins used in this study, were straight-chain hydrocarbons. In addition, for both of the straight-chain olefins examined, 1-hexene and 1-

Table 3-1. Substrates used in the hydrocarbon-cracking study.

<u>Substrate</u>	<u>Origin</u>	<u>Carbon (wt%)</u>	<u>Preparation/comment</u>
Pyrolyzed Shale	Cleveland Member shale	9.6	530 °C in N ₂ /10 min
Gasified Shale	Cleveland Member shale	7.3	800 °C in Steam/20 min
Combusted Shale	Cleveland Member shale	1.7	700 °C in air/10 min
Sand	Ottawa, Canada	0.0	20x30 mesh

Substrates are 20 x 60 mesh unless otherwise noted.

decene, the double bond was located in the alpha position. Therefore, for the sake of brevity, the prefixes *n*- and 1- will often be omitted with the understanding that reference to a non-cyclic alkane or alkene always refers to the linear isomer for the alkane and to the linear α -olefin for the alkene.

3.2.2. PROCEDURES AND CONDITIONS.

3.2.2.1. Calibration Procedures.

3.2.2.1.1. Pump calibration. Nominal pump-flow settings of either 0.1 or 0.2 mL were used for all runs. To verify the accuracy of these settings, flow rates were measured for several of the hydrocarbons by disconnecting the hydrocarbon-carrier line from the valve oven and inserting the line into a 25-mL graduated cylinder submerged in an ice bath. Each hydrocarbon was then collected at a selected pump setting for a timed interval. Volumes were recorded after allowing the collected hydrocarbon to equilibrate to room temperature. To confirm that evaporation during collection was not a significant problem, comparisons were made of the volume of decane collected in both an ice bath and a dry ice/isopropanol bath at the same pump setting. No significant differences in collection rates were found.

The results from these flow measurements, shown in Table 3-3, demonstrate that the nominal-flow settings are quite inaccurate. Further, the extent to which the nominal setting was in error was related to the selected pump setting. At a nominal setting of 0.1 mL/min, the average measured delivery was $56.8 \pm 1.5\%$ of the anticipated volume; $74.1 \pm 1.9\%$ at a setting

Table 3-2. Model hydrocarbons plus coinciding run numbers and hydrocarbon purity.

<u>Model Compound</u>	<u>MC Run numbers</u>	<u>purity (%)</u>	<u>Boiling Point (°C)</u>
<i>n</i> -hexane	MC54-82	99+	69
tetralin	MC109-111	99	207
ethylbenzene	MC112-138	99	136
1-decene	MC177-206	94	170
1-hexene	MC207-239	97	63
cyclohexane	MC240-272	99+	81
cyclohexene	MC273-304	99	83
butylbenzene	MC364-379	99+	183
<i>n</i> -heptane	MC380-448	99	98
benzene	MC449-457 MC306-334	99.9+	80
toluene	MC458-466 MC335-363	99	110
<i>n</i> -decane	MC467-475 MC139-176	99+	174

Table 3-3. Measurement of the hydrocarbon-pump flow rates.

<u>Model Compound</u>	<u>Nominal flow rate (mL/min)</u>	<u>Interval (min)</u>	<u>Anticipated flow (mL)</u>	<u>Measured flow (mL)</u>	<u>Measured/anticipated</u>
1-decene	0.1	240	24.0	13.5	0.562
"	0.2	90	18.0	13.7	0.761
"	0.2	80	16.0	12.1	0.756
"	0.3	65	19.5	15.8	0.810
1-hexene	0.2	50	10.0	7.4	0.74
"	0.2	34	6.8	5.3	0.78
cyclohexane	0.2	110	22.0	16.4	0.745
cyclohexene	0.1	75	7.5	4.4	0.587
"	0.1	100	10.0	5.8	0.58
"	0.2	95	19.0	13.4	0.705
"	0.2	140	28.0	20.4	0.729
"	0.3	50	15.0	12.0	0.800
"	0.3	20	6.0	5.0	0.833
benzene	0.1	130	13.0	7.3	0.56
"	0.2	100	20.0	14.5	0.725
"	0.2	130	26.0	19.2	0.738
"	0.3	33.3	10.0	8.2	0.82
toluene	0.1	170	17.0	9.3	0.55
"	0.2	100	20.0	14.8	0.740
butylbenzene	0.2	140	28.0	20.5	0.732
n-heptane	0.2	150	30.0	22.0	0.733

Anticipated/measured flow ratios for all measurements.....0.714 $\pm$ 0.086

Anticipated/measured flow ratios for 0.1 mL/min nominal setting....0.568 $\pm$ 0.015

Anticipated/measured flow ratios for 0.2 mL/min nominal setting....0.741 $\pm$ 0.019

Anticipated/measured flow ratios for 0.3 mL/min nominal setting....0.816 $\pm$ 0.014

of 0.2 mL/min; and $81.6 \pm 1.4\%$ at 0.3 mL/min. No bias in flow rate as a function of the study hydrocarbon was discerned.

Most adsorption and cracking experiments in this study were conducted at a nominal pump flow setting of 0.2 mL/min with the remainder conducted at 0.1 mL/min. For calculation purposes, it was assumed that the actual liquid delivery rate was 75% (0.15 mL/min) of the nominal value at a pump setting of 0.2 mL/min and 57% (0.057 mL/min) of the nominal value for the 0.1 mL/min setting.

3.2.2.1.2. Carrier-gas flows. High purity argon and nitrogen were delivered from compressed gas cylinders to the reactor system at 100 psi as read from the low-pressure gauges on the cylinder regulators. Gas-flow rates were nominally set to 150 cm³/min (ambient) in both carrier lines. The bypass carrier was composed entirely of nitrogen. In the hydrocarbon-carrier line, argon flow was adjusted to either 50 or 60 cm³/min, the vapor-phase flow rate of the model hydrocarbon was calculated assuming ideal-gas behavior, and the nitrogen flow was then adjusted to provide a total flow rate of 150 cm³/min.

Carrier-gas flows were measured with a bubble meter at a pair of two-way switching valves positioned between the inlet metering valves and valve oven. Adjustments were made with the argon and nitrogen metering valves shown in Figure 3-1. Measurements of the gas-flow rates were precise to within about ± 1 -2 cm³/min, depending on the magnitude of the flow rate being measured (lower absolute precision at higher rates).

3.2.2.1.3. Calculation of substrate density. The calculation of residence times for the vapor-phase hydrocarbons within the reactor bed required determining both packing and skeletal densities for the substrates (Table 3-4). A helium picnometer was used to determine the skeletal density of the substrate. The skeletal densities were essentially the same for all four substrates, ranging from a low of 2.70 for the pyrolyzed shale to 2.80 g/cm³ for sand and combusted shale.

For clarity, packing density is defined as the volume of the cracking-reactor tube occupied by a given weight of substrate. Packing densities were calculated by determining the weight of substrate required to fill the tube reactor then dividing by the reactor volume. Ten such determinations were made for each substrate. The packing density measurements were reasonably precise exhibiting a relative standard deviation ranging from 0.2% for sand to just over 1% for gasified shale. Although the nominal particle size range was the same for all three shale substrates, the differences in packing density shown in Table 3-4 indicate that the pyrolyzed shale tended to pack the most tightly and combusted shale the least. Additional discussion on substrate densities is deferred to the section on Substrate Analyses.

3.2.2.1.4. Calculation of hydrocarbon residence times. The difference in the substrate-bed packing volume (length of reactor occupied by substrate bed $\times \pi r^2$) and the skeletal volume from He picnometry can be attributed to the void volume within the substrate bed (Table 3-4). These data show that the void volume within the more tightly packed bed of pyrolyzed shale is, as expected, smaller. However, owing to the fact that the skeletal density of all four solids was essentially the same, the calculated reactor-void volumes were also essentially the same (5.76-5.81 cm³). This means that the residence time for the carrier gas or for a vapor-phase model hydrocarbon within the reactor was also essentially the same. Because the calculated void

Table 3-4 Substrate densities and reactor void volumes. Calculation of reactor void volume was based on a 4-g load for the processed shales and a 6 g load for sand.

<u>Substrate</u>	<u>Skeletal Density (g/cm³)</u>	<u>Packing Density (g/cm³)</u>	<u>Reactor Vol occupied by subs load (cm³)</u>	<u>Absolute Vol occupied by subs load (cm³)</u>	<u>Substrate bed void Volume (cm³)</u>	<u>Total Reactor Void Vol (cm³)</u>
Combusted	2.80	1.029	3.887	1.43	2.46	5.81
Gasified	2.76	1.119	3.575	1.45	2.13	5.79
Pyrolyzed	2.70	1.175	3.404	1.48	1.92	5.76
Sand	2.80	2.107	2.848	1.43	1.42	5.81

void volumes, an average void volume of 5.79 cm³ was assumed. This average value along with the carrier rates were then used to calculate the residence times of the model hydrocarbons within the reactor. These calculated values are shown in Table 3-5. Residence times were calculated individually for each hydrocarbon because the total flow rate varied among the different run series. As the data in Table 3-5 show, residence times for the various hydrocarbons varied substantially. However, the residence times for the four hydrocarbons that were the primary focus of this study, *n*-heptane, benzene, toluene, and *n*-decane, were quite similar at a given reaction temperature.

A second strategy for expressing the time a given hydrocarbon spent at reaction temperature in the presence of a cracking substrate was to calculate the residence time within the substrate bed instead of within the full reactor. Results of these calculations are shown in Table 3-6 as a function of exposure temperature. There are significant differences in residence times among the three substrates when calculated in this manner. However, these differences can be misleading because comparison of the packing and skeletal densities shows most of the void volume to be extraparticle. This means that the number of collisions between the vapor-phase hydrocarbon and the substrate particles is not linearly related to the residence time in the substrate bed. Therefore, it would be erroneous to correct cracking activity measurements based on the residence time within the substrate bed. A more relevant parameter in this respect is the particle surface area, which will be addressed in later sections.

Table 3-5. Residence time (s) of the model hydrocarbons within the cracking reactor as a function of reaction temperature.

Reactor Res time (s)									
Temperature (C)	flow rate (mL/min)	300	350	400	450	500	550	600	650
n-hexane	137	1.30	1.19	1.10	1.03	0.96	0.90	0.85	0.80
ethylbenzene	121	1.47	1.35	1.25	1.16	1.09	1.02	0.96	0.91
1-decene	147	1.21	1.11	1.03	0.96	0.90	0.84	0.79	0.75
1-hexene	145	1.23	1.13	1.04	0.97	0.91	0.85	0.80	0.76
cyclohexane	153	1.16	1.07	0.99	0.92	0.86	0.81	0.76	0.72
cyclohexene	156	1.14	1.05	0.97	0.90	0.84	0.79	0.75	0.71
butylbenzene	143	1.24	1.14	1.06	0.98	0.92	0.86	0.82	0.77
n-heptane	150	1.18	1.09	1.01	0.94	0.88	0.82	0.78	0.74
benzene	151	1.18	1.08	1.00	0.93	0.87	0.82	0.77	0.73
toluene	159	1.12	1.03	0.95	0.89	0.83	0.78	0.73	0.69
n-decane	149	1.19	1.10	1.02	0.94	0.88	0.83	0.78	0.74

Table 3-6. Residence time (s) of the model hydrocarbons within the substrate bed as a function of reaction temperature.

Temperature (C)	300	350	400	450	500	550	600	650
Combusted shale								
n-hexane	0.55	0.51	0.47	0.44	0.41	0.38	0.36	0.34
ethylbenzene	0.62	0.57	0.53	0.49	0.46	0.43	0.41	0.39
1-decene	0.51	0.47	0.44	0.41	0.38	0.36	0.34	0.32
1-hexene	0.52	0.48	0.44	0.41	0.39	0.36	0.34	0.32
cyclohexane	0.49	0.45	0.42	0.39	0.37	0.34	0.32	0.31
cyclohexene	0.48	0.44	0.41	0.38	0.36	0.34	0.32	0.30
butylbenzene	0.53	0.49	0.45	0.42	0.39	0.37	0.35	0.33
n-heptane	0.50	0.46	0.43	0.40	0.37	0.35	0.33	0.31
benzene	0.50	0.46	0.43	0.40	0.37	0.35	0.33	0.31
toluene	0.47	0.44	0.40	0.38	0.35	0.33	0.31	0.29
n-decane	0.51	0.47	0.43	0.40	0.38	0.35	0.33	0.31
Gasified shale								
n-hexane	0.48	0.44	0.41	0.38	0.35	0.33	0.31	0.30
ethylbenzene	0.54	0.50	0.46	0.43	0.40	0.38	0.35	0.34
1-decene	0.44	0.41	0.38	0.35	0.33	0.31	0.29	0.28
1-hexene	0.45	0.41	0.38	0.36	0.33	0.31	0.30	0.28
cyclohexane	0.43	0.39	0.36	0.34	0.32	0.30	0.28	0.27
cyclohexene	0.42	0.39	0.36	0.33	0.31	0.29	0.27	0.26
butylbenzene	0.46	0.42	0.39	0.36	0.34	0.32	0.30	0.28
n-heptane	0.44	0.40	0.37	0.35	0.32	0.30	0.29	0.27
benzene	0.43	0.40	0.37	0.34	0.32	0.30	0.28	0.27
toluene	0.41	0.38	0.35	0.33	0.30	0.29	0.27	0.26
n-decane	0.44	0.40	0.37	0.35	0.33	0.31	0.29	0.27
Pyrolyzed shale								
n-hexane	0.43	0.40	0.37	0.34	0.32	0.30	0.28	0.27
ethylbenzene	0.49	0.45	0.41	0.39	0.36	0.34	0.32	0.30
1-decene	0.40	0.37	0.34	0.32	0.30	0.28	0.26	0.25
1-hexene	0.41	0.37	0.35	0.32	0.30	0.28	0.27	0.25
cyclohexane	0.39	0.35	0.33	0.31	0.29	0.27	0.25	0.24
cyclohexene	0.38	0.35	0.32	0.30	0.28	0.26	0.25	0.23
butylbenzene	0.41	0.38	0.35	0.33	0.31	0.29	0.27	0.26
n-heptane	0.39	0.36	0.33	0.31	0.29	0.27	0.26	0.24
benzene	0.39	0.36	0.33	0.31	0.29	0.27	0.26	0.24
toluene	0.37	0.34	0.32	0.29	0.27	0.26	0.24	0.23
n-decane	0.40	0.36	0.34	0.31	0.29	0.28	0.26	0.25

3.2.2.2. Run procedure.

Preparation for a hydrocarbon-exposure run entailed packing 4 g of substrate into the substrate reactor and 6 g of sand into the bypass reactor, both centered between quartz-wool plugs. The threaded fittings on the end of each reactor tube were coated with E-Z-BreakTM, a high-temperature lubricant, to facilitate post-run reactor disassembly. The reactor train was then assembled and connected to the carrier lines. The reactor was plugged and the system was tested for leaks with soap water. The reactor train next was placed into the furnace and suspended on 4-cm-thick fire brick which were machined in the shape of split cylinders to fill the void around the reactor ends. The furnace with the loaded reactors in place was then heated to 660 °C and maintained for 5 min to remove adsorbed moisture from the substrates, then cooled to the targeted reaction temperature. As the reactor cooled, the transfer capillary to the QMS was attached to the reactor and model-hydrocarbon flow was initiated. The reactor temperature and hydrocarbon flows were allowed to equilibrate at the target temperature for a minimum of 2 min. During the multiple exposure runs to be described, the model-hydrocarbon flow was maintained for the duration of the run series. The targeted reaction temperatures were either 300, 350, 400, 450, 500, 550, 600, or 650 °C. Below 300 °C, condensation tended to be a problem for the less volatile hydrocarbons whereas 650 °C was near the upper limit of the apparatus.

The selected exposure time usually varied as a function of reaction temperature. Typical exposure intervals were five minutes for runs conducted at 300-450 °C, 10 min for the 500 and 550 °C runs, and 15 min for the 600 and 650 °C runs. These exposure times were chosen because less time was required at lower temperatures to re-establish a flat baseline following switch to expose mode. It would have been simpler to conduct all runs at 15 min, but, due to time and data-storage considerations, this approach was rejected in favor of shorter exposure times at lower temperatures.

Data collection was initiated following the 2-min equilibration at the target temperature. The temperature reading of the substrate reactor was manually maintained within ± 2 °C of the target temperature for the duration of the run. After a minimum of 100 data points (~80 s) was collected with the QMS running in the selected ion monitoring mode or two minutes when operated in the log histogram mode, the valve was rotated so that the hydrocarbon-carrier stream was switched to the substrate reactor and the bypass-carrier to the sand-packed bypass reactor. Following the selected exposure time, the valve was returned to the initial position and the baseline was re-established.

Control runs were made by packing both the bypass and substrate reactor tubes with sand to verify acceptable system operation. The bypass sand was replaced following every run at 650 °C as well as between other runs when deemed necessary.

3.2.2.3. Data collection.

Ion intensities were recorded with the QMS operating in either a log-histogram (LGH) mode or in a selected-ion-monitoring (SIM) mode. In the LGH mode, mass intensities were recorded at one-amu resolution from a mass of one to a selected upper limit (300-amu maximum). The time required to complete a scan in the LGH mode was dependent on the selected mass range and typically took several seconds (about 10 amu/s). Numerous runs early

in the study were recorded in the LGH mode. However, the relatively long scan time coupled with the fact that the LGH files could not be readily exported to the spreadsheet software used for calculating ion-intensity ratios led to a decision to discontinue this mode of data collection following run MC377. With the exception of five runs with cyclohexane and cyclohexene, little usable information was obtained from the LGH runs. Therefore, with the exception of the cyclohexane and cyclohexene runs, data from this mode of operation are omitted from this report.

In the SIM mode, up to 16 ions could be sampled over 4000 times each with the averaged intensity value being recorded at slightly less than one-second intervals. The SIM mode was the preferred operating mode due to a more rapid sampling rate but with the trade-off that all ion intensities, and thus potentially useful data, were not recorded. For most runs, in addition to the molecular ion of the model hydrocarbon and one or more of its anticipated cracking products, masses 14 and 28 (N_2), 18 (H_2O), and 20 and 40 (Ar) were recorded in the SIM mode.

It would have been preferable to record ion intensities at the full 16-ion capacity. This would have permitted the ion intensities from several cracking products formed during exposure to the substrates to be recorded, thereby providing additional information on cracking product formation as well as parent-hydrocarbon destruction. However, this was generally precluded by the fact that the measurement of a given ion intensity required up to two minutes when the partial pressure of the monitored ion dropped below 10^{-11} torr in the ion source of the spectrometer. Above this range, collection proceeded in less than one second as described. Such low partial pressures resulted in suspension of data collection for all selected ion intensities while one or more low-abundance ions were being measured. This was deemed unacceptable since monitoring the conversion of a given study-hydrocarbon required a more rapid sampling rate. Accordingly, monitoring the molecular ions of anticipated cracking products was generally limited to ions that were formed in relatively high abundance directly from the parent hydrocarbon within the ion source.

3.2.2.4. *Single- vs. multiple-exposure runs and the experiment numbering system.*

The exposure run numbers corresponded to the number of the substrate load and were numbered consecutively beginning with the number one (1). In addition, many of the run numbers contain a letter suffix, A-I, which signified that a given substrate load was exposed to the hydrocarbon being studied more than once. For a given load of substrate, such multiple exposures may have been conducted at either the same or at different temperatures, but always with the same hydrocarbon. All other exposures represented single-exposure runs, that is, runs in which the substrate load was exposed to a given hydrocarbon only once. For most of the multiple-exposure runs, the suffix A corresponded to an exposure at 300 °C, B corresponded to 350 °C, etc., up to the letter H, which corresponded to an exposure at 650 °C. With the exception of the I runs, multiple-exposure runs were always made in the order of increasing reactor temperature. The I runs were conducted at 600 °C and were always the *first* run made in the multiple-exposure series. Such runs were only conducted in the last two series of experiments in which toluene and *n*-decane were examined.

The numbering system is best be illustrated by examples. For instance, MC310 would be the three-hundred-and-tenth substrate load and represent a single-exposure run for that substrate; run MC310E would represent a 500 °C exposure run for a substrate that had been

previously exposed to the model hydrocarbon at 300, 350, 400, and 450 °C as well as at 600 °C if an MC303I run had been made for that series.

3.2.2.5. Collection and analysis of cracking products.

In an effort to determine if there were significant differences in the cracking products over time or between substrates, liquid products were collected over different exposure intervals of *n*-heptane to 4-g loads of the processed shales. Similar runs were conducted using an acid catalyst (Y-zeolite, Grace-Davison Chemical) as substrate. For the catalyst runs, the substrate reactor was loaded with 0.5 g of catalyst blended with 6.0 g of sand. Heptane exposures to gasified shale were conducted at 600 °C whereas the zeolite runs were conducted at 550 °C. This was necessitated by the substantially higher activity for the Zeolite substrate that precluded running at the higher temperature because of nearly complete destruction of the heptane.

For these experiments, each tube reactor exit was fitted with a glass tube that was bent and inserted to near the bottom of a 15-mL graduated test tube. The test tube was packed with glass wool and suspended in a dry ice/isopropanol bath during collection. Product collections were conducted for timed intervals during the initial 0-2 min of exposure to the substrate then again after a minimum of 10 min of continuous exposure.

Immediately following product collection, gas-chromatographic analyses of the cracking products were conducted on a Hewlett-Packard model 5880 chromatograph equipped with a 60 m x 0.32 mm DB-5 capillary column (J&W Sci.) and a flame ionization detector (FID). GCMS analyses were conducted on selected samples using a HP-5890 gas chromatograph equipped with a series 5971 mass selective detector and a second 60 m DB-5 capillary column.

3.2.2.6. Substrate analyses.

3.2.2.6.1. Elemental. Carbon, hydrogen, and nitrogen analyses were conducted according to ASTM-D5373.⁹ A Leco Corporation model CHN-600 analyzer was used to analyze 80-100 mg samples in duplicate. A U.S. Geological Survey round-robin sample of the New Albany oil shale was used as the standard.

3.2.2.6.2. Proximate. Proximate analyses were conducted in duplicate on approximately 50-mg samples of material according to ASTM-D5142.¹⁰ A TA-Instruments model Hi-Res TGA 2950 thermogravimetric analyzer was used for these analyses.

3.2.2.6.3. Density. As discussed before, calculating the residence time of the model hydrocarbon within the reactor required that both skeletal and packing densities be determined for each substrate. A Micromeritics Corporation model Autopycnometer 1320 was used to obtain skeletal densities in triplicate on approximately one-gram samples of uncrushed substrate.

Packing density measurements were made for the four substrates in order to determine the length of the reactor occupied by a given weight of substrate. For these measurements, the reactor tubes were repeatedly packed with a given substrate and the weight of substrate required to fill the tube was determined after each trial. Ten trials were conducted on ten different subsamples of each substrate. Packing densities were then calculated by dividing the average

packed-substrate weight by the reactor volume. Packing density values of 1.029 ± 0.009 , 1.119 ± 0.010 , 1.175 ± 0.009 , and 2.107 ± 0.002 g/cm³ were determined for the combusted, gasified, and pyrolyzed shales, and sand, respectively. For a 4-g load of shale or 6-g load of sand, this equates to a packing length in the reactor of 12.3, 11.3, 10.8, and 9.00 cm for the combusted, gasified, pyrolyzed, and sand substrates, respectively. Relative standard deviations ranged from 0.2% for sand to 0.9% for the combusted shale.

3.2.2.6.4. Surface area and pore-size distributions. Measurements of the surface area for each substrate were obtained with a Quantachrome Autosorb-6 gas-sorption system using a static N₂ volumetric flow procedure. Mercury porsimetry measurements were made with a Quantachrome Autoscan porsimeter throughout the pressure range of 0-60,000 psi. Samples for both analyses were outgassed under vacuum at approximately 250 °C for 16-20 hr prior to analysis. Surface areas were calculated using the standard BET equation.¹¹ Micropore volumes were calculated using the Dubinin-Radushkavich plot¹² over a linear range.

Substrate surface area is generally accepted as a key parameter in governing catalyst activity¹³ and has been used to explain relative coking activity in previous oil shale studies.^{2,3,4} It has been speculated that due to inaccessibility, the micro surface area (that within pores <2 nm in diameter) does not participate in coking/cracking reactions of the relatively large shale oil molecules.⁴ Accordingly, total surface areas and surface areas in meso and macro pores (>2 nm) as determined by Hg porsimetry are often treated separately in this report.

3.2.3. DATA MANAGEMENT.

3.2.3.1. Data processing.

After recording the ion-intensity values from the mass spectrometer, the data files were exported to a spreadsheet where the molecular-ion intensities of the model hydrocarbon as well as other ions of interest, were ratioed to the Ar²⁺ ion intensity (m/e 20) collected during the same scan. The argon m/e-20 (Ar²⁺) intensity was used instead of m/e-40 due to interference from C₃H₄⁺ (m/e 40), a cracking product typically produced in relatively low abundance in the ion source. The ion intensities were converted to ratios instead of using the absolute intensities directly because expressing the data in this form effectively eliminates much of the variation that arises from changing run conditions. Examples of interferences that are suppressed or eliminated by the use of ion ratios include spectrometer drift, variable flows through the QMS transfer capillary, small temperature or pressure fluctuations, and minor leaks.

3.2.3.2. Curve-fit equations.

After the spreadsheet files containing the HC/Aa ratios were processed, they were imported to a curve-fitting program (SigmaPlot Graphics System). A linear equation (Eq. 1) was then fit to the ion-intensity ratios that corresponded to the bypass-mode interval, that is the ion-intensity values collected before and after exposure of the hydrocarbon to the substrate. A function containing both linear and decaying exponential terms (Eq. 2) was then fit to the data obtained during exposure of the model hydrocarbon to the substrate (expose mode):

$$y = m*t + e \quad \text{Eq. 1}$$

$$y = -a\exp^{-b*t} + m*t + c*t + d \quad \text{Eq. 2}$$

Where,

t = time and

a - e and m are fitted constants.

The slope parameter m is the same for both equations and was determined by first fitting the bypass data to Equation 1 then including the fitted m as a constant in Equation 2 prior to fitting the expose-mode data. The m parameter served to help deconvolute baseline drift from the slope parameter c of Equation 2.

Data from several early runs were evaluated by Table Curve software (v 3.01, Jandel Corporation) in an attempt to determine the form of the equation which could best fit the data collected in the expose mode. However, after processing the data from several early runs, many of the equations that provided the best fit could best be described as physically meaningless. For example, the form of the equation which provided the best data fit often contained 5th or 6th order parameters. On the other hand, the decaying exponential form that was ultimately selected did not always provide the best fit but did always provide a reasonably good fit. Further, this form is similar to that used in both the coking study⁵ described earlier and to that often used to describe catalyst deactivation.^{14,15}

After the parameters of Equations 1 and 2 had been fitted, the two equations could be integrated thereby permitting losses due to adsorption or cracking of the model hydrocarbon to be determined. Because the hydrocarbon flow rate was known, hydrocarbon losses could also be expressed on an absolute basis, that is, grams of hydrocarbon lost per gram of substrate.

3.2.3.3. Numerical integration of the adsorption-desorption curves.

In addition to determining hydrocarbon losses by integration of fitted-equations, the magnitude of adsorption and desorption at low temperatures were also measured by numerical integration of the ion-ratio data sets. Numerical integrals were acquired by averaging the ion-ratio values between adjacent data points, multiplying the averaged value by the time increment between the two points, then summing the results over the 30-s interval immediately following valve switch to expose mode (adsorption) or return to bypass mode (desorption). A baseline-response level, which was needed for calculation of the level of hydrocarbon adsorption, was obtained by averaging approximately 20 data points immediately before and an equal number immediately after the 30-s adsorption interval. Baseline response for the desorption calculation was obtained in a similar manner using the ion-ratio values immediately before and after the 30-s desorption interval. The baseline response was then integrated over the same 30-s time interval over which the adsorption and desorption of the model hydrocarbon was measured. The ratio of the adsorption or desorption integral to the appropriate baseline integral was proportional to the extent of hydrocarbon adsorption or desorption, respectively. As before, because the QMS response during the baseline interval could be equated to the flow rate of the model hydrocarbon, the extent of adsorption and desorption could be expressed on an absolute basis. The average adsorption values to be reported actually represent an average of the numerically integrated

adsorption and desorption curves.

3.2.3.4. *Experimental obstacles.*

Numerous problems coupled with an evolving procedure and changing conditions early in the study led to the rejection of a substantial number of runs as unusable. Essentially all runs up to MC112 were rejected for a number of reasons. Problems that were encountered on one or more occasions and that could be identified included leaking check valves in the LC pump; an inadequate time allowed for the hydrocarbon flow to reach equilibrium prior to initiating a run; hot spots at the juncture between the heated-transfer capillary and the current carrying electrodes; a dirty ion source; spikes in the spectrometer signal due to flash vaporization of the hydrocarbons; leaks in the carrier-line connections, reactors, switching valve, and pump seals; a hard drive crash; failed thermocouples; defective Metricel LeaksTM; failure of the turbomolecular pump and one of the mechanical pumps; contamination of the QMS inlet with vacuum-pump oil; and obstruction of the reactor preheater coils and the transfer capillary to the spectrometer inlet.

A dirty ion source and spikes in the spectrometer signal due to flash vaporization of the hydrocarbons posed perhaps the most severe problems in terms of the number of runs affected. These problems were eventually addressed by completely replacing the ion source and by inserting a 30-in, downward-spiraling, evaporation coil in the hydrocarbon delivery line beginning at the point at which this line entered the valve oven.

Due to the cumbersome approach to data management, there was typically a several-week delay between data collection and data reduction, especially early in the study as a suitable approach to data management was being developed. These difficulties were lessened substantially by both experience and the shortening of the time interval between data collection and processing. However, it was not until several months into the study (about run MC380), that the system began to perform in a reasonably reliable and consistent manner. For this reason, only limited portions of the data set prior to MC380 will be presented with emphasis given to those runs subsequent to MC380. Additionally, selected hydrocarbon sets were repeated--benzene, toluene, *n*-heptane, and *n*-decane. The initial data set for *n*-heptane was completely discarded and only problem-free runs from the other repeat sets were retained and presented.

3.2.4. RESULTS AND DISCUSSION.

3.2.4.1. *General description of the results.*

3.2.4.1.1. Typical Run Sequence. A plot of the ion-intensity ratios obtained from a typical run sequence is shown in Figure 3-4. The data for this plot were collected with the mass spectrometer during a run in which cyclohexene was passed through a reactor packed with gasified shale. The top curve (Figure 3-4a) shows the ratio of the molecular-ion intensity for cyclohexene to that of the tracer Ar^{2+} ion (m/e 20). In the first segment labeled as *bypass mode*, the cyclohexene is being routed through the sand-packed bypass reactor. The middle segment shows the response after the valve has been switched and the cyclohexene is routed through the substrate-packed reactor, i.e., *substrate expose mode*. During this segment, the drop in the

Figure 3-4. Ion-intensity ratios from a typical exposure sequence, in this instance, during a 10-min exposure of cyclohexene to gasified shale. a)-Cyclohexene/argon (m/e 82/20) ratios; b)-propene/cyclohexene (m/e 42/82) ratios.

relative intensity of the molecular ion, $C_6H_{12}^+$, indicates loss of cyclohexene due to interaction with the gasified shale. The final segment shows the return to *bypass mode* at which time the baseline is re-established.

There is no obvious *desorption* of cyclohexene in Figure 3-4a. That is, the ion-intensity ratios do not exceed the baseline levels following return to bypass mode. This implies that essentially all the cyclohexene loss was due to cracking or coking reactions, not to reversible adsorption onto the substrate. Evidence that the loss of cyclohexene was in large part due to cracking reactions is presented in Figure 3-4b. This plot shows a substantial increase in the ratio of the m/e-42 ion (largely propene) to the m/e-82 ion (cyclohexene) during the expose-mode interval and indicates a significant level of cracking of the cyclohexene during exposure to gasified shale.

3.2.4.1.2. Hydrocarbon losses as a function of temperature. Figure 3-5 shows the ion-intensity ratios from a series of runs in which *n*-heptane was repeatedly passed through the same load of gasified shale beginning at 300 °C and progressing to 650 °C in 50-degree increments. For each run, the ratio exhibited a sharp decrease when the valve was switched to the substrate expose position ($t = 0$). In the top four runs conducted at the lower temperatures (300-450 °C), the loss of *n*-heptane immediately following the valve switch is attributed chiefly to adsorption. This is because the ion ratios during the bypass and the latter portion of substrate exposure modes were essentially equivalent and the area under the greater-than-baseline peak (desorption) that follows the return to bypass mode is roughly equal to the area under the adsorption curve that follows the initial switch to expose mode. In other words, essentially all of the heptane that entered the reactor eventually exited.

Unlike the runs at lower temperature, most of the *n*-heptane loss at higher temperatures (500-650 °C) is attributed to substrate-induced cracking and coking reactions. These higher-temperature runs are characterized by a substrate-exposure interval during which the ion-intensity ratios do not completely return to the baseline response level established in the initial bypass interval. As would be expected, this difference is most obvious in the highest temperature, 650 °C plot. There was also little, if any, observable desorption of cyclohexene following return to bypass mode in the higher-temperature plots.

The general appearance of the ion-intensity curves shown in Figure 3-5 is typical of all model hydrocarbons examined. The chief difference in these curves between hydrocarbons or between substrates was in the relative magnitude of adsorption and conversion. There were also obvious differences in the shape of the ion-ratio curves obtained from an initial versus a subsequent exposure to the same load of substrate. This latter difference will be discussed in detail in later sections.

3.2.4.1.3. Hydrocarbon losses as a function of substrate. Ion-ratio curves obtained during exposure of *n*-heptane to each of the solid substrates at 300 °C are shown in Figure 3-6a. The relative capacity of the four solids to retain heptane, or for that matter any of the other hydrocarbons examined at low temperature, generally followed the order shown. That is, the integrated area under the adsorption peak that is apparent during the 30-s interval immediately following valve-switch to expose mode ($t = 0$) followed the order of gasified > pyrolyzed > combusted shale >> sand.

Figure 3-5. Ratios of the *n*-heptane molecular-ion intensity to the Ar^{2+} ion (m/e 100/20) from exposure of *n*-heptane to gasified shale. The temperatures shown are in °C.

Figure 3-6. Ratios of the *n*-heptane molecular-ion intensity to the Ar^{2+} ion (m/e 100/20) as a function of substrate. a) 300 °C; b) 650 °C.

Analogous runs at 650 °C are shown in Figure 3-6b. A high initial level of hydrocarbon loss followed by a gradual decline to a near constant, but less than baseline response was characteristic of all the higher-temperature exposures to the processed shales. Similar to the order of adsorption losses at low-temperatures, the magnitude of the high-temperature loss of *n*-heptane also generally followed the order of gasified > pyrolyzed > combusted >> sand.

3.2.4.2. *n*-Heptane studies.

A series of experiments that were designed to evaluate overall system performance and to concurrently examine the effect of various parameters on hydrocarbon conversion, was undertaken. *n*-Heptane was selected for these studies because *n*-alkanes are a major component of the product oil generated in the KENTORT II reactor and, in particular, *n*-heptane provided a good balance between volatility (lessened condensation problems) and a relatively high level of conversion during exposure to the processed shales.

3.2.4.2.1. Heptane loss as a function of substrate and temperature. As described earlier, a linear equation was fit to the ion-intensity ratios that were derived from the QMS readings recorded during bypass-mode operation. This includes the values recorded both before the switch to exposure mode and after the return to bypass. A decaying exponential equation was then fit to the analogous data that was collected during exposure-mode operation. The two equations were then integrated beginning from the time at which the study-hydrocarbon was switched to the substrate bed. The fraction of hydrocarbon that passes unchanged through the reactor was then calculated as the ratio of the exposure-mode integral divided by the bypass-mode integral.

Results of these calculations are shown for heptane in the top half of Figure 3-7 for the initial five minutes of the exposure interval. These data are from a series of repeat runs in which heptane was exposed to a given substrate beginning at 300 °C and progressing to 650 °C in 50 °C increments without changing the substrate load (a multiple-exposure series as opposed to a single-exposure). The integrated losses of heptane appear to minimize around 450-500 °C. At lower temperatures, losses are greater due to adsorption onto the substrates, whereas at higher temperatures, coking and cracking losses dominate. The losses measured for both processes as a function of the substrate followed the order of gasified > pyrolyzed > combusted > sand.

The y-intercept ratios (*e/d* ratios from Eqs. 1 and 2) for the same runs are plotted in the bottom half of Figure 3-7. In such a plot, any low-temperature adsorption is effectively removed from the linear intercept parameter of Equation 2 by the decaying exponential term. This explains why the y-intercept ratio essentially remains at unity until cracking/coking losses become significant at higher temperatures (550 °C and above). This ratio can be used as a means to compare the more linear, continuing activity of the substrate that follows the initially high level of adsorption or cracking and coking activity.

One point concerning the plots in Figure 3-7 which warrants clarification is that, for those runs in which the substrate reactor was packed with sand, both the heptane losses and the y-intercept ratios were essentially zero regardless of the exposure temperature. This is not to imply that there was always zero cracking or coking of the heptane when routed through a sand-packed reactor. In fact, there was a significant level of cracking over sand at the higher exposure temperatures as evidenced by one experiment in which heptane was passed through a reactor

Figure 3-7. Results from runs conducted with *n*-heptane. a) Adsorption and/or cracking losses during the initial 5-min of exposure, b) y-intercept ratios from Equation 1 and 2 (e/d; bypass/expose mode intercept).

packed with sand while the furnace temperature was being ramped upward. In this test, the heptane/Ar ion ratios decreased approximately 7% during a temperature rise from 590 to 650 °C in spite of a concurrent reduction in the heptane-residence time of about 6%. Rather, the extent of heptane losses were much less for sand than for the other substrates because sand is comprised of relatively inert quartz minerals and has a very low surface area. More importantly, however, since the bypass bed was also packed with sand, loss of heptane was essentially the same in both bypass and substrate-exposure modes and such losses effectively cancel. What this means is that neither purely thermal nor sand-induced losses can be measured in the cracking reactor as configured. Therefore, the measured hydrocarbon losses presented in this report represent losses above the baseline losses over sand with thermal-cracking losses effectively removed by the parallel-reactor configuration and the manner in which baseline response was determined.

3.2.4.2.2. Cracking loss as a function of exposure time. The loss of *n*-heptane at higher temperatures is illustrated in Figure 3-8 as a function of both exposure time and substrate type. The top two plots (*a* and *c*) show average losses for multiple-exposure runs. In the multiple-exposure runs, the substrate was initially exposed at 300 °C, then again in 50 °C increments over the temperature range of 350 to 650 °C without replacing the substrate. Plots *a* and *c* represent losses during the last two exposures in this series. For each substrate, the fraction of heptane conversion declined slightly with increasing exposure times. This indicates that the substrate is deactivated to some extent during a prolonged exposure period. The bottom plots in Figure 3-8 (*b* and *d*) show more clearly that the substrates were deactivated during exposure. These plots are analogous to those of the multiple-exposure plots on top, except they represent conversion of heptane over a *fresh* or previously unexposed load of substrate (single-exposures runs). The relative activity of the substrates in the single-exposure runs was the same as in the multiple-exposure runs. However, for a given substrate, total loss was significantly greater in the single-exposure runs, again indicative of substrate deactivation.

3.2.4.2.3. Single- versus multiple-exposure runs. The ratios of the heptane/Ar ion intensities obtained during exposure to a fresh substrate load (single) and during a subsequent exposure to the same load of substrate (multiple) are plotted in Figure 3-9. As can be seen, the rate of heptane conversion over the fresh substrate was significantly greater than in the subsequent exposure. This is particularly evident during the first 1-2 min of the exposure during which time substrate activity rapidly decays. This initial high-activity interval was characteristic of the loss curves obtained with fresh substrate for all hydrocarbons studied. The shape for the conversion curve is also characteristic of that observed during deactivation of commercial cracking catalysts, that is, a period of high initial activity which rapidly decays to a more constant level. For commercial catalysts, it was shown that the rate of deactivation does not correlate with the extent of carbon deposition.¹⁶

A similar curve shape was also observed in the shale-oil-coking study discussed earlier. In that study, the initially high activity was at first attributed to diffusion of the shale oil into the substrate pores.^{5,17} However, in the tests conducted for this study, the initial interval of high activity was not observed in subsequent exposures to the same substrate load and there was little or no hydrocarbon desorption following return to bypass mode. These points suggest that the initial high activity was more likely due to coking/cracking losses and not diffusional losses of the hydrocarbons to the particle interior. In subsequent modeling studies, Carter showed that the time required for the hydrocarbon concentration within the particle to attain near-equilibrium

Figure 3-8. Loss of *n*-heptane during exposure to a fresh (single) and previously-exposed (multiple) load of substrate. a) Multiple-600 C, b) single-600 C, c) multiple-650 C, d) single-650 C.

n-heptane over Gasified Shale-600C

Figure 3-9. Loss of *n*-heptane at 600 °C during an initial (top) and a subsequent (bottom) exposure to the same load of gasified shale.

conditions was on the order of one second.¹⁸ This is substantially less than the one- to two-minute interval over which enhanced conversion was observed here, thus providing additional evidence that the relatively high initial activity is not due to diffusional losses.

To further investigate substrate deactivation, two sets of isothermal runs were conducted in which *n*-heptane was passed across gasified shale without changing the substrate and without cooling the reactor. In other words, a run was made and a second immediately initiated. Five such exposures were made at 600 °C and four at 650 °C. Each exposure was 15 min in duration with the substrate being changed between the two series.

The loss of heptane during the successive 15-min exposures is shown as a function of exposure number in the two plots on the left of Figure 3-10. With each successive exposure, a lesser fraction of the heptane is converted; a clear indication of substrate deactivation. The largest relative decline, as expected, was between the first and second exposure in each plot.

The y-intercept ratios for these same two series of runs are shown in the two plots on the right of Figure 3-10. As previously discussed, this ratio is a measure of continuing substrate activity. At equivalent temperatures, the relative declines in the y-intercept values are similar in magnitude to the relative declines in heptane loss. This indicates that the higher levels of

Figure 3-10. Successive 15-min exposures of *n*-heptane to gasified shale. Top: 600°C; Bottom: 650°C; Left: fraction converted; Right: y-intercept ratios (baseline/expose).

substrate deactivation between the first and second exposures are not due solely to loss of the high initial activity, but to declines in the more constant, continuing substrate activity as well. This is not unexpected. Although there were obvious differences in the initial portions of the hydrocarbon-loss curves, the curves shown in Figure 3-9 indicate that the amount of loss attributable solely to the initial-high-activity interval was relatively small compared to the total loss. What this means with respect to the KENTORT reactor is that, even if a strategy or treatment were devised to totally eliminate the initial high activity of the processed oil shales, the impact on oil yield may not be that substantial.

Plots of the m/e-70/100 ion ratios are shown in Figure 3-11a for the first and fifth exposures of the multiple-exposure sequence conducted at 600 °C. The relative increase in the intensity of the m/e-70 ion during the exposure interval is attributed primarily to increased production of 1-pentene, an anticipated product from free-radical cracking of *n*-heptane (m/e 100). There is an inverse relationship between the shape of these pentene/heptane ion curves and the single/multiple-exposure curves for heptane/argon that were shown in Figure 3-9. These similarities further support the contention that the initially high level of heptane loss was due to product cracking, not diffusion or adsorption. Similar behavior for the pyrolyzed and combusted shales for the single- and multiple-exposure runs was also observed.

Before concluding that the apparent increase in the relative concentration of pentene during exposure was due to increased cracking of heptane, the possibility that pentene production remained relatively constant and that the shape of the pentene/heptane ion curves merely reflect changes in the concentration of heptane must also be considered. Plots of the m/e-70/40 (pentene/argon-Figure 3-11b) ion ratios for the same two exposures revealed curve shapes more similar to those previously shown for heptane/argon in Figure 3-9. That is, the concentration of pentene during the initial exposure to fresh substrate was low, relative to that from subsequent exposures. This suggests that the high initial conversion of heptane did not result in a comparable increase in the formation of pentene. However, as discussed, the pentene/heptane plot (Figure 3-11a) showed that the concentration of pentene was relatively higher in the initial exposure interval to fresh shale than in later intervals during the exposure. Taken together, the two plots in Figure 3-11 suggest an intermediate level of heptane cracking to form pentene from the initial to the subsequent exposure. One interpretation is that the initially high rate of conversion of heptane is attributable to more than one source. The observation that the formation rate for pentene increased more than the loss rate of heptane declined (Figure 3-11a) implies that a portion of the higher initial activity was due to increased cracking. On the other hand, the decrease in the absolute concentration of pentene (Figure 3-11b) immediately following exposure to fresh substrate suggests that either a portion of the heptane loss was due to other mechanisms, such as diffusion into pores or surface adsorption, or that the higher initial substrate activity also resulted in higher destruction rates of the newly formed pentene molecules. Studies of relatively labile normal and cyclic alkenes, to be shown later, indicate the latter does occur to some extent. Regardless of the mechanism of heptane conversion, it is clear from these runs that the level of conversion was significantly greater during an initial exposure to fresh substrate.

The mechanism by which the shale substrates were deactivated is uncertain. Although there is some disagreement,¹⁶ deactivation of cracking catalysts is presumed to proceed via deposition of carbon onto the catalyst surface. In a similar manner, carbon deposition has been proposed¹⁹ as the reason for deactivation of oil-shale surfaces.

Figure 3-11. Ion-intensity ratios from an initial and a subsequent exposure of *n*-heptane to the same load of gasified shale at 600 °C. a) pentene/heptane (m/e 70/100); b) pentene/argon (m/e 70/40).

Catalyst deactivation via deposition of coke has been categorized as either direct or indirect. In *direct deactivation*, carbon deposits obstruct access to the active surface sites. As the thickness of the deposit increases, the rate of hydrocarbon cracking is thought to be mass-transfer limited. That is, the time required for the hydrocarbon to diffuse through the carbon layer limits cracking reactions. In *indirect deactivation*, the substrate pores become blocked by carbon thereby lowering the accessible surface area. A prior study showed the measured surface area of shale substrates decreased during exposure but to a much lesser extent than did substrate activity.¹⁷ However, results from that study must be viewed with caution as interaction between the coke deposits and gases (N₂ or CO₂) used to measure surface area render such measurements suspect.

An alternate explanation is that the nature of the carbon on the pyrolyzed and gasified substrates affects the activity of the substrate and that such effects vary with time. As the experiment proceeds, it is conceivable that the pool of surface carbon interacts with freshly deposited carbon and disproportionates to release small gaseous hydrocarbons relatively rich in hydrogen leaving a more aromatic residue on the substrate surface. Studies conducted with commercial cracking catalysts have shown that the H/C molar ratio of coke does in fact decrease

over time simultaneously with catalyst deactivation.¹⁶ Unfortunately, this scenario cannot explain the apparent deactivation also observed for the combusted shale which has little or no accessible carbon prior to exposure. It is possible that carbon coverage of catalytic surface sites, obstruction of interior particle surfaces, and alteration of the structure of the inherent substrate carbon all contribute to the decay in substrate activity. However, as in prior studies, the relative contribution of these factors cannot be deconvoluted here.

3.2.4.2.4. The effect of thermal pretreatment on cracking activity. The objective of this segment of the study was to determine if the thermal-pretreatment step used in this, as well as in some prior investigations, had a measurable effect on the cracking activity of the substrates. In these tests, heptane was passed over a substrate which had either been subjected to a thermal soak at 660 °C for 30 min prior to exposure at 600 °C or heated directly to 600 °C and exposed as soon as thermal equilibrium was established. Each exposure was for 15 minutes in duration.

Visual examination of the conversion curves for heptane revealed no qualitative differences in curve shape between the thermally treated and non-treated runs. The fraction of heptane loss and corresponding y-intercept ratios are shown in Figure 3-12. The trends in both plots are the same, showing insignificant difference in substrate activity with the possible exception of the pyrolyzed shale. Though only two runs each were made for samples of pyrolyzed shale that either had or had not been thermally treated, *t*-test comparisons of the average loss values (0.124 vs. 0.175) yielded a calculated *t*-value of 4.36. At a 95% confidence level, the corresponding tabular value of 4.30 suggests this difference was probably significant despite the small number of runs. Statistical evaluations conducted on larger data sets to be presented later, support this conclusion.

Pyrolyzed shale is the only processed-shale substrate for which altered activity might be anticipated following a thermal pretreatment. This is because the gasified and combusted shales had previously experienced temperatures in excess of 700 °C during preparation. In contrast, the pyrolyzed shale was prepared at 530 °C and so may be expected to undergo additional pyrolysis when exposed to higher temperatures. This would lead to additional evolution of carbon which would likely alter the surface characteristics of the particles and, as a result, potentially alter their catalytic activity as well. Thus, the conclusion that the catalytic activity of the pyrolyzed shale seems to have been altered by thermal pretreatment, whereas the activity of the gasified and combusted shales remained unchanged, is not unreasonable.

3.2.4.2.5. Adsorption and desorption studies. Due to substantially shorter integration intervals, numerical integration instead of integration of the fitted equations was used to measure the level of adsorption and desorption of *n*-heptane. Figure 3-13 shows the adsorption of heptane during the 30-s interval immediately following valve switch as a function of temperature and substrate type. Adsorption onto sand was either essentially zero or more likely, adsorption onto sand in the substrate reactor was offset by an equivalent level of desorption in the bypass reactor following the valve switch.

In addition to being plotted as fractional losses, the adsorption of heptane shown in Figure 3-13 is also expressed as mL of heptane adsorbed per gram of substrate. It is notable that the relative magnitude of heptane adsorption over the three substrates followed the same order as previously shown for cracking losses at higher temperature; gasified shale > pyrolyzed shale

Effect of Thermal Pretreatment
(Gasified shale; 600C; n-heptane)

Effect of Thermal Pretreatment
(Gasified shale; 600C; n-heptane)

Figure 3-12. The effect of thermal pretreatment on substrate activity. Top: Fraction loss of n-heptane at 600 °C, 15-min exposure. Bottom: y-intercept ratios (e/d).

> combusted shale. This was despite the fact that the combined volume in the meso and macro pores, as well as the BET surface area, was somewhat greater for the combusted shale as will

Figure 3-13. Adsorption of *n*-heptane during the 30-s interval immediately following valve switch as a function of substrate and temperature.

be discussed later. This means that not only was adsorption higher in absolute terms for the pyrolyzed and gasified shales, but adsorption per unit of surface area was greater as well.

Besides physical differences in surface areas and pore-size distributions, the primary differences in bulk chemical composition between the three shale substrates were the carbon content and the oxidation state of iron. Carbon content (Table 3-1) was highest in the pyrolyzed shale (9.6 wt%) followed by the gasified (7.3%) and combusted shales (1.7%). The bulk of the inorganic matrix was comprised of clays and silicates whose forms are apparently not chemically altered during gasification and combustion but which do undergo some disruption of crystallinity as a function of processing temperature.²⁰ On the other hand, the principal iron mineral in raw shale is pyrite, FeS_2 , with lesser quantities of iron silicates. For the most part, the principal iron-containing minerals are pyrrhotite (FeS) following pyrolysis, magnetite (Fe_3O_4) following steam gasification, and hematite (Fe_2O_3) following combustion.²¹ It is unlikely that the adsorption characteristics of the oxidized iron minerals in the gasified and combusted shales were sufficiently different to account for the relatively large differences in adsorption measured between these two substrates. Considering that total surface areas for the gasified and combusted shales are not that dissimilar, then, by the process of elimination, the logical conclusion is that the enhanced adsorption capacity of the pyrolyzed and gasified shales was due to their higher inherent carbon content. This is not an unreasonable deduction considering the high adsorptive capacity of charcoal, though high surface area plays a significant role in the latter.

3.2.4.3. Statistical evaluation of the n-heptane data set.

3.2.4.3.1. Heptane cracking losses. Tables 8 contains selected statistical analyses of the heptane loss ratios derived from integration of the fitted equations (Eq. 1 and 2). Only losses during the initial 5 minutes of exposure are considered (all exposures were for at least 5-min). Single- and multiple-exposure runs conducted at equivalent temperatures are treated separately.

Although the loss of heptane was consistently greater over pyrolyzed than over combusted shale at all temperatures, the 95% confidence intervals (Table 3-7) indicate this difference was insignificant except at 300 and 350 °C. Losses over gasified shale, however, were significantly greater by this criterion than over either of the other two substrates at 600 °C and greater than over combusted shale at 300, 350, 400, and 650 °C.

When the 95% confidence-interval method was used to compare losses over the same substrate at different temperatures, only the gasified shale exhibited a significant difference in conversion between any two sets of data at adjacent temperatures (at 600 and 650 °C). However, confidence intervals calculated with tabular t_i values at 90% probability (not shown) indicated that the measured differences in loss between all three substrates was probably significant ($p < 0.10$) at all temperatures except 400 and 450 °C.

With respect to differences in heptane losses for the single- versus the multiple-exposure runs, the t -interval approach gave mixed results. Single-exposure losses over combusted shale were significantly greater at 600 °C ($p < 0.05$) with an insufficient number of runs to make such a comparison at 650 °C. For gasified shale, this difference was also significant ($p < 0.05$) at 600 °C but not at 650 °C. There were no significant differences in the losses measured over pyrolyzed shale at either of these temperatures.

× Adsorption ○ Desorption

Figure 3-14. Comparison of the adsorption and desorption of *n*-heptane during the 30-s interval immediately following valve switch as a function of substrate and temperature.

Table 3-7. Statistical evaluation of the fractional losses for the *n*-heptane runs as determined by integration of the fitted equations (Equations 1 and 2).

n-heptane loss (5-min)											
Temperature (C)	300	350	400	450	500	550	multiple 600	multiple 650	single 800	single 850	
Combusted											
runs (n)	3	3	3	3	3	3	3	3	6	1	
maximum	0.0129	0.0102	0.0060	0.0072	0.0203	0.0460	0.0566	0.1277	0.1285	0.1031	
minimum	0.0113	0.0078	0.0045	0.0027	0.0102	0.0188	0.0428	0.0851	0.0858	0.1031	
mean (x')	0.0123	0.0093	0.0053	0.0056	0.0138	0.0327	0.0499	0.1097	0.1052	0.1031	
s (n-1)	0.0008	0.0013	0.0008	0.0025	0.0057	0.0141	0.0069	0.0221	0.0166		
%rsd	6.6	14.1	14.6	44.0	41.2	43.3	13.9	20.1	16.7		
t (95% conf.)	4.303	4.303	4.303	4.303	4.303	4.303	4.303	4.303	2.571		
x'+ts/n^(1/2)	0.0143	0.0126	0.0073	0.0117	0.0278	0.0678	0.0671	0.1645	0.1226		
x'-ts/n^(1/2)	0.0103	0.0061	0.0034	-0.0005	-0.0003	-0.0025	0.0327	0.0549	0.0878		
Gasified											
runs (n)	3	4	3	4	4	3	6	3	13	4	
maximum	0.0400	0.0381	0.0231	0.0249	0.0291	0.0764	0.2212	0.4220	0.3414	0.4358	
minimum	0.0296	0.0209	0.0194	0.0138	0.0177	0.0570	0.1595	0.3255	0.1683	0.3887	
mean (x')	0.0345	0.0299	0.0208	0.0183	0.0219	0.0636	0.1785	0.3514	0.2565	0.4182	
s (n-1)	0.0052	0.0070	0.0020	0.0048	0.0050	0.0111	0.0237	0.0294	0.0529	0.0205	
%rsd	15.2	23.5	9.8	26.3	22.7	17.5	13.4	11.6	20.6	6.0	
t (95% conf.)	4.3030	3.1820	4.3030	3.1820	3.1820	4.3030	2.5710	3.1820	2.1790	4.3030	
x'+ts/n^(1/2)	0.0475	0.0411	0.0258	0.0259	0.0298	0.0912	0.2014	0.4054	0.2884	0.4624	
x'-ts/n^(1/2)	0.0215	0.0187	0.0157	0.0106	0.0140	0.0359	0.1517	0.2974	0.2245	0.3741	
Pyrolyzed											
runs (n)	4	4	3	3	3	3	3	1	5	2	
maximum	0.0367	0.0179	0.0184	0.0143	0.0145	0.0378	0.1200	0.1644	0.1750	0.2200	
minimum	0.0240	0.0138	0.0077	0.0054	0.0079	0.0187	0.0886	0.1644	0.1235	0.2031	
mean (x')	0.0281	0.0166	0.0139	0.0096	0.0110	0.0253	0.1040	0.1644	0.1452	0.2118	
s (n-1)	0.0059	0.0019	0.0055	0.0045	0.0033	0.0108	0.0157		0.0212	0.0120	
%rsd	21.0	11.2	39.8	46.4	29.7	42.8	15.1		14.6146	5.6528	
t (95% conf.)	3.182	3.182	4.303	4.303	4.303	4.303	4.303		2.776	12.706	
x'+ts/n^(1/2)	0.0375	0.0196	0.0276	0.0208	0.0192	0.0523	0.1430		0.1715	0.3190	
x'-ts/n^(1/2)	0.0187	0.0136	0.0002	-0.0015	0.0029	-0.0016	0.0650		0.1188	0.1041	

Table 3-8. *t*-Test comparisons ($p < 0.05$) of the mean loss of *n*-heptane during single-exposure versus multiple-exposure runs.

Substrate	600 °C			650 °C		
	(n_1+n_2-1)	t_t	t_c	(n_1+n_2-1)	t_t	t_c
Combusted	7	2.365	5.407			
Gasified	17	2.110	3.502	5	2.571	3.577
Pyrolyzed	6	2.447	2.882			

A more meaningful evaluation of the single- and multiple- exposure losses for heptane was provided by *t*-test comparisons of the loss means. This approach utilizes the sum of the *n*-1 values from both data sets (greater degrees of freedom), as well as a pooled variance; thus, it is more liberal in demonstrating a significant difference between means the confidence interval approach used above. Calculated *t*-values, t_c , along with the appropriate tabular values, t_t , are shown for 95% probability in Table 3-8. In all cases, the data support the conclusion that losses over each substrate were greater during a single-exposure run than during a multiple-exposure run at both 600 and 650 °C. Comparisons for combusted and pyrolyzed shales at 650 °C are not shown since an insufficient number of runs were conducted for these substrates at that temperature.

3.2.4.3.2. Analysis of variance. An analysis of variance was conducted on the fractional losses of heptane in an effort to determine if the measured differences in loss between substrates were significant when using a *pooled* data approach. This approach first assumes a common mean value for a given data set. Specified potential sources of variation may then be examined in an effort to identify those which are significant. For this evaluation, all of the multiple-exposure runs at a given temperature were treated as being part of a common set of runs, regardless of the substrate. Each substrate was then considered as a potential source of variance. Only runs conducted at 500, 550, and 600 °C were evaluated. Adsorption losses from the low-temperature runs (300-450 °C) as measured by numerical integration are examined in a subsequent section and results at 650 °C were omitted because there was only one acceptable run with pyrolyzed shale at that temperature.

The analysis of variance (ANOVA) grids are shown in Table 3-9. Comparison of calculated- and tabular-F values (F_c and F_t) shown at the bottom of each grid indicate that the

Table 3-9. ANOVA grids prepared from the *n*-heptane loss data from repeat runs.

ANOVA-500E

Source of variation	sum of squares	degrees of freedom	mean square
between substrates	2.26E-04	2	1.131E-04
within substrate	0.00016	7	2.283E-05
Variance (total)	3.861E-04	9	4.290E-05
pooled rsd (%)			15.4
F Calculated	4.96		
F table-95 % (2,7)	4.74		

ANOVA-550E

Source of variation	sum of squares	degrees of freedom	mean square
between substrates	2.470E-03	2	1.235E-03
within substrate	8.836E-04	6	1.473E-04
Variance (total)	3.354E-03	8	4.192E-04
pooled rsd (%)			28.8
F Calculated	8.39		
F table-95 % (2,6)	5.14		

ANOVA-600E

Source of variation	sum of squares	degrees of freedom	mean square
between substrates	2.92E-02	2	1.461E-02
within substrate	1.251E-02	8	1.564E-03
Variance (total)	4.174E-02	10	4.174E-03
pooled rsd (%)			59.4
F Calculated	9.34		
F table-95 % (2,8)	4.46		

substrates were a significant source of variation ($p < 0.05$) from the overall mean at all three temperatures examined. Thus, according to this analysis, the average loss of heptane was significantly different over the three processed-shale substrates, with the differences at 600 °C being highly significant ($p < 0.01$).

3.2.4.3.3. Adsorption data. *t*-Test comparisons were made of the adsorption means from the three processed-shale substrates with both calculated and tabular *t*-values (95%) from these comparisons shown in Table 3-10. These comparisons indicate the adsorption means are significantly different for all substrates at all temperatures with the exception of the pyrolyzed and gasified shales at 300 °C. The finding that the adsorption means for pyrolyzed and gasified shales were not significantly different at 300 °C was an unexpected result since one would anticipate that the differences between means would be greatest at the lowest temperature. It is believed that the overlap in the pyrolyzed and gasified shale adsorption means reflected an inadequate equilibrium time following cool-down from the high-temperature, thermal pretreatment step rather than insignificant differences in adsorption capacities. Instead of permitting the reactor to cool completely, the furnace was often opened slightly in order to attain the target temperature of 300 °C more rapidly. This may have resulted in non-reproducible temperature gradients across the reactor and likely explains the higher level of scatter at this temperature.

3.2.4.4. Studies of benzene, toluene, and *n*-decane.

3.2.4.4.1. Fractional losses. Loss values for all runs conducted with benzene are plotted in Figure 3-15a, whereas Figure 3-15b shows average losses for both the single- and multiple-exposure runs (boxes enclose the average single-exposure run values). Analogous plots are shown for toluene and *n*-decane in Figure 3-16 and Figure 3-17, respectively. The procedure followed for the multiple-exposure runs was somewhat different for these three hydrocarbons. For benzene, as was the case for *n*-heptane, multiple-exposure runs entailed initially exposing a given substrate at 300 °C and proceeding in succession to 650 °C in 50 °C increments. For toluene and *n*-decane, the initial exposure was made at 600 °C which was then followed by the 300-650 °C exposure series. As shown in the next section, these differences in procedure had a substantial impact on the adsorption capacity of the substrates.

The extent of benzene and toluene conversion was relatively low with loss differences being statistically insignificant for all three substrates. On the other hand, the conversion of *n*-decane was substantial for all three substrates with relative conversion being significantly greater for gasified shale than for pyrolyzed or combusted shale at temperatures above 550 °C. The relative substrate-activity order for decane was gasified > pyrolyzed > combusted; the same as previously observed for heptane. However, although the conversion of decane appeared to be greater for the pyrolyzed shale relative to the combusted shale, the average conversions over these substrates were not significantly different ($p < 0.05$). The similarity in the level of conversion of decane over these two substrates can perhaps be interpreted as an increasingly important role of substrate surface area during exposure to less volatile hydrocarbons.

In terms of the single- versus multiple-exposure runs, the average level of conversion of benzene was slightly higher for the single-exposure runs, but not significantly so. Similarly, average toluene conversion was greater for single exposures at temperatures of 550 °C and higher. However, due to the small number of single-exposure runs that were conducted, only the

Table 3-10. *t*-Test comparisons of the mean adsorption levels for *n*-heptane that were determined by numerical integration.

Temperature (C)	300	350	400	450
Comparison of combusted-gasified adsorption means				
s-pooled	0.0274	0.0140	0.0131	0.0070
freedom	3	4	3	4
t-calc	6.116	9.356	7.291	9.989
t-table	3.182	2.776	3.182	2.776
Comparison of pyrolyzed-gasified adsorption means				
s-pooled	0.0396	0.0188	0.0125	0.0070
freedom	5	6	4	5
t-calc	1.306	3.271	4.845	8.052
t-table	2.571	2.447	2.776	2.571
Comparison of pyrolyzed-combusted adsorption means				
s-pooled	0.0376	0.0188	0.0063	0.0042
freedom	4	4	3	3
t-calc	3.496	4.302	6.571	4.355
t-table	2.776	2.776	3.182	3.182

Figure 3-15. Integrated fractional losses for benzene as a function of temperature. Top: all runs. Bottom: average data with single-exposure averages shown enclosed in a box.

Figure 3-16. Integrated fractional losses for toluene as a function of temperature. Top: all runs. Bottom: average data with single-exposure averages shown enclosed in a box.

Figure 3-17. Integrated fractional losses for *n*-decane as a function of temperature. Top: all runs. Bottom: average data with single-exposure averages shown enclosed in a box.

difference in conversion over gasified shale at 600 °C was significant. Single-exposure runs with decane were only conducted at 600 °C. Comparisons at this temperature indicated that loss of decane during the single-exposure runs was significantly greater than during the multiple exposures for all three substrates. Based on these results along with reasonably good precision for the multiple-exposure runs and the results from reproducibility studies with *n*-heptane, it is concluded that hydrocarbon conversion over fresh substrates (single exposure) was greater than over previously-exposed substrates (multiple exposure) for these three hydrocarbons.

Combined plots of the average losses for benzene, toluene, heptane, and decane are shown in Figure 3-18 as a function of substrate. Average losses from multiple-exposure runs are shown at all temperatures with average single-exposure losses (boxed) shown at those temperatures where available.

In those runs conducted at higher temperatures (550-650 °C), the conversion of decane was greater than conversion of the other hydrocarbons for all three substrates. With the exception of combusted shale at 550 °C, the conversion of heptane over this temperature range was also greater than was conversion of benzene or toluene, again for all three substrates. Losses for benzene and toluene during multiple-exposure runs were essentially the same for all substrates at all temperatures, including 650 °C. However, single-exposure losses for toluene were, on average, greater than for benzene. Notably, no differences in conversion trends were apparent between the four hydrocarbons as a function of substrate type.

3.2.4.4.2. Adsorption capacities. Low-temperature adsorption as a function of substrate is shown in Figure 3-19. At equivalent temperatures, adsorption was greatest for the gasified shale and lowest for the combusted shale, the same as the relative order of hydrocarbon loss at higher temperatures. As before, this order runs counter to the meso plus macro pore volumes from mercury porosimetry and to the BET surface areas, both of which were somewhat greater for the combusted shale. Since hydrocarbon adsorption does not correlate with surface area or pore volume, the adsorption capacity must be governed by some other parameter. As discussed before, the most likely parameter is the inherent carbon in the substrate.

With respect to hydrocarbon type, the relative order and magnitude of adsorption was quite unexpected. As anticipated, adsorption of decane was greatest for all three substrates, but the magnitude of adsorption relative to heptane was not as large as might be predicted based on boiling points, particularly for the pyrolyzed shale. More surprising was that larger amounts of benzene than toluene were adsorbed for all three substrates. These deviations in hydrocarbon adsorption from what might be anticipated are attributed to differences in the run procedure. As described earlier, the multiple-exposure runs with benzene and heptane were initiated with fresh loads of substrate at 300 °C, whereas, runs with toluene and decane were initiated with fresh substrates at 600 °C, then subsequently subjected to the 300-650 °C series. Thus, prior to the adsorption runs at low temperature, the substrates had been previously exposed to toluene and decane at high temperature. This likely resulted in coke deposition onto the substrates and, perhaps to some extent, obstruction of the substrate pores.

To investigate the possibility that prior exposure not only reduced cracking activity, but adsorption capacity as well, an earlier series of toluene runs was re-examined. These runs were initially rejected due to transient instrumental difficulties. Although the majority of the runs in

Figure 3-18. Comparison of losses for benzene, toluene, heptane, and decane as a function of exposure temperature. Losses represent averages from multiple-exposure runs unless shown within a box which indicates single exposures.

Figure 3-19. Average hydrocarbon adsorption as a function of exposure temperature.

Comparison of toluene adsorption over
exposed and non-exposed combusted shale

Comparison of toluene adsorption over
exposed and non-exposed gasified shale

Comparison of toluene adsorption over
exposed and non-exposed pyrolyzed shale

exposed substrate
 fresh substrate

Figure 3-20. Comparison of the adsorption of toluene onto samples of fresh substrates versus samples that had been previously exposed to toluene at 600 °C.

the initial set were not usable, several of the low-temperature runs were suitable for adsorption measurements. For these earlier runs, low-temperature exposures were conducted with fresh loads of substrate that had not been exposed to toluene at high temperature. This provided a means to compare the otherwise equivalent adsorption measurements from substrates that had been initially exposed to toluene at 600 °C. These comparisons are shown in Figure 3-20. The increase in toluene adsorption for the fresh substrates was substantial, ranging from 2-4 times that for the previously exposed substrates. Furthermore, the amount of toluene adsorbed onto the fresh substrates was greater than the amount of benzene adsorbed onto comparable substrates (unexposed), as would be expected.

The conclusion drawn from the multiple-exposure adsorption studies was that prior high-temperature exposure to hydrocarbons lowered the adsorption capacity of the substrate. In addition, although the surface area of the substrate no doubt plays an important role, it is apparently not the only parameter that governs the magnitude of adsorption, with the inherent carbon content of the substrate believed to play a significant role as well.

A final point on hydrocarbon adsorption concerns the relatively constant ratio between the amount of hydrocarbon that was adsorbed and that which was desorbed in a given run. These ratios are illustrated in Figure 3-21 as a function of substrate (top) and hydrocarbon (bottom). Although there is a significant level of scatter in these plots, there is no apparent trend with respect to either substrate or exposure temperature. The absence of a trend with respect to temperature is important because it implies that adsorption of hydrocarbons over this temperature range was reversible. This follows from the expectation that had there been non-reversible cracking losses, such losses would be increasingly significant at the higher temperatures and, therefore, a direct correlation between temperature and the adsorption/desorption ratio should be apparent. In other words, these plots provide evidence that non-reversible cracking reactions were not significant for these hydrocarbons up to temperatures of 450 °C.

The one exception may be for decane which exhibits an increase of about 50% in the adsorption/desorption ratio at 450 over that at 400 °C. However, the absolute amount of decane adsorbed at this temperature was relatively low. This means that small errors in the adsorption or desorption measurement could lead to relatively large errors in the ratio between the two. On the other hand, small levels of decane cracking losses would also have a large impact on this ratio. Examination of the y-intercept ratios from Equations 1 and 2 do not indicate a significant level of decane cracking at 450 °C. Therefore, the increase in the adsorption/desorption ratio at 450 °C for decane is concluded to be due to random scatter and not cracking losses, though the latter cannot be entirely dismissed.

3.2.4.5. Cracking losses for the complete hydrocarbon data set.

As described in the Experimental section, numerous problems were encountered in the early stages of this investigation. These problems render the results obtained early in the project both less reliable and less suitable for direct comparison with results obtained later. Nonetheless, results from these initial tests are presented with the disclaimer that the analytical precision is not as good as that for the hydrocarbons discussed to this point, that is, hydrocarbons other than benzene, toluene, *n*-heptane, and *n*-decane. Unfortunately, there were generally an insufficient number of suitable runs from the early studies to conduct a statistical evaluation; usually only

Figure 3-21. Adsorption/desorption ratios over the temperature range of 300-450 °C as a function of substrate (top) and model hydrocarbon (bottom).

one measurement was made for a given set of conditions.

For the most part, multiple-exposure runs were conducted in the later studies with benzene, toluene, heptane, and decane with only single-exposure runs conducted prior to these hydrocarbons. At 600 °C, single-exposure data are available for all hydrocarbons examined. However, at the other significant cracking temperatures of 550 and 650 °C, often only multiple-exposure data are available for benzene, toluene, and decane. As was shown for these hydrocarbons and heptane, cracking activity declined for those substrates that had been previously exposed (multiple-exposures) relative to fresh, unexposed substrates (single-exposures). Therefore, the substitution of multiple-exposure for single-exposure data in the plots to follow will be indicated in the discussion that accompanies the plots.

High-temperature losses during the initial five minutes of exposure are shown in Figure 3-22 to Figure 3-24. Figure 3-22 shows losses for a series of single-ring aromatics with *n*-alkyl side chains containing 0, 1, 2, or 4 carbons. All values for benzene at 550 °C, toluene-combusted at 550 °C, and benzene-gasified and benzene-pyrolyzed at 650 °C, are from multiple-exposure runs. As noted before, benzene and toluene, both of which have high thermal stability, exhibited minimal loss over all three substrates. On the other hand, over 40% of the butylbenzene was converted during exposure to gasified shale at 600 °C. Butylbenzene losses at 650 °C were so extensive that data collection was suspended for these runs. The magnitude of the losses measured for the single-ring aromatics is consistent with previous studies which showed the reactivity of alkylated aromatics to be directly proportional to the length of the alkyl side chain.²²

Figure 3-23 shows hydrocarbon losses for a series of C₆ hydrocarbons that include an aromatic, aliphatic, olefinic, cyclic aliphatic, and cyclic-olefinic component. As before, all values for benzene loss at 550 °C, and benzene-gasified and benzene-pyrolyzed losses at 650 °C are from multiple-exposure runs. Losses of C₆ hydrocarbons were generally greatest over gasified shale at all temperatures with losses over pyrolyzed shale being generally equal to or greater than that over combusted shale. The cyclic olefin was by far the most labile, followed by the straight-chain olefin. However, the measured loss of cyclohexane was assumed to be erroneously low due to ring cleavage to form 1-hexene. This relatively high-yield cracking product has the same molecular ion as, and is thus indistinguishable from, the parent cyclohexane in this experiment. In addition to the induced cleavage reactions, conversion of cyclohexane and cyclohexene may also proceed via ring dehydrogenation ending in the formation of stable benzene molecules. Such reactions will be shown to be a significant route for conversion of cyclic alkanes and olefins in the next section.

Analogous plots for a set of *n*-alkanes and α -olefins are shown in Figure 3-24. All losses for decane at both 550 and 650 °C, as well as the values for heptane at 550 °C are from multiple-exposure runs. Again, the alkenes were more readily converted, particularly at the lower reaction temperature. As expected, some of the measured loss was clearly related to chain length. Assuming loss of *n*-alkanes proceeds via thermal cleavage of carbon-carbon bonds via a free radical intermediate, then the measured loss should be roughly proportional to the number of aliphatic C-C bonds in the molecule, that is, 5 for hexane, 6 for heptane, etc. This was approximately the relative magnitude of loss observed. Although it is somewhat unclear from this plot, the contribution to hydrocarbon loss attributable to chain length relative to the

Figure 3-22. Relative cracking losses for single-ring aromatic hydrocarbons at 650 (top), 600 (center), and 550 °C (bottom).

Figure 3-23. Relative cracking losses for C₆ hydrocarbons at 650 (top), 600 (center), and 550 °C (bottom).

Figure 3-24. Relative cracking losses for *n*-alkanes and α -olefins at 650 (top), 600 (center), and 550 °C (bottom).

contribution by the double bond in olefins may be more important at higher temperature where the conversion of decane was greater than that of 1-hexene. Admittedly, the decane data at 550 °C represent multiple-exposure results which would explain, to an extent, the lower loss of decane relative to hexene at this temperature. However, conversion of decane at 600 °C in multiple-exposure runs (not shown) was greater than conversion of hexene in analogous runs. This reversal in the relative conversion for 1-hexene and decane as a function of temperature is perhaps explained by assuming a portion of the olefins are converted by a limited number of active surface sites. At higher temperatures, this type of conversion would be concentration (active site) limited with total conversion governed more by a combination of surface area and inherent carbon effects. On the other hand, these trends may simply reflect greater scatter in the measurement of 1-hexene conversion because the precision of the 1-hexene measurements was such that the observed conversion trends cannot be shown to be significant.

In summary, the cracking losses presented for the full hydrocarbon data set indicate increasing lability with increasing chain length for paraffins and olefins and that single-ring aromatics tended to be more stable but did exhibit a rapid increase in conversion with increasing length of the alkyl chains attached to the ring. In comparing the relative conversion of hydrocarbons with equivalent carbon numbers, 1-*n*-alkenes were shown to be more labile than *n*-alkanes and less labile than cyclic olefins. Single-ring aromatics were shown to be substantially more stable than comparable alkanes and alkenes when no more than one carbon was attached to the ring and continue to be less labile than alkanes and alkenes containing an equivalent number of carbon atoms.

3.2.4.6. *Dehydrogenation of cyclohexane and cyclohexene.*

As discussed in the Experimental Section, QMS measurements in the log-histogram (LGH) mode were terminated midway through the study because of the significantly longer scan times required in this mode, and an apparent lack of useful information being acquired. However, following the realization that cracking losses for cyclohexane and cyclohexene were relatively high, whereas the corresponding carbon depositions were disproportionately low, these data were re-examined for evidence of dehydrogenation reactions.

Only two LGH runs were available for cyclohexane, representing exposure to gasified and to pyrolyzed shale. The absolute ion intensities (as opposed to HC/Ar ratios) for six ions from these runs are shown in Figure 3-25. In addition to the mass 84 ion (cyclohexane), ion intensities are shown for masses 18 (H₂O), 56 (C₄H₈), 78 (C₆H₆), 80 (C₆H₈), and 82 (C₆H₁₀).

The mass-56 ion is believed to represent mostly butene, an anticipated cracking product from cyclohexane. The intensity for this ion decreased during exposure along with that of the parent-ion (m/e 84) intensity indicating that a significant portion of the mass-56 ion was formed from cyclohexane inside the ion source of the spectrometer. The other hydrocarbon masses (78, 80, and 82) either remain constant or increase during exposure. The C₆H₁₀ (mass 82) ion, which is attributed primarily cyclohexene (some hexadiene), exhibits a noticeable increase during exposure for both substrates. However, the increase in this ion is much less than that observed for the mass-78 ion (benzene). Also, the relative rate of formation of benzene versus cyclohexene appears to be greater during exposure to the pyrolyzed shale. Considering that the pyrolyzed shale contains more surface carbon or *char*, this finding is consistent with a previous

Figure 3-25. Ion intensities during exposure of cyclohexane to gasified (top) and pyrolyzed (bottom) shales. 550 °C; 10-min exposure; log-histogram-collection mode.

study which showed that charcoal catalyzes aromatization reactions.²³

Curiously, the C_6H_8 ion which is believed to represent mostly cyclohexadiene (and some hexatriene), did not increase during exposure despite the fact that it is a likely intermediate in the formation of benzene. There are several possible explanations which may account to some extent for the low levels of cyclohexadiene. It is likely that the rate of formation of benzene from cyclohexadiene is greater than the rate of formation of cyclohexadiene and thus newly formed cyclohexadiene would be rapidly depleted. Secondly, cyclohexadiene molecules that escape the reactor are likely to undergo substantial conversion to benzene within the ion source. Third, a portion of the cyclohexane, and perhaps neo-formed cyclohexene, goes directly to benzene while adsorbed onto the substrate surface, thus releasing little of the intermediate cyclohexadiene to the gas phase. It is also interesting to note that the benzene-ion curve was similar in shape to that of H_2O and 1-pentene collected during an exposure to fresh substrate as previously shown.

Regardless of the mechanism of benzene formation, the important point is that a significant portion of the cyclohexane was apparently dehydrogenated during exposure with little evidence of significant ring cleavage reactions. Dehydrogenation reactions have been assumed to occur during pyrolysis and are often proposed as perhaps being significant for cyclic aliphatics. However, to our knowledge, this has only been inferred from analysis of the product oil before and after exposure to hot-shale surfaces, not directly as shown here.

Similar plots are shown for cyclohexene (C_6H_{10} , mass 82) in Figure 3-26 with the results from a combusted-shale run included. Similar to cyclohexane, Figure 3-26 suggests that the high levels of conversion measured for cyclohexene were, to a large extent, due to dehydrogenation reactions. Unlike the results for cyclohexane, the substantial increase in the C_4H_8 ion indicates that ring-cleavage reactions are also a major route for the conversion of cyclohexene. As can be seen, formation of benzene was again pronounced, increasing between one and two orders of magnitude over the level formed in the ion source. Further, the relative increase in benzene production as a function of substrate type followed the same order as measured throughout the study for HC cracking and adsorption loss--gasified > pyrolyzed > combusted.

Production of C_6H_8 (cyclohexadiene) increased during exposure of cyclohexene to pyrolyzed and combusted shales but declined slightly for gasified shale. This is believed to be due to higher levels of ring-cleavage losses over the more active gasified shale as indicated by the substantially higher relative intensity of the C_4H_8 ion during exposure. That is, cyclohexadiene was likely formed during exposure of cyclohexene to gasified shale as evidenced by a higher m/e -80/82 ratio relative to the bypass mode. However, because there was a significantly lower concentration of cyclohexene in either the reactor or the ion source from which to form C_6H_8 , this ion exhibited a net decrease in intensity during exposure.

Although the demonstration of a substantial level of dehydrogenation reactions for cyclic hydrocarbons during exposure to processed shales is important, the most surprising result in Figure 3-26 comes from the C_6H_{12} -ion-intensity curve (mass 84; cyclohexane or hexene). This mass exhibits a clear increase during exposure to all three substrates, ranging from about one order of magnitude for combusted and pyrolyzed shales to about two orders of magnitude for gasified shale. Since the mass of this ion is two amu higher than cyclohexene, this curve

Figure 3-26. Ion intensities during exposure of cyclohexene to combusted (top), pyrolyzed (center), and gasified shales (bottom). 550 °C; 10-min exposure; log-histogram-collection mode.

provides evidence of hydrogen-addition reactions during exposure. There are several possible pathways to the formation of the C_6H_{12} molecules such as disproportionation in the adsorbed phase, transfer of hydrogen from surface-coke deposits, and free-radical addition or hydrogen abstraction. Since cyclohexene would be the primary source of the hydrogen being incorporated, such reactions might be expected to be concentration dependent. However, considering that the cyclohexene feed rate was the same for the three processed shales, it appears that the relative formation rates of the C_6H_{12} molecules was related to the overall rate of conversion in these runs. One possibility is that higher cracking rates over the gasified shale may have resulted in higher concentrations of free radicals within the reactor. Such species may then more readily abstract hydrogen in either the condensed or vapor phase to form higher molecular-weight cyclohexane or hexene molecules. Alternatively, higher rates of hydrocarbon coking could result in additional amounts of an active coating of coke from which hydrogen could be transferred to adsorbed-phase cyclohexene. On the other hand, the increase in mass may be explained more simply by the greater tendency of hydrocarbons to adsorb onto the gasified shale. This would lead to higher concentrations of adsorbed cyclohexene to undergo disproportionation reactions. Regardless of the mechanism, this was an interesting finding which, to our knowledge, has not previously been reported.

A final point on the role of dehydrogenation reactions concerns the results obtained for 1-hexene collected in the LGH mode. These results, which are not shown, imply that dehydrogenation is also an important mechanism of conversion for this C_6 analogue as evidenced by a substantial level of C_6H_6 (benzene) formed during exposure. In order to generate C_6H_6 from hexene, cyclization reactions must be involved. The generation of benzene from 1-hexene was much lower in magnitude than for the cyclic hydrocarbons, as one would anticipate. In summary, the studies with straight-chain and cyclic- C_6 hydrocarbons provide strong evidence for cyclization and dehydrogenation reactions that are often assumed to be important during pyrolysis of oil shales.

3.2.4.7. Carbon deposition.

Carbon and hydrogen analyses for samples of the parent, thermally-treated, and exposed substrates are shown in Table 3-11. The thermally-treated substrates were prepared in the cracking reactor by heating samples of the processed shales to 660 °C under flowing N_2 and then cooling and unloading without exposing the substrate to a hydrocarbon. The exposed substrates represent samples of processed shale that were exposed to benzene, toluene, heptane, or decane in either a multiple-exposure series (no designation), single-exposure runs (denoted by an S), or multiple exposures at one temperature (denoted by an M). The average standard deviation from repeat analyses was $\pm 0.12\%$ carbon. This deviation is quite large relative to the increase in carbon content of the substrate following exposure, resulting in a substantial scatter in the carbon deposition trends.

Comparison of the average carbon content of the parent shales (PRT) and the corresponding thermal blanks (BLK) in Table 3-11 illustrates an important point. For the combusted shale, these values were essentially the same (1.70 and 1.69%). However, the carbon content for the gasified blank was 0.09% lower and for the pyrolyzed blank was 0.17% lower than the values for the corresponding parent shales. Based on *t*-test evaluations, the respective differences in carbon content between the parent and thermal-blank samples of gasified and

Table 3-11. Elemental analyses of the parent, thermal-blank, and exposed shales. Values are from the multiple-exposure A-H series except those marked S-single exposures; M-multiple exposures at one temperature; BLK-thermal blank; and PRT-parent.

Substrate	Highest Expos. Temp (C)	Exp. Time (min)	HC	# runs	% C Avg.	% C Std. Dev.	% C % rsd	% H Avg.	H/C Molar Ratio
COMB-PRT				4	1.70	0.063	3.7	0.13	0.90
GASIF-PRT				4	7.33	0.023	0.3	0.12	0.19
PYR-PRT				4	9.61	0.100	1.0	0.49	0.62
COMB-BLK	660	10		4	1.69	0.182	10.8	0.12	0.87
GASIF-BLK	660	10		3	7.24	0.014	0.2	0.09	0.15
PYR-BLK	660	10		4	9.44	0.133	1.4	0.18	0.23
SAND-BLK	660	10		1	0.00			0.00	
COMB	650	15	benzene	2	1.84	0.042	2.3	0.14	0.91
GASIF	650	15	benzene	2	7.75	0.078	1.0	0.15	0.22
PYR	650	15	benzene	2	10.00	0.071	0.7	0.29	0.34
SAND	650	15	benzene	3	0.07	0.046	69.3	0.06	
COMB	650	15	decane	2	1.82	0.170	9.3	0.09	0.59
GASIF	650	15	decane	2	7.71	0.587	7.6	0.14	0.22
PYR	650	15	decane	2	10.11	0.021	0.2	0.25	0.29
SAND	650	15	decane	3	0.00	0.000		0.06	
COMB	650	15	heptane	4	2.02	0.063	3.1	0.26	1.51
COMB-S	600	15	heptane	5	1.72	0.057	3.3	0.18	1.29
COMB-S	650	15	heptane	3	2.01	0.119	5.9	0.18	1.08
GASIF	650	15	heptane	4	7.44	0.103	1.4	0.19	0.31
GASIF-M	651	15	heptane	1	7.83			0.12	0.18
GASIF-M	600	15	heptane	1	7.71			0.14	0.22
GASIF-S	600	15	heptane	13	7.33	0.056	0.8	0.13	0.21
GASIF-S	650	15	heptane	3	7.40	0.142	1.9	0.16	0.25
PYR	650	15	heptane	4	10.06	0.045	0.4	0.30	0.36
PYR-S	600	15	heptane	6	9.76	0.171	1.8	0.25	0.31
PYR-S	650	15	heptane	2	9.91	0.049	0.5	0.31	0.38
SAND	650	15	heptane	4	0.01	0.008	81.6	0.09	
SAND-S	599	15	heptane	8	0.06	0.045	72.4	0.04	7.20
SAND-S	649	15	heptane	1	0.08			0.08	
PYR-S	550	20	heptane	1	9.69			0.23	0.28
ZEOLITE	550	20	heptane	1	0.29			0.04	1.66
COMB	650	5	toluene	2	2.35	0.127	5.4	0.21	1.07
GASIF	650	5	toluene	2	8.08	0.396	4.9	0.17	0.25
PYR	650	5	toluene	2	10.20	0.071	0.7	0.34	0.40
SAND	650	5	toluene	3	0.07	0.059	87.9	0.07	

pyrolyzed shales were highly significant ($p < 0.01$). These results illustrate that thermal evolution of the inherent-substrate carbon is significant for both gasified and pyrolyzed shales but insignificant for the combusted shale due to the lower starting concentration of carbon in that substrate. Such thermal losses were not always considered in previous studies suggesting such studies may have underestimated the extent of coke formation onto both pyrolyzed and gasified shales but not onto combusted shale. This would make the combusted shale appear to be more catalytically active, relative to the pyrolyzed and gasified shales, than it actually is.

The average H/C molar ratios for the pyrolyzed substrates are plotted against total carbon in Figure 3-27. Comparison of the parent and thermal-blank samples illustrate that not only was the inherent-carbon content reduced during the thermal-blank run, but that on a relative basis, the inherent-hydrogen content was reduced substantially more, to about one-third of its original level. All other points represent substrate values following a multiple-exposure-series run with either benzene, heptane, toluene, or decane. These points show that as carbon deposits accumulated on the pyrolyzed shale during exposure, the resulting H/C molar ratios were higher than in the thermal blank. This implies that the H/C molar ratio of freshly-deposited coke was higher than that of the char remaining after thermal treatment. Furthermore, the H/C ratios of the fresh-coke deposits were approximately the same regardless of the hydrocarbon to which the substrate was exposed, similar to findings from studies of coke deposition onto industrial cracking catalysts.^{13,16}

In the plots to follow, the increases in substrate-carbon content resulting from high-temperature exposures were calculated as the increase above that of the appropriate thermal-blank-carbon value instead of above that of the parent shale. In addition, because of relatively high uncertainties in the elemental-analysis data, emphasis will be given to carbon deposition during the benzene-, toluene-, heptane-, and decane-exposure runs since at least two runs were made for these hydrocarbons under a given set of conditions. The lone exception was for the multiple-isothermal exposures of heptane to gasified shale. For these two sets of runs, elemental analysis was conducted in duplicate on splits of the exposed substrates.

The absolute increases in the carbon content of the substrates following exposure are shown in Figure 3-28 as a function of the substrate (top) and the hydrocarbon (bottom). Generally, coke deposition was greatest for toluene as a function of hydrocarbon and for pyrolyzed shale as a function of substrate. Measurable amounts of coke deposition onto sand were observed only during exposure to the two aromatic hydrocarbons.

To obtain an estimate of the relative rate of coke deposition versus the rate of total carbon loss to cracking reactions, the amount of carbon deposited onto each substrate as coke was ratioed to the amount of carbon contained in the hydrocarbons that were cracked during the same exposure. Such a ratio provides a rough measure of the portion of the carbon involved in cracking reaction which is converted to coke (Figure 3-29).

There are a variety of errors that are propagated in the calculation of the coke fraction: uncertainty in the extent of thermally-induced losses of the inherent-substrate carbon, scatter in the elemental analyses, and errors in the losses measured by the QMS. Of these, the uncertainty in the extent of thermally-induced carbon loss is believed to be the most significant. These errors combine to render the results in Figure 3-29 suspect, particularly for the pyrolyzed and, to a

Figure 3-27. H/C molar ratios of pyrolyzed shales as a function of total carbon. Except for parent and thrmal blk samples, analyses were conducted on substrates following a multiple-exposure series with either benzene, toluene, heptane, or decane.

lesser extent, gasified shales because of the higher initial levels of carbon on these two substrates, i.e., more susceptible to thermally-induced carbon losses and, perhaps, to additional losses induced by interactions between the inherent carbon and the model hydrocarbon during exposure. Nonetheless, certain trends in this plot are as expected. For example, a greater portion of the carbon involved in cracking reactions partitioned to the coke phase for the more thermally stable aromatic hydrocarbons--benzene and toluene. On the other hand, both heptane and decane which exhibited relatively high cracking losses exhibited much lower relative levels of coke formation. The trends in coke formation, when combined with carbon deposition and the cracking losses previously shown, demonstrate that overall cracking losses were much higher for the *n*-alkanes, with coke formation being lower on a relative basis and about the same on an absolute basis compared to the two aromatic hydrocarbons. Further, it appears that a generally higher proportion of the cracked hydrocarbons partitioned to coke during exposure to pyrolyzed and gasified shales. This is again in contrast to prior studies which reported higher rates of coke deposition onto combusted shale. A portion of this difference is likely explained by the fact that thermally-induced carbon losses from the pyrolyzed and/or gasified shales were not taken into account in the prior studies. However, it should be noted that even without the correction for thermal losses of carbon that were used to prepare these plots, the level of coke deposition was

Increase in substrate carbon content
(absolute increase over thermal blank)

Increase in substrate carbon content
(multiple exposure, A-I series)

Figure 3-28. Absolute increase in carbon content of the substrates above the appropriate thermal-blank value during exposure. Shown as a function of hydrocarbon (top) and substrate (bottom).

Carbon loss to coke (per cent of total carbon loss)

Figure 3-29. Percentage of the carbon involved in cracking reactions that is converted to coke shown as a function of substrate.

generally the same as or greater onto pyrolyzed and gasified shale than onto combusted shale.

A similar plot of coke deposition onto gasified shale during exposure to heptane is shown in Figure 3-30. From left to right, the five sets of bars in this plot represent: five consecutive 15-min exposures at 600 °C to the same load of substrate; four consecutive 15-min exposures at 650 °C to the same load of substrate; the average of two multiple-exposure series (300-650 °C); the average of 13 single-exposure runs conducted at 600 °C for 15 minutes each; and the average of three single-exposure runs conducted at 650 °C for 15 minutes each. In addition to showing the per cent of the reacted carbon which is converted to coke, this plot also shows the apparent rate of coke deposition (weight of carbon deposited divided by the exposure time). Judging from the data in Figure 3-30, it appears that even with numerous sources of error, this approach provided a reasonable level of precision when at least two substrates were analyzed.

Figure 3-30 shows that the rate of coke formation was greater for the 650 °C runs. However, the fraction of carbon in these runs that was involved in cracking reactions and that was ultimately converted to coke was about the same or slightly lower than for the otherwise similar, 600 °C runs.

Another interesting detail from this plot is that, although it was previously shown that the rate of cracking loss declined with increasing exposure time, the rate of coke deposition

Coke formation (*n*-heptane/gasified shale runs)

Figure 3-30. The fraction of total carbon loss to coke (left axis and hatched bars) and the rate of coke formation (right axis and solid bars) during exposure of *n*-heptane to gasified shale.

apparently did not decline, at least not as rapidly. This can be seen by comparing the rate of deposition between the 1st and 4th or between the 2nd and 5th pair of bars in Figure 3-30. The first and fourth pair of bars represent deposition rates measured at 600 °C for an exposure-interval equivalent of either 75 or 15 minutes, respectively. The second and fifth pair represent deposition rates at 650 °C for exposure-interval equivalents of either 60 or 15 minutes, respectively. The coke-deposition rates at these temperatures are essentially the same indicating little deactivation of the substrate over time with respect to coke deposition, i.e., a near constant rate of coke deposition. Such trends have been noted in catalyst-deactivation studies in which cracking activity declined with on-line time, but the rates of coke deposition remained essentially constant well after the high initial cracking activity had decayed.^{13,16} Coking of shale oil onto oil-shale substrates has been shown to follow a similar trend.^{1,24}

Runs that were conducted early in the investigation typically consisted of only one run under a given set of conditions. Unfortunately, scatter in the substrate-carbon analyses was so great as to render the carbon analyses from these single runs essentially unusable. Therefore, the increases in carbon content for substrates exposed for 60 min at 550 °C are shown in Figure 3-31 with little comment other than to make two points. In general, coke deposition was greater for olefinic and aromatic hydrocarbons than for straight-chain or cyclic aliphatics and carbon deposition was unusually low for cyclohexane and cyclohexene in spite of their high levels of conversion. The latter is consistent with the substantial conversion via dehydrogenation for these

Changes in the substrate carbon content during a 60 minute exposure at 550C.

Figure 3-31. Increase in the carbon content of the processed shales as a function of the hydrocarbon to which they were exposed. Exposures conducted for 60 min at 550 °C.

cyclic hydrocarbons as previously shown.

3.2.4.8. Surface area and pore volumes of the shale substrates.

It is generally accepted that surface area is one of the parameters that governs, and can therefore be used to predict, the activity of industrial cracking catalysts. Two techniques are most commonly used to measure surface area--gas adsorption and mercury porosimetry. Gas adsorption is usually applied to the measurement of surface areas within smaller diameter pores. For instance, when using N_2 as the adsorbing gas, this equates to pore diameters equivalent to the molecular diameter of N_2 (about 0.7 nm) up to an ambiguous upper limit of about 3-5 nm. Mercury porosimetry is limited to the measurement of pore volumes within particle pores that are greater than approximately 3 nm in diameter. Together, these methods provide a measure of the total surface area within particle pores that range from just under one nm to about 500 nm. Both techniques have weaknesses such as dissolution of the measurement gas into certain substrates or the creation of additional pores due to the use of Hg under high pressure. Nonetheless, they

provide reasonably precise measurements when applied to solids that have relatively large surface areas. On the other hand, neither technique is considered highly reliable when applied to solids with low surface areas such as those being examined here.

Surface areas as determined by N₂ BET analyses are shown in Table 3-12. Surface area measurements for the combusted shale were reasonably precise but were highly scattered for the pyrolyzed and gasified shales. Thus, the BET values for surface area in the plots to follow are accompanied by a high level of uncertainty.

BET surface areas are shown plotted in the top of Figure 3-32 with total surface area (BET + mercury porsimetry) shown on bottom. For the parent samples, surface area appears to be highest in the combusted shale (15 m²/g is still relatively low) and lowest in the pyrolyzed shale. This is the same order areas previously reported for these substrates.^{5,17} The surface areas for the thermal blanks was quite unexpected indicating that surface area is essentially the same for all three substrates following a thermal soak at 660 °C. Comparison to the matching parent sample indicates the combusted shales were relatively unaffected but substantial increases in surface area were induced in the gasified and pyrolyzed samples by the thermal-pretreatment step. The top plot indicates these increases were due almost entirely to increases in surface area within micro pores (BET area) which, because of size restrictions, are mostly inaccessible to the hydrocarbons examined here. However, as noted above, the relative standard deviations from replicate analyses of the pyrolyzed and gasified thermal-blank samples (81 and 86%) render the BET values in Figure 3-32 highly suspect, thus precluding reliable conclusions from BET data.

Following exposure, the surface areas for the combusted shale exhibited little change from that of the corresponding parent or thermal-blank samples. Surface areas of the pyrolyzed and gasified shales following exposure tended to be lower than those for the corresponding thermal blanks but higher than the parent values. Again, it is difficult to draw reliable conclusions about the relative surface areas of these substrates considering the scatter in the BET analysis. Thus, the BET data will not be discussed further.

Measurement of surface areas and pore volumes by mercury porsimetry is restricted to pores with diameter greater than about 3 nm (meso and macro pores). This is not believed to be a problem because, due to size restrictions, pores smaller than about two nm are considered too small to participate in the cracking of the model hydrocarbons.

A listing of the average pore volumes and surface areas within meso plus macro pores (>3 nm) is given in Table 3-13. Due to large relative standard deviations as shown for both measurements, the differences in pore volume or surface area cannot be shown to be statistically significant between the three parent shales or the thermal blanks. As with the BET surface areas, the uncertainty in pore volumes or surface areas determined by mercury porsimetry was too great to relate these parameters to substrate activity with any significant level of confidence.

Nevertheless, the average surface areas and pore volumes from mercury porsimetry are plotted in Figure 3-33 for the parent, thermal-blank, and exposed substrates. The single exposure values plotted in Figure 3-33 were derived from exposures to heptane at either 600 or 650 °C whereas the multiple-exposure values represent the 300-650 °C multiple-exposure series, also with heptane. In spite of the high level of analytical scatter, the trends in these plots are

Table 3-12. BET surface areas for processed-shale substrates.

Substrate	Treatment ^a	n	Area (m ² /g)	Std. Dev.	rsd (%)
Comb	Parent	4	10.4	1.28	12.4
Comb	Thrml blk	4	9.5	1.43	15.2
Comb	Single	3	8.5	0.44	5.2
Comb	Mult	4	8.7	0.31	3.6
Gasif	Mult-600	1	23.6		
Gasif	Mult-650	1	8.7		
Gasif	Parent	5	11.4	8.01	70.4
Gasif	Thrml blk	4	10.0	8.61	85.9
Gasif	Single	2	6.0	1.65	27.5
Gasif	Mult	4	13.0	9.41	72.7
Pyrol	Parent	6	1.5	0.30	20.3
Pyrol	Thrml blk	6	14.1	11.36	80.6
Pyrol	Single	2	2.5	0.23	9.1
Pyrol	Mult	4	2.5	0.28	11.5

^aThrml blk = thermal blank samples; Single = Single exposure runs; Mult = multiple

remarkably similar for all three substrates, particularly with respect to the pore volume measurements. In both plots, the values for the parent-combusted shale were somewhat greater than the analogous values for the pyrolyzed- and gasified-parent samples.

The apparent differences in pore volume or surface area between the parent and corresponding thermal-blank samples were also statistically insignificant for all three substrates. However, pore-volume and surface-area values were unexpectedly greater for the exposed substrates than for the corresponding unexposed substrates in all cases. These differences were significant (95% probability) according to *t*-test comparisons of the mean values for the gasified and the pyrolyzed shales but not for combusted shale. The reason for this increase in surface area and pore volume following exposure to hydrocarbons is unknown but is conjectured as due to the high surface area of the coke deposits.

It would not appear that the substrate parameters of surface area or pore volume correlate with the cracking activity reported earlier in this section. That is, the relative cracking-activity order was determined to be gasified > pyrolyzed > combusted, whereas the relative surface areas

Figure 3-32. BET and total surface areas for samples of parent, thermal-blank, and exposed substrates. Top: N_2 -BET surface areas. Bottom: Total surface areas (BET + Hg porsimetry).

Table 3-13. Surface areas and pore volumes for the processed shale as measured by Hg porsimetry (>3-nm-pore diameter).

Substrate	Treatment ^a	n	SURFACE AREAS			PORE VOLUMES		
			Area (m ² /g)	Std. Dev.	rsd (%)	Volume (cm ³)	Std. Dev.	rsd (%)
Comb	Mult	4	4.73	1.61	34.1	0.224	0.008	3.6
Comb	Single	3	6.30	0.96	15.2	0.221	0.009	4.2
Comb	Thrm1 blk	4	4.75	3.86	81.3	0.152	0.083	54.3
Comb	Parent	4	4.29	2.53	58.9	0.150	0.079	52.9
Gasif	Mult	4	4.59	2.57	55.9	0.155	0.009	5.8
Gasif	Single	2	4.63	3.62	78.2	0.159	0.021	12.9
Gasif	Thrm1 blk	4	3.52	2.67	76.0	0.102	0.055	54.4
Gasif	Parent	5	2.87	2.43	84.6	0.092	0.048	52.2
Gasif	Mult-600	1	1.27				0.065	
Gasif	Mult-650	1	2.34				0.060	
Pyrol	Mult	4	5.85	4.00	68.4	0.124	0.022	17.4
Pyrol	Single	2	6.69	3.48	52.0	0.132	0.011	8.6
Pyrol	Thrm1 blk	5	3.38	2.89	85.3	0.085	0.046	53.9
Pyrol	Parent	5	3.44	2.87	83.2	0.074	0.039	52.4
Sand	Parent	4	0.00				0.000	

^aMult = Multiple exposure A-H series; Single = single exposure runs; Thrm1 blk = Thermal blank samples; Mult-600 = five exposures at 600 °C over single substrate load; Mult-650 = four exposures at 650 °C over single substrate load.

or pore volumes (>3 nm pores) appears to follow the order of combusted > gasified ≥ pyrolyzed.

Previous studies of the coking of shale oil over processed oil-shale substrates have either demonstrated or speculated on a general relation between surface area and carbon deposition.^{3,4,25,26} Such studies have typically focused on the coking of relatively large shale-oil molecules (the heavy fractions have been shown to be the most labile) and have generally relied on BET-surface-area measurements. However, due to size restriction as discussed above, attempting to correlate coking activity with the surface area within micro pores (BET area) may not be a relevant parameter for relating coke formation from an oil with an average molecular weight on the order of 400 amu.²⁷

In addition to the potential error of including micro-pore surfaces, it is difficult to directly compare the results of previous studies which focused on carbon deposition from less volatile, heteroatom-rich, shale oils to this study, which measured the cracking of volatile, non-polar hydrocarbons. Surface area is no doubt an important parameter with respect to the absolute

Figure 3-33. Pore volumes and surface areas within meso + macro pores (>3 nm) for samples of the parent, thermal-blank, and singly- and multiply-exposed substrates.

catalytic activity of the substrate. However, it is also possible that in addition to surface area, the carbon which is inherent to the pyrolyzed and gasified shales and the nature of this carbon plays a significant role. Such surface carbon may tend to retain the more volatile hydrocarbons examined in this study, thereby providing additional time for reaction. This conjecture is supported by the trends in hydrocarbon adsorption observed at lower temperatures. On the other hand, the less-volatile shale oils would more likely condense and react more indiscriminately as a function of the accessible surface area of the substrate, which appears to be slightly greater in the combusted shale.

3.2.4.9. Evidence for a free-radical-cracking mechanism.

Typical loss curves for *n*-heptane obtained during an initial and a subsequent exposure to gasified shale were previously shown in Figure 3-9. This plot revealed an obvious difference in curve shape (cracking activity) during the first 1-2 minutes of exposure and was interpreted as evidence that the initially-high substrate activity was real and not an anomaly of the technique.

Somewhat unexpected were the $\text{H}_2\text{O}/\text{Ar}$ (m/e 18/20) ion-ratio curves (Figure 3-34) obtained from the same two exposures. Comparison of the curves in Figure 3-9 and Figure 3-34 reveals an inverse relation between the evolution of water and the loss of heptane, with the rate of change in concentration of both being quite pronounced during the early portion of the exposure interval to fresh substrate. The origin of the H_2O is unknown. It is believed to originate from either hydrated minerals that may participate in the cracking reaction, perhaps during carbon deposition, or from reactions between chemisorbed oxygen and the model hydrocarbon. The role of the H_2O (or oxygen) is also unclear. That is, does the substrate water participate directly in the reaction by catalyzing hydrocarbon cracking (perhaps as chemisorbed oxygen) or was evolution of mineral-bound moisture merely catalyzed by the substitution of coke into the mineral lattice?

One approach to resolving these questions is to examine the cracking products generated during the initial period of an exposure to fresh substrate for evidence of a reaction mechanism which differs from that which governs the later portion of the same exposure. Accordingly, cracking products were collected over timed intervals during exposure of heptane to either gasified shale or to an acid-zeolite catalyst. Capillary chromatograms of cracking products collected during these runs are shown in Figure 3-35 along with a listing of peaks identified by GCMS. The top chromatogram is of products collected during the first two minutes of exposure to gasified shale. The middle chromatogram is of products collected between 12 and 19 minutes of the same exposure. The bottom chromatogram is of products collected during exposure of heptane to an acid zeolite catalyst. Several of the peaks in these chromatograms are labelled with a number which corresponds to the hydrocarbons listed on the right side of the figure. Peak numbers which are neither encircled nor in a box are listed to the right of the top chromatogram and denote components detected in all three chromatograms. The boxed numbers in the center chromatogram denote components that are present in the top two chromatograms derived from the gasified-shale exposures but that are not detected in the chromatogram of the zeolite-derived products. Likewise, the encircled numbers in the chromatogram of zeolite-derived products (bottom) represent components that were not detected in either of the top chromatograms.

If the higher initial activity of the oil shale was due to acidic surface sites, then the

Figure 3-34. Water/Ar ion ratios during an initial (a) and a subsequent (b) exposure of *n*-heptane to the same load of gasified shale at 600 °C.

cracking products generated during this interval should show evidence of formation via an ionic intermediate, namely, more branched hydrocarbons.¹³ Comparison of the cracking products in the top two chromatograms of Figure 3-35 (from exposure to gasified shale) reveal only minor differences in component concentrations, most of which may be explained as differences in trapping efficiency between the two collections. The product suite in both of these chromatograms is enriched in 1-alkenes, components which are produced in relatively high abundance during free-radical cracking of alkanes.¹³ There are no peaks which appear in either of these chromatograms which do not appear in the other. In contrast, the circled peak numbers in the chromatogram of the zeolite-derived products at the bottom of Figure 3-35 denote branched hydrocarbons generated during exposure to the zeolite catalyst. The peak labels shown encircled were produced in relatively high abundance during exposure of heptane to the zeolite catalyst but were not detected in the top two chromatograms derived from the gasified shale. Analogous chromatograms of the products collected during exposure of heptane to combusted and to pyrolyzed shales were qualitatively similar to those from gasified shale, differing somewhat in component concentrations but not in composition. Together, these chromatograms provide strong evidence that acid catalysis does not play a significant role during the exposure, even during the initial high-activity interval. Thus, it would appear that free-radical cracking is the dominant reaction mechanism throughout the exposure interval.

Capillary Chromatograms of *n*-Heptane Cracking Products

Figure 3-35. Chromatograms of cracking products from *n*-heptane collected from: A) 0-2 minutes of an initial exposure to gasified shale; B) 12-19 min of the same exposure; and C) 0-2 min of an exposure to zeolite catalyst.

A final point on this topic concerns the plots previously shown in Figure 3-11. This figure showed plots of the m/e-70/40 (pentene/Ar) and the m/e-70/100 (pentene/heptane) ion ratios obtained from the same initial and subsequent exposures shown for the H₂O/Ar ratios in Figure 3-34. GCMS analysis of the heptane-cracking products showed the m/e-70 ion to be essentially all 1-pentene and as stated before, 1-alkenes are high-yield products from free-radical cracking.¹³ Thus, the plots in Figure 3-11 and Figure 3-34 along with GCMS analysis of the heptane-cracking products reveal that the production of 1-pentene followed a similar trend to that of water evolution and heptane conversion. In other words, production of 1-pentene during the initial high-activity interval was also enhanced. This further supports the contention that hydrocarbon cracking proceeded predominantly via a free-radical mechanism throughout the exposure interval.

3.2.4.10. Implications for KENTORT II.

The results presented in the model hydrocarbon study support the general conclusion that the use of fewer higher temperature particles for heat transfer is more detrimental to vapor-phase hydrocarbons than is use of more lower temperature particles. In other words, in order to transfer a given quantity of heat to the pyrolysis bed of the KENTORT reactor, it would be better to transfer this heat with greater quantities of cooler particles than with fewer higher temperature particles. There is, however, a limit as to how far this reasoning may be extended. For example, assuming no conductive heat losses from the reactor, theoretically it is possible to recycle solids whose temperature is, for instance, one degree above the targeted pyrolysis temperature. This would require a very high ratio of recycled to raw-shale-feed particles in order to attain the targeted pyrolysis temperature. By increasing the recycled-particle temperature to two degrees above target, this ratio would be cut in half. In this instance, the detrimental effect of the slightly higher temperature would be more than offset by such a drastic reduction in the number of *hot* particles recycled to the pyrolyzer. This line of reasoning can be extended but a point is quickly reached at which further reductions in the number of particles being recycled does not compensate for the detrimental effects of the higher temperatures required for those particles. Thus, in general terms, the temperature of the recycle particles must be held to a reasonable minimum. However, the optimum combination of recycle temperature and recycle rate can only be addressed in a KENTORT-prototype reactor in which shale oil is being freshly generated and exposed to recycled particles as described earlier in this chapter.

The next question is then, what is the optimum composition for this recycle stream in terms of the ratio of gasified to combusted shale. Although previous coking studies conducted with shale oil indicated that gasified shale is the preferred heat carrier, results shown here clearly demonstrate that gasified shale was more active than combusted shale, at least with respect to the more volatile, non-polar hydrocarbons examined in this study. With the exception of one portion of the study by Rubel et al.,³ previous studies showed that shale oils tend to coke at higher rates onto the combusted-shale surfaces. Considering that the hydrocarbons examined in this study are more representative of the lighter components found in shale oil, that is, the more valuable components, it can be inferred that a high ratio of combusted to gasified shale should be used for heat transfer. This is because the combusted shale, with its higher surface area, appears to selectively deplete the less valuable heavy-oil components (and perhaps heteroatom containing components) whereas gasified shale may be more detrimental to the more volatile and

more valuable hydrocarbons. Therefore, even though the extent of coking of shale oil may be greater over combusted shale than gasified shale, the implications of the combined results from this and prior studies indicate a potential improvement in oil quality may be realized by using greater quantities of combusted shale for heat transfer than previously believed. However, such reasoning is not in complete agreement with the results from a prior study in which shale oil was found to coke more rapidly over combusted shale but the oil produced with gasified-shale recycle tended to be of higher quality in terms of a lower molecular weight, viscosity, and density and a higher volatility and H/C ratio.^{28,29} It should also be noted that the prior conclusion that combusted shales was the more active substrate was not confirmed by the results of this study. On the other hand, this prior conclusion cannot be refuted by this study due to the reasons discussed above, that is because of differences in volatility of the hydrocarbons examined. Additional discussion and possible reasons for this discrepancy are given in the Summary section.

It was demonstrated in this investigation that the magnitude of cracking reactions at high temperature declined as a function of exposure time for all three shale substrates. It is believed that this loss in activity following exposure of the substrates to hydrocarbons at high temperatures may provide a means to lessen oil losses during solids recycling, e.g., exposing the solids to be used for heat transfer to less valuable hydrocarbons before routing them to the pyrolysis bed.

Finally, it is clear that cracking and coking reactions do not proceed at the same rate for different hydrocarbon types. For instance, olefins are selectively eliminated by exposure to all three of the processed shales and particularly by the gasified shale. The gasified shale also tends to more rapidly dehydrogenate cyclic olefins and aliphatics. Thus, the oil product can be controlled to some extent by variation of the recycle ratio and recycle composition. This must also be considered when selecting the final operating conditions.

3.2.5. SUMMARY.

The reactor and measurement system constructed for this investigation provide a novel means for measuring adsorption and cracking of hydrocarbons over solid substrates at elevated temperatures. A major advantage of this apparatus relative to many of those used in prior investigations was a short vapor-phase residence time (about 0.2-0.5 s within the substrate bed) which is similar to that for the oil products generated in a fluidized-bed reactor.

The relative extent of both adsorption and cracking losses of hydrocarbons over the processed shales generally followed the order of gasified > pyrolyzed > combusted for all of the hydrocarbons examined. This order of substrate activity differs from that reported in most prior coking studies of shale oil in which, with one exception, combusted shale was reported as being the most active. However, these previous studies relied entirely on measuring the carbon content of the shales before and after exposure to the shale oil in order to determine the extent of coke deposition. Thus, these differences in substrate activity order may well be due to the loss of inherent carbon from the pyrolyzed and gasified shales which were shown to be a potentially significant factor in this study. When the appropriate corrections were made for thermal evolution of the substrate carbon, it was determined that the order of carbon deposition as measured by elemental analysis generally correlated with the order of hydrocarbon-cracking

activity as determined by mass-spectrometric measurements.

Another possible explanation of the differences in substrate activity order is that the inherent carbon on the pyrolyzed and gasified shales may tend to retain lighter, more volatile hydrocarbons such as those examined here, thereby providing additional time for reaction. This reasoning is consistent with the observed trends in hydrocarbon adsorption as a function of substrate. On the other hand, less volatile shale-oil components, may tend to condense and react more indiscriminately as a function of the available surface area of the substrate, which was highest in the combusted shale.

In addition to the potentially greater impact of surface area on less volatile hydrocarbons, carbon deposition onto the shale substrates in each of the prior coking studies was generally more than an order of magnitude greater than in this study. Such a high level of carbon deposition is well in excess of that needed to completely cover the accessible surfaces of each substrate with a monolayer of coke. This means that after a layer of coke was deposited onto a given substrate, subsequent hydrocarbon cracking is likely governed more by the properties of the coke layer than by the original surface properties of the non-exposed substrates. Thus, for a given surface area, these subsequent reactions should proceed at roughly the same rate regardless of the substrate, and the overall rate of deposition should therefore be proportional to the accessible surface area. The implication is that the results reported here are related more to the initial substrate activity whereas prior studies were more impacted by the rate of deposition of coke-on-coke.

Complicating the comparison of catalytic activity of the substrates was an apparent increase in cracking activity for the pyrolyzed shale following thermal pretreatment (660 °C) relative to that over pyrolyzed shales which had not been thermally pretreated. Such a thermal-pretreatment step was not used in previous coking investigations, rendering direct comparisons of the results from low- versus high-temperature exposures in those studies less reliable for the pyrolyzed shale. Thermal pretreatment of the combusted and gasified shales was found to have no measurable effect on the cracking activity of these substrates.

The magnitude of cracking reactions at high temperature declined as a function of exposure time for all three shale substrates. Similarly, the adsorption capacity of these substrates was shown to be substantially diminished following exposure to hydrocarbons at high temperature. This loss in activity following such an exposure may provide a means to lessen oil losses in the KENTORT reactor via deliberate exposure of the solids used for heat transfer to less valuable hydrocarbons (heavy oils or methane) prior to recycling to the pyrolyzer.

Each of the oil-shale substrates exhibited a relatively high initial activity that correlated with increased evolution of H₂O. The source of the H₂O is unknown but is thought to originate from either hydrated minerals or from reactions with chemisorbed oxygen.

Analysis of the cracking products revealed no evidence of significant acid catalysis during exposure. This conclusion was based on the absence of branched hydrocarbons in the cracking products that were collected during exposure of *n*-heptane to the processed oil shales. This was in contrast to the substantial quantities of branched hydrocarbons produced during an otherwise equivalent exposure to a commercial acid-zeolite catalyst. In the exposures to processed shales, the production of straight-chain cracking products and the absence of branched hydrocarbons in

both the initial and later portions of the exposure interval indicated that the primary loss mechanism throughout the exposure was free-radical cracking.

The rate of coke formation did not differ significantly between aromatic and aliphatic hydrocarbons and tended to be highest over pyrolyzed shale. However, when only those hydrocarbons which were cracked during exposure are considered, the fraction of the cracking products that partitioned to coke was much greater for the aromatic than for the aliphatic or olefinic hydrocarbons. The fraction of the cracked products that partitioned to coke was also shown to be higher at higher exposure temperatures. Unlike the decline in substrate-cracking activity with increasing exposure time, coking rates appeared to remain relatively constant throughout the exposure.

In terms of cracking rates for the different hydrocarbons, cyclic olefins were found to be the most labile followed in order by cyclic aliphatics, α -olefins, and *n*-alkanes. Small single-ring aromatics were substantially more resistant to cracking, with the relative rate of cracking for these components increasing in proportion to the length of alkyl side-chains attached to the ring. Although the cyclic olefin and cyclic aliphatic hydrocarbons studied were the most labile of the hydrocarbons examined, carbon analysis of the substrates from these runs revealed relatively low levels of coke formation. These cyclic components were converted, to a large extent, via dehydrogenation reactions, ultimately forming benzene. In the case of cyclohexene, there was a significant yield of either hexene and/or cyclohexane, both of which have a molecular weight 2 amu higher than the cyclohexene being fed to the reactor. Thus, these tests clearly showed that hydrogenation reactions also occur in addition to cyclization and dehydrogenation reactions.

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3.3 FLUIDIZED BED COKING KINETICS

3.3.1 Experimental Approach

The secondary cracking and coking of oil vapors produced from oil shale retorting have been previously shown to depend upon the nature and temperature of the substrate over which these reactions occur. To realistically examine the kinetics of these reactions during fluidized bed retorting, an apparatus was developed which permitted shale oil vapors generated continuously in one fluidized bed to pass over solid particles in a second fluidized bed. The solid particles to be contacted with the shale oil vapors could be fed in batch or continuous mode. In each mode, raw shale was fed continuously to the pyrolysis bed to create a steady stream of shale oil vapors. Coking kinetics were determined with the apparatus in the batch mode. By this method, the batch of solid particles (also referenced as "substrate" throughout the text) was heated to reaction temperature in flowing nitrogen, and was then continuously exposed to a constant concentration of shale oil vapors for a certain period of time. Carbon deposition on the solids was monitored in real-time by combusting the pyrolysis products and measuring the oxides of combustion with an on-line mass spectrometer. Detailed procedures are described in section 3.3.1.3. The extent of carbon uptake was also determined by elemental analysis of the coked solids. The apparatus was also operated in the continuous mode, where both raw shale and the solids to be tested for coking and cracking reactivity (substrate) were fed continuously, for the cracking chemistry studies which are described in section 3.4.

3.3.1.1 Shale Samples. The master sample of oil shale utilized in this study was from the Cleveland Member of the Ohio Shale from northeastern Kentucky, USA (Table 3-14). This master sample and the processed shales derived from it were used for all of the experiments described in section 3.

The shale was prepared to a size range of $-841\mu\text{m} +250\mu\text{m}$ and was used for the production of shale oil vapors and as the starting material for the generation of pyrolyzed, gasified, and combusted shale residues. Processed shales were produced at atmospheric pressure in a 7.6-cm diameter fluidized bed reactor, under conditions similar to those that occur during normal operation of the KENTORT II process. The pyrolyzed shale was produced at 530°C with nitrogen as the fluidizing gas; the gasified shale was produced at 800°C using steam; and the combusted shale was generated in air at 700°C . In addition, portions of the pyrolyzed and gasified shales were subjected to low-temperature ashing to remove carbon with minimal disturbance to the mineral matrix. Finally, a sample of the combusted shale was fluidized in steam at 730°C to study the effects of steam pretreatment on coking rates. Ultimate analyses of these materials are given in Table 3-14.

The mineralogy of Devonian oil shales is reasonably constant stratigraphically which means that all Cleveland member oil shales have approximately the same mineral composition. The silicate fraction of the shale is composed primarily of illite, which

Table 3-14. Ultimate Analyses (as-received wt% basis) of the Raw Oil Shale, Processed Shales and Reference Minerals.

	C	H	N	S	Ash
Raw Shale	16.0	1.9	0.8	1.9	74.1
Pyrolyzed Shale	9.6	0.7	0.7	1.2	84.8
Pyrolyzed-LTA	6.5	0.5	0.6	1.3	88.5
Gasified Shale	7.3	0.2	0.6	0.4	91.0
Gasified-LTA	3.3	0.1	0.5	0.4	95.4
Combusted Shale	1.4	0.2	0.6	0.2	97.0
Combusted-Steamed	1.2	0.1	0.5	0.1	97.8
Kaolin-Fine	<0.1	1.6	0.6	<0.1	85.0
Kaolin-Coarse	<0.1	1.4	0.5	<0.1	86.3
Huron Shale (illite)	0.2	0.6	0.6	1.4	92.9
Illite-Heat Treated	<0.1	<0.1	0.5	<0.1	99.1
Ottawa Sand (quartz)	<0.1	<0.1	0.3	<0.1	99.6

constitutes about 2/3 of the minerals, followed by quartz (~20%) and the clay minerals, chlorite (~10%) and kaolinite (~5%).^{1,2} Naturally occurring kaolinite, illite, and quartz samples were also tested as coking substrates. Pure chlorite occurs as thin flakes and was not amenable to fluidized bed processing, and it was not tested. Two kaolin samples (fine- and coarse-grained) obtained from a commercial mine in Georgia, USA and a low-carbon shale (high illite content) from the Huron Member of the Ohio Shale in Rowan Co., KY, USA were dried and prepared to a size range of $-841\mu\text{m} + 250\mu\text{m}$. The quartz sample was unmodified Ottawa sand ($-841\mu\text{m} + 600\mu\text{m}$). A portion of the low-carbon shale ("illite") was heat treated to 600°C in air to investigate the possible significance of oxidizing the minerals. The surface area and porosity measurements of the coking substrates (Table 3-15) show that none are especially porous materials.

3.3.1.2 Apparatus. The apparatus consisted of two vertically aligned fluidized beds (7.6-cm internal diameter) which shared a common fluidizing medium and which were heated externally by two dual-zone (each zone independently controlled) electrical resistance furnaces (Figure 3-36). The fluidizing gas, nitrogen in this study, was preheated in a separate furnace and introduced into the plenum chamber beneath the lower fluidized bed. Raw oil shale was metered by a nitrogen-purged screwfeeder into the lower fluidized bed operating at 530°C. The level of solids in the bed was held constant by a standpipe through which the pyrolyzed oil shale was removed from the reactor. The lower fluidized bed contained a baffle to narrow the residence time distribution of the solids.

In the upper portion of the apparatus, a vertical baffle divided the pipe into two unequal sections; one covered 73% of the cross sectional area and the other 27%. The larger section contained a fluidized bed of solids, and the smaller section provided a bypass-path for the fluidizing stream. The temperature of the upper fluidized bed was controlled independently from the pyrolysis bed. A semi-butterfly valve beneath the baffled section was used to select which of the routes the upward flowing vapors and gases would follow. A gas injection port was located on each side of the baffle so that gas-flow was maintained through each side of the reactor regardless of the butterfly valve position. The flow of balancing gas was important for four reasons: 1) the total flow of gas in the reactor remained constant regardless of the position of the semi-butterfly valve; 2) the upper bed always remained fluidized; 3) the balancing gas acted as a seal for the semi-butterfly valve which was not completely leak-free; and 4) it was possible for the balancing gas to have a different composition than the fluidizing gas and could have served as a pretreatment gas for the solid substrate. The flow of balancing gas was switched by a three-way valve connected in tandem with the semi-butterfly valve through a pneumatic valve actuator. The fluidizing gas flow was thus diverted simultaneously with the change in the injection point of the balancing gas. A purge gas (He or Ar) was introduced into the seal assembly of the semi-butterfly valve to inhibit coke formation within the valve assembly and to serve as a tracer gas. This tracer gas facilitated mass spectrometer analyses by correcting for pressure surges, changing flowrates, and instrumental fluctuations.

Table 3-15. Surface Area (m²/g) and Pore Volume (cm³/g) of Coking Substrates by Hg Porosimetry (macro- and meso-pores, >3.5nm dia.), and N₂ Adsorption (micro-pores, <3.5 nm dia.).

Pore Diameter	Surface Area (Pore Volume)			
	> 50 nm macro	3.5-50 nm meso	Total macro+meso	<3.5 nm micro
Pyrolyzed Shale*	2.1(0.125)	11.3(0.030)	13.4(0.155)	0.1(0.000)
Pyrolyzed-LTA	2.4(0.147)	7.3(0.025)	9.7(0.173)	na
Gasified Shale*	2.5(0.164)	9.2(0.024)	11.6(0.188)	15.8(0.034)
Combusted Shale*	3.6(0.230)	9.1(0.031)	12.7(0.261)	12.0(0.058)
Combusted-Steamed	4.0(0.252)	6.2(0.026)	10.3(0.279)	na
Kaolinite-Fine**	8.3(0.190)	13.9(0.106)	21.7(0.296)	1.1(0.001)
Kaolinite-Coarse	6.8(0.346)	3.7(0.022)	10.5(0.368)	0.5(0.000)
Illite*	1.0(0.044)	8.1(0.030)	9.1(0.074)	0.8(0.000)
Illite-Heat Tr'd	1.8(0.080)	7.6(0.023)	9.3(0.103)	0.4(0.000)
Ottawa Sand*	0.0(0.000)	1.0(0.001)	1.0(0.001)	0.0(0.000)

* average of two analyses

** average of three analyses

na- not available for analysis

Overflow pipes for the solids in the upper bed were located adjacent to the gas distributor and at 5 cm and 10 cm above the distributor (the two higher overflow pipes are not illustrated in Figure 3-36). In the coking kinetics mode of operation, the lowest port was used to completely drain the solids from the reactor once the flow of purge gas, that prevented the solids from exiting the bed, ceased. The use of the overflow pipes located high above the distributor plate would not have allowed complete drainage of the bed of solids by gravity. Coked solids were collected in a flask that had been evacuated and filled with nitrogen gas to prevent oxidation of the carbon on the hot particles.

The flows of balancing gas and the pyrolysis/ fluidization stream converged in the uppermost portion of the reactor and the mixture was then directed to two insulated cyclones in series to remove entrained fines. Most of this gas stream was then cooled and vented, but a portion was sampled at approximately 530°C at the outlet of the second cyclone and drawn through a combustion tube. The gases/vapors were withdrawn in a direction opposite to the main flow, so only very small particles could break away from the main fluid streamlines and enter the sampling tube. Oxygen was metered into the heated combustor tube downstream of the sampling location. To ensure thorough combustion, the majority of the tube was filled with a Pt/Al₂O₃ catalyst. The temperature of the combustion tube was maintained at approximately 600°C.

Following combustion, a small sample of the combustion gases was withdrawn through a 0.3 mm fused silica capillary maintained at 277°C. The sample was then routed directly to the inlet of a VG model EGA 300MM quadrupole mass spectrometer (QMS) operating in the multiple ion monitoring (MIM) mode. This mode permitted the monitoring of up to 16 masses at a more rapid rate and with greater accuracy than does, for instance, monitoring a wide mass range in an analog or log histogram mode. The masses that were selected for continuous monitoring in this study included 4 or 40 (He or Ar tracer); 12 (carbon-to confirm mass 44 intensity); 18 (H₂O); 28 (fluidization N₂); 32 (excess O₂ from the combustion tube); 44 (CO₂); 46 (NO₂); 64 (SO₂); and 42 (a typical hydrocarbon fragment to check for adequate combustor performance). All selected masses were sampled at approximately 1.5 second intervals.

3.3.1.3 Procedure. The following text describes the procedure used for the kinetic mode of operation utilizing the products of oil shale pyrolysis as reactants (Figure 3-37). After system heat-up, raw shale was metered into the pyrolysis bed with the semi-butterfly valve positioned so that the pyrolysis products bypassed the upper fluidized bed (i.e. the valve is in the "bypass" position). Once conditions reached steady state, the QMS was used to scan from 1 to 82 amu to ensure that combustion of the pyrolysis products was complete. When proper combustor operation was confirmed, the QMS was put into MIM mode and 9 selected masses (see previous section) were scanned to ensure that steady operation was achieved.

Once stable system operation was verified, a weighed aliquot of substrate was loaded into the upper fluidized bed and allowed to reach thermal steady state. The heat-up time varied from three to ten minutes depending on the solid particles that were tested. The

Figure 3-36. Schematic diagram of the dual fluidized bed reactor used for coking kinetics studies.

pressure drop across the bed was monitored because it was a direct indication of the mass of solids in the bed, and provided an on-line measure of the entrainment of particles from the bed. After conditions were again stabilized, QMS data collection was initiated. After at least 100 scans of the 9 selected masses were collected, the semi-butterfly valve was rotated so that the upper bed of solids was fluidized by the gases and vapors from the lower bed (i.e. "fluidize" position). When the selected time interval elapsed (5 to 15 minutes is typical), the valve was returned to the bypass position and the bed of solids was immediately drained from the bed by halting the flow of purge gas to the drain pipe. Ten minutes were allowed for solids to completely drain from the reactor; most exited within one to two minutes. The solid receiver flask was removed and replaced with an empty one, which was then evacuated and purged with nitrogen before the procedure was repeated. The batch of processed solids was weighed, and ultimate analyses were performed on each sample by standard methods. Surface area and pore volume measurements by Hg porosimetry and N₂ adsorption were performed on selected solid specimens.

Post-run data manipulation included taking the ratio of the combustion gas intensities to the tracer gas intensities. By doing so, changes in selected elemental concentrations, particularly carbon, were observed with minimal interference from variations in the measurement conditions that could typically occur over the course of a run. These uncontrolled measurement variations included reactor pressure fluctuations, variations in the combustor tube or capillary transfer tube flowrates, slow changes in the QMS sensitivity, etc. These variations result in absolute changes in combustion gas intensities as measured by the QMS which are unrelated to coking loss. In the absence of the carefully metered tracer gas, it would be impractical to resolve elemental changes due to coking from those due to measurement variations.

3.3.2 Method Validation

The method which was described accounted only for coking losses due to contact with solid particles. Cracking products will be identified in section 3.4, which describes the results from the continuous mode of operation. Because coking losses constitute a large portion of the oil yield reduction in solid recycle systems, and carbon deposition can affect the activity of solids, the study of coking kinetics is invaluable for yield optimization.

There were two independent measures of carbon deposition available in the kinetics mode of operation. One measure was obtained simply through elemental analysis of the coked substrate in comparison to the original substrate. An advantage of this method was that ultimate analysis is a well known and reliable technique. A disadvantage of post-run analysis of the solids was that numerous runs were required to establish the deactivation of a particular solid under a set of specific conditions as a function of time. In addition, at low conversion and short solid residence time, the analytical uncertainty of the ultimate analyses can become significant. The accuracy of the ultimate analysis is generally considered to be ± 0.1 wt%. [As an aside, the journal *Fuel* will not accept data of greater precision.] Therefore, a complementary measure of carbon deposition was developed which could provide an on-line

Figure 3-37. Diagram illustrating the valve switching sequence for the coking kinetics study.

determination of coke formation and which could possibly be more sensitive at low conversions.

In the batch mode of operation, the rate of carbon deposition onto the solid substrate can be inferred from differences in total vapor phase carbon exiting the reactor. Some success has been reported by workers in using a flame ionization detector (FID) to measure the quantity of vapor phase products during pyrolysis kinetics experiments,^{3,4,5} but the response of the FID becomes increasingly nonlinear as the molecular size of the hydrocarbons increases. In addition, the FID cannot distinguish among heteroatoms. The combustion/QMS approach was adopted because of these limitations. If combustion in the catalyst tube was complete, then linearity was not considered a problem because concentration changes of 40% or less were experienced. By monitoring the combusted pyrolysis products with a QMS, total nitrogen and sulfur deposition (or evolution) could potentially be measured as well as carbon.

A typical coking sequence is illustrated by the CO_2/Ar ratio in Figure 3-38a. For all experiments, the ion of interest was normalized by the tracer gas in order to account for differences in sampling flowrates during the course of a run. For the initial runs, helium was used as the tracer gas. However, helium-normalized baselines tended to shift excessively, which was attributed to the high rate of helium diffusion into the QMS. The tracer gas was switched to argon, and more stable baselines were then obtained. With the semi-butterfly valve in the bypass position, the CO_2/Ar ratio initially remained constant. Following the turn of the valve to the fluidize position, the ratio immediately dropped to a minimum value before it gradually returned to a steady value. The initial plunge in the CO_2/Ar ratio must be due to carbon deposition because any transient mass transfer effects were determined to occur within a second (see Appendix). Finally, when the valve was returned to the bypass position, the original baseline was restored. Similar response was observed for the NO_2/Ar ratio, and in most cases, the curves tracked the CO_2/Ar response almost exactly (Figure 3-38b). Measuring sulfur deposition as a result of oil coking was complicated because H_2S can react with the iron species in the substrates. In addition, quantifying SO_2 was found to be sensitive to sampling conditions that were not correctable by the tracer gas, especially cool spots in the sampling train where condensation occurred. Many of the SO_2/Ar response curves contained large baseline shifts that could not be explained by substrate exposure, and were considered to be unreliable for these reasons.

One concern about the apparatus was that shale oil vapors could leak into the substrate bed when the semi-butterfly valve was in its bypass position. Therefore, several blank runs were made in which batches of solids were loaded into the upper bed with the valve in the bypass position and then drained from the reactor following approximately 15 minutes. In all cases, the carbon content of the exiting solids was equivalent to or slightly less than the original carbon content. Therefore, no incidental contact with vapors was evident, and there was in fact some possible carbon loss which was likely due to methane generation by secondary pyrolysis. Another consideration was the possibility that the measured response could be due in part to carbon deposition onto the reactor walls following the switch to the fluidized mode. Figure 3-39 illustrates that a reduction in the CO_2/Ar ratio can only be due to

Figure 3-38. QMS response to shale oil vapor exposure to combusted oil shale at 530°C for 15 minutes: a) CO₂/Ar ratio (44/40 m/e ratio); b) NO₂/Ar ratio (46/40 m/e ratio).

deposition onto the solids in the upper bed. Ottawa sand, which has little potential to induce coke formation because of its minimal surface area, was used as the bed material, and no evidence of shale oil conversion is observable. Also shown in Figure 3-39 is the tracing of argon concentration which illustrates two points. The first point is that the noise associated with Ar is much lower than that of the CO₂/Ar ratio. Secondly, overall system response is very rapid as demonstrated by the negative spike in Ar concentration due to the first valve switch and the positive spike from the second valve switch. Note that after the return of the valve to the bypass position, a step increase in Ar concentration occurs because the nitrogen purge to the drain pipe is simultaneously terminated.

It is obvious from Figures 3-38 and 3-39 that there is a large amount of baseline noise. Of the nine ion intensities monitored, the four that exhibit the most noise are 12(C), 44(CO₂), 46(NO₂), and 64(SO₂), and all originate primarily from pyrolysis of the oil shale. Other m/e signals such as 32(O₂), 28(N₂) and 40(Ar) were relatively more stable and represent gases that were metered into the reactor. The primary source of noise has been determined to be fluctuations in the feedrate of oil shale to the reactor. The raw shale was fed to the reactor by a screwfeeder, and by nature, screwfeeders cannot feed solids without pulsation. To compensate, the flights of the screw were made as thin as possible. As a consequence, periodic oscillations in QMS response could no longer be discerned relative to screwfeeder speed, and the noise level was reduced. Other sources of noise which also must be considered are the chaotic nature of fluidized beds and particle-to-particle variation in the kerogen content of the raw shale.

A consequence of utilizing a fluidized bed technique is the entrainment of fines, and there is little that can be done to avoid it completely. In the current study, fines entrainment presented greater problems than just the nuisance factor associated with dust accumulation in downstream equipment. The residual organic material carried by fine particles reaching the combustion tube, rapidly combusts, and produces oxides which generate spikes in the QMS response and create another major source of noise. The raw shale was screened twice in order to exclude fines, which is a method that has been found to be just as effective as prefluidization. Nevertheless, entrainment is always a problem when fluidizing friable solids, and special efforts made to exclude fines from the combustion tube included the additions of a second cyclone and the reverse orientation of the sampling tube to the apparatus.

In the coking kinetics apparatus, fines could be entrained from both the pyrolysis and substrate beds, making it difficult to perform a mass balance on the substrate. However, from elemental analyses of the fines trapped by the cyclones, it appeared that the majority of the entrained solids originated from the upper (coking) bed. The mass of solids lost from the upper fluidized bed following a coking sequence was roughly comparable to the amount of solids collected in the cyclones. The loss of solids by entrainment was determined during operation by monitoring the pressure drop across the upper bed. In most cases, the majority of the solid loss occurred during the preheating period of the substrate, so there was little loss while the shale oil vapors were in contact with the tested substrate. Entrainment was more severe in the coking bed because the fluidizing velocity was higher than in the pyrolysis bed.

Figure 3-39. QMS response to shale oil vapor exposure to Ottawa sand at 580°C for 5 minutes: a) CO₂/AR ratio (44/40 m/e ratio); b) absolute Ar intensity (relative units).

The mass of each batch of particles contacted with oil vapor was determined from the amount of material recovered from the reactor following exposure, since it was more representative of the mass during vapor contact than the initial substrate weight. By monitoring the pressure drop across the bed throughout the procedure, it was found that most entrainment occurred during the preheating period for most of the coking substrates studied. The coarse-grained kaolinite was so friable that significant bed loss occurred during vapor/solid contact. Therefore, utilizing the final bed mass overestimated the conversion per unit mass. From pressure drop measurements, the bed loss during vapor/solid contact was estimated from a straight line correlation and the conversion was continuously adjusted for the loss of coarse-grained kaolinite.

Although the baseline noise in the QMS data was large, the conversion of shale oil vapor to coke was higher than the noise level under all the conditions of the study. Therefore, the data were determined to be suitable for further analysis. Since the amount of carbon deposited on the solid must be proportional to the area under the QMS response curve during vapor contact, the area was integrated and compared to the post-run analysis of the solids to check the validity of the QMS data. A least-squares line fitted to the baseline data before and after exposure to the solids was determined first (Figure 3-40a). The fraction of carbon loss was then determined as a function of time for each QMS data point (Figure 3-40b). Conversion was assumed to be directly proportional to the reduction in QMS response compared to the least-squares baseline. The conversion data were then integrated using the trapezoid rule, and the area under the QMS curve was related to the increase in carbon content of the substrate through a proportionality constant (Figure 3-40c). This constant was calculated by taking the ratio of the rate of volatile carbon production from the pyrolysis zone (determined by elemental analysis of the pyrolyzed shale) to the baseline CO_2/Ar ratio.

The QMS-determined carbon uptake data is compared with the data determined by post-run elemental analysis for combusted shale in Figure 3-41a. While there was a certain amount of scatter, the linear regression which was forced to pass through the origin was nearly equivalent to the unity line. However, the correlation was not as good for the other processed shales (Figure 3-41b,c). For example, gasified oil shale (Figure 3-41b), which contained approximately 7.3 wt% carbon before the coking treatment, deviated more from the unity line and contained more scatter than for the combusted shale (Figure 3-41a). The regression line had a slope of 1.115 which means that the QMS data indicated more extensive coke deposition than the ultimate analysis. One reason for this phenomenon is that during preheating, especially at temperatures above 600°C, pyrolysis of the residual carbon in the substrate may occur which could measurably lower the actual starting carbon content of the substrate and result in lower carbon deposition reported by post-run analysis. To help account for this, the initial C content of the gasified shale was assumed to be 7.1 wt% for each run, which was the value observed when gasified shale was processed in a typical coking sequence without contact with oil vapor. The results for the pyrolyzed shale deviate even further from the unity line (Figure 3-41c). Compared to the gasified shale, the carbon content of the pyrolyzed shales is higher and the organic matter is more labile, so even more extensive secondary pyrolysis is expected.

Figure 3-40. Example of data reduction results from the raw QMS responses shown in Figure 3-38a: a) least squares line fitted to the baseline data, b) fractional carbon loss, c) carbon deposition as a function of time.

Figure 3-41. Comparison of carbon uptake data as determined by the QMS and post-run elemental analysis methods for: a) combusted, b) gasified and c) pyrolyzed oil shale.

Another possible explanation for the deviation from the unity line for the gasified and pyrolyzed shales is that carbon-covered shales display reversible gas and vapor adsorption properties at high temperatures. Taulbee⁶ (1994) observed that gasified shale had higher adsorptive capacity compared to combusted and pyrolyzed shales when exposed to various model compounds. When removed from exposure to the shale oil vapors and cooled, significant amounts of gases and vapors can then desorb. A particularly conspicuous case of this is illustrated in Figure 3-42 by a peak following the switch of the semi-butterfly valve back to the bypass position. Other occurrences were generally more subtle, making compensation for the apparent desorption difficult to standardize, and no manipulation of the data was performed in this regard.

To a lesser extent, trace oxygen impurities in the fluidization gas may lead to reduced apparent carbon content of the substrate by the post-run analysis method. Partial oxidation of the high-carbon solids would be transparent to the QMS because it would become part of the CO₂ baseline, before, during, and after vapor/solid contact.

To provide further evidence that the high residual carbon content was responsible for the imperfect correspondence between the two measurement methods for the gasified and pyrolyzed shales, the agreements between the two methods for low-carbon solids are displayed in Figure 3-43. The linear regression of the illite occurs almost exactly on the unity line. However, the fine-grained kaolinite displayed a slightly larger slope than unity. This is attributed to the entrainment of fine substrate particles during carbon deposition which was originally not determined to be significant enough to require compensation, as was done for the coarse-grained sample. The results for the coarse-grained kaolinite, following compensation for entrainment, fall around the unity line.

The scatter in the data for the illite and the two types of kaolinite was approximately equivalent to that for the combusted shale. Only the increased slope of the data for the gasified and pyrolyzed shales in Figure 3-41b,c can be attributed to secondary pyrolysis or desorption because those are systematic sources of error. As will be shown in later sections of this chapter, the increased scatter for the gasified and pyrolyzed shales is mostly attributable to the relatively low rate of coke formation that occurs on predominantly carbon-covered surfaces. Because the coking rate is slow on these surfaces, baseline noise and baseline shifts by the QMS become more significant, introducing more uncertainty to the QMS data. Therefore, the on-line method of measurement for coke deposition is no more accurate at low conversion than the post-run method, but it does provide essential, real-time information about the initial rate of coking and the slowing of the coking rate as carbon continues to deposit on the substrate.

3.3.3 Results Using Post-Run Carbon Analysis

3.3.3.1 Relative Coking-Forming Affinities of the Substrates. As shown in the previous section, the determinations of carbon deposition by either the post-run analysis of the solids or the real-time integration of vapor-phase carbon reduction are equivalent. Both

Figure 3-42. Illustration of coking sequence for gasified shale at 625°C where desorption of carbonaceous material from the shale following exposure to shale oil vapors is evident.

Figure 3-43. Comparison of the QMS and post-run analysis methods for determining carbon uptake for the illite, and the two kaolinite samples.

techniques will be utilized later in this chapter to discuss the rates of carbon deposition. However, only the post-run carbon analysis data will be used in this section because, they are viewed as a way to reliably confirm the results that were generated by the real-time measurements. Even carbon deposition kinetics can be discerned in an average sense by post-run carbon analysis because a range of solid holding times (typically 5 to 15 minutes) was employed in the test matrix.

The combusted oil shale gave the highest coking activity compared to the gasified and pyrolyzed shales (Figure 3-44). Similar observations have been made by other workers,^{7,8,9,10} including a recent study by Rubel et al.¹¹ (1991). In each of the studies, it was concluded that the surface area of the substrate was an important parameter. It was also found that substrates which originally had contained large amounts of carbon had lower coking activity. The data in Figure 3-44 indicate that surface area and the initial carbon content are important factors to consider in the current study. Measurements showed that the surface areas (for pores >3.5 nm in diameter) of the three processed shales were similar (Table 3-15). Therefore, the parameter which was apparently responsible for the differences in carbon uptake was the initial carbon content (Table 3-14). The coking activity of the low-carbon substrates that were tested, showed that surface area was apparently an influential parameter (Table 3-15, Figure 3-44). The two kaolinite samples produced the highest coke formation and had higher surface areas than the illite. In the following sections, the effects of surface area and initial carbon content will be examined more closely.

3.3.3.2 Relationship of Surface Area to Coke Formation. Surface area measurements based on N₂ adsorption (BET method) and Hg porosimetry were made for uncoked and coked substrates, Tables 3-15 and 3-16, respectively. Of the uncoked substrates, significant micro-pore surface area (by N₂ adsorption) was measured for only the combusted and gasified shales. The two kaolinite samples, which had among the highest coking activities of the substrates studied, did not contain appreciable micro-pore surface area, showing that meso- and macro-pores are capable of accommodating relatively high amounts of coke formation.

The micro-porosity of all the coked substrates, except pyrolyzed shale, was essentially zero. Perhaps the additional exposure to >500°C temperatures during coking resulted in the formation of micro-porosity in the substantial residual carbon of the pyrolyzed shale. It is possible that carbon deposition blocked the micro-pores of the combusted and gasified shales, but the accuracy of N₂ adsorption measurements for these solids must also be taken into consideration. For low surface area solids (i.e. the substrates in this study), the quantity of adsorbed nitrogen is small compared to the total amount of nitrogen in the apparatus, making the accuracy of the measurement poor.¹²

This paragraph and the next are concerned with the applicability of micro-pore surface area as a parameter to characterize the coking activity of the substrates in this study based on the measurements obtained by N₂ adsorption for various processed and unprocessed substrates (Tables 3-15 and 3-16). The measured micro-pore surface areas were essentially zero for the

Figure 3-44. Carbon deposition measured by post-run carbon analysis of the solids after 15 minutes of exposure to shale oil vapors at a concentration of $8.33\text{E-}4$ gmol C/liter.

combusted shale samples that were processed in the reactor without oil vapor contact (CRK's 48-1 and 48-2 in Table 3-16). These measurements were taken well after those for the parent samples of combusted shale listed in Table 3-15. In the case of run CRK48-1, water vapor was present in the fluidizing gas while the shale was maintained at 600°C for 15 minutes. For run CRK48-2, the same procedure was performed except that water vapor was absent. It is doubtful that significant alteration of the mineral matrix could have occurred in either case, especially for the non-steam treatment, because the combusted shale was produced at a much higher temperature (700°C).

There are at least two possible explanations for the substantial differences in the measured micro-pore surface areas between the uncoked combusted shale samples. The first is that the analytical uncertainty of the N₂ adsorption technique is too great to reasonably measure the micro-porosity of the combusted shale. If this is the case, then it is difficult to predict whether significant micro-porosity actually exists. However, if micro-pore surface area is present, then it is probably low. The second possible explanation is that the N₂ adsorption measurements can be taken at face value and that the heating period in N₂ (or N₂/steam) at 600°C somehow resulted in the loss of micro-pore surface area of the combusted shale. Therefore, micro-porosity would not have been present in the combusted shale during coke formation. In either scenario, it does not appear likely that substantial micro-porosity was available for carbon deposition.

Even if the micro-pore surface areas that were measured for combusted and gasified shales prior to processing can be considered accurate, the amount of coke formation that was observed does not correlate with these values. The average molecular weight of the oil vapors from fluidized bed pyrolysis of this shale is at least 300 amu,¹³ and little access to micro-pores by such large molecules is expected. Therefore, unless otherwise indicated, the total meso- plus macro-pore surface area (pores >3.5 nm as measured by Hg porosimetry) will be utilized as the characteristic surface area in the following discussions in relation to the coking activity of the substrates in this study. The usual convention of assigning 2 nm as the division between the micro- and meso-pore ranges has been modified to 3.5 nm in this study for convenience because the Hg porosimetry procedure can only measure pore diameters above 3.5 nm.

The meso- plus macro-pore surface area of the pyrolyzed shale was actually the highest of the three processed shales, but this substrate consistently displayed the lowest rate of carbon deposition. The combusted shale had the highest surface area for pores greater than 50 nm in diameter, and the gasified shale had the highest total surface area when the N₂ adsorption data was used to include pores smaller than 3.5 nm. For these materials, it is apparent that these measures of surface area cannot alone explain the observed results. The differences in carbon content of the processed shales appear to more significantly influence the rate of subsequent carbon deposition.

Naturally occurring minerals, which were both low in organic carbon, and represent a significant portion of the mineral matrix in eastern U.S. Devonian shales, were tested as

Table 3-16. Surface Area Measurements of Coked Substrates. Micro-pores (<3.5 nm, BET), Meso-pores (3.5 - 50 nm, Hg Porosimetry), and Macro-pores (> 50 nm, Hg porosimetry).

Substrate	Temp., °C	Solid Exp. Time, min.	Surface Area, m ² /g					Run#
			Micro	Meso	Macro	Total	Mes+Mac	
Combusted	530	15	na	24.8	3.2	28.0	28.0	CRK30-6
Combusted	545	5	na	10.2	3.5	13.7	13.7	CRK25-5
Combusted	545	10	na	32.7	3.5	36.2	36.2	CRK25-6
Combusted	545	15	na	9.4	3.5	12.9	12.9	CRK25-4
Combusted	585	5	0.3	8.1	3.5	11.9	11.5	CRK24-2
Combusted	585	10	0.1	8.3	3.5	11.9	11.8	CRK24-3
Combusted	585	15	0.0	7.8	3.5	11.3	11.3	CRK24-1
Comb-St. Tr.	600	0	0.8	7.0	3.8	11.6	10.8	CRK48-1
Combusted	600	0	0.6	8.0	3.7	12.2	11.7	CRK48-2
Combusted	620	5	0.4	6.1	3.6	10.1	9.7	CRK23-2
Combusted	620	10	0.3	8.0	3.6	11.9	11.6	CRK23-3
Combusted	620	15	0.3	8.4	3.6	12.4	12.0	CRK23-1
Combusted	625	5	na	4.2	3.7	7.9	7.9	CRK52-4
Combusted	625	30	0.3	6.3	3.5	10.1	9.8	CRK47-1
Combusted	625	60	0.3	5.1	3.1	8.5	8.2	CRK47-3
Gasified	530	5	na	7.6	2.5	10.1	10.1	CRK30-4
Gasified	530	15	na	5.0	2.3	7.3	7.3	CRK30-5
Gasified	545	5	1.0	9.0	2.6	12.6	11.6	CRK25-3
Gasified	545	10	1.0	6.8	2.5	10.3	9.3	CRK25-1
Gasified	545	15	1.0	10.4	2.5	13.8	12.9	CRK25-2
Gasified	585	5	0.8	10.9	2.5	14.2	13.4	CRK24-5
Gasified	585	10	0.9	10.5	2.3	13.7	12.9	CRK24-4
Gasified	585	15	1.0	8.7	2.5	12.2	11.1	CRK24-6
Gasified	620	5	0.6	6.2	2.5	9.4	8.8	CRK23-4
Gasified	620	10	0.6	6.8	2.5	9.8	9.2	CRK23-6
Gasified	620	15	na	6.8	2.4	9.2	9.2	CRK23-5
Gasified	620	15	na	5.3	2.5	7.7	7.7	CRK52-1
Gasified	620	15	na	6.8	2.5	9.3	9.3	CRK52-2
Gasified	625	15.2	na	5.2	2.5	7.6	7.6	CRK52-3
Gasified	625	30	1.2	7.8	2.4	11.4	10.2	CRK47-2
Illite	620	5	0.3	6.9	1.4	8.6	8.3	CRK35-2
Kaolinite-F	545	5	0.0	12.9	9.1	22.0	22.0	CRK34-4
Kaolinite-F	545	10	0.0	13.8	8.7	22.5	22.5	CRK34-6
Kaolinite-F	545	15	0.0	11.7	8.1	19.8	19.8	CRK34-5
Kaolinite-F	585	5	0.0	14.6	9.4	24.0	24.0	CRK34-2
Kaolinite-F	585	10	0.0	11.1	8.8	19.9	19.9	CRK34-3
Kaolinite-F	585	15	0.0	10.7	8.0	18.7	18.7	CRK34-1
Kaolinite-F	620	0	0.4	17.5	8.1	26.0	25.6	CRK32-0
Kaolinite-F	620	5	1.0	14.3	8.2	23.5	22.6	CRK32-2
Kaolinite-F	620	11	1.1	13.8	7.9	22.8	21.7	CRK32-3
Kaolinite-F	620	15	1.4	13.9	8.0	23.3	21.9	CRK32-1
Kaolinite-F	650	10	0.0	10.6	9.8	20.4	20.4	CRK33-1
Kaolinite-F	650	15	0.0	11.5	7.8	19.3	19.3	CRK33-3
Pyrolyzed	530	5	na	12.1	2.1	14.2	14.2	CRK30-2
Pyrolyzed	530	10	na	33.0	2.0	35.0	35.0	CRK30-1
Pyrolyzed	530	15	na	6.6	2.2	8.8	8.8	CRK30-3
Pyrolyzed	585	5	13.1	10.4	2.0	25.5	12.4	CRK31-5
Pyrolyzed	585	10	5.2	11.5	2.2	18.9	13.7	CRK31-1
Pyrolyzed	585	15	7.9	11.3	2.1	21.3	13.4	CRK31-3
Pyrolyzed	650	5	0.0	8.4	2.3	10.8	10.8	CRK33-4

substrates to help elucidate the contribution of any surface area effects. The fined-grained kaolinite sample had the highest surface area (in > 3.5 nm pores) and displayed the highest coking activity. The coarse-grained kaolinite sample had the next highest coke-forming affinity, and the illite had the lowest rate of coke formation (Figure 3-44). Therefore, in the absence of carbon in the substrate, the affinity for coke formation was found to increase with surface area. When the results for the combusted shale are included in the low-carbon mineral data, the trend of increasing coke formation with surface area remains consistent (Figure 3-45). The surface area relationship for the low-carbon samples was also apparent for samples that had been pretreated. The coke deposition results for the air-oxidized illite sample and the steam-pretreated combusted shale are also shown in Figure 3-45.

The size and distribution of pores have a large influence on the rate of diffusion in particles, and it is important to consider pore volume as a coking parameter. The measured pore volumes were directly proportional with the surface areas for most of the substrates of this study (Table 3-15). Therefore, it was important to determine which parameter was most related to coking activity, and the differences in the pore structures between the kaolinite samples provided the opportunity to do this. The coarse-grained kaolinite sample had the highest pore volume (especially in the meso-pore range) of all the substrates, but its surface area was average for the group. The fine-grained kaolinite sample, on the other hand, had the highest surface area of the substrates, but its pore volume was substantially less than the coarse-grained kaolinite. The high rate of carbon deposition on the fine-grained kaolinite therefore indicates that available surface area is more important for coke formation for these substrates than the average pore size.

3.3.3.3 Effects of Carbon Content on Coke Formation. To further investigate the effects of the initial carbon content of the solids on coke formation, the pyrolyzed and gasified shales were subjected to a low-temperature ashing (LTA) procedure that is designed to remove carbon while minimizing the alteration of the associated minerals. The LTA procedure lowered the carbon content of the pyrolyzed shale from 9.6 to 6.5 wt% and of the gasified shale from 7.1 to 3.3 wt%. Longer processing times were apparently necessary to completely remove the carbon, which may be due to comparatively restricted access to the organic matter because of the large mineral/organic matter ratio.

Because of the small amount of sample that could be processed in each batch and the length of time required for the LTA procedure, sufficient LTA materials from the pyrolyzed and gasified shales were produced for only two runs in each case. The amount of carbon deposition for the LTA-processed samples was significantly higher than over the parent samples. When plotted as a function of original carbon content, a clear relationship of increasing coke formation with decreasing carbon content emerges (Figure 3-46). The extent of carbon deposition on the pyrolyzed-LTA sample was somewhat higher than the trend suggested by the rest of the data. Perhaps the LTA procedure was more effective in removing carbon that was important for the coking process than for the other materials. Nevertheless, for processed shales which have similar pore structures, there is a strong correlation between the initial carbon content of the shale and the affinity for subsequent coke formation.

Figure 3-45. Effect of meso- and macro-pore surface area on carbon deposition measured by post-run analysis for low-carbon solids (<1.3wt%). Solids residence time: 10 minutes, oil concentration: 8.33E-4 gmol C/liter.

3.3.3.4 Effects of Steam on Coke Formation. Contact with steam was a method used to pretreat the solids to investigate activity changes. This was of particular interest because Rubel et al.¹¹ (1991) indicated that steam treatment of combusted shale lowered its coking activity by approximately 50%. This treatment did not reportedly lower the surface area of the shale, so it was concluded that some chemical alteration of the minerals caused the decrease in activity. It is surprising that no change in surface area was found for the steam-treated shale because steam enhances the sintering of catalyst supports which are not unlike the minerals in eastern U.S. shale.¹⁴ Although the minerals subject to sintering are dispersed in oil shale and the effect of steam should not be as great, steam was shown in the current study to measurably lower the surface area. No mechanism or reaction pathway was offered by Rubel et al. (1991) to explain the decreased coking activity.

In this research, three different methods of introducing steam to the bed of solids were studied in order to examine the effect of steam treatment on coking activity. First, instead of utilizing pure N₂ as the balancing gas for the upper section of the reactor, steam (30% by volume) was blended with N₂ during the preheating period for runs with combusted shale (these runs are subsequently referred to as "steam pretreated"). No significant effects on the rates of carbon deposition were observed (Figure 3-47), at this severity of treatment. In the second case, more severe contact between steam and combusted shale was achieved by pre-processing a batch of combusted shale in the fluidized bed reactor at 700°C using steam for fluidization (heretofore called "steamed" shale). It was determined that this treatment produced a slight decrease in coking activity (approximately 20%). However, there was also a 20% decrease in surface area (see Figures 3-45 and 3-47). Consequently, there are some discrepancies between these results and those reported by Rubel et al. (1991).

The third method of steam treatment was to utilize steam for fluidization during the coking experiments (heretofore called "steam-fluidized" runs). The steam-fluidized runs differed from the two other types of treatments because there was a significant partial pressure of steam during pyrolysis and during carbon deposition onto the solids in the upper fluidized bed. There were, however, no detectable differences in the rate of carbon formation for the steam-fluidized runs compared to the nitrogen-fluidized runs (Figure 3-47). In summary, these results suggest that treatment does not affect carbon deposition onto combusted oil shale, with the exception that steam pretreatment at 700°C reduced the surface area of the shale with a commensurate reduction in coking activity.

The finding that steam treatments of various types did not hinder coke formation for the solids studied has significant implications for the remainder of the current study and for the development of commercial oil shale processes like KENTORT II. For practical reasons, steam was used for fluidization in the cracking chemistry study described in section 3.4. Since the presence of steam did not affect coking rates, then more confident comparisons between the coking kinetics study, which used primarily nitrogen for fluidization, and the cracking chemistry study can be made. A complete discussion of the possible effects of steam during the pyrolysis and thermal cracking of hydrocarbons is presented in section 3.4. In terms of oil shale process development, it is unfortunate that steam did not appear to be a

Figure 3-46. Effect of initial carbon content of processed shales on subsequent carbon deposition as measured by post-run analysis. Solid residence time: 10 minutes, oil concentration: 8.33E-4 gmol C/liter.

Figure 3-47. Effects of various steam treatments on carbon deposition onto combusted shale as measured by post-run analysis. Solid res. time: 10 minutes, oil conc.: $8.33\text{E-}4$ gmol C/liter.

coking inhibitor in this research, because steam is a common commercial agent that possibly could have provided an economical means of improving oil yield.

3.3.3.5 Effects of Other Substrate Pretreatment Methods on Coke Formation. With the evidence that has been presented to this point, there is nothing to suggest that there are any intrinsic activity differences between the different mineral surfaces of the substrates that have been tested. Figure 3-45 shows that surface area can account for the differences in coking rates that were observed for the various low-carbon solids that were studied. The data in Figure 3-45 also includes samples that were pretreated in different ways to simulate the process history of the shale samples. An aliquot of illite was preheated in air at 600°C to see whether oxidative conditions could affect some mineralogical or other change that would influence coking rates. If something among these lines were to occur, then the increased coking activity of combusted shale compared to the gasified and pyrolyzed shales might also be attributed to the influence of oxidative treatment, and not necessarily to the removal of carbon. However, the effect of the illite pretreatment on coking was found to be insignificant and barely affected the surface area or the coking rate (Figure 3-45).

Surface acidity is generally related to the coking activity of cracking catalysts, so pretreatments aimed at altering the surface acidity of combusted and gasified shales were also performed. Shales that were soaked in highly concentrated acid and base solutions physically deteriorated, so lower concentrations were then utilized that did not induce this behavior. No difference in coking activity was observed for any of the substrates treated in this manner compared to the parent samples. However, firm conclusions cannot be drawn from the results of this exercise because the acid/base treatments were possibly too mild to affect a significant change in the surface acidity of the washed samples.

3.3.3.6 Effects of Temperature and Oil Vapor Concentration on Carbon Deposition. Increasing the temperature of the upper fluidized bed consistently resulted in enhanced carbon deposition, but the effect was small (Figures 3-44, 3-47, and 3-48), and none of the substrates appeared to be more or less sensitive to temperature. For the reactions of hydrocarbons in this temperature range, such a small increase indicates that the carbon deposition process is either mass-transfer controlled or the reaction pathway has an extremely low activation energy. A complete kinetic analysis will be presented in later sections to properly quantitate these results, but the presentation of the data in this form was useful in the search for a kinetic model. The result that all of the solids responded similarly to temperature changes provided more evidence that there were no fundamental differences in the chemical activity of the mineral surfaces for the samples studied.

A parametric test matrix to examine the effects of temperature, oil vapor concentration, and substrate residence time was performed for the combusted and gasified shales so that kinetic measurements could be made. For the other solids in the study, only temperature and substrate residence time were varied. The oil vapor concentration was varied by adjusting the feedrate of the raw shale to the pyrolysis zone. The superficial velocity of the fluidizing gas

Figure 3-48. Effect of oil vapor concentration on carbon deposition measured by post-run carbon analysis following 15 minutes of vapor-solid contact time.

was held constant, so the oil concentration was directly proportional to the raw shale feedrate. The concentration of oil vapor had a significant effect on carbon deposition over combusted shale, but coke formation on gasified shale was almost unaffected by concentration (Figure 3-48). From this result, it could be supposed that there is some fundamental difference between the pathways for coke formation on combusted shale and gasified shale. Identifying the phenomena responsible for this difference in concentration dependence is probably the key issue in formulating a proper kinetic model.

3.3.3.7 Effect of Vapor-Solid Contact Time on Carbon Deposition. For all of the solids studied, the rate of carbon deposition decreased as the substrate residence time increased (Figure 3-49). The data were fitted reasonably well to a power function corresponding to the "coke clock" first identified by Voorhies¹⁵ (1945). The important thing to notice about the data is that the rate of carbon deposition continues to decline with time, but does not go to zero. Extended runs of up to 60 minutes were performed with combusted and gasified shale to demonstrate this point. While real-time carbon deposition measurements provide data that are more useful for kinetic analysis, demonstrating the effect of contact time with post-run carbon-on-solids data is important because it helps to validate the results of the kinetic analysis and strengthens the case for the kinetic model that is introduced later.

3.3.3.8 Carbon-Concentration Profile in Particles. This section describes the results of studies to examine the carbon distribution in coked particles. The distribution of carbon can provide an important indication of how carbon deposition progresses. The coked oil shale substrate samples (pyrolyzed, gasified, and combusted) exhibited particle-to-particle variations in total carbon content and spacial carbon distribution because they were produced in fluidized beds. Therefore, individual particles could not provide a representative carbon distribution. Further, because the original carbon distributions could not be well characterized, attention was focused on the pure mineral substrates. The kaolinite and illite samples contained essentially no carbon before contact with the shale oil vapors, and these samples were better suited to this study.

The two kaolinite samples (fine- and coarse-grained) were selected for carbon-profile analysis to determine if there were significant effects due to pore structure. It is to be noted that these samples (coarse- and fine-grained) had the same particle size range ($-841\mu\text{m} + 250\mu\text{m}$), but the individual grains that comprised the particles were relatively large and small, respectively. The two sets of particles were contacted with shale oil vapors for 5 minutes so that the carbon distribution could be observed during the early stages of deposition. Particle size effects were investigated by choosing a $-841\mu\text{m} + 250\mu\text{m}$ illite sample and a $+841\mu\text{m}$ illite sample. The selected illite samples were contacted with shale oil vapors for 10 minutes so that the total carbon content was similar to that of the kaolinite samples. The four samples each had a carbon content of approximately 1 wt%.

The particles were examined by scanning electron microscopy (SEM) with an Hitachi S-2700 with energy dispersive X-ray (EDX) attachment. The particles were embedded in a binder which was then sawn, exposing the cross sections of the particles. Usually, an epoxy

Figure 3-49. Effect of vapor-solid contact time on carbon deposition at 620°C measured by post-run analysis. Oil vapor concentration: 8.33E-4 gmol C/liter.

binder was used to facilitate polishing. For EDX analysis, however, the carbon content of the epoxy binder would complicate carbon analysis and a silica-based castable ceramic was substituted. Even then, as the lowest atomic mass that is detectable by the Hitachi S-2700 is 11, carbon detection is difficult. It transpired that the carbon content of the coked particles was below the sensitivity of the instrument, and no distinguishable carbon peaks were observed above the baseline noise for the coarse-grained kaolinite sample.

The preparation of the particle cross sections in the white ceramic binder provided visual evidence that coke formation had significantly darkened the interior of the particles. The original kaolinite samples were brilliant white, and the illite samples were light gray. With the naked eye it could be seen that carbon had been deposited throughout the interior of each of the coked particles, with a variation in color from gray to black. Optical microscopic examination of mixtures of original and coked particles of kaolinite and illite most clearly illustrate these color changes.

The coked -841+250 μ m illite particles are much darker than the original substrate (Figure 3-50). The dark color appears to be uniform throughout the interior of each coked illite particle. Likewise, the coarse-grained coked kaolinite particles in Figure 3-51 are also much darker than the original material, and no appreciable color gradient is evident. Coked illite particles larger than 841 μ m (Figure 3-52) show a dark rim near the outer edge of the particle which gradually becomes lighter towards the center. However, it is also apparent that the interior of the particle was substantially darkened by carbon deposition.

Photomicrographs of the -841+250 μ m fine-grained kaolinite particles showed a lighter outer band (100-150 μ m wide) containing a darker region in the interior of the particle (Figure 3-53). The sharp division between the lighter and darker regions made it seem unlikely that carbon deposition could be responsible for this appearance. An explanation for the apparent zoning in the particles is that the epoxy binder permeated the pores of the particles during sample preparation. To validate this explanation, EDX analysis was used to obtain an elemental map of a particle cross section from the same epoxy pellet. The EDX images of the particle (Figure 3-54) show the sharp division between the inner and outer regions of the particle, as was illustrated for other particles in the reflected light photomicrographs (Figure 3-53). The elements detected in the pellet by EDX were Al, Si, and C. Since the attempt to obtain a C map by this method using a ceramic binder was unsuccessful due to the low concentration of carbon, the C detected by EDX analysis was clearly due to the resin.

The maps of Si and Al coincided perfectly with each other (Figure 3-54). The inner region of the particle showed higher intensities of Si and Al while they were distinctly lower in the outer region. The intensity of C was highest on the exterior of the particle where the epoxy resided. A faint, but distinct, band of C is shown on the outer edge of the particle which corresponds to the low-Si/Al region and represents the region of epoxy penetration. These results are consistent with the explanation that epoxy resin had penetrated the pores of the kaolinite during curing to affect the optical properties of the particle cross sections in reflected light. One important conclusion that can be made from these observations is that

fluids have ready access to the interiors of the fine-grained kaolinite particles. If the fairly viscous epoxy liquid was able to penetrate the pores of the kaolinite particles, then gaseous diffusion should not be a rate-influencing factor for coke formation from shale oil vapors.

To possibly reduce the penetration of the epoxy into the pores of the kaolinite during pellet preparation, the epoxy was allowed to harden to the point that it was extremely viscous, but still soft enough that the particles could be imbedded into the binder. Microphotographs of the fine-grained kaolinite pellet prepared in this manner (Figure 3-55) showed none of the zoning that was prevalent for first pellet that was prepared (Figure 3-53). Like the coarse-grained sample, there was no obvious color gradient (Figure 3-55), again indicating that the pore structure was conducive to fluid transport.

In general, there are two significant observations to be made about the microphotographs. The first is that the color of each of the particles was significantly darkened indicating that carbon had been deposited to some extent throughout the particles. Therefore, the pore structure was well enough connected to freely permit the transport of fluids. The second observation is that a color gradient for the +841 μ m illite particles was evident, indicating that pore diffusion may become a factor for large (illite) particles.

3.3.3.9 Summary of Carbon Deposition Results. The following rank of coking activity was observed for the solids in this study: fine-grained kaolinite > combusted shale > coarse-grained kaolinite > illite > gasified shale > pyrolyzed shale > sand. The differences in activity between the substrates investigated were determined to be mostly attributable to surface area and initial carbon content of the solid particles. The rate of carbon uptake declined as greater amounts of carbon were deposited onto the solids with time. Similarly, solids with high initial carbon content were found to induce less coke formation than solids with little or no initial carbon. Reaction temperature had little effect on the amount of carbon deposition. The concentration of oil vapor affected carbon deposition onto combusted shale more than gasified shale. The data appear to suggest that once the mineral surfaces are covered by coke, the subsequent adsorption and coking of oil vapor is slowed significantly.

Figure 3-50. Photomicrographs at 100x for a mix of coked (dark) and uncoked (light) illite particles ($-841\mu\text{m}+250\mu\text{m}$). Coked particles were exposed to oil vapor for 10 min. at 550°C .

Figure 3-51. Photomicrographs at 100x of a mixture of coked (dark) and uncoked (white) coarse-grained kaolinite particles. The coked particles were exposed to oil vapors for 5 minutes at 620°C.

Figure 3-52. Photomicrographs at 100x magnification of coked illite particles which were greater than $841\mu\text{m}$ in diameter. Particles were exposed to oil vapor for 10 min. at 550°C .

Figure 3-53. Photomicrographs at 100x magnification of coked fine-grained kaolinite particles. The coked particles were exposed to oil vapors for 5 minutes at 620°C.

Figure 3-54. EDX maps (Al, Si, and C) of a cross section of a fine-grained kaolinite particle from the epoxy pellet shown in Figure 3-53.

Figure 3-55. Microphotographs of fine-grained kaolinite at 400x magnification with reduced penetration by the epoxy binder.

3.3.4 Kinetic Analysis of Coking Rates

In this section a kinetic model for coking rates will be presented. The model was developed from the real-time carbon deposition measurements as described in section 3.1. In all cases the rate of coking declined with increasing process time. Since the batch of solids was contacted with a continuous flow of oil vapors at a constant inlet concentration, the reduction in coking rate was due to the deactivation of the solids. A crucial part of this type of kinetic analysis is to evaluate the deactivation process. The most commonly used approach is to apply a deactivation function, Φ , to the main rate equation.

$$r' = r^o \Phi \quad (3-1)$$

where r^o is the reaction rate without deactivation and r' is the reaction rate after the solids have been processed for a certain period of time.

3.3.4.1 Empirical Deactivation Function. The deactivation function can be expressed as a function of contact time or the carbon content of the solid, and it is usually empirically derived. The advantages of using time as the independent variable for Φ are that these data are easy to obtain, and the mathematics of the resulting kinetic equations are relatively simple. However, a time-based deactivation function is dependent on the conditions of the experiment and is purely empirical. A deactivation function based on the carbon content of the solid is more difficult to develop experimentally and the kinetic expressions become more complex because an additional equation is needed to relate the gas-phase coke precursors to the carbon on the solid. The carbon-based deactivation function is much less empirical because the agent that is the cause of the deactivation, namely carbon, is the parameter in the function.¹⁶

While the coking rate data in the current study were obtained as a function of process time, integration of these data yielded the carbon concentration on the solid. Therefore, both time-based and carbon-based deactivation functions could be evaluated for the current study. However, because it was the intent of the present study to investigate the basic mechanisms of carbon deposition, the carbon-based approach to rate reduction was emphasized the most.

A typical set of coking-rate vs. carbon-on-solid data (Figure 3-56) shows a substantial amount of noise. Without any further manipulation or smoothing of the data, the noise makes it difficult to unambiguously determine the initial rate of coking or the apparent asymptotic rate that is reached at high levels of carbon deposition. In addition, the number of data points is so large that their direct utilization in this form would be impractical. Therefore, to smooth the data and to provide a mathematical description of the rate data by a small number of parameters, a curve fitting procedure was adopted.

The goals of the curve fitting procedure were to find a simple expression that adequately modeled the essence of all of the rate vs. carbon-on-solid data that were collected.

PC-based software (TableCurve 2D for Windows) was used to fit candidate equations to each set of data. The software was capable of automatically fitting and ranking up to 3456 linear and non-linear equations. To reduce the set of candidate equations, only functions with two terms plus an intercept value were evaluated. Furthermore, for reasons to be discussed later, only equations with continuous first derivatives at $x=0$ were considered. The equation with the fewest parameters that met these criteria and that had the consistently highest goodness-of-fit ranking (r^2) was

$$y=A+B*\exp(-x/C) \quad (3-2)$$

where A, B, and C are fitted parameters, y is the measured rate of carbon deposition and x is the carbon-on-solid concentration, C_c . Dumez and Froment¹⁷ (1976) found a similar exponential function (without a constant term) to adequately represent the deactivation of catalytic 1-butene dehydrogenation. The exponential deactivation equation, however, is not viewed at this point in the current study as having any physical significance other than providing an empirical means of describing the data for further analysis. The equation provides the initial coking rate, r_i , from the sum of parameters A and B, and the final coking rate, r_f , from A.

3.3.4.2 Critical Carbon Content. All of the data consistently displayed an initially rapid decrease in rate followed by a relatively constant rate period. The parameter C in the deactivation function is a measure of how quickly the rate falls from r_i to r_f . While performing the curve fitting evaluations, it was noticed that a fundamental difference between the shapes of the curves for each type of solid was the rate at which the coking reaction deactivated relative to the added carbon content, C_c . There appeared to be a characteristic value of C_c for each type of solid that divided the rate data between a rapidly decreasing rate period and a constant rate period. To evaluate this critical value of C_c , a line tangent to the fitted equation at $C_c=0$ was extended to the x-axis (Figure 3-56). For this reason, it was necessary for the fitted equation to have a continuous first derivative at $C_c=0$. This "critical" carbon-on-solid content, C_{crit} , was then calculated from the fitted parameters by the equation: $C(A+B)/B$. The validity of this linear extrapolation will be later demonstrated in light of the kinetic model that is proposed.

The average values of C_{crit} for each of the solids tested were found to follow the same general order as the coking reactivities identified in the previous section (Table 3-17). The kaolinite samples had the highest values of C_{crit} followed by the combusted shale, illite, pyrolyzed shale, and gasified shale. The values of C_{crit} for the coarse-grained kaolinite and the pyrolyzed shale were somewhat higher than expected from the relative coking tendencies that were observed, but the values are still in agreement with the general trends. The relatively low number of determinations for the coarse-grained kaolinite and the pyrolyzed shale are expected to increase the uncertainty of the respective C_{crit} values. In addition, high rates of attrition experienced by the coarse-grained kaolinite placed additional uncertainty on the C_{crit} measurement. The pyrolyzed shale, on the other hand, displayed such a brief

Figure 3-56. Coking rate data for combusted shale at 625°C for 60 minutes of exposure as a function of the added carbon-on-solid concentration as measured in real time.

transition to the steady-rate period that linear extrapolation is also expected to be subject to uncertainty.

The value of C_{crit} appears to directly relate to the capacity of the solid for rapid carbon deposition. Since surface area was also shown to influence the rate of carbon deposition, it would be expected that this is also related to C_{crit} . For the low-carbon solids, a good correlation between surface area and C_{crit} are found (Table 3-17). The high-carbon solids (gasified and pyrolyzed shales) displayed lower C_{crit} values which is consistent with the observation from the previous section that high initial carbon content inhibits additional carbon deposition.

To investigate the theory that the initial rapid deposition of carbon is associated with coking onto exposed mineral surfaces, the theoretical monolayer coverage according to the >3.5nm-pore surface area was calculated and compared to the measured C_{crit} values (Table 3-17). Excellent agreement was found for the two measures with the exception of the coarse-grained kaolinite. The percentage of the theoretical monolayer that was utilized during the initial rapid-rate period, as measured by C_{crit} , is shown in the last column of Table 3-17. For the low-carbon solids, the percentage should be close to 100% for the monolayer coverage theory to be valid. The monolayer utilization for the high-carbon solids is approximately 35% which indicates that the much of the available surface area was already carbon covered prior to the coking experiments. Therefore, the monolayer utilization may also be interpreted as the percentage of surface area that is not originally covered by carbon.

3.3.4.3 Overall Rate Equation. While it has been shown that exposed mineral surfaces are associated with the rapid deposition of carbon, it is also apparent that coking takes place on carbon-covered surfaces. As shown in Figure 3-56, coking continued for the combusted shale long after the surface was covered by a theoretical monolayer of carbon (ca. 1 wt%). Therefore, under the conditions of this study, the rate of the coking reaction does not proceed to zero, but it declines to a nonzero value that is presumably similar to that for coking onto a pure carbon surface. A kinetic model must provide for both the initial rapid-rate period that declines quickly and the constant-rate period. It will be assumed that the rate of coking that is observed, r_{tot} , is the sum of the rates due to coking over exposed mineral substrates, r_{min} , and due to coking onto carbon-covered surfaces, r_{car} . Each of these rate functions has its own deactivation function associated with it, as follows

$$r_{tot} = r_{min} \bar{\Phi}_{min} + r_{car} \bar{\Phi}_{car} \quad (3-3)$$

The deactivation function associated with coking over pure minerals can be defined non-empirically as suggested by Froment and Bischoff¹⁶ (1979):

Table 3-17. Carbon Coverage Capacities of the Coking Substrates Compared to the Mean Critical Carbon-on-Solid Content, C_{crit} .

	Mean Measured C_{crit} , wt%	Meso/Macro Surface Area, m^2/g	Calculated Monolayer C Content, wt%**	Number of Measure- ments	Monolayer Util- ized, %
Combusted Shale	0.87	12.7	0.99	60	87.9
Gasified Shale	0.31	11.6	0.91	57	34.1
Pyrolyzed Shale	0.37	13.4	1.05	12	35.2
Illite	0.56	9.1	0.71	22	78.9
Kaolin (Fine)	1.67	21.7	1.70	11*	98.2
Kaolin (Coarse)	1.48	10.5	0.82	9*	180.5

* Only solid holding times of 10 minutes or greater were evaluated.

** Calculated assuming surface mono-layer packing of 1 C atom/ $0.0255nm^2$.

$$\Phi_{\min} = \frac{(C_{\min} - C_{\min})}{C_{\min}} \quad (3-4)$$

Note that $C_{\min}$ is equivalent to the term C_{crit} that was defined previously, and it represents the total amount of carbon that can be deposited in a monolayer on the exposed mineral surfaces. $C_{\min}$ is the amount of new carbon that is deposited during vapor/solid contact as a monolayer on the bare mineral surfaces. Therefore, by definition, $C_{\min}$ cannot exceed $C_{\min}$. The deactivation function for the carbon surface coking reaction is a misnomer because it actually increases as $C_{\min}$ increases, and it cannot exceed unity:

$$\Phi_{\text{car}} = \frac{C_{\min}}{C_{\min}} \quad (3-5)$$

When monolayer coverage of the mineral surface is minimal, or at the beginning of the experiment, the total coking rate is reflected by the mineral coking rate and the second term in Equation 3 is insignificant. Therefore, differentiating Equation 3-3 with respect to $C_{\min}$ at $C_{\min}=0$ yields

$$C_{\min} = \frac{-r_{\min}}{\left(\frac{dr_{\text{tot}}}{dC_{\min}} \right)_{C_{\min}=0}} \quad (3-6)$$

which is the linear extrapolation that was demonstrated in Figure 3-56 to obtain C_{crit} . This procedure is also valid for solids that have a moderate initial carbon content, like gasified shale, because the coking reactions over the exposed minerals dominate during the initial stages of vapor/solid contact.

3.3.4.4 Determination of Deactivation Functions. Empirical determination of the deactivation function is normally applied because $C_{\min}$, as indicated in Equations 3-4 and 3-5, is not a readily measurable quantity. The quantity that is measurable by experiment is C_{tot} which is the sum of $C_{\min}$ and C_{car} . Therefore, a relationship between C_{tot} and $C_{\min}$ is needed to complete this model. Due to the inclusion of the term for coking onto carbon-covered surfaces in the overall rate equation, it is possible to derive a relationship between $C_{\min}$ and C_{tot} based on the assumed deactivation functions, $\Phi_{\min}$ and Φ_{car} , in Equations 3-4 and 3-5, respectively. Taking the ratio of the coking rate associated with carbon on minerals to the total rate yields

$$\frac{dC_{\min}}{dC_{\text{tot}}} = \frac{r_{\min}(1-\Theta)}{r_{\min}(1-\Theta) + r_{\text{car}}\Theta} \quad (3-7)$$

where $\Theta = C_{\min}/C_{\min}$.

In Equation 3-7 it is assumed that the individual coking rates, $r_{\min}$ and r_{car} , are constants that are indicative of the initial and final coking rates for a particular experiment, respectively. These reaction rates will be shown to depend on oil vapor concentration, but in the context of this analysis, they are treated as constants because it is the changing carbon content that is causing the coking rate to slow down. Rearrangement and integration of Equation 3-7 gives

$$\int \frac{1-\Delta\Theta}{1-\Theta} d\Theta = \frac{1}{C_{\text{mon}}} \int dC_{\text{tot}} \quad (3-8)$$

where $\Delta = (r_{\min} - r_{\text{car}})/r_{\min}$. Evaluation of the integral yields the non-empirically based relationship between C_{tot} and C_{mon} .

$$\frac{C_{\text{tot}}}{C_{\text{mon}}} = (\Delta - 1)\ln(1 - \Theta) + \Delta\Theta \quad (3-9)$$

Unfortunately, Equation 3-9 is not particularly useful because it cannot be easily inserted into Equation 3-3. The plot of Equation 3-9 shows that Θ rises quickly initially and then asymptotically reaches unity when viewed as a function of C_{tot} (Figure 3-57). The parameter Δ is shown to influence the rate at which carbon coverage of the bare minerals is achieved. When $\Delta=1$, coverage of the mineral surface proceeds linearly to $\Theta=1$ which corresponds to zero coking onto carbon-covered surfaces. As the rate of carbon-on-carbon deposition increases relative to coking onto minerals (i.e., decreasing Δ) the coverage of minerals diminishes as a function of the total carbon added. The functionality of Equation 3-9 resembles the simple exponential function of C_{tot} :

$$\Theta = 1 - \exp\left(-\frac{C_{\text{tot}}}{C_{\text{mon}}\Delta}\right) \quad (3-10)$$

In fact, Equation 3-9 becomes Equation 3-10 when the second term on the R.H.S. of Equation 3-9 is dropped.

Utilizing Equation 3-10 in the general rate equation (Equation 3-3) yields Equation 3-11 which has the same functional form that was derived from the least squares fitting procedure of the experimental data (Equation 3-2).

$$r_{\text{tot}} = (r_{\min} - r_{\text{car}})\exp\left(\frac{-C_{\text{tot}}}{C_{\text{mon}}\Delta}\right) + r_{\text{car}} \quad (3-11)$$

Figure 3-57. Relationships between $C_{\min}$ and C_{tot} according to Equations 3-9 and 3-10.

This means that the $C_{min}=f(C_{tot})$ relationship in Equation 3-10 provides the best fit for the data of the current study. A graphical comparison of Equation 3-10 to Equation 3-9, in Figure 3-57, shows that the mineral surfaces were covered at a slower rate than was predicted by the theoretical deactivation functions. The functions defined in Equations 3-4 and 3-5 assume a localized phenomenon that is first order with respect to available surface and is not dependent on changing transport conditions such as pore narrowing and pore blocking. Under the conditions of the current study, coking is expected to occur initially on the outer surfaces of the particle and then proceed inward. This assumption is based on the hypothesis that coke precursors are adsorbed onto the particle from the gas-phase in parallel to the cracking reactions that occur. Therefore, oil vapor that is diffusing through the pores experiences contact with carbon-covered surfaces prior to reaching the uncovered mineral surfaces, which serves to increase the amount of carbon deposition onto carbon-covered surfaces over that predicted by the theory.

The theoretical deactivation function also underestimates the amount of carbon needed to cover the minerals because it assumes that coke precursors will adsorb onto either a clear mineral site or a carbon-covered site, with no overlap. Any adsorbed molecule on the mineral surface which does not completely occupy the maximum amount of surface for its number of carbon atoms will result in underestimation by the theoretical model. Therefore, considering the relative simplicity of the theoretical coverage function and its similarity to the functional form of the empirical model, the discrepancy between the models is not excessive. The use of the empirically-derived surface coverage equation is simpler to implement than the theoretical model and it still fits in well with the concept that C_{mon} is a parameter of a solid that can be used to predict the potential for carbon deposition.

3.3.4.5 Kinetic Measurements for Coking onto Solids. Since the gas flow patterns through fluidized beds are not easily characterized, some assumptions are required before a kinetic analysis can be attempted. The simplest hydrodynamic model of a fluidized bed consists of a bubble phase and an emulsion phase. Gas bubbles increase in size and mix the particles as they rise through the bed, although there is relatively little gas-solid contact. The gas flows evenly through the solids in the emulsion phase, much as it does through a packed bed. The majority of gas-solid contact occurs in the emulsion phase, and it typically involves only a small portion of the total gas flow. The minimum fluidization velocity is equivalent to the emulsion-phase velocity, so gas velocities in excess of the minimum are generally representative of the bubble-phase velocity. As the superficial gas velocity is increased, the bed becomes more turbulently mixed, but more gas bypassing also occurs. A detailed description of the two-phase fluidized bed model as applied to the conditions of this study is given in Appendix A.

Two characteristics of the fluidized bed used in the current study served to minimize the amount of gas bypassing. First, the bed was shallow (5 cm in height, 7.6 cm in diameter) which means that the growth of bubbles with height in the bed was small. Second, the superficial gas velocities were no higher than twice the minimum fluidization velocity, which indicates that the emulsion-phase gas flow was roughly half of the total gas flow. Operation

at lower velocities was not attempted because a gas velocity well in excess of the minimum is necessary to ensure proper solids mixing. Levenspiel¹⁸ (1972) showed that the performance of a fluidized bed with small- to medium-size bubbles was approximately equivalent to that of a mixed flow reactor (gases are perfectly mixed). Fluidized beds with large bubbles give much lower conversions than mixed reactors. Even though the gas flow regime can approximate to plug flow in a fluidized bed, the bypassing caused by the bubbles lowers the performance so much, that plug-flow conversion cannot be approached even with the smallest bubbles. In this study, it was assumed that the fluidized bed could be characterized by plug flow of gas through a mixed bed of solids, but that the performance was more akin to mixed flow of gas because of bypassing in the bubble phase.

Another factor that must be considered in the kinetic analysis is whether the reactor is integral or differential. A reactor can be termed differential if the bed is shallow or if the conversion is relatively small. Unfortunately, as Froment and Bischoff¹⁹ (1979) indicate, "it is always a matter of debate how small the conversion has to be to fulfill the requirements." The fluidized bed used in the current study was shallow (5 cm), but the initial loss of gas-phase vapors to carbon on the solids was as high as 40% for some runs. After a certain amount of carbon had accumulated on the solids, the conversion dropped to approximately 5% in most cases. Therefore, for carbon-covered solids, the justification for a differential reactor is clear, but for the initial period of rapid carbon deposition the case is not so clear. The performance equation for a differential reactor assumes that the concentration remains constant throughout the bed of solids where:

$$-r_A = \frac{F_{A0}X_A}{W} \quad (3-12)$$

This equation can also be applied in mixed reactors because the concentration of gas is constant throughout, due to mixing. Therefore, it is argued that Equation 12 can be used as the performance equation for the current study because the reactor can be characterized both as differential (for carbon-covered solids) and as having the performance characteristics of a mixed reactor. The application of the integral-reactor methods of analysis (either differential or integral) for fixed beds were not appropriate for the current study because of the aforementioned gas bypassing in fluidized beds.

A range of shale oil vapor concentrations was included in the test matrix for the combusted and gasified shales so that kinetic measurements could be made. The oil vapor concentration was held constant for the other solids of the study to keep the number of experiments at a manageable level. The three parameters for the test matrix involving the combusted and gasified shales were upper bed temperature, oil vapor concentration, and substrate residence time in the flowing vapors. The temperature was varied from 530 to 660°C, and the data were grouped into four temperature ranges for subsequent analysis: 530-550, 570-600, 610-630, and 655-660°C. The average temperature for each of these temperature groups will be used in the following sections: 540, 580, 620 and 660°C, respectively. The shale oil vapor concentration was varied by a factor of three by changing

the rate of raw shale feed to the pyrolysis (lower) bed. By keeping the other flow parameters constant, the rate of reactant input, F_{A0} , and the concentration of reactant, C_{A0} , were changed simultaneously with the changing feedrate. The substrate residence time was not considered a parameter in this analysis because on-line measurements of coking rate were utilized, and the total residence time was only needed to perform the numerical integration of the data.

The initial rate of coking for combusted shale was found to be dependent on the average concentration for each of the temperature ranges (Figure 3-58). Better linear and nth-order correlations were obtained when using the average oil vapor concentration, $C_{Ai(avg)} = (C_{A0} + C_{Ai})/2$, compared to the concentration exiting the fluidized bed, C_{Ai} . The average concentration was likely more representative of the concentration that was experienced by the solids because of the assumed plug-like gas flow. For a differential reactor, it is the average concentration that is used in the rate equation. However, when a reactor is classified as a non-differential mixed reactor then it is assumed that the exit concentration, C_{Ai} , is prevalent throughout the bed also. For the current study, the mixed-flow equation is being used because it estimates the performance of a fluidized bed and not necessarily the fluid-flow characteristics of a fluidized-bed reactor. Therefore, it is argued that the use of the average concentration is also appropriate even if the reactor cannot be classified as non-differential. In practice, however, this issue does not impact upon the present work because the relatively small shift caused by the use of $C_{Ai(avg)}$ rather than C_{Ai} did not affect the apparent order of reaction.

Due to the scatter in the data, the application of simple nth-order kinetics was assumed to be the most reasonable approach. At each of the four temperature levels, the least-squares line, and the best nth-order equation from a non-linear curve fitting procedure, were determined for the initial rate data for combusted and gasified shales (Figures 3-58 and 3-59, respectively). The nth-order and linear equations fit each set of data similarly except at 540°C where no data were obtained at the highest oil vapor concentration. Without the data at the highest concentration, the nonlinear fit was skewed horizontally making the information provided by the nth-order equation questionable. The order for the nonlinear equations at the higher temperatures ranged from 0.60 to 0.94. The nth-order equations fit the data better than the least-squares line at the lowest concentration, but the fit was worse at the higher concentrations. Because there did not appear to be a common order for the nonlinear equations and the linear equations fit all of the data adequately, first-order kinetics were applied in the subsequent analysis.

In a similar fashion to the initial coking rate data, the "final" coking rates were plotted as a function of the average oil vapor concentration for combusted and gasified shales (Figures 3-60 and 3-61, respectively). The final rates in this case were derived from the fitted "A" parameter of Equation 3-2. These data displayed much more scatter than the initial rate data and most of the values were at or near zero. The very low values made the data unacceptable for subsequent analysis. In two cases the fitted least-squares line with a non-zero intercept had a negative slope. There was a non-zero coking rate throughout the timeframe of each experiment, but in some cases the fitted exponential curve extrapolated the

Figure 3-58. Initial coking rate, r_{Ai} , onto combustured shale vs. the average oil vapor concentration. The smooth curves are the least-squares first- and nth-order fits to the data.

Figure 3-59. Initial coking rate, r_{Ai} , onto gasified shale vs. the average oil vapor concentration. The smooth curves are the least-squares first- and nth-order fits to the data.

rate to zero at infinite time or carbon content. In most cases, this occurred for runs with up to 5 minutes of solid contact with the vapors, because there was no data at longer times to influence the fitted curve. Convergence to zero for longer contact times also occurred in a few instances because of baseline shifts during measurement by the mass spectrometer.

To utilize all of the final rate data without eliminating the obviously low results, revised "final" rates within the timeframe of the experiments were used for analysis. In order to do this a new definition for the "final" coking rate was established. Because the critical carbon content, C_{crit} or C_{mon} , was shown to indicate the breakpoint between the two apparent coking rate mechanisms, it should also serve as a standardizing parameter for the carbon content. The coking rates for combusted and gasified shale were determined from the fitted exponential equation at multiples of one, two and three times the value of C_{mon} calculated for each run (Figures 3-62 and 3-63, respectively). The rate data derived from this procedure were more closely grouped, especially at $1 \cdot C_{mon}$, and there were no rates of zero. Although the rates at $1 \cdot C_{mon}$ correlated better, the rates at $3 \cdot C_{mon}$ were more representative of the "final" coking rate because they were within 5% of the extrapolated final value.

Both linear and nth-order equations were fitted to the $3 \cdot C_{mon}$ data. The fitted order for the non-linear equations was slightly higher than for the initial rate data. The order ranged from 0.7 to 1.1 for the data at 580°C and above. Like the initial rate data, the order derived from the 540°C data was low because of the lack of data at the highest oil vapor concentration. Since the best non-linear fits for each temperature were so close to unity, first-order kinetics were applied to the final rate data.

The first-order rate constants for the initial coking period and their relationship to temperature were similar for the combusted and gasified shales (Figure 3-64). The activation energies derived from the Arrhenius plot of these rate constants yielded similar values of 10,456 and 9,902 J/gmol for combusted and gasified shale, respectively. The similarities of the reaction orders, the rate constants, and the activation energies indicate that the same initial rate mechanism prevailed for combusted and gasified shales. The initial rate constants for the combusted shale were consistently higher than for gasified shale because the exposed mineral surface area was higher for the combusted shale.

Similar correspondence was found in the rate parameters for the final coking rates of combusted and gasified shales (Figure 3-64). These similarities suggest that the same rate mechanisms apply for both the combusted and the gasified shales, following substantial carbon deposition. The first-order rate constants became more dependent on temperature as the rates were evaluated at higher multiples of C_{mon} . The activation energies shifted from approximately 16,600 J/gmol at $1 \cdot C_{mon}$ to 62,127 and 72,273 J/gmol at $3 \cdot C_{mon}$ for combusted and gasified shale, respectively. It is apparent from these results that the fundamental mechanism for coking changed as a result the extent of carbon deposition.

The Arrhenius plots in Figure 3-64 also indicate that a change in rate mechanism may have occurred as the temperature was raised from 540 to 660°C. There is an unexpected dip

Figure 3-60. Final coking rate, r_{Af} , onto combusted shale. These data were obtained from the parameter "A" in Equation 3-2, and were determined to be unsuitable for subsequent analysis.

Figure 3-61. Final coking rate, r_{Af} , onto gasified shale. These data were obtained from the parameter "A" in Equation 3-2, and were determined to be unsuitable for subsequent analysis.

Figure 3-62. "Final" coking rate data for combusted shale at multiples of C_{mon} . A least-squares line is shown for each set of data.

Figure 3-63. "Final" coking rate data for gasified shale at multiples of C_{mon} . A least-squares line is shown for each set of data.

in the rate constants for both shales and for both rate periods at 620°C. This short-lived decrease is probably not attributable to experimental error, because it occurred for both shales and it was derived from the most abundant data set of the study. There is also evidence of a drop in coking rate at approximately 620°C, from the post-run carbon analysis of the coked solids. Second-order regression was performed on the data plotted in Figures 3-44 and 3-48 to highlight the trends as a function of temperature for the various solids. For much of the data, including all of the solids studied, there was a shallow but evident fall in the amount of deposited carbon at temperatures ranging from 580 to 620°C. This may be due to a change in structure of carbon on the surface. For typical pore diffusion limitations to be involved, the rate would be expected to settle to a relatively constant value at the highest temperatures. This was not the case, because the rates at the highest temperature returned to the level projected by the two lower temperatures on the Arrhenius plot.

The observed dip in rate at 620°C should not, however, obscure the overall significance of the findings. The two rate mechanisms that were described in general by Equation 3-3 were each well characterized by first-order kinetics and by an Arrhenius-type temperature dependency. The two coking mechanisms or modes were distinguished by significant differences in rate and apparent activation energy. These results are now included in Equation 3-2 to further define the kinetic model.

$$r_A = -\frac{dC_A}{dt} = \left[k_{0i} \exp\left(\frac{-E_i}{RT}\right) \Phi_{\min} + k_{0f} \exp\left(\frac{-E_f}{RT}\right) \Phi_{\text{car}} \right] C_A \quad (3-13)$$

The kinetic parameters are presented for convenience in Table 3-18. The empirical deactivation functions, $\Phi_{\min}$ and Φ_{car} , which were derived in the preceding section can also be inserted in Equation 3-13 to complete the kinetic model.

$$r_A = -\left[\left[k_{0i} \exp\left(\frac{-E_i}{RT}\right) - k_{0f} \exp\left(\frac{-E_f}{RT}\right) \right] \exp\left(-\frac{C_{\text{tot}}}{C_{\text{mon}} \Delta}\right) + k_{0f} \exp\left(\frac{-E_f}{RT}\right) \right] C_A$$

$$\text{where } \Delta = \frac{k_{0i} \exp\left(\frac{-E_i}{RT}\right) - k_{0f} \exp\left(\frac{-E_f}{RT}\right)}{k_{0i} \exp\left(\frac{-E_i}{RT}\right)} \quad (3-14)$$

3.3.4.6 Discussion of Coking onto Exposed Mineral Surfaces. The activation energy of approximately 10,000 J/gmol that was observed for the initial coking rate is low for hydrocarbon reactions in this temperature range. This activation energy is equivalent to the

Figure 3-64. Arrhenius plots of the first-order rate constants for: a) the initial coking period, and b) and the final coking period as determined at multiples of C_{mon} .

Table 3-18. First-Order Kinetic Parameters Determined from On-Line Measurement of Coking Rate as Defined in Equation 3-13.

	Combusted Shale	Gasified Shale
Initial Rate		
E_i , J gmol ⁻¹	10,456	9,902
k_{oi} , cm ³ g ⁻¹ s ⁻¹	35.770	27.774
Final Rate		
$E_f(1 \cdot C_{mon})$, J gmol ⁻¹	16,938	16,280
$E_f(2 \cdot C_{mon})$, J gmol ⁻¹	37,126	38,578
$E_f(3 \cdot C_{mon})$, J gmol ⁻¹	61,983	71,936
$k_{of}(1 \cdot C_{mon})$, cm ³ g ⁻¹ s ⁻¹	31.303	23.663
$k_{of}(2 \cdot C_{mon})$, cm ³ g ⁻¹ s ⁻¹	258.63	240.93
$k_{of}(3 \cdot C_{mon})$, cm ³ g ⁻¹ s ⁻¹	5301.3	14137.7

resistance expected for pore diffusion at these temperatures.²⁰ However, it does not appear that pore diffusion plays a significant role under these circumstances. The results of the fluidized bed model in Appendix A, which includes diffusion in porous solids, indicated that pore diffusion should not be a significant factor under the conditions of this study. The Weisz-Prater criterion²¹ for pore resistance for first-order reactions, $L^2(-r_{\text{obs}})/(D_e C_A)$, was found to be less than one for the conditions of the study. This also indicates that pore resistance is a relatively insignificant rate influencing factor. In addition, optical microscopy of substrate cross sections showed uniform darkness due to the presence of carbon, which also indicates that pore diffusion resistance is low.

With the absence of diffusional constraints, the low activation energy is indicative of some other process with a low energy barrier. The on-line measurement of the initial coking rate actually reflects the adsorption of oil vapors onto the solid. It is assumed from the decrease in measured oil vapor concentration that coke eventually forms on the surface. However, the transformation of the adsorbed oil to a coke-like substance proceeds unnoticed by the on-line measurement technique, except for small quantities of gas production. The activation energy for the rapid coking rate is within the range that is generally assumed for physical adsorption (4-40 kJ/gmol), and in this context Szekely et al.²² (1976) refer to this energy range as being approximately equivalent to that of the condensation of a vapor. Physical adsorption involves attractive forces that are much weaker than those involved in covalent chemical bonding and can result in the formation of multiple layers. The latter two characteristics are not congruent with the observations made for the rapid coking period, however. Although small amounts of desorption (which would be expected for physical adsorption) were observed in some cases, when the coking substrate was cooled, this was likely due to desorption from carbon-covered sites and not from clear mineral surfaces. Also, the data appear to indicate that the initial rapid coking period ceases once a significant portion of the exposed mineral surfaces are covered by coke. Therefore, the formation of multiple layers of carbon does not contribute to the initial rapid coking rate.

Chemisorption onto solid surfaces involves the formation of covalent chemical bonds between the adsorbent and the adsorbate, and hence can only occur in a monolayer on the surface. The activation energy for this type of process is typically in the range of 40-600 kJ/gmol. The high energy required may appear to eliminate chemisorption as a mechanism for the observed results, but Szekely et al.²² (1976) also note that chemisorption has been found with small activation energies.

Appleby et al.²³ (1962) found that large aromatic compounds were especially susceptible to coke formation over a silica-alumina cracking catalyst. For anthracene coking, the acidity of the surface was found to be important because the acidic catalyst produced much more coke than a neutral pH pure silica gel with equivalent surface area. It is important to note that coke formation also occurred, albeit to a lesser extent, through so-called thermal processes onto neutral solids. Appleby et al. (1962) also observed that the basicity of the compounds was related to the extent of coke formation on catalyst. The basicity constants used in the Appleby study were derived by Mackor et al.²⁴ (1958) who developed a basicity

measurement scale based on the partitioning between HF and n-heptane or CCl₄. Appleby et al. (1962) suggested that the interaction between the aromatics and catalyst that initiated coke formation involved proton transfer to the aromatics or electron transfer to the catalyst, or both. They also found that coke formation for the four-member rings (chrysene and pyrene) appeared to be more related to their large size than basicity, and suggested that dimers or trimers of such very large molecules should be the most reactive coke intermediates compared to the smaller species that they studied.

The significance of the work by Appleby et al.²³ (1962) to the current study is that the large and heteroatomic aromatics produced by fluidized bed pyrolysis should be at least as prone to coke formation over acidic surfaces as the model compounds used in the former study. Unfortunately no activation energies were determined in the former study, but the strong attractive forces between basic hydrocarbons and acidic surfaces should be consistent with a low energy barrier for adsorption. Wallaston et al.²⁵ (1975) assumed activation energies ranging from 0 to 20 kJ/gmol for coking in their fluid catalytic cracking model, which is in the same range as the results of the current study.

While the rapid coking period was characterized by carbon deposition onto clear mineral surfaces, the nature of these surfaces has not yet been discussed. For whatever reason, these surfaces are more conducive to coke formation than carbon-covered surfaces. If coking occurred through purely thermal reactions then it would seem that the total accessible surface area, whether carbon-covered or not, would be the primary factor controlling the coking rate.

The majority of the mineral matrix of Eastern U.S. shales consists of so-called clay minerals which are expected to display some activity under the conditions of this study. Listed in order of abundance, the clay minerals in eastern U.S. oil shales are illite, chlorite, and kaolinite. The basic building blocks for clays are layers of tetrahedral sheets of SiO₄ units and octahedral sheets of Al(OH)₆ or Mg(OH)₆ units. The differences in the various clay types arise from the proportions of the different sheets in the layers and any interlayer substitution that may be present. Illite (Table 3-19) has a highly variable composition and is characterized as a 2:1 layer clay which means that 2 tetrahedral SiO₄ sheets enclose an octahedral cation hydroxide sheet.²⁶ Kaolinite is a 1:1 layer clay with a better characterized pure structure. Chlorite is a 2:1:1 layer clay which means that an octahedral interlayer occurs between a 2:1 layer arrangement.

Heating the minerals above 500°C leads to the dehydroxylation of octahedral sheets and a general decrystallization of the mineral structure. Robl et al.¹ (1990) showed that the original illite and kaolinite had almost completely decrystallized in a sample of combusted oil shale from the KENTORT II bench-scale reactor. They also found that the extractability of Al, Fe, K, and Na by H₂SO₄ increased as a function of heating. These results are consistent with the discussion by Gates et al.²⁷ (1979) concerning the removal of water from a silica-alumina catalyst upon heating. They state that water removal exposes the aluminum ions which can then create Lewis acid sites due to the electron-pair-acceptor properties of

aluminum. While the structure of decrystallized clay minerals are not identical to manufactured silica-alumina catalysts, the same tetrahedral silica and octahedral alumina units are present in each.

There is more direct evidence from a study by Rubel et al.²⁸ (1992) to show that combusted Cleveland oil shale possesses surface acidity. Temperature programmed desorption (TPD) studies were performed with combusted and gasified oil shale samples similar to those used in this research. Low levels of ammonia were found to adsorb onto both samples, with the gasified shale adsorbing more than the combusted shale. The temperature of desorption was much higher for the combusted shale than for the gasified shale. It was concluded that the combusted shale contained fewer but stronger acid sites. No differentiation was made between Bronsted and Lewis acid sites.

In summary, the rapid period of carbon deposition during the initial stage of vapor-solid contact is believed to be due to adsorption of oil vapor onto exposed mineral surfaces followed by polymerization, condensation, and hydrogen elimination reactions. This adsorption process requires little energy, and it is not apparently affected to a significant extent by diffusional limitations which could have lowered the apparent activation energy. It is proposed that the process is energetically favorable because of acid-base attractions between the mineral surfaces and the large, condensed aromatic compounds. The extremely high nitrogen content of the shale oil in this study (ca. 1 wt%), coupled with its high aromaticity (40% by ¹³C NMR),¹³ makes it likely that the oil vapor has a highly basic character. Further, it appears that the dehydroxylated clay minerals in the solids that were tested possess sufficient activity to promote the adsorption process. Observations concerning possible catalytic cracking activity will be presented in section 3.4.

3.3.4.7 Discussion of Coking onto Carbon-Covered Surfaces. The significant differences in kinetic parameters for coking onto carbon-covered solids compared to coking onto uncoated mineral surfaces is indicative of a major difference in mechanism. The difference in activation energy between the two apparent regimes cannot be totally explained by diffusion limitations because they differ by more than a factor of two. The deposition rate for coking onto carbon was found to be first order with respect to the oil vapor concentration, so that the surface reactions are unlikely to be rate limiting. The activation energy for the coking period on carbon-covered shale was within the range that is typical for gas-phase hydrocarbon cracking and addition reactions involving free radicals. Depeyre et al.²⁹ (1989) tabulated kinetic parameters for several classes of hydrocarbon reactions. They reported that the formation of radical species from a paraffin had the highest activation energies of approximately 250 kJ/gmol. Recombination reactions involving a free radical (paraffinic or olefinic) and a paraffin (or olefin) to form another free radical (paraffinic or olefinic) and/or paraffin (olefin) had activation energies that ranged from 0 to 69 kJ/gmol. One reaction that was well outside this range was the production of a hydrogen radical and butadiene from ethene and an ethene radical at 205 kJ/gmol.

Table 3-19. Normalized Composition and the Ideal Chemical Formulas of the Main Silicate Minerals in Cleveland Oil Shale.

<u>Mineral</u>	<u>Wt%*</u>	<u>Ideal Formula**</u>
Kaolinite	3	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Chlorite Group	10	
Clinochlore		$(\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$
Chamosite		$(\text{Fe}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$
Illite	63	$\text{K}_{\leq 1}\text{Al}_{\leq 2}(\text{Fe}^{3+}\text{Mg}^{2+})_{>0}(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2$
Quartz	23	SiO_2

* Normalized composition from XRD analysis by Robl et al.¹

** Formulas from Hathaway.²⁶

An important point about the preceding information is that the measured activation energies from the current study were approximately equivalent to those for gas-phase radical reactions. There are two main reasons why comparisons of the activation energies from the current study should be made in only general terms to the literature values. First, the uncertainty in determining the activation energies for the coking-on-carbon periods was rather high. The coking rates that were used for the determinations were not fully extrapolated to full carbon coverage to improve the precision of the data. Therefore, the actual coking-on-carbon activation energy is expected to be slightly higher than those reported. Second, there is a danger in measuring the lumped activation energy of a large number of parallel reactions than have a wide range of activation energies. Golikeri and Luss³⁰ (1972) showed that the activation energies obtained from lumping groups of parallel reactions can be dependent on conversion if the individual activation energies occur over a relatively wide range.

According to one mechanism proposed by Reyniers et al.³¹ (1994) for carbon formation onto carbon-covered solids, tar droplets formed in the gas phase can impinge on carbon-covered solid surfaces and continue the process of dehydrogenation, cyclization, and hydrogen abstraction on the growing coke layer. This type of mechanism does not appear likely for the current study because coke formation which could have resulted from substantial droplet impingement has not been noted as being significant on the interior surface of the reactor. The reactor has been operated for several years under similar conditions, and there has never been a need to clean coke from the interior walls. In addition, if droplet impingement were a significant contributor to carbon formation onto the solids, then it would seem reasonable to expect rapid pore mouth blockage near the particle exterior and the inability to subsequently collect significant amounts of coke on the interior of the particle. There was never any evidence of glazing on the exterior of the particles to suggest that droplet impingement had occurred (Figures 3-50 to 3-55).

According to another mechanism proposed by Reyniers et al.³¹ (1994), a heterogeneous noncatalytic mechanism was concluded to be responsible for the majority of coke formation during naphtha cracking, once the metal surfaces of the reactor were covered by filament coke. In their mechanism, free radicals in the gas phase create free-radical sites on non-dehydrogenated polyaromatics at the gas-surface interface. The free radicals then act as sites for addition reactions with unsaturates to increase the size of the macromolecules. Further hydrogen abstraction then occurs to regenerate the free radical sites so that the number of sites remains constant during the addition reactions. For pyrolysis of propylene over carbon active sites, Hoffman et al.³² (1985) observed that the rate of propylene consumption remained unchanged after extensive deposition, suggesting that carbon deposits on the active surface area and then replicates the active sites. Venkateswaran and Back³³ (1994) came to similar conclusions based on methane decomposition over pyrolytic carbon films.

The theory that free-radical sites are important for the coke formation process over carbons is consistent with the results from the present research because coking was found to be constant for substantial periods following the formation of a monolayer of carbon. Also, the measured activation energy for this coke-forming period is suggestive of free-radical

chemistry processes. This theory requires that the gas-phase reactions remain unchanged in nature, but they are increased in rate by the active sites on the coke-forming layer. The cracking chemistry study in section 3.4 will show whether contact with the substrates changed the composition of the gas phase products.

3.4 FLUIDIZED BED CRACKING CHEMISTRY

The purpose of this set of experiments was to complement the coking kinetics study by identifying the major liquid and gaseous cracking products under similar, but steady-state conditions. It is important to characterize the distribution of these products because of the potential impact on the economics of the oil shale process. The loss of oil to gas due to secondary cracking is nearly as detrimental to the economics, as oil loss to coke. The raw gas produced during oil shale retorting has, at best, moderate heating value and contains many contaminants (H_2S , CO_2 , N_2 , etc.) that need to be separated before it can be sold. In addition, accessibility to gas pipelines may be a problem. Therefore, in most cases, the gases are generally considered for in-plant use and are much less valuable than the shale-derived liquids. Minimization of gas production in favor of liquids is preferred. The ideal scenario would be to establish reaction conditions that would crack the heavy liquids to lighter liquids without excessive gas and coke production. For this to be the case, catalytic activity similar to fluid catalytic cracking (FCC) catalysts would be required for the processed shales. This is not completely unrealistic because the first cracking catalysts were natural clays.

The unsteady-state nature of the coking kinetics experiments made it necessary to conduct a completely separate set of experiments to adequately characterize the cracking products. Because carbon continued to accumulate on the batch of solids with time, and possibly change the catalytic activity (if present), a changing slate of products could have been anticipated. The apparatus used to determine coking kinetics was not configured to sample or quantify the liquid products during the progress of the experiment. This is because the coking kinetics system was designed around the constraints of the original system which was a steady-state retorting apparatus. It was deemed more effective to conduct two sets of experiments, rather than make major modifications to the original retort in order to perform a single, comprehensive slate of experiments that included observations for both coking and cracking.

3.4.1 Experimental

3.4.1.1 Apparatus. The apparatus used for the coking kinetics study required only minor modification for the cracking study (Figure 3-65). One of the principal changes was that the coking/cracking (upper) bed was adapted to allow the continuous feed and withdrawal of solids. A feeding system (Items 6 and 8 in Figure 3-65) was added which was identical to the one used in the pyrolysis (lower) bed. In addition, the solids drain at the bottom of the upper bed was sealed, and the overflow pipe in the wall 5 cm above the distributor plate was put into use to control the height of the solids in the bed. A larger solids receiver (Item 10 in Figure 3-65) was installed to collect the greater volume of solids that would pass through the upper bed.

The other modifications to the system were that the combustion tube (in conjunction with the mass spectrometer) was no longer used, and the oil collection system used in previous retorting studies was made operable again. Steam, rather than nitrogen, was the

selected fluidizing medium in order to facilitate efficient trapping of the oil. The use of steam increases the amount of low boiling products that are collected, compared to fixed fluidizing gases, because the condensation of the steam raises the dew point of the vapors. Possible effects of steam fluidization are discussed in the results section of this chapter. Saturated steam was produced in an electrode-type generator, and it was then superheated (Item 5 in Figure 3-65) before it was introduced to the plenum of the lower bed. The semi-butterfly valve was set in the "fluidize" position throughout this series of tests so that the gases and vapors generated by pyrolysis would be directed through the upper bed. Steam, pyrolysis vapors and gases, and entrained solids exited the freeboard of the upper fluidized bed and were directed into an insulated cyclone (Item 13 in Figure 3-65) for solids removal without liquid condensation. The stream then entered an air-cooled heat exchanger (Item 14 in Figure 3-65) to initiate the oil condensation process. An impingement baffle at the inlet of the heat exchanger collected some of the fine solids that passed through the cyclone. It was important to remove as many fines as possible at this point: blockage of the heat exchanger outlet with solids-laden heavy oil has been a difficulty in the past. Some heavy oil collected in the heat exchanger, but the main purpose of this component was to cool the vapor stream and condense the heavy oil in the form of a stable aerosol. Steam, the oil aerosol, fixed gases and uncondensed oil vapors were then directed into an electrostatic precipitator (ESP) to collect the heavy oil. The ESP was maintained at approximately 150°C to prevent the condensation of steam and to lower the viscosity of the oil so that it would drain freely from the collection plates.

The remaining gases, comprising steam, fixed gases and uncondensed oil vapor were then sent to the tube side of a water-cooled shell-and-tube heat exchanger to condense the steam and light oil. The condensate was collected in a receiver for further processing. Now cooled to approximately 25°C, the gases, vapors, and mist were cooled further in two traps immersed in ice-water. Glass wool was placed at the trap exits to aid the collection of water and oil mist. A continuous sample of the remaining gases and vapors was pumped to a gas chromatograph for analysis. The remaining gas/vapor stream was vented into the building fume exhaust system.

3.4.1.2 Procedure. A charge of raw oil shale (nominally 3500 g) was weighed, loaded into the feed hopper, and the hopper was sealed. A similar quantity of processed shale was weighed and loaded into the other feed hopper for these runs which used solids in the upper bed. With nitrogen flowing through the system, all of the electric furnaces and heat tapes were energized to heat the system to the prescribed temperature levels. Once the appropriate temperatures were established, the flow of N₂ for fluidization was replaced by steam. The steam flow rate was checked by measuring the rate of water collected in the condenser receiver. Once all system conditions were stable, the run was initiated by simultaneously starting the screwfeeders for the raw oil shale and processed shale (if used) to meter the solids to the lower and upper beds, respectively. The feeding period lasted approximately 3 hours for each of the runs.

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During the steady state period, the gas chromatograph (Carle Series 400 Model 04397-B) was used for on-line gas sampling every 30 minutes. Hydrocarbons from C_1 to C_5 were separated and detected by a flame ionization detector (FID) and a backflush peak of C_6+ hydrocarbons was eluted and detected by the FID to measure uncollected vapor-phase oils. A second series of columns, which was connected to a thermal conductivity detector (TCD), separated H_2 , CO_2 , CO , H_2S , C_2H_4 , C_2H_6 , CH_4 , N_2 , and O_2 . The condensate from the shell-and-tube condenser (water and light oil) was drained every twenty minutes, weighed, and stored in sealed bottles for subsequent separation and processing. All other liquids were allowed to accumulate in the system for later retrieval.

At the end of the experiment, the system was allowed to cool overnight, and was opened for inspection the next day. The processed shale, in the receiving bins for the upper and lower beds and the cyclone, was weighed and sampled for analysis. The air-cooled heat exchanger was removed and thoroughly cleaned with dichloromethane. Any oil clinging to the inside of the ESP was cleaned with this solvent and the washings were combined with those from the heat exchanger. These washings were then filtered and the solvent was evaporated to determine the weight of oil. The filtration residue was dried, weighed and sampled for analysis. The majority of the oil collected by the ESP accumulated in a receiving bottle beneath the unit. Water was decanted from the more dense ESP oil, and the oil was sampled for analysis. The water and light oil removed from the condensate receiver were decanted in a separatory funnel. Sometimes centrifugation of materials near the oil/water interface was required to achieve good separation. The oil/water mixtures collected in the two ice-water traps were combined with the liquids from the condensate receiver. In all, the oil was combined into three separate oil fractions for mass determination and chemical analysis: heat exchanger oil, ESP oil, and condenser oil. A fourth oil fraction, vapor-phase C_6+ detected by GC, was included in the mass balance. A sample of the separated water was analyzed for total carbon and sulfur, suspended and dissolved solids, and pH.

Ultimate analyses were performed on all processed solids and the three oil fractions. One of the most important reasons for this was to determine component balances (carbon in particular) for each run. The carbon balance closure for the runs in this series averaged above 95% which is a good indication that the operating and analytical procedures were satisfactory. Another important function of the ultimate analysis is to characterize both the oil and solid fractions. Many inferences about the physical and chemical properties of oils may be obtained by ultimate analysis, and it can provide an important basic tool in characterizing such a complex material as shale oil liquids.

3.4.1.3 Materials. The same shale materials that were used in the coking kinetics study (Tables 3-14 and 3-15) were also used in this study. Only processed shales (combusted, gasified, and pyrolyzed) were used as substrates in the upper bed. The low-carbon mineral analogs (kaolinite and illite) were not used in these experiments.

3.4.2 Results and Discussion

3.4.2.1 Operating Conditions. Five runs were performed, two without vapor/solid contact, and three with solid contacting. The test matrix was established so that the run conditions would be similar except for the absence or presence of solids in the upper bed and the type of solids used (Table 3-20). Additionally, in order to obtain an indication of the importance of vapor-phase thermal cracking reactions, one run was performed in which raw shale was pyrolyzed in the upper bed, thereby reducing the vapor residence time by more than 50%. This method of reducing the vapor residence time was more favorable than the alternative of increasing the fluidizing gas velocity. By increasing the rate of steam flow, the bed would become more turbulently mixed and the concentration of vapors would decline making the operating conditions sufficiently different to put into question any comparisons of the results.

The mean pyrolysis temperature for each of the runs was between 532 to 540°C. This temperature range was shown in a previous fluidized bed pyrolysis study to produce the maximum oil yields for eastern U.S. oil shale.³⁵ The goal for each of the runs was to reproduce the pyrolysis conditions as closely as possible so that the concentration and character of the pyrolysis vapors contacting the substrate in the upper bed would be nearly identical. In general, the mean run conditions that were recorded for each run were essentially the same (Table 3-20), and it is assumed that any differences in product distribution can be assigned directly to the conditions in the upper bed. The pyrolysis conditions for Run-3 were slightly different than the other four runs because the size of the upper bed was smaller which caused the solid residence time to be reduced significantly. The shorter solid residence time could cause a slight decrease in oil production, but it has been shown in previous studies that 6.8 minutes is sufficient for pyrolysis to be greater than 99% complete under these conditions.^{5,34}

3.4.2.2 Mass And Carbon Balances. In addition to providing important information about the product distribution, the closure of mass and carbon balances indicates whether the accuracy of the operating and analytical procedures were satisfactory. Mass balance closure for the 5 runs ranged from 91.5 to 94.2 wt% on a water-free basis. The shortage is attributed principally to water that is not accounted in the balance procedure. Since steam was used for fluidization, it was not possible to differentiate the relatively small amount of moisture released from the shale. The moisture content of the shale, including mineral-bound water, is approximately 4 wt%, which significantly improves the water-free balances listed in Table 3-21. Since the steam rate was so high, it is possible that appreciable amounts of volatile pyrolysis products became dissolved in the condensed steam. These materials were also not included in the water-free mass balances. Also, it is to be noted that the mass balance closure is approximately 1.5 wt% lower for the solid/vapor contact runs compared to the others. The reason for this is that the surface moisture on the processed shale, which was approximately 1.5 wt%, was not accounted in the balances. If the mass balances included the approximately 4 to 5.5 wt% of the moisture in the solids, the overall mass balances would all be greater than 97%.

Table 3-20. Mean Run Conditions for the Steady-State Cracking/Coking Experiments with Eastern U.S. Oil Shale

Run#	1	2	3	4	5
Upper Bed Weight (g)	108	0	135	108	108
Upper Bed Substrate	Comb.	none	n/a	Gasif.	Pyrol.
Mean Pyrol. Temp. (C)	540	533	532	538	537
Mean Cracking Temp. (C)	548	542	na	524	524
Recycle Ratio	0.68	0.00	0.00	0.74	0.84
Freeboard Height (cm)	112	112	44	112	112
Mean Shale Residence Time (min.)	14.3	13.2	6.8	13.7	13.5
Mean Shale Feedrate (g/minute)	19.2	20.8	19.8	20.1	20.3
Mean Steam Flowrate (g/minute)	47.2	49.0	45.8	47.1	47.1
Superficial Velocity (cm/s)	64.3	66.1	61.8	64.0	63.9
Vapor Residence Time (s)	1.74	1.69	0.71	1.75	1.75
Pyrolysis Bed Location	Lower	Lower	Upper	Lower	Lower
Run Length (minutes)	183	169	177	175	153

Table 3-21. Mass Distribution for Steady-State Cracking/Coking Experiments with Eastern U.S. Oil Shale.

Run#	3	2	5	4	1
Substrate	None	None	Pyrol.	Gasif.	Comb.
Pyrolysis Bed	Upper	Lower	Lower	Lower	Lower
	Yields, % of Raw Shale Weight				
<i>Raw Shale (as received)</i>	100.00	100.00	100.00	100.00	100.00
<i>Substrate (Comb Shale)</i>	0.00	0.00	84.46	74.47	67.64
<i>Processed Solids (Total)</i>	84.47	85.07	167.01	157.73	150.91
Pyrolyzer Bin	79.88	81.39	80.77	80.44	79.26
Substrate Bin	0.00	0.00	80.01	72.17	65.72
Cyclone	3.89	2.99	5.45	4.37	4.59
Heat Exchanger	0.70	0.70	0.77	0.76	1.34
<i>Liquids (Total)</i>	6.61	6.33	5.91	6.10	5.45
Heat Exchanger	2.06	2.42	1.97	1.91	2.25
ESP	2.50	1.70	2.01	1.96	0.54
Condenser	1.48	1.55	1.41	1.41	1.72
C5+ Vapor	0.58	0.65	0.51	0.82	0.93
<i>Gases (Total)</i>	2.40	2.79	3.08	3.02	3.29
CH ₄	0.27	0.34	0.35	0.37	0.41
C ₂ 's	0.26	0.39	0.40	0.43	0.46
C ₃ 's	0.22	0.28	0.29	0.31	0.33
C ₄ 's	0.17	0.23	0.24	0.26	0.26
CO ₂	0.61	0.60	0.92	0.68	0.71
CO	0.20	0.21	0.29	0.24	0.25
H ₂ S	0.60	0.70	0.54	0.67	0.80
H ₂	0.06	0.05	0.05	0.07	0.07
<i>Total (less water)</i>	93.49	94.19	91.53	92.38	92.01
<i>Water Collected</i>	231.83	235.48	231.20	233.98	245.93

Due to the high ash levels and the problems in dealing with moisture, the carbon balance closure provides a more accurate assessment of the validity of the analytical and operating procedures. Carbon balance closure was higher than that of the mass balances and ranged from 93.9 to 98.5 wt% (Table 3-22). While the water-soluble products could not be included in the overall mass balances, they were included in the carbon balances by determining the carbon content of the water. Up to 8 wt% of the carbon in the raw shale was detected in the condensed steam. The concentration of dissolved carbon in the water was not particularly high (0.4-0.5 wt%), but due to the large volume of water used, water-soluble species can contribute significantly to the overall carbon balances. Further, the levels of dissolved carbon in the condensed steam may have been underestimated because of the loss of dissolved gases prior to analysis.

The carbon distributions for the five runs were reasonably similar to those obtained in previous fluidized bed pyrolysis experiments with eastern U.S. oil shales.³⁵ Approximately 50% of the carbon partitioned to the solid phase as char, 29.9-33.1% was collected as oil, 6.3-9.4% formed gas and 5.3-8.2% was detected in the aqueous phase. However, the primary conversion to oil was slightly lower than that reported for fluidized bed pyrolysis. Carter and Taulbee³⁵ (1985) have reported a carbon conversion to oil of 49% and conversion to char of approximately 45% in a 7.6-cm diameter retort with Cleveland member oil shale. Since the char yield is high in the current study, it appears that inefficient oil collection cannot be the primary reason for the low oil yield, as does the good average carbon balance closure of 95.8%.

The carbon residue resulting from the primary pyrolysis reactions is referenced as "char" in this context to distinguish it from the coke that is formed by secondary reactions away from the original shale particle. The use of the term char may not be strictly correct, because it is arguable whether the kerogen components that produce the "char" remain in a solid state during carbonization.

As a point of clarification, organic carbon represents approximately 99% of the total carbon in Cleveland oil shales,³⁶ so the total carbon distributions in Table 3-22 essentially reflect the organic carbon distribution. For many oil shales of the world, however, carbonate minerals are abundant, so the distinction between organic and mineral carbon then becomes important.

3.4.2.3 Oil Shale Sample Aging. One possibility for the unexpectedly low oil yield obtained in the present study is that aging of the oil shale diminished its oil yield potential. The master sample of oil shale used in the present studies was in storage, following crushing and screening, for approximately five years. Coburn and Rubel³⁷ (1983) reported that aging of eastern U.S. oil shale can significantly reduce its oil yield potential. Coburn and Barron³⁸ (1985) later attributed the loss of oil yield to the oxidation of pyrite which caused enhanced hydrogen abstraction from the kerogen and lowered the oil yield. In these studies, the decrease in oil yield over a period of a year was found to be approximately 10% and to correlate with the square root of time. Longer studies were not carried out. The oil shale

Table 3-22. Carbon Balances for the Steady State Cracking Runs

Run#	3	2	5	4	1
Substrate	None	None	Pyrol.	Gasif.	Comb.
Pyrolysis Bed	Upper	Lower	Lower	Lower	Lower
	Yields, % of Raw Shale Carbon				
<i>Raw Shale (as received)</i>	100.00	100.00	100.00	100.00	100.00
<i>Substrate (Comb Shale)</i>	0.00	0.00	51.53	32.95	6.38
<i>Total Carbon Input</i>	100.00	100.00	151.53	132.95	106.38
<i>Processed Solids (Total)</i>	49.49	48.63	48.90	51.23	52.30
Pyrolyzer Bin	45.91	46.34	47.63	47.06	45.62
Substrate Bin*	0.00	0.00	-3.22	0.74	4.43
Cyclone	3.03	1.85	3.93	2.92	1.75
Heat Exchanger	0.55	0.43	0.56	0.51	0.51
<i>Liquids (Total)</i>	33.12	32.17	29.88	30.50	28.65
Heat Exchanger	10.48	12.18	10.52	9.63	11.83
ESP	11.69	8.27	8.87	8.92	2.55
Condenser	7.75	8.15	7.68	7.49	9.11
C5+ Vapor	3.20	3.57	2.81	4.46	5.16
<i>Gases (Total)</i>	6.29	7.88	8.95	8.75	9.43
CH4	1.26	1.59	1.65	1.74	1.94
C2's	1.38	2.03	2.11	2.24	2.43
C3's	1.14	1.48	1.53	1.61	1.76
C4's	0.91	1.20	1.28	1.36	1.39
CO2	1.05	1.02	1.60	1.17	1.24
CO	0.55	0.56	0.78	0.64	0.68
H2S	0.00	0.00	0.00	0.00	0.00
H2	0.00	0.00	0.00	0.00	0.00
<i>Total (less water)</i>	88.89	88.68	87.73	90.48	90.38
<i>Water</i>	5.26	7.69	6.18	5.56	8.15
<i>Total</i>	94.15	96.37	93.90	96.04	98.53

* The amount of carbon contained originally in the substrate was subtracted from the amount collected in the "coked" substrate. Therefore, a small negative value could mean that the carbon content of the substrate dropped slightly or that a significant amount of substrate was entrained and collected in the cyclone and the air-cooled heat exchanger.

sample in the current study was stored in sealed bags that were placed within 55-gallon drums. Although closed, the drums were not rendered air tight. The potential for air oxidation during such an extended period of time was certainly high, and it appears reasonable to expect that some loss of oil yield potential could have occurred.

However, the extent of aging of the master sample is only a secondary issue here. The most important issue is whether the characteristics of the sample changed significantly between the coking kinetics study and the current cracking study. The master sample had been stored for approximately 3 years when the coking kinetics study commenced, and another 2 years passed before the steady-state cracking study was initiated. Carbon analyses of the pyrolyzed oil shales from the coking kinetics study were routinely performed to verify the performance of the pyrolysis zone. The average carbon removal from the raw shale for the coking study was 50.3% which was identical to the results that were obtained in the current cracking study. Therefore, it does not appear that the additional two years of storage significantly affected the oil generating potential of the raw oil shale.

3.4.2.4 Effects of Steam on Pyrolysis/Cracking. While every effort was made to keep the conditions of the coking kinetics study and the cracking chemistry study as similar as possible, it was necessary to use different fluidizing media in each case to accommodate practical considerations. In the case of the coking kinetics study, nitrogen fluidization was essential because a large steam partial pressure caused condensation problems in the sampling system to the mass spectrometer. In the case of the steady-state cracking study, steam was used because the oil collection system was most efficient when used with steam. Moreover, the oil collection system that was used for the cracking study could not handle the larger volume of fixed gas from nitrogen fluidization at room temperature and below because the system was designed specifically for steam. The potential effects of steam compared to nitrogen during oil shale pyrolysis cannot be dismissed lightly, however. There has been a longstanding debate in the oil shale literature concerning this issue. A full examination of the topic would require a digression that is too extensive for this work, but a brief evaluation will be given in the following paragraphs for completeness.

Various investigators have argued that steam plays either a direct chemical role by somehow donating hydrogen to the kerogen to improve oil yield, or an indirect role by capping free radicals or passivating shale surfaces to reduce oil cracking reactions. Many of these studies were performed under a variety of different conditions which do not relate to the fluidized bed pyrolysis of eastern U.S. oil shale. High pressure steam pyrolysis studies have produced the most significant results. Higher quality oil^{39,40} and increased kerogen conversion to soluble products⁴¹ have been reported for high pressure steam conditions. In attempts to simulate natural petroleum generation from oil shale under "hydrous pyrolysis" conditions, workers have observed petroleum-like oil⁴² and lower olefinic unsaturation of the oils.⁴³ While the precise role exerted by steam under these conditions is still uncertain, there is little doubt that it could function as a reactant.

Studies performed at atmospheric pressure, however, have been less convincing on the subject of the reactive nature of steam. Modest increases in collected oil yield for steam-swept experiments in fixed-bed reactors, over that obtained with inert-gas sweep, have been reported by several workers,^{44,45,46,47} but no specific details were presented to clarify the role of the steam. In fixed-bed retorts, reaction times are generally long because of the relatively slow heat-up rate, so there is some opportunity for chemical reactions between the kerogen and steam to take place if, indeed, these types of reactions do proceed. In fluidized bed reactors, however, any contact between kerogen (or its pyrolyzate) and steam is short-lived. The high heat and mass transfer rates in fluidized beds cause pyrolysis to occur quickly, and any attendant reactions must also be rapid. Even though steam has exhibited some reactivity in the fixed-bed studies, these effects do not necessarily translate to fluidized bed systems.

Literature on the rapid steam pyrolysis of oil shale was sparse in the early 1980's, and a study was performed at the University of Kentucky's IMMR (now CAER) by Carter and Taulbee³⁵ (1985) to evaluate steam as a fluidizing medium for eastern U.S. oil shale. The experiments were performed in a single-stage, fluidized-bed apparatus which was a predecessor to the one used in the current cracking study. The basic conclusion of this work was that the major effect of steam was to improve the collection efficiency of light oil products. Steam improves oil collection through its condensation and the subsequent increase in oil vapor partial pressure, allowing the condensation of more light components. During inert-gas retorting, a significant portion of the lighter oils remains in the vapor phase and is not physically collected. An important feature of the Carter and Taulbee experiments was that the concentration of the vapor-phase (non-condensed) oils was determined, so that the collection efficiency was not a factor in determining the true oil yield.

It is possible that the oil yield enhancement attributed to steam for some of the studies cited may be due, in part, to the improved oil collection efficiency with steam and not to any reactivity that it may possess under those conditions. Slightly greater carbon removal (2%) by steam was reported by Carter and Taulbee which was reflected by greater amounts of water soluble carbon and increased CO₂ production. It is possible that a small amount of residual carbon was gasified by steam to achieve those results. Otherwise, the quality of the oils and the hydrocarbon gases were identical for steam and nitrogen fluidization. The comparison of the carbon removal from the coking kinetics runs and the more recent cracking chemistry experiments indicates that the production of volatile pyrolysis products was not significantly enhanced by steam.

In the present research, it is relevant to resolve whether steam was reactive during the steady-state cracking experiments. If it appears that steam could have played a reactive role, then comparisons between the steady-state cracking experiments and the coking kinetics study must be approached with caution. There is a large body of information relating to the industrial pyrolysis (or steam cracking) of various petroleum fractions because it is the preferred method of production for olefins worldwide.⁴⁸ Since ethylene is produced in greater volumes than any other organic chemical in the world,⁴⁹ a tremendous amount of expertise has been developed in steam cracking processes. The conditions within a steam cracker are

generally similar to those in a fluidized bed oil shale retort using steam for fluidization. The main differences are that a cracking unit operates at a higher temperature (650-870°C)⁴⁸ and there is no contact with solids except for the walls of the cracking furnace. It is well documented that steam is used primarily as a diluent for the cracking process and that it has no effect on the homogeneous gas-phase cracking reactions.^{48,49,50,51,52} The control of the hydrocarbon partial pressure is critical for selectivity to olefins and the reduction of coke formation due to recombination reactions.

At the same time, steam has been found to act chemically on the surfaces in steam crackers. It can gasify the coke formed on the walls of the cracker to produce carbon oxides, and it can also alter the surface properties of the metal and indirectly influence the coke forming tendencies.⁵³ Steam is also useful as a diluent commercially because its condensation at a relatively high temperature results in smaller volumes of gas to be fractionated and separated at low temperatures compared to lower boiling materials such as nitrogen, hydrogen, hydrogen sulfide, ammonia, etc. This is analogous to the improved oil collection efficiency for steam retorting of oil shale.

Considering the convincing body of evidence in the steam cracking literature and the conclusions of the steam retorting study by Carter and Taulbee,³⁵ it will be assumed in the following discussions that steam did not cause a significant difference between the gas-phase cracking reactions that occurred in the coking kinetics and the steady-state cracking studies. These studies did not, however, necessarily rule out the possibility that steam can alter the surface properties of the shale which can, in turn, affect the rate of subsequent carbon deposition. As described previously in the coking kinetics section, mild steam pretreatment and moderate steam partial pressures did not apparently affect the rate of carbon deposition. Also, at temperatures of less than ~600°C, steam gasification of coke is slow.⁵⁴ Therefore, even the surface effects of steam are expected to be minimal.

3.4.2.5 Oil Fractionation During Collection. Four separate oil fractions were specified in the mass and carbon distributions that have been previously discussed: heat exchanger, ESP, condenser, and C₆+ vapor. Due to the step-wise lowering of the temperature in oil collection system, the separation of the oil products into a few major fractions was automatic. Experience has shown that these oil fractions have general physical properties that are fairly independent of reaction conditions, but the relative amount in each fraction changes as a function of the reaction parameters.

The oil that is collected in the air-cooled heat exchanger and the ESP is always blackish, viscous and dense. The oil boils above 150°C because the ESP is maintained at least at that temperature. Oil that is characterized as heat-exchanger oil also contains oil that is washed from the ESP, so it is often most appropriate to lump the two quantities together and describe them as "heavy" oil. The heavy oil is always more dense than water for the products of eastern U.S. oil shales. It is necessary to decant any condensed steam from the collected oil because it clings to the bottom of the container. The oil that is collected downstream of the water-cooled condenser is always less dense and viscous than the heavy oil and usually

has a brownish appearance. The specific gravity of this "light" oil is less than 1.0 when the ESP is operating properly. By comparing the relative amounts of "heavy" and "light" oil, significant information regarding the character of the oil and the effects of reaction conditions may be obtained.

3.4.2.6 Gas-Phase Cracking. By comparing the results from the two non-solid-contact runs, the importance of gas-phase cracking can be observed. The total yield of oil decreased slightly when the residence time of the pyrolysis vapors was increased from 0.7 s to 1.7 s (Run-3 and -2 in Figure 3-66). This loss in oil yield was reflected by a decrease in the heavy oil fraction as described above. The amount of light oil appeared to be unchanged. The aromaticity (as indicated by the H/C molar ratio) of the oil fractions, and the oil as a whole, was also similar for the two runs. The loss in oil yield was accompanied by an increase in hydrocarbon gas production (Table 3-22). Not only was the yield of gas increased, but the composition of the gas shifted as a result of the increased vapor-phase residence time (Table 3-23). The yield of olefins, with the exception of 1-pentene, increased at the longer residence time. Methane and ethane increased slightly but the higher n-alkanes were slightly reduced. The isobutane yield was also reduced, but the change should not be over-emphasized, because the levels of isobutane were near the detection limits of the gas chromatograph.

The shift to greater α -olefin production and a predominance of C_1 - C_3 products is consistent with the free- radical/thermal cracking mechanism (generally referred to as the Rice-Kossiakoff mechanism) for paraffins as first outlined by Rice and coworkers^{55,56,57,58,59} (1931-1943). The first step in this mechanism is the cleavage of a carbon-carbon bond to form free radicals:

The free radical may then undergo β -scission to form a secondary free radical and an α -olefin:

Free radicals can also abstract hydrogen from other hydrocarbon molecules to form new radicals:

The Rice-Kossiakoff theory predicts that hydrogen abstraction from primary, secondary, and tertiary carbon atoms occurs at the relative rates of 1.0:3.7:13.4, respectively. Experimental studies by Greensfelder, et al.⁶⁰ (1949) showed good agreement with theory for the thermal cracking of n-hexadecane. Under normal cracking conditions, hydrogen abstraction is slow compared to β -scission.⁶¹ The β -scission and hydrogen abstraction reactions (Equations 3-15 and 3-16) proceed so that the most stable olefin is formed and continue until mostly C_1 to C_3 's and α -olefins are produced. No isomerization involving migration of alkyl groups or

Figure 3-66. Oil yield for the steady-state cracking experiments. Numbers are the H/C molar ratios for each fraction and the weighted mean H/C ratio.

Table 3-23. Composition of the Gas (Vol%) from the Steady-State Coking/Cracking Runs on a N₂-Free Basis.

Substrate	None	None	Pyrol.	Gasif.	Comb.
Pyrolysis Bed	Upper	Lower	Lower	Lower	Lower
Run#	3	2	5	4	1
Methane	15.36	17.79	17.14	17.02	16.91
Ethene	2.86	5.41	5.39	5.44	5.13
Ethane	5.33	5.82	5.31	5.25	5.07
Propene	2.63	3.74	3.62	3.62	3.54
Propane	1.99	1.82	1.70	1.66	1.62
1-Butene	0.77	1.07	0.97	0.99	0.89
N-Butane	0.83	0.60	0.68	0.65	0.65
Isobutene	0.38	0.49	0.48	0.50	0.43
Isobutane	0.09	0.04	0.08	0.07	0.06
T-2-Butene	0.26	0.30	0.33	0.31	0.29
C-2-Butene	0.19	0.22	0.24	0.22	0.22
1,3-Butadiene	0.27	0.58	0.60	0.64	0.54
1-Pentene	0.47	0.47	0.48	0.41	0.50
N-Pentane	0.49	0.42	0.40	0.38	0.37
C6+	5.44	5.68	3.95	6.35	6.51
Hydrogen	26.78	20.62	21.38	24.47	24.83
Hydrogen Sulfide	16.31	17.24	12.64	14.39	15.68
Carbon Monoxide	6.73	6.25	8.07	6.23	5.95
Carbon Dioxide	12.82	11.43	16.54	11.39	10.82

shifts in the radical position occurs,⁶² but double bonds do shift slowly.⁶⁰

The thermal cracking of paraffins produces aromatics by cyclization and condensation reactions, but the extent of these reactions is small.⁶² The participation of aromatics in thermal cracking is limited to the side-chain cracking of alkyl aromatics within the side chain so that toluene is the smallest major product.⁶⁰ Aromatics are also expected to be involved in condensation reactions to form tars and coke because of the ability of the benzyl radical to combine readily with other aromatics.⁵⁰ Therefore, the aromatic fraction of the pyrolyzate from eastern U.S. shales is expected to produce both condensed products and lighter hydrocarbons upon exposure to high temperatures.

The compositions of the gases produced in the steady-state runs (Table 3-23) are similar to those obtained by Griswold et al.⁵² (1976), whose goal was to maximize ethene production by steam cracking of western U.S. shale oil. Methane, not ethene, was the major gaseous product in the current study, but at higher severity (i.e. longer residence time), higher ethene concentrations were produced. The higher ethene production from the western U.S. shale oil was attributed to its more aliphatic nature. Because of the high aromatic content of eastern U.S. oil shale, paraffin-type thermal cracking was not as significant. Another major difference between these studies is that non-hydrocarbon gases were more prevalent in the current study because all of the retorting products, including mineral byproducts, were contained in the gas stream. The Griswold study involved cracking of previously produced shale oil, so the whole slate of pyrolysis products that would be obtained with raw shale was not represented. Significant levels of H_2 , H_2S , CO_2 , and CO were present in the gases from the current study. The high level of H_2 is probably due to the charring reactions that accompany the pyrolysis of the most aromatic kerogen components (which yield little or no oil). Eastern U.S. shale contains significant quantities of iron disulfide minerals (pyrite and marcasite) which decompose to form pyrrhotite (FeS) and H_2S in the presence of a hydrogen donor. It is possible that the carbon oxides originated from trace carbonate minerals, organic oxygen, and steam gasification reactions.

The influence of diluents (H_2 and H_2S , in particular) other than steam have been shown to be significant in terms of affecting the rate of thermal cracking. For example, Rebick⁵⁰ (1983) concluded that H_2S acted as a catalyst for hydrogen abstraction which reduced C_1 - C_2 gas yields due to the stabilization of intermediate alkyl radicals. These effects are not expected to be significant in the current study, however, because the high steam:shale oil ratio (approximately 25:1 on weight basis) caused the gas species within the reactor to be extremely dilute. The partial pressure of H_2S in the current study was at least an order of magnitude lower than that reported for the Rebick study.

3.4.2.7 Cracking Reactions over Solids. The contact of oil shale pyrolyzate with solids during these experiments reduced oil yield (Figure 3-66). As would be assumed from the coking kinetics studies, some of this loss in oil yield must be attributable to coke formation on the solids. To determine the amount of carbon deposited on the substrate as a percentage of the raw shale carbon, the entrained fines of the substrate in the cyclone and

heat exchanger, and the small amount of solids that weep through the upper gas distributor, must be taken into account. Therefore, the net carbon gain for the solids collected in the substrate bin compared to the carbon contained in the substrate which was fed into the upper bed for Run-5 (Table 3-22) is negative. However, by using Run-2 as the baseline for carbon distribution on the shale particles due solely to pyrolysis, the net amount of coke formation on the processed shales in the upper bed may be determined readily. For Run-5, the percentage of carbon in the raw shale that was deposited onto the pyrolyzed shale in the upper bed was $48.90 - 48.63 = 0.27\%$. By making the same adjustment for the three solid-contact runs, the percentage of raw shale carbon that resulted in coke formation on the substrates was:

Run#	Substrate Type	Coke Formation on Substrate, % Raw Shale C
5	Pyrolyzed Shale	0.27
4	Gasified Shale	2.60
1	Combusted Shale	3.67

As would be expected, the same order of coking activity was observed for the steady-state cracking study as for the coking kinetics study.

Contact with pyrolyzed and gasified shales in the upper bed resulted in similar increases in gas yield (Table 3-22) over the solid-free run (Run-5 and -4 vs. -2). The decrease in oil yield for the two runs was found to be almost evenly distributed among the oil fractions. Contact with the gasified solids produced slightly less heavy oil and more light oil (Figure 3-66). The relative gas composition for Run-4 and -5 was essentially identical with that of the solid-free run (Run-2, Table 3-23). Therefore, contact with the solids apparently increased the rate of cracking reactions, thereby increasing the yield, but the mechanism was still apparently consistent with a free radical type of process. Greensfelder and coworkers⁶⁰ (1949) proposed that so-called "inert" solids can enhance the cracking rate through a free-radical pathway. They also showed that activated carbon can enhance cracking by a thermal cracking pathway where free radicals are formed at the surface, β -scission occurs, and the primary radical is rapidly quenched by a hydrogen atom at the surface. Their calculations for this mechanism and the actual experimental results were reasonably consistent. This quenched type of free-radical pathway produces gases that are higher in carbon number compared to homogeneous cracking, and the product slate is approximately intermediate to the results for acid-catalyzed reactions.

It is not expected that the carbon-rich shales in the current study would come close to the behavior of an activated carbon because of differences in surface area and surface activity. However, the gasified shale is expected to possess at least a low level of surface activity due to the introduction of oxygen functional groups in the carbon surfaces and due to partial uncovering of mineral surfaces by steam-carbon gasification. Taulbee⁶ (1994) showed in model-compound studies that gasified oil shale was more active than pyrolyzed or combusted oil shales in terms of promoting cracking. In Taulbee's work, it was concluded that free

radical mechanisms were dominant because of the absence of branched products. In the present research, it appears that the gasified shale introduced an increase in free radical activity compared to the pyrolyzed shale, as indicated by the higher light oil yield, lower heavy oil yield, and increased coke production. Because of the high aromatic content of eastern U.S. shale oil, condensation of multi-ring aromatics to form coke and increased light oil production at the expense of heavy oil is an expected outcome of an increase in free radical activity.

Contacting the shale oil vapors with combusted shale produced even greater amounts of gas than the other solids, and effected a significant shift in the yields and H/C atomic ratios of the oil fractions (Figure 3-66). With this evidence alone, it may be tempting to attribute some sort of catalytic cracking activity to the combusted oil shale. However, the gas composition was basically the same as in the other solid-contact runs, which again favors a free-radical pathway. As shown in the coking kinetics study, the bare mineral surfaces of the combusted shale cause the rate of coking to be more rapid during the initial exposure period. It was proposed that polycyclic and heterocyclic aromatics which have relatively high levels of basicity were more strongly attracted to the acidic surfaces of the carbon-free shale minerals than the more "inert" carbon-covered surfaces. It is possible that chemisorption can occur between these molecules and surface sites with the formation of covalent bonds.

The adsorption of a gas-phase molecule and the creation of a carbonium ion on a solid surface are the first steps in acid-catalyzed cracking. It is generally recognized that acid catalysts like amorphous silica alumina and the crystalline zeolites promote cracking through a carbonium ion intermediate on the surface of the catalyst.^{62,61} The products of this type of mechanism are C_3 - C_6 including many branched components. Since these types of cracking products were not observed, the shale minerals in the current study, while slightly acidic in nature, clearly do not function in the same way as cracking catalysts.

In catalytic cracking, charge transfer must occur on the surface of the solid in order for isomerization to occur along the hydrocarbon chain. Otherwise, the charge separation would be too great to allow the process to proceed. The mechanism for this charge transfer is still not completely understood, but Gates et al.⁶² (1979) suggest that a charge may be distributed over the oxygen anions in zeolites to facilitate charge movement. They also point out that it has also been suggested that a combination of Lewis and Bronsted acid sites may participate in concert during catalytic cracking to accomplish solid-state charge transfer. Therefore, the creation of a carbonium ion alone does not necessarily mean that cracking will follow.

It is proposed that, in the systems studied in this research, polycyclic and heteroatom-containing aromatics are adsorbed onto the shale minerals. The ensuing processes are non-catalytic in the sense that the surfaces do not function as cracking catalysts. The immobilized species can support free radical sites at the adsorbate-vapor interface that promote thermal cracking and polycondensation. The product distribution for the combusted-shale run (Run-1) is consistent with polycondensation to form more carbonaceous deposits and a more highly unsaturated heavy oil, and it is also indicative of increased thermal cracking to produce lighter

liquids and more gases. The production of more gas and higher boiling liquids was also found by Appleby et al.²³ (1962) in a study of coke formation on amorphous silica-alumina catalysts by aromatics. They found that the major products of aromatic cracking were coke, light gases (mainly methane), and liquids of equal or higher boiling range than the feed material. They assumed that catalytic processes had influenced the formation of coke, but in the current study there is no evidence to support acid-catalyzed behavior of the shale minerals. One could argue that the highly aromatic materials used in the study could have masked catalytic pathways. However, Taulbee⁶ (1994) observed no branched species when utilizing n-alkanes in experiments with combusted oil shale, and free-radical pathways afford the most favorable explanation for coke formation in the current study.

3.4.3 Summary and Conclusions

The principal cracking mechanisms for the conditions of this study are:

- 1) Adsorption and possible chemisorption of polycyclic and heterocyclic-containing aromatics onto clay minerals.
- 2) Typical gas-phase thermal cracking involving free-radical mechanisms.
- 3) Creation of "active sites" on deposited carbons by gas-phase free radicals that promote additional cracking and polycondensation reactions.
- 4) Evidence of acid-catalyzed reaction products was not observed.

3.5 FIXED-BED PYROLYSIS AND HYDROPYROLYSIS

The design of the fluidized bed cracking and coking apparatus used in the current study limited its operation to atmospheric pressure, which can be a constraint when studying the rate-influencing phenomena for carbon deposition over porous solids. Voorhies¹⁵ (1945), for example, showed that the rate of carbon deposition onto cracking catalysts is largely unaffected by the partial-pressure of oil vapor, over a relatively small range. While a recent study by Mieville⁶³ (1991) did show a slight dependence of the coking rate on space velocity, for the most part, catalytic coke formation has been found to be relatively insensitive to space velocity. In the current fluidized bed studies, however, it has been clearly shown that carbon deposition is influenced by space velocity. The difference in behavior between the current study and the study by Voorhies may be due to differences in the type of coke formed in each of these studies. According to the coke classification system described by Venuto and Habib⁶¹ (1979), the cracking of highly aromatic shale oil is expected to produce mainly additive coke, while the more saturated petroleum feeds used in the Voorhies study should produce mainly catalytic coke. As the formation of additive coke has been reported to be dependent on oil vapor concentration, the goal of this part of the current study was to examine this dependence at much higher total pressures.

A two-stage fixed-bed reactor at the University of Strathclyde, Glasgow, Scotland, capable of operating at pressures up to 15 MPa, was used for this test series. In addition to providing more information concerning the effects of oil vapor partial pressure on the coking mechanisms of shale oil vapors, the study was also applicable to elucidating the coking reactions that may be expected during the catalytic hydrotreating of shale oils.

The apparatus was originally designed for research on the two-stage hydrolysis of coal, Bolton et al.⁶⁴ (1989) and Snape et al.⁶⁵ (1989). It provided the capability to examine the effects of hydrogen partial-pressure on coking and to characterize the volatile products of coking and cracking. Pyrolysis (or hydrolysis) occurs in the first stage of the reactor, and solids may be loaded into a second stage to study secondary reactions. The same combusted oil shale used in the fluidized bed studies, and a commercial Ni/Mo/ γ -alumina catalyst, were used as the second-stage substrates. The catalyst was used to provide some comparisons with the combusted shale, as it possesses drastically different surface characteristics, and could allow some insights into the processes of coking onto hydrotreating catalysts.

3.5.1 Experimental

3.5.1.1 Materials. The samples of raw and combusted oil shales utilized in these studies were from the same master samples as used in the fluidized bed coking and cracking experiments. Prior to using the commercial Ni/Mo/ γ -alumina hydrotreating catalyst, it was precalcined at 400°C for 12 hours to remove water and trace organics, and to improve its mechanical strength at the reaction temperatures.

3.5.1.2 Apparatus and Procedure. The reactor was fabricated from high-pressure stainless steel tubing (0.79 cm I.D.) and was configured for both single- and two-stage operation (Figure 3-67).^{64,65} The first stage consisted of a bed of raw oil shale supported by a wire wool plug. By establishing a low-voltage potential across the first stage using a high-ampere transformer, electrical current passed axially through the reactor tube and heated the shale to pyrolysis temperature. This method of heating provided a uniform temperature within the bed of shale and enabled high heating rates to be achieved (up to 5°C s^{-1}). When a second stage was utilized, it was heated by a furnace which enclosed the reactor tube. The second stage was preheated to its target temperature prior to heating the first stage. Sweep gas (N_2 or H_2) flowed downward and carried the reaction products to a dry-ice-cooled coil where liquids were condensed and collected.

In all tests, the bed of raw oil shale (first stage) was heated at 5°C s^{-1} to a temperature of 520°C and held there for 10 minutes. Sweep gas (N_2 or H_2) constantly flowed through the reactor during the heat-up and constant-temperature periods. The gas flowrate was measured downstream of the pressure let-down valve, and a representative sample was collected for analysis of $\text{C}_1\text{-C}_4$ by gas chromatography. Following each run, the cold trap was weighed and rinsed with toluene to recover the liquids. In all cases the water content of the toluene wash from the trap was too low to be detected by the Dean-Stark method. Instead, it was assumed that the raw shale produced 4 wt% water which was completely collected in the trap. Oil analyses included: size exclusion chromatography using a PL gel column (30 cm long, $5\text{ }\mu\text{m}$ particles, 10 nm pore size) with UV detection, and polystyrene standards for column calibration; $^1\text{H-NMR}$ on a Bruker AMX 400 instrument using chloroform- d as solvent; gas chromatography on a bonded-silica capillary column, 25 m long; and silica gel adsorption chromatography. The weight loss of the reactor was recorded following each run, and the pyrolysis char and second stage material (if present) were recovered for ultimate analysis. It is recalled that the carbon residue resulting from the primary pyrolysis reactions is referenced as "char" in this context to distinguish it from the coke that is formed by secondary reactions away from the original shale particle.

A series of single-stage experiments was performed to provide baseline data for the two-stage runs. Approximately 15 g of raw oil shale was loaded into the reactor, resulting in a fixed-bed height of 28 cm. The bed of shale was situated near the outlet of the heated zone (61 cm length) to reduce secondary reactions. Single-stage tests involved sweeping with either nitrogen at 0.1 MPa and 5 MPa pressure, or hydrogen at 5 MPa. For these runs, the superficial gas velocity ranged from 0.2 to 2 m/s because of the large differences in total pressure and the limits of the gas metering system. In all cases, the sweep gas represented at least 99% of the total outlet gas volume.

For the two-stage tests a smaller charge of raw shale (10 g, 19-cm bed depth) was used because of space limitations in the first stage (33-cm heated length). Approximately 5 g of substrate was used in the second stage with a bed height of approximately 14 cm. The heated length of the second zone was 46 cm, and it was maintained at 520°C . Two-stage tests involved nitrogen sweep at 0.1 and 15 MPa or hydrogen sweep at 5, 10, and 15 MPa.

Figure 3-67. Schematic diagram of the two-stage fixed-bed hydropyrolysis reactor used at the University of Strathclyde.

In addition, a "single-stage" run was performed in the two-stage configuration because no comparable run at 15 MPa H₂ pressure was performed in the single-stage configuration.

3.5.2 Results and Discussion

The determination of oil yield was one of the most uncertain measurements from this set of experiments, as it is in most pyrolysis experiments. Eastern U.S. oil shales tend to form an aerosol (especially when a sweep gas is used) that is particularly difficult to trap: the dry-ice-cooled trap was not sufficiently efficient to completely collect the oil in this study. Light oil and water were present in the glass wool at the outlet of the trap, following each run, which suggests that some liquids escaped. The overall carbon balances (Table 3-24) averaged 91% ($\pm 10\%$ std. dev.), and were considered acceptable because gas analyses were not available for some of the runs and others were believed to be low for reasons to be discussed later. Generally, the balances suggest that only small amounts of oil were lost. The problem of oil vapor losses is compounded during two-stage operation because of the lighter products that are produced. Inferences from relatively small changes in oil yield should, therefore, be considered in this context.

The measured gas yields were somewhat erratic, especially between high- and low-pressure runs, and this appears to be due to the sampling procedure. The apparatus was designed for high-pressure operation, so a relatively large sweep-gas flowrate, measured at ambient conditions, is required to attain a high sweep velocity within the reactor. At atmospheric pressure, however, a much lower gas flowrate is required, and much less gas is collected for analysis. Because of the small volume of gas and the relatively large gas sampling system, it was not possible to fully eliminate air contamination.

The measured gas yields, with a few exceptions, are, however, comparable with those obtained in previous studies of oil shale pyrolysis.^{35,66} Regardless of the absolute gas yields, the alkene/alkane ratios were determined with accuracy, and were used to provide indications of the relative extent of cracking, coking, and hydrogenation reactions (Table 3-25).

3.5.2.1 Single-Stage Results. Since the reaction conditions in the second stage were, by design, identical to those in the first stage (except temperature which could be controlled independently), the relevant variables are the type and velocity of the sweep gas and the total pressure. The pyrolysis conditions can be categorized as either thermal pyrolysis or hydropyrolysis depending on the use of N₂ or H₂ as the sweep gas. Intra- and interparticle mass transfer limitations, which are particularly important in thermal pyrolysis, are expected to be small for these experiments because of the rapid particle heat-up and the high sweep gas rate. Organic carbon removal from the shale, for the all thermal pyrolysis runs, was approximately 115% of the Fischer assay conversion (40-45% for the Cleveland member oil shale) and nearly as high as that reported for fluidized bed pyrolysis (125% of Fischer assay) using the same type of oil shale.³⁵ With increasing total pressure during thermal pyrolysis, the carbon removal decreased only slightly (Table 3-24).

Table 3-24. Run Conditions and Carbon Distribution for Single- and Two-Stage Pyrolysis and Hydropyrolysis Runs.

Run	Sweep Gas	2nd Stage Substrate	Press., MPa	No. of Stages	Gas Vel., m/s	2nd Stage Temp., C	1st Stage C Conv. (%)	Alkene/Alkane Ratios		
								C2	C3	C4
2	N2		0.1	1	0.99		50.22	na	na	na
3	N2		0.1	1	1.98		53.35	na	na	na
7	N2		0.1	1	1.98		51.73	0.489	1.015	0.882
4	N2		5.3	1	0.19		49.10	na	na	na
5	H2		5.1	1	0.19		71.75	na	na	na
6	H2		5.1	1	0.19		73.41	0.326	0.701	0.702
18	H2	none	15.0	2	0.07	520	75.58	0.354	0.612	nd
14	N2	NiMo	0.1	2	2.47	520	51.73	0.524	1.141	0.992
10	N2	Comb Shale	0.1	2	2.47	520	49.50	0.518	1.134	0.995
19	N2	Comb Shale	15.0	2	0.07	520	47.51	0.382	0.944	nd
9	H2	Comb Shale	4.9	2	0.30	520	73.18	0.441	0.748	nd
17	H2	Comb Shale	15.0	2	0.07	520	81.12	0.209	0.475	nd
12	H2	NiMo	4.8	2	0.31	400	69.32	0.112	0.278	nd
13	H2	NiMo	10.0	2	0.15	400	80.97	0.064	0.205	nd
15	H2	NiMo	15.0	2	0.07	400	79.75	0.000	0.000	0.000

Run	Sweep Gas	2nd Stage Substrate	Press., MPa	C Distribution (wt% C/wt% C in r.s.)				C Balance (%)
				Char	2nd Stage	Oil	Gas	
2	N2		0.1	0.498		0.195	na	69.31
3	N2		0.1	0.467		0.412	na	87.83
7	N2		0.1	0.483		0.389	0.050	92.15
4	N2		5.3	0.509		0.322	na	83.11
5	H2		5.1	0.283		0.685	na	96.75
6	H2		5.1	0.266		0.677	0.159	110.23
18	H2	none	15.0	0.244	---	0.608	0.076	92.87
14	N2	NiMo	0.1	0.483	0.168	0.273	0.048	97.17
10	N2	Comb Shale	0.1	0.505	0.038	0.266	0.048	85.83
19	N2	Comb Shale	15.0	0.525	0.023	0.157	0.058	76.27
9	H2	Comb Shale	4.9	0.268	0.007	0.509	0.144	92.81
17	H2	Comb Shale	15.0	0.189	0.000	0.669	0.034	89.23
12	H2	NiMo	4.8	0.307	0.117	0.465	0.109	99.75
13	H2	NiMo	10.0	0.190	0.143	0.546	0.154	103.36
15	H2	NiMo	15.0	0.202	0.150	0.509	0.056	91.65

na- not available for analysis

nd- not detected

The composition of the oil produced by single-stage thermal pyrolysis at 0.1 MPa is characterized by a bimodal distribution of n-alkanes which span from C_{11} to C_{32} as determined by gas chromatography (Figure 3-68). The oil was high in number average molecular weight (370 amu) and relatively low in aromaticity (55%), Table 3-25.

One of the effects of hydropyrolysis on the composition of the oil was to eliminate the high molecular weight n-alkanes in favor of a uni-modal distribution that is shifted to lower carbon numbers (Figure 3-68). The other effects of H_2 pressure were to lower the C_2 - C_4 alkene/alkane ratios and to increase the aromaticity (Tables 3-24 and 3-25). The increase in aromaticity of the oil under elevated H_2 pressure is due to the increase in overall organic carbon conversion. Highly aromatic materials which would have formed coke during thermal pyrolysis were stabilized and collected as volatile compounds during hydropyrolysis. Carbon conversion maximized at 81% at H_2 pressures above 10 MPa (Table 3-24). These results are slightly lower than the hydropyrolysis results reported by Roberts et al.⁶⁶ (1992) for a similar eastern U.S. oil shale (New Albany) under otherwise similar conditions, with the exception that 25 minutes solid residence time was used in their study. The increased conversion at this extended residence time is attributable to increased hydrocarbon gas production.

3.5.2.2 Two-Stage Results. Carbon deposition in the second stage onto combusted shale under 0.1 MPa nitrogen accounted for 4% of the carbon in the raw shale, and is similar to coke deposition on combusted shale in the fluidized bed cracking chemistry study (section 3.4). Under otherwise similar conditions, except lower superficial gas velocity, carbon deposition on the combusted shale was observed to be slightly lower at a nitrogen pressure of 15 MPa, despite the much higher average oil vapor partial pressure for the 15-MPa run (10.3 kPa) than the 0.1-MPa run (0.28 kPa). (Partial pressures were determined assuming an average molecular weight of 300 for the products of each run.) It is suggested that the surface coking reaction may be the rate-limiting step at such high oil vapor partial pressure. This behavior is in contrast to that reported for catalytic coke formation under these conditions, because enhanced catalytic coke deposition would be expected.

The heavy n-alkanes in the oil, when passed through a bed of combusted shale during thermal pyrolysis, largely disappeared (Figure 3-68), and the aromaticity of the oil increased (Table 3-25). The C_2 - C_4 alkene/alkane ratios also increased slightly as a result of contact with combusted shale. It appears that the combusted shale substrate promoted the generation of cracking products more than coke deposition under these circumstances. Cracking of alkanes, in the absence of H_2 , produces olefins and aromatics which can then form coke. Therefore, in classifying products as resulting more from either cracking or coking, the issue is the extent of reaction, rather than the type of reaction, because cracking and coking always occur together to some extent.

When the Ni/Mo catalyst was used as the 2nd-stage substrate with 0.1 MPa nitrogen, nearly 17% of the carbon originally present in the raw shale was deposited on the catalyst. This is consistent with the hypothesis that carbon deposition is controlled to a large extent by

Figure 3-68. n-Alkane distributions of the oils, determined by GC, produced at (a) 0.1 MPa N₂ and (b) 15 MPa H₂. Open bars, 1-stage; shaded bars, 2-stage with combusted shale.

the available surface area of the substrate: the catalyst has a total surface area of 180 m²/g compared to 20 m²/g for the combusted shale. The conversion of such a large fraction of the oil vapor to coke did not, however, measurably affect the yield, aromaticity or the molecular weight of the oil (Tables 3-24 and 3-25) compared to the oil produced by passage over combusted shale. There was also no measured difference in the gas yield or composition between these runs. Since the carbon balances for these runs were so dissimilar (85.8 and 97.2%), it is possible that the aforementioned yield measurement difficulties masked actual differences in the oil and gas yields.

At hydrogen partial pressures of 5 and 15 MPa, the carbon deposition was effectively reduced to zero over the combusted shale, and the oil yield was not seriously affected, compared to single-stage runs under high pressure hydrogen. The elimination of larger molecular weight n-alkanes, when the oil vapor is contacted with combusted shale, is evident in Figure 3-38. A significant decrease in the number average molecular weight and increase in the aromaticity of the oil are also indicated under these conditions (Table 3-25).

When hydrotreating conditions were employed in the second stage with the catalyst (hydrogen pressure: 4.8 to 15 MPa, temperature: 400°C), the resultant oil was of higher quality (lighter in color and more stable with time as judged by its unchanging tint), compared to all the other oils produced in the study. Unfortunately, the boiling range was so low that it could not be distilled from the toluene used to extract the liquids from the dry-ice-cooled trap; also no neat oil samples were obtained. Therefore, no analyses could be made on the hydrotreated liquids to quantitatively show the extent of upgrading. Hydrogenation was apparently quite extensive at 15 MPa hydrogen pressure, as evidenced by the complete disappearance of C₂ to C₄ 1-alkenes (Table 3-24). A detailed study of these hydrotreating reactions is beyond the intended scope of this research, and is suggested as an area for further investigation.

The most interesting result from the hydrotreating runs, as it pertains to the main theme of this research, is that carbon deposition remained high on the Ni/Mo catalyst (12 to 15% of the carbon originally in the raw shale), even at 15 MPa hydrogen pressure. A similar amount of carbon (17% of raw shale C) was deposited on the catalyst at 0.1 MPa nitrogen and 520°C. It is recalled that 15 MPa hydrogen pressure completely eliminated coke formation on combusted shale at 520°C. It is possible that the lower temperature (400°C) used during the hydrotreating experiments could have enhanced the carbon deposition by collecting high boiling molecules that would otherwise vaporize at 520°C, but this is considered unlikely due to the definite increase in coking activity of the catalyst compared to the combusted shale using N₂ as sweep gas.

An effect of high-pressure hydrogen is to cap unpaired electrons and thus lower the free radical concentration in the system. In the case of combusted shale, 15 MPa hydrogen resulted in essentially no coke formation which implies that free-radical processes are important for carbon deposition on that type of surface. It is unlikely that hydrogen adsorption inhibited the subsequent adsorption of oil vapors because of the marginal

Table 3-25. Oil Properties from Selected Single- and Two-Stage Runs.

Run	Press	Sweep	2nd	$^1\text{H}_{\text{Ar}}$	MW ^a	SGAC ^b		
	(MPa)	Gas	Stage	(%)	(amu)	Alk.	Aro.	Pol.
7	0.1	N ₂	none	12.5	370	23	55	21
14	0.1	N ₂	NiMo	15.4	250	n.a.	n.a.	n.a.
10	0.1	N ₂	Comb. Shale	14.4	250	21	62	17
18	15	H ₂	none	18.4	320	7	67	26
17	15	H ₂	Comb. Shale	24.7	180	5	72	23

^a Number-average molecular weight

^b Silica gel adsorption chromatography

n.a.-Not available for analysis

adsorption characteristics of combusted shale for other gases.²⁸ Carbon deposition on the catalyst, however, was largely unaffected by hydrogen pressure, indicating that free radical processes are not important for coking on the catalyst surface.

3.5.3 Summary and Conclusions

Single-stage, thermal pyrolysis at 0.1 MPa resulted in carbon conversion averaging approximately 115% of Fischer assay, which indicates that heat and mass transfer limitations were minimal in the reactor system. Transport effects were also apparently low at high pressure because carbon conversion remained relatively high (49.1%) for pyrolysis at 5.3 MPa nitrogen pressure. As was anticipated, significantly increased oil yield and carbon conversion were attained by single-stage hydrolysis.

The effect of combusted oil shale in the second stage was to significantly lower the molecular weight and increase the aromaticity of the shale oil under both thermal pyrolysis and hydrolysis conditions. The primary effect of the combusted shale was to increase cracking, but coke formation was also significant under thermal pyrolysis conditions. Coke formation was found to be insensitive to oil vapor partial pressure over the range of 0.28 to 10.3 kPa, which is contrary to the first-order dependency observed from the fluidized bed coking study (section 3.3). It is suggested that at high partial pressure, the surface reactions may be rate-limiting. This result also provided more evidence that additive coke is predominant in this study, rather than catalytic coke which is dependent on oil vapor partial pressure if the range is wide enough.

High pressure hydrogen (15 MPa) essentially eliminated carbon deposition on the combusted shale, which suggests that a free radical mechanism is important for coking onto combusted shale. A significant amount of carbon was deposited on the hydrotreating catalyst under both thermal pyrolysis and hydrolysis conditions. Such high amounts of coke formation on the catalyst could significantly reduce the yield of saleable liquids and increase the cost of upgrading for an oil shale process. However, catalysts can remain active with relatively large amounts of coke, and the subsequent coke loading decreases significantly with time on stream, so the situation for shale oil upgrading may not be as severe as the current results indicate. Therefore, shale oil upgrading studies are suggested for further research.

3.6 SUMMARY OF SHALE OIL COKING AND CRACKING STUDIES (3.3-3.5)

A two-stage fluidized-bed reactor was developed to investigate the secondary coking and cracking reactions that can occur within a fluidized bed of processed oil shale particles and other related solid particles. The purpose of the study was to examine the secondary reactions caused by the recycle of hot processed solids to a fluidized bed pyrolyzer. Shale oil vapors, which were continuously generated in one fluidized bed, were passed through a second fluidized bed which contained either pyrolyzed shale, gasified shale, combusted shale, fine-grained kaolinite, coarse-grained kaolinite, illite (Huron shale), or Ottawa sand. On-line and post-run methods for measuring carbon deposition as a function of solid residence time were developed and were found to be equally accurate. The on-line technique proved to be especially useful for measuring the initial rate of carbon deposition. Fixed-bed experiments were also utilized to investigate the effects of nitrogen and hydrogen pressure (up to 15 MPa) on coking and cracking over combusted shale and over a hydrotreating catalyst.

The process of coke formation from nascent shale oil vapors on substrates derived by processing eastern U.S. oil shales, and related materials, has been found to be characterized by two distinct rate periods. The initial rate is rapid, but declines quickly, and the rate of decline is more rapid if the substrate has a significant carbon content prior to coking. After a certain amount of carbon deposition, the rate of coke formation falls to a low steady value.

The initial rate period is attributed to coke formation onto mineral surfaces which were not previously covered by coke. The rate of deposition of oil vapor onto the mineral surfaces to form coke is well-described by first-order kinetics and has a low apparent activation energy of approximately 10,000 J/gmol. The shale particles are sufficiently porous that pore diffusion is unlikely to be a rate-limiting step. Rather, the low activation energy is attributed to favorable attractions between the shale oil vapors and the exposed clay surfaces. One possible interaction, which is usually assigned to catalytic cracking systems, is the adsorption of basic components such as multi-ring and N-containing aromatics onto the exposed clay surfaces which may develop Lewis acid sites upon heating. The low energy barrier is especially suggestive of a condensation or physisorption process, because many of the multi-ring aromatics are near their boiling point at the temperatures used in this study.

The second rate period is characterized by a constant rate of carbon deposition onto carbon-covered surfaces, and also adhered to first-order kinetics. The apparent activation energy ranged from 62,000 to 72,000 J/gmol which is roughly equivalent to that for free-radical hydrocarbon addition reactions. The rate of coke formation during this period was approximately 10 to 20% of the initial rate.

The reduction in coking rate as the carbon content of the shale particles increased was attributed to the coverage of the minerals by a layer of carbon in large pores (>3.5 nm). The reasons for the selection of a carbon-coverage deactivation theory over a pore-blocking theory are outlined below:

- o The calculated effective diffusivities of the oil vapors in the particles that were studied and the measured coking rates indicated that pore diffusion should not have been a rate influencing factor. In fact, the fine-grained kaolinite sample was so porous that a viscous epoxy resin used for petrographic pellet preparation was shown to readily penetrate the interior of the particles prior to curing.
- o Photomicrographs of coked kaolinite and illite particles showed that coke had been deposited uniformly throughout their interior. It was concluded that the pore system in the particles freely permitted the transport of fluids. Evidence of a carbon concentration gradient between the exterior and the interior of the largest illite particles is consistent with the prediction from mass transfer modeling that coking over particles with diameters of $>1200\mu\text{m}$ would begin to suffer from pore diffusion limitations.
- o For particle types with low carbon content (combusted shale, illite, coarse- and fine-grained kaolinite), the surface area associated with the meso and macro pores ($>3.5\text{nm}$ diameter) correlated well with coke formation. With the exception of the kaolinite samples, pore volume also correlated well with surface area. The fine-grained kaolinite which had higher surface area and lower pore volume than the coarse-grained kaolinite displayed significantly higher coke formation. If pore blockage had been the major factor controlling the rate of coke formation, then less carbon deposition would be expected for the fine-grained kaolinite with the smaller average pore size.
- o The rate of carbon deposition onto carbon-covered particles remained constant for up to an hour which indicates that there was no appreciable pore blockage during this period and that multiple layers of coke could form in large pores. Therefore, if pore blockage were a rate controlling factor, the pores must have been blocked during the initial stages of carbon deposition before substantial amounts of coke had formed.
- o A characteristic coke content, C_{crit} , was identified for each type of solid tested that divided the coking process into two rate periods in terms of the carbon added. At carbon contents of less than C_{crit} , coking proceeded according to the rapid rate mechanism, and at carbon contents greater than C_{crit} , the slower, constant rate period applied. The value of C_{crit} for each type of solid showed good correspondence with the amount of carbon that could theoretically be deposited in a monolayer on the surface area available in the macro and meso pores. For solids which had substantial carbon concentrations prior to the coking experiments (i.e. gasified and pyrolyzed shales) the measured values of C_{crit} were lower than the amounts that would be expected from monolayer coverage because residual carbon was already covering a portion of the meso and macro surface area before carbon deposition began.
- o The empirical deactivation function which gave the best fit to the data was similar to the theoretical function that can be derived based on simple monolayer coverage theory. The latter did not account for pore diffusion and was based upon the assumption that oil vapors had instantaneous access to all available surface area.

Regardless of the validity of the mono-layer coverage theory for coking-rate deactivation, the empirical relationships based on added-carbon and time-on-stream are found to apply over the range of conditions used in these studies. While the kinetic functions based on the added-carbon content of the solid particles are more theoretically based, the time-on-stream deactivation function is more convenient to implement. Excellent agreement was found with the experimental results for the time-dependent deactivation function when applied to the conditions of the 2.3-kg/hr KENTORT II retort. The model accurately reproduced the effects of solid-recycle ratio and the coking activity of the particles. The results from the 22.7-kg/hr PDU were not adequately predicted because a fluidized bed model was not implemented that could account for the large bubbles and excessive gas-bypassing in the large fluidized bed.

The gas-phase products were indicative of the incidence of free-radical thermal cracking reactions (i.e., predominance of C_1 to C_3 species, high 1-alkene content, and the absence of branched components) whether or not there was contact with solids. Therefore, acid catalyzed reactions by any of the substrates studied was not indicated, and the mineral surfaces were assumed to function primarily as sites for the adsorption of the most heavy and aromatic shale oil vapors that subsequently formed coke. Oil vapor contact with the shale particles was shown to increase the amount of gases at the expense of oil yield, but the gas composition was not affected. Combusted shale was a more active cracking agent than the gasified and pyrolyzed shales, which is consistent with its relatively high coking activity.

The coke formed under the conditions of this study corresponds to the classification of "additive" carbon, as defined by Venuto and Habib.⁶¹ The high molecular weight, N-containing, and aromatic pyrolyzate from oil shale is consistent with their description of the precursor materials that produce additive coke. The largely temperature-independent formation of coke from heavy aromatics in the current study is also consistent with a study by Wiwel et al.⁶⁷ (1991) which indicated that polyaromatics of 4 or more rings were responsible for coke formation on a hydrotreating catalyst. Coke formation in the current study was found to occur on what were determined to be non-catalytic surfaces, and the rate adhered to first-order kinetics. These are both characteristics of additive coke. The "coke clock" as first observed by Voorhies¹⁵ for catalytic coke formation was not strictly observed in the current study because the rate of coke formation was shown to be dependent on the partial pressure of oil vapor. However, the power-law relationship for coke formation versus time was observed.

In the fixed-bed tests, there was no apparent effect of total nitrogen pressure (0.1 to 15 MPa) on coking rate, when the oil vapor partial pressure was varied from 0.28 kPa to 10.3 kPa. However, the fluidized bed experiments at 0.1 MPa total pressure showed that carbon deposition was first-order dependent on oil vapor concentration. To rationalize this disparity, it is proposed that, at high pressures, the coking process is more dependent on the rate of the surface coking reaction than on the rate of adsorption, whereas at lower pressure, adsorption is rate-limiting.

Hydrogen pressure of 15 MPa almost completely eliminated the formation of coke on combusted shale particles, whereas carbon deposition on the hydrotreating catalyst remained high under similar conditions, illustrating the substantial differences in surface chemistry between the two materials. For the catalyst, strong adsorption of the shale oil vapors at acidic sites on the alumina support could ultimately lead to the formation of a substantial amount of coke, even in high-pressure hydrogen. This sort of coke-forming pathway is well established in the literature. The reasons for the elimination of coke formation onto combusted shale as a result of high-pressure hydrogen are less straightforward and not well documented. The results of the present study allow only conjecture. However, it is apparent that the elucidation of this coke-eliminating mechanism may also provide valuable information concerning the nature of the initial adsorption of shale oil vapors onto exposed clay minerals. Although possible explanations have been advanced in the preceding sections, it seems appropriate to provide in this final chapter some additional propositions with a view to defining the needs for future research.

Hydropyrolysis in the absence of secondary oil vapor/substrate contact resulted in the formation of a more aromatic oil product, with a lower molecular weight than that produced by thermal pyrolysis. High-pressure hydrogen can serve to cap unpaired electrons and reduce free-radical reactions. Therefore, the difference in oil properties between hydropyrolysis and thermal pyrolysis is attributed to the inhibition of addition and condensation reactions through the action of hydrogen.

While it may appear initially that the more aromatic hydropyrolysis oil should be more susceptible to coke formation than the thermal-pyrolysis oil, the types of aromatic compounds must also be considered. Kopinke et al.⁶⁸ (1993) showed that the number of aromatic rings and the chain length of alkyl substituents are the most important factors in determining coking propensity (i.e., benzene is a poor coke precursor, but toluene and naphthalene are much better). Therefore, the smaller aromatics produced by hydropyrolysis may be considered to be generally less susceptible to coke formation than the higher molecular weight products from thermal pyrolysis. Taulbee⁶ (1994) showed that, for the same combusted shale sample used in this study, small model compounds (one-ring aromatics and up to C₁₀ paraffins) were not significantly adsorbed. It is possible that only the largest molecules (4 aromatic rings or more) may be significantly adsorbed onto these fairly inert clay minerals. The apparent absence of temperature dependence for coking onto exposed clay surfaces could then be explained as a balance between the gas-phase production of coke precursors that are more likely to adsorb and the reduced ability of the shale to adsorb materials at higher temperatures. The observed dip in coking rate onto the minerals at approximately 620°C is consistent with the existence of such competing processes.

The elimination of coke formation over mineral surfaces in the presence of high-pressure hydrogen could be due to a combination of factors. Under hydrogen pressure, the pyrolyzate (as discussed) has reduced molecular weight which will tend to reduce the driving force for adsorption and also to lower the surface residence time of adsorbed species. Hence, the potential for surface reactions (dehydrogenation and addition) that lead ultimately to the

formation of a carbon-rich (coke) deposit will be much less. In addition, the presence of hydrogen or dissociated hydrogen on the surface will help to stabilize free radicals and oppose the formation of higher molecular weight species.

Conversely, in thermal reactions, the higher molecular weight species will adsorb more readily on the mineral surfaces, they will have more extended residence time, and hydrogen is not present to suppress the propagation of dehydrogenation and addition reactions. Therefore, the apparent irreversible adsorption of shale oil vapors to eventually form coke on the surface of shale minerals is not due to strong oil/mineral attractions, but the growth of the coke precursors due to uninhibited free-radical reactions.

In summary, in thermal pyrolysis it appears most likely that high molecular weight and polar compounds adsorb onto the exposed mineral surfaces, and subsequent dehydrogenation, addition and condensation reactions occur which lead ultimately to the formation of a layer of coke. This process of coke formation can be prevented in the presence of high-pressure hydrogen due to the production of lower molecular weight pyrolyzate which is less likely to adsorb onto the mineral surfaces, and due to the inhibition of surface reactions due to the presence of adsorbed and possibly dissociated hydrogen. This explanation is consistent with the observations of low activation energy for the deposition of carbon onto minerals, the non-selective coking on the mineral surfaces, the correlation between coking and total accessible surface area, and the coke-reducing effects of hydrogen.

Once a coke layer has been formed by the surface reactions, coke formation continues, but at a slower, more temperature-dependent rate. More rapid rates of carbon deposition onto non-carbon versus carbon-covered surfaces have been observed in other studies. Tesner⁶⁹ (1984) found that coking onto quartz was more rapid than onto carbon black. Similarly, Scaroni⁷⁰ (1981) found the coking rates of anthracene to be higher over alumina-supported catalysts than carbon black and glassy carbon. In neither study was an explanation given for these results. In the current study, the increase in activation energy and the decrease in rate indicate that coking onto carbon covered surfaces is controlled by the surface reaction rather than adsorption. Several recent studies agree that coking onto carbon-covered surfaces occurs primarily by addition reactions between gas-phase components and free-radical sites on the coke surface.^{31,32,33,68} The activation energy observed in this study for coking onto carbon-covered surfaces is similar to that expected for these types of free-radical addition reactions. While this explanation may not be valid for all the different coke precursors and coking substrates that are of academic and commercial interest, it is suggested that research along these lines be continued. Due to the wide variety of research interests, materials used, and experimental methods utilized, there continues to be little in the way of a comprehensive coking model in the fields of hydrocarbon/petroleum processing or carbon production.

3.7 NOMENCLATURE (3.3-3.6)

$a =$	coking activity of solid particle (current rate/initial rate)
$A =$	constant in Voorhies power function related to the catalyst, feedstock, and temperature
$A =$	pre-exponential factor for 1st-order coking reaction, s^{-1}
$A =$	parameter in Equation 3-2
$B =$	parameter in Equation 3-2
$C =$	parameter in Equation 3-2
$C_{A0} =$	concentration of oil vapor entering the coking bed, $gmol\ C\ l^{-1}$
$C_{Ai} =$	conc. of oil vapor exiting coking bed at time=0, $gmol\ C\ l^{-1}$
$C_{Af} =$	conc. of oil vapor exiting coking bed at final coking rate, $gmol\ C\ l^{-1}$
$C_b =$	conc. of oil vapor in bubble phase, $gmol\ cm^{-3}$
$C_c =$	carbon content of the catalyst, wt%
$C_{crit} =$	C content on solid identifying the division between the rapid and constant rate periods, wt. fraction
$C_e =$	conc. of oil vapor in emulsion phase, $gmol\ cm^{-3}$
$C_{e,avg} =$	avg. conc. of oil vapor in emulsion phase, $gmol\ cm^{-3}$
$C_{in} =$	inlet oil vapor concentration, $gmol\ cm^{-3}$
$C_{mon} =$	theoretical carbon content associated with monolayer coverage of minerals, wt. fraction
$C_r =$	conc. of oil vapor in particle phase, $gmol\ cm^{-3}$
$C_r(R) =$	conc. of oil vapor at particle surface, $gmol\ cm^{-3}$
$d_p =$	particle diameter, cm
$D_{12} =$	mol. diffusivity of oil in fluidizing gas, $cm^2\ s^{-1}$
$D_{12,eff} =$	effective mol. diff. of oil in fluidizing gas, $cm^2\ s^{-1}$
$D_{eff} =$	effective diffusivity of oil vapor in particle, $cm^2\ s^{-1}$
$D_K =$	Knudsen diffusivity, $cm^2\ s^{-1}$
$D_{K,eff} =$	effective Knudsen diffusivity, $cm^2\ s^{-1}$
$E_b =$	axial diffusion coefficient in bubble phase, $cm^2\ s^{-1}$
$E_e =$	axial diffusion coefficient in emulsion phase, $cm^2\ s^{-1}$
$E_o =$	activation energy of coking reaction, $J\ gmol^{-1}$
$E_s =$	exit age distribution of solids in fluidized (well-mixed) bed
$F_{A0} =$	feedrate of oil vapor to coking bed, $gmol\ C\ g^{-1}\ s^{-1}$
$F_s =$	throughput rate of solids, $g\ min^{-1}$
$g =$	gravitational constant, $980.665\ cm\ s^{-2}$
$k_d =$	first-order deactivation constant, min^{-1}
$k_e =$	first order chemical reaction constant in emulsion, s^{-1}
$k_i =$	first-order rate constant for initial coking period, $cm^3\ g^{-1}\ s^{-1}$
$k_f =$	first-order rate constant for final coking period, $cm^3\ g^{-1}\ s^{-1}$
$k_{oi} =$	frequency fractor (pre-exponential) for first order coking rate constants, $cm^3\ g^{-1}\ s^{-1}$
$k_p =$	mass transfer coef. between emulsion and part. surf., s^{-1}
$k_r =$	n-th order reaction constant in particle, $(cm^3)^n\ cm^{-2}\ mol^{-(n-1)}\ s^{-1}$

K_{bc}	bubble-cloud mass transfer interchange coefficient, s^{-1}
K_{be}	bubble-emulsion mass transfer interchange coefficient, s^{-1}
K_{ce}	cloud-emulsion mass transfer interchange coefficient, s^{-1}
L	axial length of fluidized bed, cm
M_1	molecular weight, amu
n	order of Voorhies power function which depends slightly on catalyst, feedstock, and temperature, dimensionless
n	order of coking reaction, dimensionless
r	radial position in particle, cm
r'	apparent coking rate, $gmol\ C\ s^{-1}\ g^{-1}$
r^0	initial coking rate, $gmol\ C\ s^{-1}\ g^{-1}$
r_c	mean effective radius of pore in solid particle, cm
r_A	rate of disappearance of oil vapor, $gmol\ C\ g^{-1}\ s^{-1}$
r_{final}	asymptotic coking rate, $gmol\ C\ s^{-1}\ g^{-1}$
r_{tot}	total coking rate, $gmol\ C\ s^{-1}\ g^{-1}$
P	pressure, atm
R	radius of particle, cm
R	gas constant, $82.057\ atm\ cm^3\ gmol^{-1}\ K^{-1}$, $1.9872\ cal\ gmol^{-1}\ K^{-1}$
R	solid-recycle rate (feedrate of recycle solids/feedrate of raw shale)
Re_{mf}	particle Reynolds number at minimum fluidizing velocity
S_p	surface area of particle, $cm^2\ g^{-1}$
t	time, s or min.
T	temperature, K or $^{\circ}C$
T_c	critical temperature, K
U_b	velocity of emulsion gas, $cm\ s^{-1}$
U_e	velocity of bubble gas, $cm\ s^{-1}$
U_{mf}	minimum superficial fluidization velocity, $cm\ s^{-1}$
U_o	superficial gas velocity, $cm\ s^{-1}$
V_b	molar volume of oil at normal boiling temperature, $cm^3\ gmol^{-1}$
W	total weight of solids in coking bed, g
x	added-carbon content in Equation 3-2, wt. fraction
X_A	fractional conversion of oil vapor to non-volatile products
X_f	fractional conversion during final coking period
X_i	fractional conversion during initial coking period
y	rate of C deposition in Equation 3-2, $gmol\ C\ s^{-1}\ g^{-1}$
Y	logarithmic mean of nondiffusing component
z	axial position in fluidized bed, cm

Greek Letters

ε	Lennard-Jones force constant
ε_{mf}	void fraction in the emulsion phase
θ	catalyst residence time in Voorhies power function, minutes

θ =	void fraction within particle
θ =	fraction of the theoretical mineral coverage by monolayer of carbon
κ =	Boltzmann Constant, $1.3805\text{E-}16 \text{ erg K}^{-1}$
μ =	gas viscosity, $\text{g cm}^{-1} \text{ s}^{-1}$
ρ_g =	density of gas, g cm^{-3}
ρ_p =	density of particle, g cm^{-3}
σ =	Lennard-Jones force constant
Φ =	deactivation function, dimensionless
τ =	tortuosity of the porous solid
Ω =	Lennard-Jones collision integral

Subscripts

1 =	oil vapor
2 =	fluidizing medium (steam or nitrogen)
min =	exposed mineral surfaces
carb =	carbon-covered surfaces
i =	initial coking rate
f =	final coking rate

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4. KENTORT II PDU DEVELOPMENT AND DESIGN

4.1 COLD-FLOW MODELING

4.1.1 Introduction

Even though the understanding of fluidization has greatly improved, particularly in the area of catalytic cracking, there are still some uncertainties associated with scale-up. This is especially true for a multiple-bed process such as KENTORT II, which includes solid recirculation and utilizes coarse-grained solids. To better overcome the potential problems of increasing the size of the KENTORT II process from a 5-lb/hr unit, a full-scale cold-flow model was built to verify the preliminary design of the 50-lb/hr retort.

An area of particular concern was the solid recycle loop between the gasification and pyrolysis zones. The most uncertain aspect of this recycle loop was the downflow standpipe which delivers shale by the force of gravity from the pyrolysis zone to the gasification zone. Since shale must move from a zone at low pressure to one of high pressure, a balance between the resistances to downward solid flow and upward gas flow must be achieved. Otherwise, either insufficient downward flow of shale will occur or excessive amounts of gas will pass through the standpipe and cause shale to be entrained upward rather than move downward. The efforts to experimentally refine this downflow standpipe are described.

One of the reasons for scale-up to the 50-lb/hr retort is the ability to investigate different particle size ranges. Due to slugging, only a relatively narrow range of particle sizes could be tested in the 3-inch diameter KENTORT II unit. The size and nature of solids in a fluidized bed system influence its behavior significantly. Therefore, an important function of the cold-flow model was to evaluate the effects of particle size on fluidization quality and solid recirculation behavior. Three particle size ranges, which were identified as candidates for testing in the 50-lb/hr retort, were evaluated in the cold-flow model. The results of these tests as a function of the important operating parameters (superficial gas velocity, solid recycle rates, solid throughput rate) are discussed.

4.1.2 Experimental

Apparatus. The cold-flow model (Figure 4-1) includes four dense phase fluidized beds. The beds representing the pyrolysis, gasification and the cooling zones are aligned vertically and share a common fluidizing gas. The fourth bed which represents the combustion zone is aligned adjacent to the other three, and the fluidizing gas is supplied separately. A cyclone is connected downstream to collect entrained fines from each gas stream before the air is vented.

The main body of the unit is constructed of transparent acrylic tubes. The beds that represent the pyrolysis and combustion zones have a 6-in. I.D., and the beds representing gasification and cooling zones have an 8-in. I.D. The sections of the unit are separated by gas distributors which are sandwiched between flanges. The total height of the unit is about 20 feet.

Figure 4-1. Diagram of the 50-lb/hr cold-flow model.

Due to the smaller diameter of the pyrolysis zone, the fluidizing gas velocity is 78% greater than in the gasification and cooling zones because the beds share a common fluidizing gas. This situation will not be as strongly pronounced in the PDU because of the temperature difference between the gasification and the pyrolysis zones. The gas passing through the pyrolyzer will be cooler and more dense, thereby reducing the gas velocity. This will effectively offset the differential and bring the gas velocity within the pyrolyzer to 127% of the other zones.

To compensate for the diameter differential, the cold-flow model had a bleed-off tube mounted near the top of the gasification zone. By bleeding off some of the air from the gasifier before it entered the pyrolyzer, the gas velocity within the pyrolysis zone could be lowered. An orifice flowmeter measured the gas flowrate through the bleed-off tube. The pyrolysis and the gasification zones each had a vertical baffle which split the zones into two equally sized beds. The purpose of the baffles was to narrow the particle residence time distribution by creating two beds in series within each zone. By narrowing the particle residence time distribution, greater chemical conversion can occur per unit reactor volume.

Standpipes and their corresponding diplegs, or downcomers, penetrated the gas distributors of the pyrolysis, gasification and combustion zones. These pipes provided passage for solids to flow from the upper to the lower sections of the unit. The standpipes also controlled the bed heights of each zone, where the height of the pipes were roughly equivalent to the minimum fluidized bed height. The heights of the standpipes above the gas distributors during this study were:

- Pyrolyzer	12 inches
- Gasifier	30 inches
- Combustor	12 inches

Oversized steel pipes are attached to the walls of the unit to provide inlet and exit ports for the recirculation systems. Aerated J-valves (Figure 4-2) which controlled the solid recirculation rates to the pyrolysis and the combustion zones, were connected to the angled standpipes extending from the gasification section. The J-valves delivered shale to vertical lift pipes which served as pneumatic conveyers for the solids.

The liftgas velocity was held constant at 20 ft/s in each of the liftpipes. The pressure drop across the liftpipes was measured, and by using previously developed pressure-drop correlations versus mass flowrate (Figure 4-3), the recirculation rates were determined. The required capacity of the two recirculation loops was determined from the anticipated range of temperatures to be studied in the 50-lb/hr retort.

A screwfeeder was used to meter the shale into the pyrolysis zone at a rate of 50 lb/hr. Shale left the system through the side port in the cooling zone 10 inches above the distributor.

Figure 4-2. J-valve with liftpipe.

Figure 4-3. Mass flowrate vs. pressure drop in pneumatic liftpipe.

Procedure. The air blower was started and the air flowrate to each side of the system was adjusted to its target value. During the initial start-up period, any excess solids which had settled into the cooling zone from the previous test were forced upward as a slug through the gas distributor and into the gasification zone. The holes in the gas distributors for the gasification and the pyrolysis zones were larger than the particles, so these beds drained into the cooling zone when not fluidized.

The pressure difference between the gasification and the combustion zones was adjusted to zero. Aeration gas was then introduced to the J-valves to start the recirculation of solids. The screwfeeder motor was turned on, and solids were metered into the pyrolysis zone. Once proper bed levels were attained, the exit port in the cooling zone was opened. Following at least 10 minutes of steady operation under a particular set of conditions, the bed heights, net throughput rate and the recirculation rates of solids were recorded.

For this study, the cold-flow model was tested with 20x60 mesh retorted oil shale, 8x20 mesh raw oil shale and a 50/50 blend, by volume, of the 8x20 and the 20x60 mesh shales.

4.1.3 Results and Discussion

Fine-Grained Solids. The fine-grained particles, 20x60 mesh retorted oil shale, showed very smooth flow and fluidization behavior. The recirculation loop for the pyrolysis zone was shown to work flawlessly. The rate of solid recycle was easily adjustable and could meet the 200-lb/hr requirements with a comfortable margin under a wide range of operational conditions.

The second recirculation loop, which transported solids from the gasification to the combustion zone, needed a 500-lb/hr capacity. With the pressure difference between the two beds adjusted to zero, it was impossible to meet the required recirculation rate. Further tests showed that some of the aeration gas to the J-valve escaped backwards up the angled standpipe to the gasification zone. This restricted the solid flow to the J-valve and ultimately caused the low recirculation rate. By slightly pressurizing the gasification zone, smaller amounts of aeration gas then escaped to the gasifier, and the recirculation rate approached 500 lb/hr. However, running the unit with the gasifier pressurized clearly restricted the flow of solids from the combustion to the gasification zone, and caused the combustor bed to grow in height.

To remedy these problems, the entrance port for solids to the combustor was elevated to the solid-gas interface. This effectively created greater static head within the angled standpipe, and forced more aeration gas to flow towards the liftpipe. Also, the inlet port to the gasifier from the combustor was elevated to lessen the potential pressure differential between the zones. With these changes, the pressure between the two zones could then be balanced while the required recirculation rate was achieved (see Table 4-1).

The nozzle geometry for the recirculation port connecting the combustion to the gasification zone also strongly influenced the flow of solids. In general, it is expected that exit port 2 (see Figure 4-4) will permit greater solid flow than exit port 1 because the solids in the pipe are agitated through more intimate contact with the fluidized bed. By changing to the design of exit port 2, the solids-transfer pipe from the combustor to the gasifier was shown to easily handle the required capacity.

From previous cold-flow experiments it was found that the pressure drop across the beds, measured in inches of water column, was roughly equivalent to the dense bed height in inches. As can be seen from Table 4-1, this held fairly well for all the beds. With gas velocities above the minimum for fluidization, the pressure drop across the bed remained practically unchanged with a rise in gas flow, as one would expect.¹

Table 4-1. Average Operating Conditions for the Cold-Flow Model.

Zone	Pyrolysis			Gasification			Combustion			Cooling		
Particle Dist.	20x60	8x20	8x60	20x60	8x20	8x60	20x60	8x20	8x60	20x60	8x20	8x60
Fluidizing Gas Vel. (ft/s)	3.2	5.1	3.8	2.5	4	3	2.5	4	3	2.5	4	3
Lift Gas Vel. (ft/s)	20	20	20				20	20	20			
Aeration Gas (scf/hr)	5	14	9				14	35	23			
Solid Recycle (lb/hr)	200	200	200				500	500	500			
D.P. Beds (in H ₂ O)	8	11	10	22	28	25	8	11	10	6	9	7
Dense Bed Height (in)	12	12	12	30	30	30	12	12	12	10	10	10
Max Bed Height (in)	18	18	18	40	40	40	16	16	16	14	14	14

Figure 4-4. Types of pipe exits studied.

Coarse-Grained Solids. The coarse-grained raw shale, 8x20 mesh, had a bulk density of about 1.1 g/cm^3 compared to the fine-grained processed shale which has a bulk density of about 0.85 g/cm^3 . This difference was mainly due to increased porosity from the removal of oil, sulfur and carbon during previous pyrolysis, gasification and combustion.

The density and the particle size differences were found to influence the flow and fluidization dynamics significantly. Due to the higher gas velocity required for fluidization, large bubbles and slugging were strongly pronounced within the standpipes, causing the solids to be entrained with the upward flowing gas. Short-circuiting through the standpipes was so severe that the standpipes acted like pneumatic lifts, and the solids in the lower beds eventually emptied into the ones above. These factors made it impossible to operate the unit with the 8x20 mesh raw shale as a bed material without design changes.

As mentioned earlier, the design of the downcomers is a crucial element in a circulation system for solids.^{2,3,4} The function of a downcomer is to transfer solids from an upper zone at low pressure to a lower zone of higher pressure. During operation, the fluidizing gas tries to flow up the standpipe to the low pressure region but is hindered by the downflowing solids. With proper design, the gas may remain approximately stationary and the solids will move downward.

A packed, moving-bed of solids, or stick-slip flow, provides the most resistance to gas short-circuiting. In stick-slip flow, the movement of gas relative to the solids determines the pressure gradient. Small pressure gradients in the standpipe will lead to moving bed flow, larger gradients sufficient to counter the weight of solids in the standpipe will result in aerated flow. Gradients larger than this cannot be maintained.

The length of the downcomer is determined from the static head requirements. The diameter is determined from the desired mass flowrate and velocity requirements for stick-slip flow. An orifice attached to the bottom end of the standpipe is one way to make a restriction for the flow of solids. Without this orifice the solids would descend much faster causing the solids to flow in a lean phase. This lean phase flow creates a static head that is too small to

prevent the gas from short-circuiting up the pipe. The greatest static head is created when the pipe stays filled and the solids descend in stick-slip fashion.

For the cold-flow model, the downcomer from the pyrolyzer to the gasifier needed a capacity of 250 lb/hr. The downcomer from the gasifier to the cooling zone needs a 50-lb/hr capacity. The pipe and orifice diameters for these downcomers are listed below.

Pipe D.(mm)	Orif. D.(mm)
- Pyr. 25.4	22.0
- Gasif. 19.0	14.9

The downcomers tested yielded a solid descending velocity of less than 10 cm/s, which was well below what is needed to ensure stick-slip flow.³

The orifice diameters were experimentally determined by trial and error. Preliminary tests were done with both ends of the downcomer exposed to atmospheric pressure, and the rate at which a packed-bed of shale passed through the downcomer in stick-slip flow was measured.

The standpipe was then mounted back in the cold-flow model and tested. After a few iterations, the orifice diameters that gave the required solid flowrates were determined. As a rule of thumb, only half the flowrate could be achieved with the standpipe mounted in the cold-flow model, compared to what was achieved outside.

As can be seen from Table 4-1, the coarse-grained solids acted well for fluidizing gas velocities of about 4 ft/s, compared to the fine-grained solids which showed the best results with fluidizing gas velocities of around 2.5 ft/s. Even though the fluidization behavior was somewhat more vigorous for the coarse-grained solids, the overall flow characteristics were demonstrated to be very stable and smooth. More aeration gas was required for the J-valves to achieve the same solid flowrates with the coarse-grained solids. In addition, the pressure drop across the beds was slightly higher due to the higher bulk density.

Due to the redesign of the standpipes, the fine-grained shale was retested in the cold-flow model. It was verified that the design changes made to accommodate the coarse-grained shale did not influence the flow and fluidization behavior of the 20x60 mesh retorted oil shale.

Blend of Coarse- and Fine-Grained Solids. The 50/50 blend, by volume, of the two particle sizes gave an 8x60 mesh size distribution. It is difficult to handle such a wide particle size distribution in a fluidized bed because the heavy particles will hardly fluidize while the light particles will spout high into the freeboard region causing elutriation of the bed.

Table 4-1 shows that the 8x60 mesh particle size distribution behaved somewhat in between the fine-grained and the coarse-grained solids. Fluidizing gas velocities of about 3 ft/s gave the best results. It was observed that the mixing was poorer with this size distribution, causing segregation of the bed material and leaving the coarsest particles at the bottom of each of the beds.

4.1.4 Summary and Conclusions of Cold-Flow Modeling

A full-scale cold-flow model of the 50-lb/hr KENTORT II reactor was built and tested with 20x60 mesh retorted oil shale, 8x20 mesh raw shale and a blend of these two. The coarse-grained solids, 8x20 mesh, showed best fluidizing and flow behavior for a superficial velocity of about 4 ft/s. The fine-grained, 20x60 mesh shale behaved best with a fluidizing gas velocity of 2.5 ft/s. The blend of the two, 8x60 mesh, showed best results for a velocity of about 3 ft/s. Overall, the 20x60 mesh fluidized more smoothly and provided the most stable operating characteristics.

Following modifications, it was demonstrated that the operation of the unit was stable for all the particle sizes tested at the design throughput rate of 50 lb/hr. The required recirculation rates to the pyrolysis and the combustion zones were achieved with a comfortable margin. All aspects of the system were demonstrated to work flawlessly, and at the completion of the cold-flow modeling study, the final design and construction of the 50-lb/hr PDU was initiated.

4.2 DESIGN OF 50-LB/HR KENTORT II RETORT

4.2.1 Process Overview

Reactor. The KENTORT II process is a fully integrated four-stage fluidized bed oil shale retort. The pyrolysis, gasification and cooling zones are aligned vertically and share a common fluidizing gas. The combustion zone is adjacent to the gasification section and a separate gas stream (air) is used for fluidization (see Figure 4-5). All beds are designed to operate in the bubbling mode, and the cold-flow studies from the previous section showed that a gas velocity of about 2.5 ft/s provides proper fluidization for 20 x 60 mesh particles.⁵

Raw shale at a rate of 50-lb/hr is fed over-bed to the pyrolysis zone which is the uppermost bed of the reactor. The fluidizing medium is a mixture of steam and product gases from the gasification stage below. Heat is provided to the pyrolysis section by a combination of fluidizing gas and recirculating solids from the gasification zone which are injected directly into the bed. The rate of solids which are recycled from the gasifier is controlled by an aerated J-valve. The pyrolysis zone is baffled to narrow the particle residence time distribution. The design conditions for the pyrolyzer are: temperature, 500-550°C; raw shale feedrate, 50 lb/hr; mean shale residence time, 3 minutes; bed depth, 12 inches; maximum solid recirculation rate, 200 lb/hr.

Shale from the pyrolysis zone is transferred to the gasifier section via a downcomer. The bed depth in the gasification zone is designed to be adjustable between 15-30 inches so that solid residence time may be varied from 30 to 60 minutes. The design temperature range for the gasification zone is from 750 to 850°C. Hot solids from the combustor enter the lower part of the bed at a rate of up to 500 lb/hr to heat the gasification zone. Steam from the cooling section below is used as the fluidizing medium.

A downcomer transfers shale from the gasification zone to the cooling zone which also serves to preheat the steam that fluidizes the gasification bed. The cooling zone is the primary exit point for solids from the reactor. An overflow outlet in the wall of the vessel creates a 15-inch deep bed.

The combustor provides all the heat required for the pyrolysis and gasification sections of the KENTORT II process. The gasification and the combustion zones are closely aligned to facilitate the transfer of solids. To minimize mixing of the gas streams, however, the pressure between the two vessels is balanced. The bed depth in the combustor is determined by the height of an overflow standpipe. The design bed depth is 12 inches, although this can be adjusted from 6 to 24 inches if necessary. The combustor is fueled primarily by carbon-containing shale which is recycled from the gasification section via a pneumatic lift pipe. Fines recovered by the pyrolysis cyclone are fed into the combustion bed to provide additional fuel. Air is used for fluidization in the combustor.

Oil Collection and Gas Conditioning. Gases and vapors from the pyrolyzer enter a cyclone for fines removal. A combination convection/liquid-injection heat exchanger then cools the vapor stream to 150°C which causes an oil aerosol to develop. This aerosol is trapped by an electrostatic precipitator (ESP) which contains over 100 ft² of collection surface area and includes two, two-stage Penney-type collection cells in series to ensure high collection efficiency. Downstream of the ESP, a shell-and-tube condenser is then used to condense steam and light oil that remain. Light oil and water from the condenser are separated, and the water is sufficiently treated to be fed back into the steam generator. Mist collection, further cooling and more mist collection are performed before the gas stream is sampled by an on-line gas chromatograph and mass spectrometer.

Fines are removed from the combustion gas stream by a cyclone before the gas is cooled to approximately 250°C and released to the ventilation system. Fines and water are removed from a small portion of the gas stream for analysis by on-line combustion gas analyzers which provide a continuous measure of all major flue gas components.

Auxiliary Systems. A propane burner is used to heat the fluidizing air for the combustor during start-up. By circulating solids among the zones, most of the heat required for preheating is provided by the burner. A superheater upstream of the cooling zone provides the rest of the energy needed to preheat the system. Nitrogen, rather than steam, is used during most of the preheating period so that the amount of steam condensate is kept as small as possible. Once steady state conditions are approached, the energy provided by the burner and superheater is reduced.

Raw shale is metered at 50 lb/hr into the pyrolyzer by a screwfeeder which is supplied by a bin with a 300-lb shale capacity. Additional shale can be loaded into the bin during operation, so truly continuous operation may be realized. Processed shale at approximately 400°C exits the cooling zone through a rotary valve and into a sealed bin with a capacity of approximately 500 lb. Although the bin was designed so that it was possible to remove hot solids from the bin during operation, this practice was never actually implemented because of the potential hazards of handling the hot shale. Therefore, the practical operating duration for the PDU was 10 hours or the processing of 500 lb of shale.

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Figure 4-5. Schematic diagram of the 50-lb/hr KENTORT II process.

4.2.2 Reactor Design and Fabrication

The cold-flow model provided significant information for the final design of the PDU while accounting for the density differences of the gases at reaction temperatures. It was important to have experimental, cold-flow information available because the positions and nozzle geometries of the inlet and outlet ports and the sizing of downcomers are extremely important in an integrated fluidized bed system. Again, with the aid of experimental data, the materials of construction were specified, and the final blueprints of the reactor were completed. A machining subcontractor was selected to complete fabrication of the reactor, and the unit was secured into the scaffolding. Installation of auxiliary systems, the oil collection system, and instrumentation was then completed. The following sections describe the design of the retort and the rationale behind the design.

Reactor Material Selection. Previous experience with the 5-lb/hr retort⁷ demonstrated the inherent material problems associated with the combination of high temperatures and corrosive gases that characterize the different zones of the KENTORT II process. Rapid scaling and spalling was observed for type 304 SS that was exposed to the fluidized bed region of the gasification section. By aluminizing the base metal of the 3-inch diameter KENTORT II system, however, it was shown that corrosion could be effectively reduced to acceptable levels. Aluminizing is a process where aluminum diffuses at high temperature into the surface of a base metal for a minimum depth of 100 microns producing an aluminum-rich alloy on the surface.

Because of the success of the aluminized metal for the 3-inch unit, this measure of corrosion protection was adopted for the 50-lb/hr retort. The base metal used for some of the internals of the 3-inch system, however, displayed evidence of high-temperature failure, so heat-resistant base metals were a requirement for critical areas of the reactor. Commonly used high-temperature alloys such as Inconel and Hastelloy were rejected because of possible difficulties during fabrication. Furthermore, high-nickel alloys do not necessarily provide protection against the type of sulfidation that has been evident in the 3-inch unit, so the additional expense for these types of materials would be wasted. Other alloys such as cast stainless steels were also considered. While the cast stainless steels are relatively inexpensive, have very high tensile strength and creep resistance at elevated temperatures, the fracture toughness is poor. The alloy which appeared to most closely meet all of the system requirements was TP 316H stainless steel. This alloy is covered under ASTM A312 as a modification of grade TP 316 and is intended for high temperature service.⁶ This material was used as the primary construction material for the high temperature zones of the PDU.

Seals Between Reactor Sections. The sections of the KENTORT II unit were separated by gas distributors which were sandwiched between standard ANSI 150-lb flanges. The selection of the type of device to seal the sections of the reactor was, again, made difficult by the high-temperature, corrosive conditions of the KENTORT II system. A test rig which was made from two 3-inch 150-lb flanges was utilized for evaluating different sealing devices. Ceramic fiber sheets and ropes were tested and were found not to provide a quality

gas-tight seal. A ceramic based gasket forming compound was tested and was found to be woefully inadequate for sealing large flanges. A gasket made from Grafoil, a flexible graphite material, was also tested. Grafoil is rated for temperatures up to 3000°C, but only under neutral atmospheres. When exposed to air at temperatures above 525°C on the outer surface of the gasket, the graphite material burned and disintegrated. While Grafoil was unsuitable for the highest temperature flanges, it was appropriate for the less severe areas of the reactor such as the thermowell ports.

NASA Lewis Research Center provided four custom-made metallic O-rings for testing purposes. The O-rings were fabricated from 5/16-inch stainless steel tubing which was joined at the ends with an electron beam weld. To accommodate the metallic O-ring, the sealing surface of the test rig was smoothed to a roughness of 32 micro-inches. Subsequent tests showed that the O-rings did seal properly, but they required heavy torquing and were not reusable after being thermally cycled.

Two spring energized metallic C-rings (see Figure 4-6) were obtained for testing purposes. The C-rings consist of a limiting plate and a spring-energized seal. The limiting plate, made from a 300 series stainless steel, centers the seal between the mating flanges and eliminates the need for a groove in the flange. The seal consists of an Inconel X-750 spring inside a C-shaped Inconel X-750 jacket, which is nickel coated. The nickel coating has dual functions: it penetrates the imperfections of the mating surfaces to improve sealing capability and increases the corrosion resistance. Tests conducted with the prototypes showed that the C-rings provided a quality seal and were reusable after thermal cycling. The C-rings were, therefore, selected for use in the 50-lb/hr PDU.

Figure 4-6. Spring energized C-ring.

Since the C-rings could not be aluminized, protection against corrosion was an important consideration. If the seal was directly exposed to the shale particles, especially in the gasification zone, the potential for corrosion was increased. By using an extension ring to mount the gas distributor above the C-ring (see Figure 4-7), the seal became isolated from the solids. Since the C-ring was at the bottom of the fluidized bed, the concentration of corrosive gases was low and sulfidation was not expected to be a problem.

Reactor Assembly. Figures 4-8 and 4-9 show an assembly view and cross-section of the KENTORT II reactor, respectively. The gasification and combustion sections were each mounted at the same level above the floor (10 feet) so that thermal expansion would have a minimal effect on the connecting pipes between the sections. Expansion joints were still required, however, for connection to downstream equipment and connections between sections. The scaffold which supported the reactor system was constructed of eight 4 x 4-inch, 22 feet-long columns which are tied together with channel-type bars.

The main reactor sections were sealed with the aforementioned spring energized C-rings. The ports for the solid recirculation loops which link the pyrolysis, gasification, and combustion zones were also sealed with C-rings because of the high temperatures. Temperature and pressure ports are located at 6-inch intervals within each fluidized bed and at 1 foot intervals in the freeboard areas. These ports consisted of 1/2-inch schedule 40 pipe with 150-lb flanges. The temperature of these flanges was below 525°C, so graphite foil gaskets could be used. All ports extended approximately 5 inches from the vessel wall and were covered by one inch of the six-inch layer of insulation. High-temperature electrical

Figure 4-7. Gas distributor mount.

Figure 4-8. Assembly view of KENTORT II reactor.

Figure 4-9. Cross-section of KENTORT II reactor.

heating elements were located beneath the layer of insulation surrounding the pyrolysis and cooling zones to compensate for heat loss and to aid the preheating of the system.

Pyrolyzer Design. The pyrolysis section was 6-feet tall and consisted of 6-inch schedule 40 pipe. A modified 8-inch 150-lb flange for mating with the gasifier was connected to the bottom of the pipe (see Figure 4-10). A 46-inch tall baffle split the pyrolysis zone into two equally sized beds to narrow the residence time distribution of the solids. Raw shale was introduced above the bed through an angled 1-inch pipe on one side of the baffle, and shale exited the zone through a downcomer, which was attached to the distributor, on the other side of the baffle. There were 12 ports along the vertical axis (6 on each side of the baffle) which accommodated a combined thermowell and pressure tap assembly.

The recirculation inlet to the pyrolysis zone was a 1-inch pipe (Figure 4-10, section A-A), which was connected directly to the lift pipe from the gasifier. It was placed 3.5 inches above the gas distributor. This position was successfully tested on the cold-flow model and was incorporated into the final design.

The fluidizing gas and product vapors left the pyrolysis zone through a 2-inch pipe at the top of the vessel (Fig. 4-10, section A-A) and entered a cyclone that separated the fines from the gas stream. The original design specified that these fines would be fed directly into the combustor by a rotary valve. Cold-flow testing of this arrangement, however, was not successful. There was enough gas leakage past the rotary valve to fluidize the fines in the bottom of the cyclone, and this prevented the very fine particles from entering the combustor. Instead, the design of the system was modified so that fines collected in the cyclone from a previous run could be loaded into a sealed bin to be fed into the combustor at a rate that was not necessarily related to the rate of fines entrainment from the pyrolyzer. This new arrangement allowed the accurate determination of fines carry-over which was another important benefit.

Gasifier Design. The gasification zone was 6-feet high and was constructed of 8-inch schedule 40 pipe with 150-lb flanges at each end. The gasification zone had a larger diameter than the pyrolyzer for two reasons. First, a longer solids residence time is required for gasification, so it was desirable to increase the diameter to reduce the L/D ratio of the bed. Second, a larger diameter was required to keep the gas velocity in the gasification zone similar to the pyrolysis and cooling zones. Since the pyrolysis, gasification and cooling zones share a common fluidizing gas, the density and velocity (if the vessel diameter is constant) of the fluidizing gas vary according to the temperatures of the zones.

A 1.5-inch inlet for the recirculation port from the combustor, was placed 15 inches above the distributor and cut at a 60° angle (see Figure 4-11, section A-A). This was observed from cold-flow studies⁵ to be the most favorable arrangement to permit the free-flow of solids into the gasification zone. A 1-inch schedule 40 pipe, placed in the freeboard region, was available for feeding raw shale during start-up and during periods of upset when

the dipleg of the downcomer which feeds the gasifier became uncovered. Six 1/2-inch ports on each side of the baffle were available for temperature and pressure readings.

A 46-inch tall baffle was located 2 inches above the gas distributor to provide staging for the particles to narrow the residence time distribution. Three brackets attached 21 inches from the top on the gasifier were used to mount the unit to the scaffold.

Cooling Zone Design. Because the cooling zone was designed to operate between 350-500°C, a slightly smaller inside diameter was required compared to the pyrolyzer, so a 6-inch schedule 80 pipe was specified as the vessel shell. A concentric reducer was used to ensure a smooth transition between this zone and the gasification zone (see Figure 4-12). The reducer eliminated any dead space around the edges of the gasifier distributor. A 1-inch pipe was used as the outlet port for the spent shale (Figure 4-12, section A-A). This pipe, which also controlled the bed height, was mounted at a 30 degree angle from the vessel wall. The cooling zone was 3-feet tall and the bed height was 15 inches.

A 7-inch long plenum chamber made from 6-inch schedule 40 pipe and a 6-inch 150-lb flange served as the base for the cooling zone. The steam used for fluidization was introduced through a vertical 2-inch pipe attached to the bottom of the unit.

Combustor Design. The combustor consisted of 6-inch schedule 40 pipe which was slightly modified from the cold-flow design. The height was increased from 4.5 feet on the cold-flow model to 6 feet on the hot unit. This change was introduced so that CO would have the opportunity to completely combust in the taller freeboard section of the unit. High CO levels were recorded in the 3-inch unit because of a very short freeboard section in the combustion zone. Additionally, a taller freeboard should reduce entrainment of non-fine particles.

Shale from the gasification zone was injected pneumatically into the combustor bed through a 1.5-inch pipe which was placed 3.5 inches above the distributor (see Figures 4-5 and 4-13). Gases and entrained solids exited the combustor through a horizontal 1.5-inch pipe at the top which was connected to a cyclone for fines removal.

A 7-inch long plenum chamber with a 2-inch inlet port for the fluidizing gas and a 2-inch outlet port for the recirculation loop to the gasifier served as the combustor base. The standpipe which controlled the depth of the combustion bed extended through the gas distributor and through the outlet port at the bottom of the plenum chamber. This configuration made it easy to adjust the standpipe height and thereby allow for a study of the mean solid residence time. Three brackets attached to the plenum mounted the combustor to the scaffold. The combustor was covered with 6 inches of high temperature insulation to minimize heat losses. A propane burner was used to preheat the fluidizing air during start-up and during steady state operation, if necessary.

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Figure 4-12. Cooling zone.

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MODIFIED 8" 150# FLANGE

SECTION A-A

SECTION B-B

NOTE: 8" FLANGE IS OFFSET 0.75 IN. AS IN SECTION A-A.

MAIN PLENUM

Figure 4-13. Combustor.

4.3 REFERENCES

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5. KENTORT II PDU TEST RESULTS

5.1 SHAKEDOWN RUNS

5.1.1 Introduction

The objectives of the shakedown procedures were two-fold. The first was to evaluate the operating capabilities and to identify any deficiencies of the system. The second was to develop and refine operating procedures and to modify the PDU so that design conditions could be achieved. The first task was the verification of proper shale movement throughout the system at ambient temperatures. This was done initially at room temperature because the subsequent modification or replacement of retort components would be facilitated without the presence of insulation, heating tapes, etc. Once reactor stability in terms of shale dynamics was verified, the next task was to evaluate the start-up/supplemental heating systems and the resultant temperature distribution throughout the system. Therefore, the two major tasks associated with the start-up of the 50-lb/hr PDU can be roughly termed cold-flow and hot-flow testing, respectively.

5.1.2 Cold-Flow Testing

The major objectives of the cold-flow tests were to determine the capacity of the recirculation loops, assess the operating stability of the retort, and measure the amounts of fines entrained into the combustor and pyrolyzer cyclones. Tests were conducted using room-temperature air which was supplied by a 220-ft³/min blower. Raw oil shale (20 x 60 mesh) was continuously fed to and withdrawn from the retort at a rate of 50 lb/hr.

The rates of solid recycle from the gasifier to the pyrolyzer and combustor were observed at the design levels of 200 and 500 lb/hr, respectively. These recycle rates were calculated from previously determined empirical relationships for pressure drop and mass-flow rate for this system. The control of the solid-recycle rates by the aerated J-valves was steady, and there were no disruptions of solid recirculation during the tests. Therefore, no modifications to the J-valves or lift pipe designs were deemed necessary.

During 9.5 hours of continuous cold-flow testing, no incidents of unexpected system instability were experienced. The PDU behaved very much like the full-scale cold-flow model except for the cooling zone. The diameter of the cooling zone in the PDU was 2 inches smaller than the cold-flow model because of the temperature difference between the gasifier and the cooling zone in the PDU. Therefore, when operated at room temperature, the superficial gas velocity in the cooling zone was 92% higher than in the gasifier, so the cooling zone was more vigorously fluidized. In spite of this, the stability of the system was not compromised and no elutriation of the bed or bypassing of the fluidizing gas into the gasifier via the downcomer was apparent.

Fines generation during cold-flow testing was not excessive. Approximately 11% of the feed was recovered in the pyrolysis cyclone (10% carryover was the design basis). Most of these collected fines were fed into the retort as undersized material clinging to particles in the 20 x 60 mesh range. Minimal attrition of the particles can be expected at room temperature as demonstrated by the small amounts collected in the combustion cyclone. Since the gasifier and pyrolyzer were the feed points for shale into the retort, most fines which were fed to the system would be entrained before circulation to the combustor. The cyclone was designed to trap most of these fines, but like all cyclones, it was not 100% efficient, so significant quantities of fines were also transported to the pyrolyzer heat exchanger and the electrostatic precipitator.

5.1.3 Hot-Flow Testing - Phase 1

Nitrogen was used for fluidization of the cooling, gasification, and pyrolysis (CGP) zones during the hot-flow tests. This was done for convenience because condensation of steam in undesirable areas of the system would cause unnecessary difficulties during this early phase of testing. The nitrogen was heated by the steam superheater to approximately 500°C which, in turn, heated the CGP zones during the start-up process. The maximum temperature of the nitrogen from the superheater was achieved within three hours when starting from room temperature (see Figure 5-1). The electrical heating tapes surrounding the cooling and pyrolysis zones also provided some energy during start-up. The heat tapes for the pyrolyzer provide enough energy to make it hotter than the gasifier during this portion of the heat-up process (see Figure 5-1).

Start-up heat for the combustor was provided by a propane burner which was in line with the fluidizing air. Early in the start-up process, no solids were recycled to the combustor so that the temperature would be quickly elevated. Typically, the combustor temperature reached 800°C within one hour (see Figure 5-2). To avoid over heating the combustor and to heat the remainder of the system, the next step in the start-up procedure was to initiate the recirculation of shale between the combustor and the gasifier. This caused an initial drop in the combustor temperature (Fig. 5-2), but it caused a corresponding increase in the rate at which the gasification zone was heated. The burner provided approximately 40,000 Btu/hr of gross energy input while the superheater contributed approximately 20,000 Btu/hr of gross heat. The 100% greater energy input by the propane burner is appropriately reflected by the more rapid heat-up rate of the gasifier during the period of solids-recycle between the combustor and gasifier compared to the period when heat was only supplied by the steam superheater.

The most significant findings were that the system displayed stable operating tendencies and that the design temperatures and shale recycle rates were achieved for each zone. The problems that were encountered had nothing to do with the retort itself as they were all associated with ancillary pieces of equipment. A brief description of each shakedown run and the corrective action taken, if any, follows:

KT930902. From a cold start, the run lasted approximately 8 hours which included about 3 hours where the temperatures of the 4 beds were at near steady state. The propane burner raised the temperature of the combustor to 650°C before it ceased operation following the initiation of solid recycle between the combustor and gasifier. The combustor sustained temperatures ranging from 700 to 780°C without the aid of the start-up burner. Shale was fed to and withdrawn from the retort continuously to provide enough carbon to sustain combustion. The pressure in the gasifier could not be sufficiently adjusted downward so that it was the same as in the combustor at the balance point. This hindered the operation of the unit, and was at least partly responsible for a process upset that caused termination of the run. The temperature of the ESP was too low (less than 120°C) to permit operation with steam, so

Figure 5-1. Heat-up profiles of the cooling, gasification, and pyrolysis zones from run KT930902 as a result of heated nitrogen from the steam superheater.

nitrogen fluidization was used for the duration of the test. Some oil was produced and collected, but because of the relatively short duration of the steady state period and the inability to operate with steam, the amount of oil collected was not meaningful.

KT930920. Combustion flue gas analyzers were placed on line. A higher-pressure source of propane was used to fuel the burner, and it operated flawlessly. Pyrolyzed shale was periodically fed to the system in order to provide carbon for fuel yet not produce oil. Design temperatures for each of the zones were achieved: Pyrolyzer (500-600°C), Gasifier

Figure 5-2. Temperature profiles for the combustor, gasifier, and pyrolyzer from run KT930920 illustrating the effect of shale recycle between the combustor and gasifier on the heat-up rate of the system.

(750°C), and Combustor (850°C). Pressure balance between the combustor and gasifier could not be achieved. The ESP temperature was still too low to permit steam fluidization.

KT930927. No shale was fed to the system in order to test the capabilities of the start-up heaters without aid from carbon in the shale. Proper pressure balance between the gasifier and the combustor was maintained due to the installation of a gate valve at the outlet of the combustor flue gas stream. The temperatures attained for each of the zones were: Pyrolyzer (600°C), Gasifier (725°C) and Combustor (775°C). Additional insulation was not sufficient to raise the outlet temperature of the ESP above 100°C.

KT931007. Excessive heat losses from the piping between the pyrolyzer and the air-cooled heat exchanger continued to be a problem for this run. The run was terminated following about 8 hours of heat-up time because it was apparent that the equipment downstream of the pyrolyzer would heat up no further. Excessive heat loss was a problem between the pyrolyzer and the air-cooled heat exchanger because low temperatures can cause heavy oil to condense, accumulate, and eventually restrict the flow of gas through the piping, especially in bends. Runs had previously not been sufficiently long enough to experience this problem. However, the heat loss problem that was experienced was that the temperature of the electrostatic precipitator (ESP) was lower than 100 °C. It was an important priority to minimize steam condensation in the ESP because water is nearly impossible to remove from this heavy, viscous oil. Water-laden ESP oil presents problems because the water cannot be uniformly dispersed even after vigorous stirring and mixing, so obtaining a representative sample for analysis is difficult. Following the run, heat losses were then reduced by adding extra insulation to the piping and by installing electrical heating pads beneath the insulation of the ESP. No such problems with heat losses were observed since.

KT931014. The preheating portion was successfully completed, but the run was then aborted prematurely because a successful switch to steam from nitrogen fluidization could not be achieved. The dynamics of the attempted switch to steam were so severe that steady operation of the system could not be regained in a reasonable amount of time. It was also determined that any subsequent attempts to switch to steam would have a similar result, so the unit was shut down. To make the transition to steam more smooth, a steam-bypass system was installed. In addition, a condensate trap was installed to minimize water mist entering the steam flowmeter.

KT931021. Following approximately 3 hours of preheating, a section of pipe between the propane burner and the combustor plenum burst due to high-temperature oxidative fatigue. Plumbing constraints during construction dictated that the burner be situated at a 90° angle with the inlet pipe to the combustor plenum. The elbow-fitting and the pipe section immediately downstream became an area of intense heat impact due to the turbulence induced by the bend and was the site of the failure. Examination of the plenum chamber itself showed signs of oxidative scaling, inside and out. It was determined that modifications to the burner configuration and the plenum chamber were needed, not only to solve the materials problem, but also to make the heating of the combustor more efficient.

These planned changes will be described in a following section. Rather than making any major changes immediately, the damaged section of pipe was replaced as a temporary measure so that the shake-down process could be completed. The reasoning for this was that more problems could become apparent during subsequent shake-down runs, and modifications could then be performed all at once during an extended down-time period.

KT931029. During this run, the preheating period was completed without incident, the switchover to steam was smooth, and the start of raw shale feed was successful. This was the first time that the system had gone through all steps of the start-up procedure. Steam flow was maintained for 51 minutes during the shale-feed period, but the steam generator was not even able to sustain lowered steam rates, so N₂ fluidization was restored for the remainder of the run. Raw shale feed was continued for an hour following the switch to N₂ because it was the first time that the system had successfully fed raw oil shale under prime oil generating conditions, and an assessment of the performance of the oil collection system was needed. Oil and small amounts of water drained continuously from the ESP, and light oil was collected in the receiver for the shell-and-tube condenser according to design. While relatively little oil was collected during this period, the basic functionality of the system was demonstrated. The robustness of the oil collection system during prolonged periods of operation was still yet to be confirmed, however. Although the conditions during the two-hour raw-shale-feed period fluctuated somewhat, the average temperatures of all beds were at or near their design levels (see Table 5-1).

Much more ESP oil was recovered during the clean-up process than was drained from the unit during the run due to its shortness. It was expected that once the internals of the ESP become coated, the oil would drain from the unit steadily without additional hold up. The collection of light oil in the shell-and-tube condenser receiver most likely occurred during the portion of the run when steam was used for fluidization. Much fine oil mist was visible in the exhaust during the nitrogen-fluidization phase because the mist filters were not then in use. The compositions of each of the two gas streams were measured during the run and were generally in line with what was expected (see Table 5-2). The combustion gas composition was the average of on-line measurements, and the gasifier/pyrolysis gas composition was determined chromatographically from one sample taken during the steady-state period. While the gas measurements are fine for qualitative purposes, enough samples were not taken by the gas chromatograph for the results to be viewed quantitatively.

A high concentration of SO₂ from the combustor was observed which was attributable to the low conversion of pyrite to magnetite in the gasifier because of its relatively low temperature. The average carbon monoxide concentration was high in the combustor flue gas because at times there was a rich fuel/air ratio in the burner which starved the combustor of oxygen. When the propane flow was reduced so that it served only to preheat the fluidizing air, enough oxygen remained so that the carbon in the shale particles would readily combust. Under these conditions excess oxygen became present in the flue gas, CO was reduced, and the combustor temperature increased. Therefore, a rich fuel/air mixture in the burner worsened the operation of the combustor when there was an adequate level of carbon in the

Table 5-1. Average Conditions for the Two-Hour Steady-State Period of Run KT931029.

	Bed Temp., °C	Lift Pipe, °C	Recirc. Rate, lb/hr
Pyrolyzer	520	615	280
Gasifier	685		
Combustor	800	670	380

solids. It is estimated that 25% of the CO₂ in the combustion flue gas was from the propane gas and the balance was from the carbon in the oil shale. The combustor can sustain operation without aid from the propane burner, but the temperature gradually decreases to an unacceptably low level because of the cool fluidizing air.

A slight pressure differential between the gasifier and combustor caused the CO₂ content in the gasification/pyrolysis gas stream to be relatively high. Otherwise, the relative amounts of these gases were similar to previous fluidized bed pyrolysis studies. The pressure imbalance was not detrimental to the generation of oil because the combustion flue gas generally contained little or no oxygen during the oil-producing period. The combustor was operated under oxygen-starved conditions for much of the run which meant that the combustion flue gases which were leaking into the gasifier and pyrolyzer did not contain oxygen that could oxidize the freshly generated shale oil vapors.

In summary, this run demonstrated the functionality of all parts of the 50-lb/hr KENTORT II system and showed that the product yields were generally similar to what was found in the 3-inch diameter KENTORT II system. The oil collected from this run was roughly equivalent to Fischer assay. The shortcomings of the system left to be resolved after the run were the low capacity of the steam generator and the low temperature of the gasification zone. In an attempt to increase its capacity to at least 50 lb/hr (the design capacity is 86 lb/hr), the steam generator was thoroughly cleaned and one partially clogged pipe was cleared. The low gasification temperature was felt to be related mainly to heat losses from the burner/combustor-plenum configuration so this problem was set aside until the scheduled modification down time.

KT931104. The objective of this run was to sustain steam fluidization for at least a 3-to-4-hour period. Once again, the steam generator was not able to sustain its target rate of 50 lb/hr, so fluidization by N₂ was restored. Because of the large effort involved with performing a run, operation with N₂ was continued just to gain more experience with the unit.

Raw shale was fed continuously for three hours but little or no oil generation was apparent. A major reason for this was that the pyrolysis temperature was rather low (450-500°C), but it was not low enough to explain almost a complete lack of oil generation. Another, and more significant factor, was that much leakage of combustion flue gas into the gasifier and subsequently into the pyrolyzer was occurring. This was confirmed by high CO₂ concentrations in the pyrolysis/gasification gas stream. While this was also the case for run KT931029, the oxygen content of the flue gas was much higher for this run and apparently oxidized much of the oil that was generated in the pyrolyzer. In addition, there were portions of the run when the pyrolysis bed was poorly fluidized as indicated by a non-uniform axial temperature distribution in the bed region. Poor fluidization occurred in the pyrolyzer when the pressure differential between the combustor and gasifier was adjusted so that there was no flow of combustion gases into the gasifier. Therefore, at no time during this run were the conditions favorable for oil generation.

There were two fundamental causes for the problems that were observed during this run. The first was that the temperature of the gasifier was too low for its superficial gas velocity to be equivalent to the velocities in the cooling and pyrolysis zones. At temperatures less than 800°C the thermal expansion of the gas was too low to compensate for the increased cross sectional area of the gasifier. Inconsistent gas velocities among the zones were shown to contribute to unstable behavior during testing of the cold-flow model. However, higher gasifier temperatures were expected to alleviate this problem.

The second cause for the problems associated with this run was the low height of the gasifier bed. A low bed height can expose the dipleg of the gasifier/combustor standpipe to the freeboard region of the gasifier and make balancing the pressure between the combustor and gasifier more difficult. When the dipleg is immersed in the bed, there is more resistance to gas flow and large amounts of flow between the two zones is less likely. It was expected that both of these problems could be resolved by the changes that are described in the next section.

Table 5-2 Gas compositions from run KT931029 during the two-hour steady-state period

Combustor		Pyrolyzer/Gasifier	
CO ₂ (vol%)	13.5	H ₂ (vol%)	5.1
CO (ppm)	649	CO ₂ (vol%)	6.9
O ₂ (vol%)	1.1	CO (vol%)	1.2
SO ₂ (vol%)	0.5	H ₂ S (vol%)	2.3
		CH ₄ (vol%)	2.2
		C ₂ 's (vol%)	1.0
		C ₃ -C ₅ (vol%)	0.8

5.1.4 System Modifications

Burner/Plenum Configuration. The failure of the elbow-joint fitting between the propane-gas burner and the combustor plenum was the most serious problem to be addressed. In the original configuration (Figure 5-3a), the hot gases from the burner impinged directly onto the elbow joint, causing it to overheat and eventually rupture. The elbow fitting and the distance of the burner from the plenum also caused significant heat loss. To resolve both problems, the burner was mounted horizontally so that a short, straight length of pipe could direct the hot gases to the plenum (Figure 5-3b). To prevent the same sort of heat-related failure that the elbow fitting experienced, the entire surface of the plenum was aluminized and then the inside surfaces were lined with a 0.5-inch thick layer of castable ceramic (SiO_2). The ceramic layer served to protect the metal and to reduce heat losses from the plenum. In addition, a ceramic-sheathed R-type thermocouple was installed in the plenum chamber to more efficiently control the operation of the burner and the fluidized bed combustor.

Distributor Plates. During inspection of the combustion plenum chamber it was found that a significant amount of shale particles had fallen through the holes of the distributor plate and into the plenum. In addition, many of the holes had become clogged with particles. A similar situation was revealed in the cooling zone plenum and distributor plate. There was no problem with the distributor plates for the pyrolysis and gasification zones because they were designed to permit the passage of solids. Rather than attempt a major redesign of the distributor plates that would require cold-flow modeling, new distributor plates were fabricated with smaller holes that would not permit particles to pass through when the beds are slumped (0.0625 inch dia.). The new distributors had the same open area as the original ones but were thinner to facilitate the drilling of so many small holes.

Gasifier Standpipe. To double the height of the gasifier bed, a 30-inch long pipe was aluminized and was placed over the existing 15-inch pipe so that the total height of the standpipe was 30 inches above the distributor plate.

Steam Generator. Steam is produced by electrodes that pass electric current directly through the water in the main vessel of the steam generator. The rate of steam generation is directly related to the current flow through the water. The rate of current flow is effected by the conductance of the water and the percentage of the electrodes that are covered by water. A pressure regulator controls the level of water in contact with the electrodes, and therefore, the rate of electric current. This regulating process was found to be facilitated at higher generator pressures. Since the generator was being fed directly by city water, the line pressure was limited to 70 psig. Therefore, a water holding tank and a feed-water pump were installed so that the steam generator could be operated above 100 psig. This arrangement also permitted the recycle of condensed steam in the system.

a) Original Burner/Combustor Plenum Configuration

top view

side view

b) Modified Configuration

top view

Figure 5-3. Top and side views of (a) the original plenum chamber and top view of (b) the modified plenum chamber without the elbow fitting.

5.1.5 Hot-Flow Testing - Phase 2

Following the completion of the system modifications, a final series of shakedown runs was performed. All the runs utilized nitrogen for fluidization to simplify the operating procedures. Since steam fluidization was required for efficient light oil trapping, the oil yields generated during these runs were not considered representative and will not be reported. The emphasis of these shakedown runs was to establish proper temperatures and solid-recycle rates among the zones. A synopsis of each run will follow to emphasize the successes and the difficulties that were encountered.

KT940222. This was a successful first run for the PDU following the extended down time for system modifications. Raw shale was continuously fed to the pyrolyzer for over three hours and the temperatures that were achieved for each of the zones were within the design ranges (see Table 5-3). Significant amounts of oil were collected in the electrostatic precipitator (ESP), so this run provided an opportunity to develop and refine oil-yield-measurement procedures.

While this was considered to be an excellent non-steam run in most respects, a disappointing aspect was that the temperatures of the gasifier and the combustor were approximately 100°C cooler than what was expected. Gasification temperatures of approximately 800°C are required for the steam/carbon gasification reaction to proceed at a reasonably fast rate, so an increase of 100°C was required in this regard. Additionally, higher gasifier temperatures are required for the solid-recycle rate to the pyrolyzer to be reduced. In the previous burner configuration, the plenum and the burner-inlet pipe were not thickly insulated because of the material-failure problems in the region. Therefore, thermal losses were tolerated in order not to overheat the plenum area. This approach was carried forth to the new configuration, but these heat losses essentially negated the thermal-efficiency gains of the new burner arrangement.

Consequently, additional layers of thermal insulation were added to the exterior of the plenum region. Also, more insulation was added to the lift pipes for the pyrolyzer and the combustor to further reduce thermal losses from the system.

KT940308. The purpose of this run was to test the temperature capabilities of the

Table 5-3 Average temperatures (and standard deviation) recorded during the periods of raw shale input to the pyrolysis zone for runs: KT940222 and KT940317.

		Temperature+/-Std. Dev. (C)	
		<u>KT940222</u>	<u>KT940317</u>
Pyrolysis	Bed	516 +/- 8	520 +/- 20
	Lift	632 +/-13	704 +/- 26
Gasification	Bed	701 +/- 15	809 +/- 30
Combustion	Bed	788 +/- 18	896 +/- 25
	Lift	670 +/- 15	801 +/- 25

combustor and gasifier with the new layers of insulation intact. During the start-up period, the propane burner was used aggressively to quickly raise the temperature of the combustor by maintaining the plenum chamber above 1200°C. A disturbance in the system during heat up resulted in the loss of solid recycle between the combustor and gasifier. Since solid recycle was the primary means of removing heat from the combustor, the temperature of the combustor rose quickly to over 950°C for several minutes before the flow of fuel to the burner could be ceased. Following this event, the recycle of solids between the combustor and gasifier could not be resumed and the whole system became inoperable. The system was then cooled down for examination on the following day. Large, fused masses of shale which had been previously in a molten state were found in the combustor. These slag-like materials were primarily located on the gas distributor and needed to be broken loose using a hammer and chisel. The combination of the high plenum temperature (>1200°C) and the temporarily high bed temperature in the combustor (950°C) probably caused the temperature near the gas distributor to well exceed 1000°C and reach the melting point of the minerals in the shale. Ash-fusion analysis of the shale according to ASTM D-1857 indicated that initial deformation occurred at 1168°C (see Table 5-4). It should be noted that slagging or ash agglomeration has been observed at temperatures hundreds of degrees lower than the initial deformation temperature of this test. According to the ASTM test and the temperatures that seemed to cause the agglomeration, the Cleveland oil shale should experience temperatures of no more than 950°C for safe, non-slagging processing.

KT940310. The slag was removed from the retort and a repeat of the run was attempted with the exception of maintaining the plenum temperature below 1200°C. Early in the heat-up process, it became apparent that something had clogged either the J-valve or the lift pipe to the combustor. To avoid additional slag formation, the retort was immediately cooled down. A marble-sized piece of agglomerated shale (apparently from run KT940308) was found to be trapped in the J-valve and was definitely determined to be the cause of the malfunction. To facilitate future cleaning of the J-valve, a flanged connection was installed near the inlet to the lift pipe.

KT940317. This run was characterized by relatively trouble-free operation with the exception of some interruptions in solid recycle to the pyrolysis zone during heat up. These breaks in recycle were probably due to small slag particles that had not yet been purged from the system and that got temporarily hung up in the J-valve or lift pipe or both. The plenum temperature was maintained between 1100 and 1150°C throughout the heat-up process. Like run KT940222, raw shale was fed continuously to the pyrolyzer for over three hours and a

Table 5-4 Ash fusion analysis (ASTM D-1857) of the master oil shale sample.

Initial Deformation Temperature-	1168°C
Softening Temperature-	1206°C
Hemispherical Temperature-	1244°C
Fluid Temperature-	1485°C

steady-state period of operation was achieved during that time. Temperatures in the combustor and the gasifier were at least 100°C higher than the previous successful run (see Table 5-3). The temperature of the combustor was actually a little bit higher than ideal because of the potential particle agglomeration problem. However, while the combustor bed temperature was above 900°C for over two hours, the plenum temperature was maintained at approximately 800°C so that there was no possibility of over heating the gas distributor. With the high end of the temperature range demonstrated by this run, it was determined that the system was ready for a steam-fluidized run to begin the parametric test matrix.

KT940329. The start-up period was riddled with solid-recycle interruptions to both the combustor and pyrolyzer. After attempting for several hours to heat up the system, it was determined that the J-valve or lift pipe to the combustor was clogged again and needed to be cleaned out. Indeed, shale agglomerates were found throughout the system and in the J-valve. As opposed to run KT940308, however, the agglomerates were few in number and small in size. In fact, no agglomerates were recovered from the combustor itself, but it is possible that they could have formed there and migrated throughout the rest of the system. The production of these agglomerates during the heat-up period is difficult to explain because the conditions were in all respects less severe than run KT940317. One possibility is that a thin layer of molten shale formed on the distributor plate of the combustor during KT940317 and remained there throughout the run without causing any problems. There was a four-hour-long period where the plenum temperature was held between 1100 and 1150°C which could have overheated the gas distributor and caused the thin layer of molten material to form. All of the agglomerates were 1/8" or less in thickness. The molten material could have cracked following solidification from cooling after run KT940317. The agglomerates would have then been present at the start of run KT940329. A detailed discussion of the characteristics of the agglomerates will follow in a separate section. This is an important matter because particle agglomeration can be a serious problem in this type of system. Only when over-sized particles have been in the system have the solids-recycle systems displayed any inconsistencies.

5.1.6 Start-up Procedure

The final start-up procedure which was developed during the shake-down period involved three different periods: 1) preheating, 2) switch-to-steam and 3) start-shale-feed. Refer to Figure 4-5 for the flow diagram of the system.

1) Preheating. The two major sources of energy for the preheating period were the electric steam superheater and the propane-fired burner. Some energy for heat up was also provided by heat tapes surrounding the cooling and pyrolysis zones. Approximately three hours were required for the N_2 gas from the superheater to reach its maximum temperature at approximately $500^\circ C$. The N_2 gas fluidized the cooling, gasification, and pyrolysis (CGP) zones. The fluidizing gas completely preheats the cooling zone but it was not sufficient to completely heat the gasification and pyrolysis zones. This extra energy was provided by recirculating solids between the combustor and gasifier which had been heated in the combustor with the aid of the propane burner. Through a combination of gas and solid heat transfer, the pyrolysis zone was subsequently heated by the gasification zone. During this period, processed shale could be fed to the pyrolyzer or gasifier to increase the levels of the beds. Pyrolyzed shale could also be fed during this period to increase the inventory of carbon in the combustor so that less heat was required from the propane burner. Raw oil shale was not added during this period because generation of oil and gas under unfavorable or transient conditions can compromise the operation of the system. In addition, solids could be withdrawn from the cooling zone so that its proper height could be attained, but generally, the preheating period occurred without continuous inflow and outflow of solids. The entire preheating process lasted up to 8 hours.

2) Switch-to-Steam. Once the system, including the retort and the oil collection system, were up to specified temperatures, steam then replaced nitrogen as the fluidizing gas for the CGP zones. The switch to steam had to be done smoothly because there was a possibility that beds could become slumped and the operating stability of the system put into jeopardy. Once steam flow was established, the system was allowed to reach steady-state conditions again, and the rate of water collected was matched against the measured rate of steam injection to ensure the accuracy of the flowmeter. This period typically lasted less than one hour.

3) Start-Shale-Feed. The start of shale feed to the pyrolyzer basically represented the beginning of the steady state period because temperatures, bed heights, and flowrates were already near their specified levels. However, some operating adjustments were required shortly after the feeding commenced. Fine tuning of the temperature in the pyrolyzer was done by adjusting the shale-recycle rate to the pyrolyzer. The flowrate of propane to the burner was then decreased because the level of carbon in the combustor increased. The recycle rate between the combustor and gasifier also needed adjustment to change those temperatures. In general, the preparation for the start of feed to the pyrolyzer was done so that this transition period was as short as possible.

5.1.7 Ash Agglomeration and Fusion

The occurrence of ash agglomeration and fusion during shakedown tests was identified as a serious operational problem. Therefore, it is important to understand the conditions under which these large masses of material form. There is no great mystery concerning the formation of the fused shale during KT940308 because of the extraordinarily high temperatures that were experienced. While no accurate measure of the temperature of the combustion distributor plate was recorded, it is quite certain that localized temperatures exceeding 1000°C were attained at least for a short period of time. The more disturbing occurrence of shale agglomerates was observed during the attempted heat up of run KT940329 because there were no obvious over-heating episodes or other disturbances which could definitely explain the formation of the fused particles. As noted previously, the fused particles from KT940329 were thin flakes. With the naked eye, one side of each flake had a greenish tint, was almost completely molten, and evidence of individual shale particles had nearly disappeared. The other side of each flake had a more granular texture consisting of imbedded, reddish particles which were approximately the size of the raw oil shale. In addition, the molten side had no obvious curvature that would indicate formation on the inside or outside surface of a pipe. From these observations, it appears that the flakes were formed on a flat surface which was hotter than the environment on the granular side of the flakes.

Scanning electron microscope-energy dispersive X-ray analyses (SEM-EDX) were performed using a Hitachi S-2700 SEM with $\times 10^4$ magnification. Materials included a glassy phase that is intergrown with residual shale particles and red and white mineral precipitates that formed preferentially on the surface of the flakes. Figure 5-4 illustrates how partial melting and cooling of mineral grains resulted in the formation of glassy regions that engulfed residual shale particles. Figure 5-5 is an enlargement of the previously viewed area and illustrates the glassy structures which include some fibrous networks. Mineral grains and shale particles are observed at higher magnification in the SEM as a matrix bounded by glassy structures (Figure 5-6a). EDX analyses further indicate that the mineral matrix is composed predominantly of Si, Al, K, and Ca, with smaller amounts of Fe (Figure 5-6b).

White precipitates were present in all samples and were identified as hexagonal calcium hydroxide ($\text{Ca}(\text{OH})_2$) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) crystals that were formed by hydration of CaO and MgO upon exposure to moisture after sampling. Calcination of limestone and dolomite impurities in the raw oil shale sample is the principal origin of the CaO and MgO. Please recall that a small amount of contamination by limestone and dolomite occurred during crushing, accounting for the presence of Ca in the SEM-EDX analyses.

The reddish color of the granular surface is the result of the formation of oxidized iron phases (hematite, Fe_2O_3). Clusters of iron-rich mineral agglomerations are shown in the SEM microphotograph of Figure 5-7a. Almost all areas of the hardened crust are intergrown with the glassy matrix. The EDX analyses reflect the presence of a Ca-Si rich glassy phase together with the Fe-rich precipitates (Figure 5-7b).

Figure 5-4. SEM photograph of shale agglomerate at x70 magnification illustrating a glassy phase engulfing shale particles.

Figure 5-5. Enlarged view of the sample shown in Figure 5-4 at x900 magnification illustrating the fibrous nature of the glassy melt.

Figure 5-6. a) SEM photograph of the mineral clusters between the glassy phases of the agglomerated shale at x5000 magnification; b) EDX analyses of the mineral clusters.

The clay minerals which dominate the composition of the shale (illite, kaolinite and chlorite) are most likely to dewater first and to then melt. The dehydration of the clays, which starts at approximately 600°C, will increase P_{H_2O} which lowers the melting point of various silicate phases, including clays, quartz, feldspars, etc. Therefore, the clays are believed to influence the agglomerating behavior of the shales the most. The glassy regions were characterized by compositions that are representative of the shale matrix as a whole. The formation of mineral agglomerates is, therefore, expected to be primarily influenced by temperature and to a lesser degree by P_{H_2O} . From experiences in this study, a maximum processing temperature of 950°C is suggested for these shales because of the potential for hotspots that can be hundreds of degrees hotter. For the KENTORT II process, combustor plenum temperatures of no more than 1100°C are now being employed because it appears that a thin layer of molten material can form on the distributor plate if higher temperatures are achieved.

a)

b)

Figure 5-7. a) SEM photograph of red deposits at x450 magnification; b) EDX analysis of the red deposits.

5.2 RESULTS FROM STEADY-STATE OPERATION

5.2.1 Experimental

Start-Up. With spent shale remaining in the cooling zone and the combustor from the previous run, flows of nitrogen and air to these zones, respectively, were initiated. The steam superheater was activated and the propane burner for the combustor was started. The slumped bed of solids in the cooling zone was expanded to transfer some of the shale into the gasification section. Subsequently, the recycle of solids from the gasifier to the pyrolysis and combustion zones was initiated. The propane burner was adjusted so that the temperature within the combustor plenum remained at approximately 1100°C. As indicated previously in this chapter, operation at higher temperatures are believed to be responsible for slag formation near the distribution plate of the combustor. Several hours of operation in this mode were required to elevate the temperatures in the beds to their working levels. During this period the carbon content of the shale was diminished to essentially zero because of repeated passes through the combustor.

Steady-State Operation and Shut-Down. Once the desired operating temperatures within the reactor were achieved and the temperature of the electrostatic precipitator (ESP) was comfortably above 100°C, nitrogen was replaced by steam as the fluidizing gas for the cooling, gasification, and pyrolysis zones. After this transition, approximately 30 minutes was required to establish steady-state conditions once again. Raw shale was then fed to the pyrolysis zone resulting in a drop in the pyrolysis temperature to the prescribed level and an increase in the carbon inventory within the reactor. To maximize the temperature within the combustor, the flow of propane was gradually reduced so that sufficient oxygen was available in the fluidized bed to burn the increasing amount of carbon on the recycling shale. The optimal plenum temperature was found to be slightly less than the fluidized bed temperature of the combustor. Therefore, under steady-state conditions, the propane burner was providing the energy to preheat the fluidizing air only, and it provided no net heat to the shale. The system was operated in this manner for up to 10 hours. During this time, gas samples were taken every 30 minutes from the product gas stream for gas chromatography. Analysis of the combustor flue gas stream was conducted continuously and recorded by the computerized data acquisition system. Light oil was removed from the oil/water separator as required, and oil from the ESP was continuously collected in clear containers for visual inspection. Shut down of the system involved: 1) terminating shale feed, 2) de-energizing all heaters and the propane burner, 3) replacing the flows of steam and air with reduced flows of nitrogen, and 4) allowing the system to cool overnight.

Oil and Solids Recovery. On the day following the run, the solids from the cyclone bins and the spent shale bin were removed, weighed and sampled. The heavy oil trap beneath the air-cooled heat exchanger and the ESP oil containers were removed, weighed, and set aside for further processing. A substantial amount of heavy oil remained held up in the heat exchanger and the ESP at this point. These areas were then thoroughly cleaned with CH_2Cl_2 and the rinsings were distilled to separate the solvent from the shale oil so that the weight of

the oil could be determined. Ultimate analyses on all of the solid and oil samples were then performed. The detailed oil preparation and analysis procedures follow in Chapter 6.

5.2.2 Results and Discussion

The average conditions recorded for each of the seven runs were within the prescribed operating window for the 50-lb/hr KENTORT II PDU (See Table 5-4). In two cases, 500 lb of raw oil shale was processed during steady-state conditions, which was the practical limit of the system. In nearly all cases, premature termination of runs was due to malfunction of the ESP. Inoperability of the reactor itself was never the cause of involuntary shut-down.

Thermal losses from the system were substantial, so it was necessary to operate the cooling zone at a high temperature (ca. 600°C) and the gasifier at a relatively low temperature. Due to the heat losses, nearly complete carbon burn-out was required to maintain the gasifier temperature at the lower end of its expected operating range. Since it was impossible to achieve the range of temperatures in the gasifier that had been originally planned, the result was a series of runs that had very similar average temperatures for each of the major zones. Pyrolysis temperatures ranged from 519 to 534°C which was well within the temperature window for maximum oil production. The measured recycle-solid temperature was quite consistent among the runs with the exception of the last run when it was rather low (612°C). In all cases a significant temperature differential existed between the average gasifier temperature and the measured lift pipe temperature to the pyrolyzer. Much less apparent heat loss was observed for the recycle-solid lift pipe to the combustor. While air was used as the lift gas and there was some combustion occurring to offset heat losses, the

Table 5-5 Average Run Conditions During Steady-State Periods of Operation of the KENTORT II PDU.

Date	940405	940414	940511	940518	940607	940614	940622
Run Number	1	2	3	4	5	6	7
Pyrolysis Temp. (C)	519	534	534	520	531	522	527
Pyr. Lift Temp. (C)	660	656	661	687	656	680	612
Gasifier Temp. (C)	735	728	734	754	704	752	779
Combustor Temp. (C)	810	817	813	836	793	828	849
Comb Lift Temp. (C)	729	733	729	751	705	747	773
Run Length (minutes)	349	194	335	615	444	549	514
Shale Feed Rate (lb/hr)	48.3	62.0	52.7	48.9	47.3	54.6	46.4
Steam Rate (lb/hr)	32	35	36	33.5	35	32	37

much higher recycle ratio to the combustor certainly had an impact on the magnitude of heat loss. The relatively low gasifier temperatures, compounded by relatively large apparent heat losses in the lift pipe, required that the maximum recycle-solid rates to the pyrolyzer for all the runs (4:1) be utilized. The maximum recycle-solid rate to the combustor (10:1) was also necessary for each of the runs to optimize residual carbon combustion and heat transfer.

The carbon, sulfur and mass balances for the runs were quite acceptable (see Tables 5-6 to 5-8). Total accountability for carbon and sulfur was generally higher for runs in which the steady-state run duration was greater than 7 hours. The total weight of spent shale produced was determined by forcing an ash balance on the quantity of raw shale that was fed. The amounts of solids collected in the cyclones and the solids recovered from solvent rinsing (reservoir bottoms) were then deducted from that amount to determine the amount of spent shale recovered in the overflow bin during steady-state operation. The average analysis of two to four samples taken from the inlet of the overflow bin during steady-state conditions were used to calculate the average composition of the spent shale. The oil weight was determined from 5 separate fractions: 1) neat heavy oil from the heat exchanger trap, 2) neat ESP oil, 3) solvent-recovered oil hold-up (still bottoms), 4) neat light oil, and 5) vapor phase C_5+ from gas chromatography. The major combustor flue gases were CO_2 and SO_2 . CO contributed little to the mass and carbon balances, and NO_x was not determined because of difficulties with the analyzer. The rest of the carbon, sulfur and mass balance categories should be self explanatory.

The carbon distributions were well in line with the design conditions of the KENTORT II process. Residual carbon ranged from 6-8% of the total carbon. Approximately 2.5% of the total carbon was recovered in relatively high concentrations in the pyrolysis-cyclone solids and the solids recovered by solvent washing downstream of the cyclone. Injection of these materials directly into the combustor would be an efficient method of utilizing this carbon. The approximately 4% of the carbon that remained as residual carbon in the spent shale is basically unrecoverable because of the wide residence time distribution in the KENTORT II system. Inordinately high mean solid residence times would be required to recover this carbon more fully.

Approximately 10% of the carbon reported to hydrocarbon and synthesis gases produced from the pyrolysis and gasification zones. This amount is on the low side of the design quantity, but it is not unreasonable considering the relatively low gasification temperatures that were reached. Combustor flue gases comprised 37-46% of the carbon balances which was somewhat high. Again, these figures are not unreasonable because of the large thermal losses that had to be overcome. The propane to preheat the fluidizing air and the resulting CO_2 were not included in the mass and component balances. During all of the runs it was necessary for the combustor to be slightly pressurized compared to the gasifier, which resulted in some leakage of combustion flue gases into the gasifier. The amount of combustion CO_2 which was detected in the pyrolysis/gasification gas stream was determined

Table 5-6 Carbon Distribution for PDU Runs 1-7 as Mass Fraction of Total Carbon.

Date	KT940405	KT940414	KT940511	KT940518	KT940607	KT940614	KT940622
Run No.	1	2	3	4	5	6	7
<i>Processed Solids (Total)</i>	0.0686	0.0801	0.0766	0.0743	0.0693	0.0596	0.0954
Spent Shale Bin	0.0393	0.0487	0.0437	0.0375	0.0406	0.0348	0.0411
Pyrolyzer Cyclone	0.0229	0.0138	0.0216	0.0262	0.0194	0.0159	0.0453
Combustor Cyclone	0.0007	0.0006	0.0038	0.0004	0.0011	0.0009	0.0014
Reservoir Bottoms	0.0057	0.0169	0.0075	0.0102	0.0082	0.0080	0.0076
<i>Liquids (Total)</i>	0.2997	0.3103	0.2804	0.3876	0.2975	0.3730	0.3495
Heat Exchanger	0.0202	0.0142	0.0134	0.0285	0.0198	0.0267	0.0263
ESP	0.0672	0.0865	0.0632	0.1223	0.0445	0.1170	0.1086
Still Bottoms	0.0846	0.0785	0.0919	0.0899	0.1047	0.0837	0.1030
Condenser	0.0828	0.0885	0.0815	0.0982	0.0802	0.0861	0.0665
C5+ Vapor	0.0448	0.0427	0.0304	0.0487	0.0483	0.0596	0.0451
<i>Gases (Pyrol/Gasif)</i>	0.0936	0.0756	0.0763	0.1222	0.1138	0.0987	0.1271
CH ₄	0.0194	0.0166	0.0160	0.0242	0.0228	0.0193	0.0230
C ₂ 's	0.0146	0.0137	0.0127	0.0194	0.0191	0.0151	0.0178
C ₃ 's	0.0120	0.0115	0.0104	0.0162	0.0169	0.0126	0.0152
C ₄ 's	0.0030	0.0030	0.0028	0.0049	0.0141	0.0037	0.0046
CO ₂	0.0290	0.0197	0.0211	0.0346	0.0260	0.0306	0.0450
CO	0.0157	0.0111	0.0133	0.0229	0.0149	0.0174	0.0216
<i>Gases (Comb)</i>	0.3802	0.3742	0.3661	0.4537	0.4582	0.3969	0.4349
CO ₂	0.3802	0.3742	0.3661	0.4537	0.4582	0.3969	0.4349
CO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Water (incl. cond. steam)</i>	0.0267	0.0242	0.0238	0.0265	0.0383	0.0398	0.0566
Total	0.8688	0.8644	0.8232	1.0643	0.9771	0.9680	1.0636

Table 5-7 Sulfur Distribution for PDU Runs 1-7 as Mass Fraction of Total Sulfur.

Date	KT940405	KT940414	KT940511	KT940518	KT940607	KT940614	KT940622
Run No.	1	2	3	4	5	6	7
<i>Processed Solids (Total)</i>	0.3942	0.3936	0.3242	0.4139	0.4226	0.4791	0.5735
Spent Shale Bin	0.3074	0.3496	0.2688	0.3401	0.3467	0.4176	0.4336
Pyrolyzer Cyclone	0.0572	0.0323	0.0341	0.0551	0.0488	0.0392	0.1128
Combustor Cyclone	0.0156	0.0118	0.0152	0.0117	0.0138	0.0137	0.0164
Reservoir Bottoms	0.0140	0.0000	0.0061	0.0069	0.0132	0.0086	0.0106
<i>Liquids (Total)</i>	0.0536	0.0526	0.0471	0.0819	0.0571	0.0595	0.0566
Heat Exchanger	0.0063	0.0038	0.0025	0.0074	0.0046	0.0066	0.0046
ESP	0.0130	0.0146	0.0094	0.0211	0.0093	0.0191	0.0191
Still Bottoms	0.0147	0.0151	0.0172	0.0221	0.0211	0.0170	0.0220
Condenser	0.0196	0.0191	0.0180	0.0314	0.0221	0.0168	0.0109
C5+ Vapor	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Gases (Pyrol/Gasif)</i>	0.3257	0.2892	0.2234	0.5080	0.5034	0.3552	0.4279
H2S	0.3257	0.2892	0.2234	0.5080	0.5034	0.3552	0.4279
<i>Gases (Comb)</i>	0.1071	0.1147	0.0408	0.2045	0.1279	0.1261	0.0647
SO2	0.1071	0.1147	0.0408	0.2045	0.1279	0.1261	0.0647
<i>Water (incl. cond. steam)</i>	0.1148	0.0755	0.0762	0.1765	0.1369	0.1252	0.0744
Total	0.9955	0.9257	0.7117	1.3847	1.2478	1.1451	1.1970

Table 5-8 Mass Distribution for PDU Runs 1-7

Date Run Number	Mass of Component, wt%						
	KT940405	KT940414	KT940511	KT940518	KT940607	KT940614	KT940622
	1	2	3	4	5	6	7
<i>Processed Solids (Total)</i>	82.44	82.12	83.57	83.09	82.82	83.03	83.60
Spent Shale Bin	67.51	70.34	69.87	67.33	67.98	70.28	63.40
Pyrolyzer Cyclone	6.23	5.24	5.10	8.48	7.57	4.90	10.94
Combustor Cyclone	7.65	5.74	7.99	6.69	6.43	7.20	8.55
Reservoir Bottoms	1.05	0.81	0.61	0.59	0.85	0.65	0.70
<i>Liquids (Total)</i>	4.47	4.87	4.47	5.81	4.68	5.47	5.01
Heat Exchanger	0.35	0.27	0.23	0.46	0.35	0.51	0.38
ESP	1.22	1.62	1.13	2.00	0.85	1.92	1.75
Still Bottoms	1.17	1.16	1.57	1.46	1.70	1.19	1.48
Condenser	1.14	1.25	1.13	1.28	1.12	1.11	0.85
C5+ Vapor	0.59	0.57	0.40	0.61	0.66	0.74	0.56
<i>Gases (Pyrol/Gasif)</i>	3.13	2.58	2.58	4.02	3.75	3.17	4.11
CH4	0.29	0.26	0.25	0.35	0.36	0.28	0.33
C2's	0.20	0.19	0.18	0.26	0.27	0.20	0.23
C3's	0.16	0.16	0.14	0.21	0.24	0.16	0.19
C4's	0.04	0.04	0.04	0.06	0.20	0.05	0.06
CO2	1.21	0.84	0.89	1.38	1.12	1.21	1.77
CO	0.42	0.30	0.36	0.58	0.41	0.44	0.54
H2S	0.68	0.69	0.64	1.05	1.07	0.75	0.88
H2	0.12	0.10	0.09	0.14	0.08	0.09	0.12
<i>Gases (Comb)</i>	16.33	16.48	15.67	18.86	20.33	16.15	17.33
CO2	15.91	15.97	15.45	18.07	19.82	15.64	17.08
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO2	0.42	0.51	0.22	0.79	0.51	0.50	0.25
NOx	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Total (less water)</i>	106.37	106.05	106.29	111.78	111.59	107.81	110.06
<i>Water (incl. cond. steam)</i>	66.19	56.36	68.37	68.46	74.00	58.60	79.75
<i>Total</i>	172.56	162.41	174.66	180.24	185.59	166.41	189.81

by performing a four-component balance on the system (total flow, carbon dioxide, nitrogen, and oxygen) and this amount was assigned to the combustion zone.

Compared to the carbon distribution that was typical from the operation of the 3-inch diameter, 5-lb/hr bench-scale KENTORT II system, only the amounts of carbon partitioning to char and the combustion flue gases were significantly different (see Figure 5-8). The

Figure 5-8. Comparison of the average carbon distribution from the bench-scale KENTORT II system to the carbon distribution from PDU Run 6.

bench-scale system was limited to a 5:1 recycle ratio between the combustor and gasifier. This limited the amount of heat that could be transferred out of the combustor and caused the combustor to become too hot when air was used for fluidization. To reduce the temperature, N_2 was blended with the fluidizing air which limited the extent of combustion and caused approximately 25% of the carbon to remain unconverted. Otherwise, the amounts of carbon reporting to oil and to the pyrolysis/gasification gases were nearly identical.

The same sort of comparison can be made for the sulfur distributions from the bench-scale unit and the PDU (see Figure 5-9). In the bench-scale unit, over 50% of the sulfur was converted to H_2S , but this was somewhat lower for the PDU runs. The SO_2 yield from the PDU was correspondingly higher which highlights the more efficient operation of the combustor. Substantially more residual sulfur was recovered in the spent shale from the PDU. This was likely due to the recapture of H_2S in the pyrolysis zone by iron oxides contained in the more rapidly recirculating spent shale. Nevertheless, the distribution of sulfur from the operation of the PDU remained favorable in that the two major goals for sulfur management were met. First, the gaseous sulfur emissions were skewed toward H_2S rather than SO_2 production. The stoichiometry is favorable for the direct implementation of the Claus reaction by combining the two gas streams after appropriate scrubbing. Second, all the pyrite appears to have been converted which means that acid leaching from the shale should be reduced.

Figure 5-9. Comparison of the average sulfur distribution from the bench-scale system to Run 6 in the KENTORT II PDU.

Oil yields from the PDU were most affected by the length of the steady-state operating period (see Figure 5-10). The runs of longest duration had the highest percentage of stable and uninterrupted pyrolysis conditions. In addition, the longest runs had enough time to establish a higher level of residual carbon on the recirculating shale. From the bench-scale coking and cracking studies, it was found that the level of carbon on the spent shale had a tremendous impact on the rate of subsequent carbon deposition in a pyrolysis environment. Fully combusted shale with little residual

Figure 5-10. Oil yields from the KENTORT II PDU runs.

carbon had high reactivity toward forming carbonaceous deposits on its surfaces when exposed to oil vapor at pyrolysis temperature. However, the rate of deposition declined as more carbon was deposited. Please recall that the heat-up procedure required extensive recycling of shale through the combustion zone which rendered the shale within the retort devoid of carbon prior to the start of the raw shale feeding period. Therefore, at the start of each run, the spent shale in the retort was highly reactive toward carbon deposition, but as the run progressed, the carbon inventory increased and oil coking decreased due to the recycle of solids.

In comparison to the oil yields obtained from the bench-scale KENTORT II system, there was relatively little reduction in yield for the two longest duration runs. The Fischer assay conversion to oil was taken in Figure 5-10 to be 35.5%, but recent assays on the shale sample have been significantly lower (ca. 30%). It is uncertain whether aging of the sample was the cause or if the original Fischer-assay recipe was not totally reproduced. The Fischer-assay equipment at the CAER had been idle for a significant period of time. Nevertheless, oil yields of at least 109% of Fischer assay have been produced in the PDU and it appears that there are no significant effects of scale. If there is indeed some reduction in oil yield due to the scale-up from 5-lb/hr to 50-lb/hr, it can reasonably be attributed to the corresponding increase in the recycle-solid rate to the pyrolysis zone.

5.2.3 Summary

A successful series of seven steady-state, mass-balanced runs was completed in the 50-lb/hr KENTORT II Process Development Unit. The testing showed that the system operated according to design conditions with the exception that heat losses did not permit operation at gasification temperatures higher than 800°C. However, the runs were successful enough that it was concluded that the concept of the KENTORT II process was verified at this scale. Enhanced oil yield was demonstrated (109 wt% of Fischer assay) which is a high oil yield for a solid-recycle retort of this size. Following is a listing of the highlights from the test series:

- o When the retort did not contain oversized particles (i.e. slag particles from the combustor), it performed flawlessly and was not the cause of any involuntary shutdowns.
- o The system operated autothermally even with thermal losses. Although the two fluidizing gas streams were preheated by external means, this quantity of heat was approximately equivalent to the energy that would be recovered in a commercial system (i.e. sensible heat from the effluent gases and the spent shale).
- o The system worked well with an oil shale that was average in kerogen content for the eastern U.S. oil shale deposits. Richer shales, which would be the first in line for commercial development, would perform even better. Shale with higher kerogen content would contain more residual carbon on an absolute basis and would have more carbon available as fuel to provide greater margins for adjustment in the heat balance.
- o Oil yield was mostly affected for this run series by the length of the steady-state operating period. Once the carbon-free shale had been displaced or partially carbon covered, the yield of oil increased. It does not appear that scale-up in itself had a significant impact on oil yield or the overall slate of products. The solid-recycle ratio to the pyrolysis zone appears to be the most influential parameter with regard to scaleup of this type of process. As the size of the retort increases, so does the required recycle-solid ratio. But even at this small scale, the pyrolysis zone was being heated approximately 80% by hot solids.
- o The gasification zone was influential in minimizing solid-recycle-induced oil losses because it contained shale with a relatively high average carbon content, and those solids were used to transfer much of the heat to the pyrolyzer. The average carbon

content of the shale in the gasifier was relatively high because high-carbon solids from the pyrolyzer were mixed with low-carbon shale from combustor.

5.3 APPLICATION OF TIME-DEPENDENT COKING DEACTIVATION MODEL TO KENTORT II RESULTS

The purpose of this chapter is to summarize the bench-scale KENTORT II process development efforts and to show how a simple, time-dependent coking deactivation model can be used to aid the interpretation of the experimental data. The most important function of this coking model is to predict the effects of solids recirculation on coke formation in the pyrolysis zone. The pyrolysis zone of the KENTORT II process is heated by a combination of fluidizing gas and solids recycled from the gasification zone. A consequence of this combined-phase heating is that the contribution of heating by gas decreases as the size of the retort increases. Therefore, retort scale up involves increases in solid-recycle rates to the pyrolysis zone in addition to the usual effects of scale up.

The coking kinetics section (3.3) stressed the development of a carbon-based coking deactivation model over a time-based model because carbon is the deactivating agent, not time. However, the carbon-based kinetic model is not as easy to implement as the time-based version. As will be shown, the time-based deactivation model is particularly suited for solids recirculation in a fluidized bed system. By adhering to the limitations of the time-dependent coking model, its implementation is much simpler and just as valid as carbon-based versions. A particular advantage of this model is that the mathematical solution is analytical, not numerical. Because it illustrates the important effects of recycling solids to the pyrolysis zone clearly and simply, the time-based coking deactivation model was chosen for application to the KENTORT II results. The time-dependent coking model will be developed following the description of the KENTORT II bench-scale system to facilitate the discussions about scale up and the recycle of solids to the pyrolysis zone.

5.3.1 Bench-Scale Unit (7.6-cm diameter, 2.3-kg/hr)

Apparatus. This system consisted of the three critical zones of the KENTORT II process: pyrolysis, gasification, and combustion. The pyrolysis and gasification zones were aligned vertically and shared steam as the common fluidizing gas. The combustion zone was adjacent to the gasification section and a separate gas stream (air) was used for fluidization (see Figure 5-11). All beds were designed to operate in the bubbling mode at a superficial velocity of approximately 76 cm/s.

Raw shale at a rate of 2.3 kg/hr was fed over-bed to the pyrolysis zone which was the uppermost bed of the reactor. The fluidizing medium was a mixture of steam and product gases from the gasification stage below. Heat was provided to the pyrolysis section by a combination of fluidizing gas and recirculating solids from the gasification zone. The rate of solids which were recycled from the gasifier was controlled by an aerated J-valve. The pyrolysis zone was split in half by a baffle to narrow the particle residence time distribution.

Shale from the pyrolysis zone was transferred to the gasifier section via a gravity-fed downcomer. The gasification zone was also divided in half by a baffle to narrow the

residence time distribution of the solids. The solids from the combustor entered the lower part of the gasifier to heat the incoming solids from the pyrolyzer. The gasification stage, therefore, operated at a temperature between that of the combustion and pyrolysis zones. Preheated steam from an electrically-heated furnace was the fluidizing medium.

A downcomer transferred solids from the gasification zone to an aerated J-valve which controlled the rate of solids transferred to the combustion zone by a pneumatic lift pipe. The gasification and the combustion zones were closely aligned to facilitate the transfer of solids. Air was used for fluidization in the combustor. To minimize mixing of the gas streams, however, the pressure between the two vessels was balanced.

The entire integrated fluidized bed system was enclosed within two double-zone split-tube furnaces. The furnaces were used to raise the temperature of the system to operating conditions and then compensate for heat losses once the system was at steady-state conditions. For example, the temperature of the furnace zone adjacent to the pyrolysis section was maintained at the same temperature as the pyrolysis bed. Therefore, all the heat to the pyrolysis zone was provided by the fluidizing gas and the recycled solids from the gasifier, so no net heat was provided from the furnace.

The treatment of the gases and vapors generated in the gasification and pyrolysis zones was identical to that performed in the cracking chemistry study. Please refer to Section 3.4 for the detailed description of the product collection and measurement procedures.

Results and Discussion. The results from the operation of the integrated KENTORT II bench-scale system have been summarized in the literature.^{1,2,3} The same master batch of oil shale that was used for the bench-scale KENTORT II study was also used in the coking and cracking studies described in section 3.3. The results that will be presented here pertain mainly to the effects of recycling solids to the pyrolysis zone. Due to the external furnaces, it was also possible to operate the reactor without recycling solids and without the combustor.

To gain experience with the system in a simple configuration, it was first operated with only the pyrolysis and gasification zones. In that mode of operation, the pyrolysis zone could be heated by recycling solids from the gasification zone or by increasing the temperature of the external furnace so that no solid recycle was required (gas-heated mode). The heat for the gasifier in this mode was provided by the preheated steam and the external furnace. Several runs were initially performed without solid recycle in order to establish baseline oil and gas yield data. The average carbon conversion to oil for the gas-heated runs was 46.5 wt% of the carbon in the raw shale.

The operation of the system without the combustor on line was also beneficial because the gasification reactions as functions of solid residence time and temperature could be more clearly identified. Steam gasification of carbon was the major reaction under the conditions studied because of the high partial pressure of steam. Little difference in the amount of gasification was identified for mean solid residence times of 20 and 30 minutes. Temperature

was the more influential parameter as gasification rates doubled from 730 to 830°C.

For a given raw shale feedrate, the same quantity of heat could be supplied to the pyrolysis zone by either a high rate of low-temperature solids, a low rate of high-temperature solids, or any combination in between. In order to decouple the relationship between solid-recycle rate and temperature, the heat load to the retort (i.e. raw shale feedrate) had to be a variable also. To study the effects of solid recycle and solid temperature most fully, the test matrix in the combustor-less mode of operation was set up for a range of recycle ratios, gasification temperatures, and raw shale feedrates.

Oil loss for solid-recycle runs was defined as the decrease in carbon conversion to oil compared to the average conversion to oil from the gas-heated runs (46.5 wt%). Increased recycle ratio for solids of similar temperature resulted in increased oil loss (Figure 5-12). This was an expected result because greater proportions of solids in the pyrolysis zone that are active toward coke formation should promote greater oil loss. Another observation was that higher solid temperature also resulted in greater oil loss. This result was not as easily explained because the temperature of the pyrolysis bed was held at 530°C for all of the runs. The hot shale that was injected into the bed was expected to equilibrate to the average bed temperature within a second. If the oil loss reactions were extremely sensitive to temperature then even a small hot region near the solids inlet could result in temperature-related oil loss in the pyrolyzer itself. However, the results of the coking kinetics study of Section 3.3 do not support this explanation because of the insensitivity to temperature for the rapid coking reactions.

For combustor-less runs at a constant raw shale feedrate, the same sort of apparent temperature effect was observed. Recall that the solid-recycle rate and the solid temperature are inversely related for runs at constant shale feedrate. For that series of runs, greater oil loss was observed at lower solid-recycle rate and higher solid-recycle temperature (Figure 5-13).

Results for the runs in which the combustor was integrated with the rest of the system were not significantly different. All of the runs in that test series were conducted at the same raw shale feedrate which means that the solid-recycle rate and temperature were coupled. The oil yield remained relatively constant as a function of gasification temperature for the master batch of Cleveland shale used throughout the study (Figure 5-14). Increased gasification temperature resulted in lower carbon content of the spent shale. Irati oil shale from Brazil was also tested in the bench-scale unit in a subsequent test series, and a slight apparent reduction in oil yield was found at increased gasification temperature. The reduction in the carbon content of the spent shale was more pronounced at higher gasifier temperatures for the Irati shale compared to the Cleveland shale.

For each test series in the bench-scale unit, increased gasification temperature was apparently offsetting any increases in oil yield that would be expected by a decrease in the recycle ratio of the solids to the pyrolyzer. It was this puzzling result that provided the

Figure 5-12 Oil loss as a function of temperature and solid-recycle ratio for combustor-less runs in which the raw shale feedrate was a variable also.

Figure 5-13 Oil loss at a constant raw shale feedrate for the combustor-less runs. The recycle ratio is inversely proportional to the gasification temperature.

motivation for the coking kinetics study (Section 3.3). A large temperature sensitivity toward coke formation would have affirmed the hypothesis that hot regions in the pyrolyzer caused by solid recycle could have been responsible for the oil losses. The coking kinetics study showed that coking was not sensitive to temperature, but the carbon content of the solids was an important factor relating to coking activity. It is now clear that the effect of gasification temperature on oil yield was a result of increased carbon burn off by gasification and/or combustion which created solids with higher coking activity that were recycled to the pyrolysis zone.

Figure 5-14 Oil and char yields for the Irati and Cleveland shales tested in the KENTORT II bench-scale unit with the combustor on line.

5.3.2 Time-Dependent Coking Deactivation Model

A time-dependent coking deactivation model will be presented in this section to show how the effects of coking activity and solid-recycle rate can be quantified in a simple framework. In its simplest form, the time-dependent activity for a solid, a (current rate/initial rate), is represented by

$$\frac{da}{dt} = -k_d a \quad (5-1)$$

which assumes that k_d is independent of concentration. The model assumes that the activity is asymptotic to zero at long times which is apparently at odds with the results of the coking kinetics study (section 3.3), where it was shown that the coking activity always attained a non-zero asymptote. These non-zero rates were concluded to be representative of coking onto carbon-covered sites. In formulating a model that predicts the amount coke formation due to solids recirculation, it is the amount of coking that occurs on uncovered mineral surfaces that is important. Coking that occurs on carbon-covered solids (i.e. pyrolyzed shale or shale undergoing pyrolysis) proceeds whether solids recirculation is used or not. Therefore, the coking activity of carbon-covered surfaces is taken as zero so that the additional coking attributable to solid recycle is represented.

The coking rate data for combusted and gasified shales were adjusted according to the above discussion so that the coking activity was unity at $t=0$ and it was zero at $t=\infty$. The integral of Equation 5-1 was fitted to the data as a function of time.

$$a = \exp(-k_d t) \quad (5-2)$$

Equation 5-2 was found to fit the data reasonably well (Figure 5-15) and the average deactivation constants, k_d , were found to be 0.44 and 0.56 min^{-1} at 540°C and $C_{A0} = 8.33\text{E-}4$ gmol/liter for the combusted and gasified shales, respectively.

In general, the average activity for a bed of solids is represented by the relationship:

$$\bar{a} = \int_0^{\infty} a \cdot E_s dt \quad (5-3)$$

For a mixed bed of solids, which is well approximated by a fluidized bed, the exit age distribution, E_s , is⁴

$$E_s = \frac{1}{\bar{t}} \exp(-t/\bar{t}) \quad \text{where } \bar{t} = W/F_s \quad (5-4)$$

W is the weight of solids in the bed and F_s is the rate of throughput of the solids. Equation 5-2 is representative of the activity of the solids recycled to the pyrolysis zone. The activity of the entire bed of solids, by including a weighting factor to account for pyrolyzing shale which has been assumed to have zero coking activity, is given by

$$a = \frac{R}{(R+1)} \exp(-k_d t) \quad (5-5)$$

where R = (feedrate of recycled solids/feedrate of raw shale). Integration of Equation 5-3 following the substitution of Equations 5-4 and 5-5 yields the time-dependent coking activity model

$$\bar{a} = \frac{R}{(R+1)} \left(\frac{1}{1 + \frac{W}{F_r} \frac{k_d}{(R+1)}} \right) \quad (5-6)$$

where F_r = feedrate of raw shale. The model, Equation 5-6, is valid for a particular apparatus configuration assuming that the oil vapor concentration does not significantly affect the value of k_d . The value of W/F_r is representative of the mean solid residence time of raw shale in the pyrolyzer in the absence of solid recycle. The values of W/F_r were 8.84 and 21.25 minutes for the bench-scale and PDU systems, respectively. The higher non-recycle residence time was necessary for the PDU because higher solid recycle rates had to be used. When operating at normal levels of solid recycle, the mean solid residence time for each of the units was approximately 4 minutes. The plot of Equation 5-6 shows that the lower value of W/F_r for the bench-scale system was reflected by higher average coking activity (Figure 5-16). Consistent with the average values determined for the combusted and gasified shales, lower values of the deactivation constant, k_d , are shown to result in higher levels of coking activity. Coking activity is quite sensitive to small changes in k_d for the solids in this study.

Comparisons of the time-dependent model to the results from the bench-scale unit are not as accurate as they could be, because the precise values of k_d for the solids from those particular runs were not determined. This is a drawback not only of the time-dependent model, but also of the carbon-based model, because the characteristic constant for coking activity of each solid, either k_d or C_{mon} , must be determined by experiment. As was shown for the combusted and gasified shales in the coking kinetics study, a relatively small difference in the available amount of mineral surface area can have a large effect on the rate at which the coking activity declines. As was also shown, the total carbon content of the

Figure 5-15 Fit of the time-dependent deactivation function to the adjusted coking rate data (see text) for a) gasified and b) combusted shale at 540°C and $C_{A0} = 8.33\text{E-}4$ gmol/liter.

Figure 5-16 Calculated average coking activity from the time-dependent coking model as a function of solid recycle ratio and the deactivation constant, k_d (min^{-1}).

shale is related to its coking activity, but the relationship is not straightforward. For example, the gasified shale had a C content of 7.3 wt% and the combusted shale had a C content of 1.6 wt%, but the combusted shale had only twice the capacity for rapid carbon deposition. Therefore, the relationship between total carbon burn off and coking site reactivation should be more fully investigated before more refined coking deactivation models can be developed.

While the uncertainty about the relationships between the deactivation constants and the carbon burn-off reduces the accuracy of the deactivation model, good agreement has been found between the model and the results for the bench-scale unit. Using the value of $k_d = 0.56 \text{ min}^{-1}$ for the gasified shale and assuming a recycle ratio of 1.5 the average coking activity from Figure 5-16 is 0.2. Then, applying the first-order rate constant for the rapid coking period and employing the performance equation for a mixed flow reactor, the predicted conversion to coke was 11.5%. The conversion was low enough that the plug performance equation was similar at 12.2% conversion. These predictions correspond well with the results from the bench-scale unit where oil losses of 11 to 14% were experienced.

In general, the oil losses in the bench-scale unit remained relatively constant with increasing gasification temperature and the accompanying decrease in solid recycle rate. According to Figure 5-16, this can only happen when an increase in the recycle ratio is compensated by a corresponding increase in the value of k_d to keep the activity constant. The differences in carbon burn off at the high and low ends of the gasification temperature range were large enough that such differences in the coking activity constant appear to be possible. For example, the spent shale processed to 760°C in the gasification zone (solid-recycle ratio=2.22) contained 8.0 wt% C and an otherwise similar run at 839°C (solid-recycle ratio=1.48) contained 6.3% carbon. It is possible that this difference in carbon content could be responsible for the 0.2 difference in k_d necessary to maintain constant activity under those conditions.

Application of the deactivation model to the PDU results was not as successful as for the bench-scale unit. Utilizing the mixed flow performance equation with an average coking activity of 0.25, which corresponds to a recycle ratio of 4, predicted that 44% conversion to coke should occur. The best of the PDU runs had oil losses of approximately 20%. The over-estimated conversion is due to the extrapolation of kinetics derived from a small fluidized bed reactor. Fluidized beds with large bubbles display conversion that can be much lower than of a mixed reactor, due to gas bypassing. The pyrolysis bed of the PDU had an L/D ratio of 3:1 which undoubtedly caused substantial bubble growth and occasional slugging behavior. The simple fluidized bed model which is described in the following chapter is not sufficient to characterize that type of behavior, so no further attempts were made to extrapolate the coking kinetics to the PDU. It is interesting to note that in this case the poor vapor-solid contacting behavior of large fluidized beds is actually preferable because it reduces coke formation in the pyrolysis zone. It was not the validity of the coking deactivation model that caused the failure to predict the PDU results, but the deviation from standard kinetic performance models by the fluidized bed pyrolyzer of the PDU.

5.4 REFERENCES

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6. PRODUCT CHARACTERIZATION.

6.1 ANALYSIS OF PRODUCT STREAMS AND PROCESS WATER.

6.1.1. Sampling and sample handling

In the KENTORT reactor, the products generated in the pyrolysis and gasification sections exit the reactor in a single stream. After the liquid components were condensed from this stream, a split of the remaining stream was passed through the sampling loops of a Carle refinery-gas analyzer in order to measure fixed gases and any non-condensed liquid components. This unit automatically cycled at ~30 minute intervals. A minimum of five analyses were conducted and averaged for each run. Combustion gases exited directly from the combustion bed from which selected components (CO , CO_2 , SO_2 , and O_2) were continuously monitored with a series of on-line Beckman industrial gas analyzers.

Unadulterated oil streams were collected from one of three locations (see reactor schematic-Chapter 4). These include #1) the electrostatic precipitator (ESP), #2) a water-cooled condenser, and #3) a pair of filter mist coalescers. In addition to these three neat samples, #4) the weight of oil that passed through the oil collection train and remained in the vapor phase was measured with an on-line gas analyzer as C_5^+ hydrocarbon vapors (C_5^+ fraction); #5) the oil that coated the interior surfaces of the reactor was measured by rinsing the reactor with methylene chloride (CH_2Cl_2) followed by evaporation of the CH_2Cl_2 (rinsings) and correction for residual ash content (fines); and #6) the weight of oil collected in the air-cooled heat exchanger was determined in a similar manner (H-X oil). Solvent extraction rendered the latter two fractions unsuitable for subsequent physical testing. Likewise, additional analyses of the C_5^+ vapor-phase hydrocarbons were not feasible since these materials were measured with a gas chromatograph using a flame ionization detector (FID) and not physically collected.

Two of the three remaining oil streams, i.e., the water-cooled condenser (#2) and the filter coalescers (#3), were combined into one sample termed the *light oil (LO)*. A portion of the third neat-oil stream, the *ESP oil*, was then combined with the light oil at levels proportional to the production of heavy and light oils. More specifically, the LO and ESP oils were combined by first determining the total weight of heavy oil produced, i.e., the weight of heavy oil collected in the air-cooled heat exchanger (H-X oil; fraction #6) plus the weight of oil coating the reactor surfaces (rinsings; fraction #5) plus the oil recovered in the electrostatic precipitator (fraction #1). Total light oil production was then calculated as the weight of light oil collected in the water-cooled heat exchanger and mist coalescers (fractions #2 and #3) plus the weight of the C_5^+ components remaining in the gas phase and determined with the gas analyzer (fraction #4). With the ESP oil representing the total weight of heavy oil and the LO sample representing the total weight of light oil, the ESP and LO samples were combined in proportion to the total production of heavy and light oils. This combined ESP/LO sample was thoroughly blended and is subsequently referred to as the *composite oil (CO)*. This approach yielded five oil samples for subsequent testing as follows:

1) *Light oil (LO)*-a combination of the oil collected in the water-cooled condenser and the filter mist coalescers. Oil from the condenser comprised the bulk of the LO sample. This sample was analyzed without further treatment;

2) *ESP oil (ESP)*-Taken directly from the electrostatic precipitator and analyzed after removing as much water as could be easily decanted;

3) *Heat-exchanger oil (HX)*-The oil recovered from the air-cooled heat exchanger. This oil was recovered by dispersing the mixture of ash, oil, and water collected in the heat exchanger in CH_2Cl_2 , decanting most of the water, evaporating the CH_2Cl_2 and remaining water, and measuring the carbon content of the residue. This was a relatively minor stream;

4) *Reactor rinsings (rinsings)*-The oil obtained by rinsing down the reactor interior with CH_2Cl_2 . Solids were permitted to settle from the rinse solution, the solvent was distilled, and the carbon content of the residue was measured;

5) *Composite oil (CO)*-A combination of Samples 1 (LO) and 2 (ESP) which were combined according to their weight production ratios as described on the preceding page.

Though not all oil streams were collected and combined into the composite oil, this sample was presumed to be representative of the total product. This reasoning is based on the fact that the heavy-oil fractions that are absent from the CO sample (the HX and rinsings oils) are produced in quantities similar to and exhibit properties that are diametric to (offsetting) the omitted light oil fraction (C_5^+ vapors). That is, the omitted streams represent the extremes in properties such as H/C ratio, average molecular weight, density, etc. Thus, the net effect of omitting these extremes from the composite oil is presumed to be reasonably minor.

All process oil samples were blanketed with nitrogen and stored in a freezer at -10°C as soon as practical following a given run. These samples were maintained at -10°C (except during sampling and analysis) for the duration of the study.

Process waters were sampled from the water-cooled heat exchanger in which the bulk of the fluidizing steam was condensed. The process waters were analyzed without treatment for suspended/dissolved solids and pH. A base-treated split (10 g NaOH/L) was analyzed for total sulfur and organic carbon as soon as practical after the run. Likewise, an acid-treated split (10 mL/L concentrated HNO_3) was analyzed for metals content.

6.1.2. Procedures.

A synopsis of the analytical procedures is as follows. Ultimate, heating value, water content, and physical testing of the product oils were conducted according to ASTM procedures. Proximate analyses were obtained by TGA, average molecular weights were determined by vapor phase osmometry, oil density was measured with an oscillating density meter, and oil aromaticity was determined by ^{13}C -NMR. For the process water, anion/cations were measured by ion chromatography and metals were analyzed by ICP.

Retort off-gases were analyzed on an EG & G Chandler Engineering Carle Series 400 AGC equipped with both FID and TC detectors. Splits of the non-condensed gas stream were automatically sampled at ~30 minute intervals during steady state portions of each run. Primary gas standards were used for calibration. Additional details of the analytical procedures follow.

Analysis. (Procedure and/or Comments)

Aromatic Carbon

Determined by ^{13}C -NMR on a Varian XL-200. Composite oil samples were dissolved in CDCl_3 at ~25 wt%. At least 25,000 transients were acquired with phased decoupling and a 1-sec delay between pulses. The aromatic (100-190 ppm) and aliphatic regions (0-60 ppm) were phased corrected and integrated separately. The reported values represent the fraction of aromatic carbon (f_a).

Anions/cations

Anions and cation concentrations were determined on a Dionix model 2020i ion chromatograph for samples of untreated process water. Anions were resolved on a Dionex ASA-4 column and cations separated on a Dionex CS3. The unit was calibrated daily with standards purchased from VHG Labs, Inc.

Average Molecular Weight

Measured by vapor phase osmometry (VPO; Wesken Model 233) at three sample concentrations in pyridine. Benzil was run daily for calibration.

C-H-N

Both solids and oils were analyzed in duplicate on a Leco model 600 using acetanilide as standard. Base-preserved process waters were analyzed for carbon content.

Conradsen Carbon

Determined according to ASTM D189-76.

Density

Oil densities were determined with a Mettler DMA-40 oscillating densitometer. Deionized water was used as the calibration standard.

Dissolved/suspended solids

Duplicate 100 mL aliquots of process water were filtered through 0.45 μm MetricalTM membrane filters and dried to determine suspended solids. Dissolved solids were determined by evaporation of the filtrate.

Fixed Gases

Following condensation of the liquid components, pyrolysis-gasifier offgases were analyzed on a Carle Series Sx-AGC Gas analyzer using Carle App. #397-B, both FID and TC detection, and an approximate 30-min automatic sampling interval. A minimum of five injections were during each run. Reported results represent the average of multiple analyses. Combustion gases (CO , CO_2 , O_2 , and SO_2) were continuously monitored with

on-line Beckman industrial gas analyzers (models 865, 864, 755, and 865, respectively). Primary gas standards were run daily to calibrate all gas analyzers.

Heating Value

The composite-oil samples were analyzed in duplicate according to ASTM-D3286 using a Parr adiabatic calorimeter-model 1242. Benzoic acid was used as the daily calibration standard.

Metals

Reported heavy-metal values were obtained on a Spectra-Span IIIB ICP unit ($\pm 3\%$ rsd). High purity standards from VHG scientific were employed for calibration. Analyses were conducted on acid-treated process waters as well as composite oils that were filtered through 0.45- μ teflon-filters prior to analysis.

Pour Point

Determined according to ASTM D97-66

Proximate

Conducted on a Perkin-Elmer TGS2 thermogravimetric analyzer; details given in Elder, *Fuel*, 62, 580 (1983).

Sulfur

Solids, oils, and base-treated process waters were analyzed in duplicate on a Leco SC132 sulfur analyzer according to ASTM-D4239-84. Leco-supplied standards were used for calibration.

Water content

Product oils were analyzed by Karl-Fischer Titration in triplicate according to ASTM D1744-64 using a Fischer model 392 titrator. The unit was calibrated daily with distilled water.

Viscosity

Composite oils were analyzed at 25 °C with a Brookfield HBT viscometer. This unit was equipped with a ThermocellTM for temperature control.

6.2. CHEMICAL/PHYSICAL ANALYSIS.

Analytical data for the various product streams are shown in Table 6-1 to Table 6-7. It was not the objective of this project to systematically vary reactor conditions between runs. Rather the objective was to demonstrate the feasibility of operating the integrated reactor on a larger scale. Therefore, it is not realistic to express the product properties as a function of reactor conditions i.e. there was too little variation in reactor conditions relative to the analytical scatter. Accordingly, in the discussion to follow, emphasis will be given to the average properties from the five selected runs since it was our intent to demonstrate typical product properties, not how those properties vary with conditions. It should be noted that, in general, the analytical data for a given product stream were relatively constant for all five runs.

6.2.1 Light Oil Analyses.

Table 6-1 shows chemical analyses for the light oils (LO). LO properties and relative production rates were reasonably constant for all runs. Scatter which is present is attributed more to run-to-run differences in ESP trapping efficiency (resulting in differences in oil partitioning between LO and ESP) than to inherent differences in the production of LO. The LO fraction represents a premium oil product as evidenced by the low density (0.897 g/mL) and high H/C ratio (1.56). Sulfur content is relatively high (3.7 wt%) and is believed to be due in part to dissolved H₂S. On the other hand, the average nitrogen content was reasonably low (0.61 wt%).

6.2.2. ESP Oils Analyses.

Analogous analytical data for the ESP oils are shown in Table 6-2. Again, run-to-run variation in the data is reasonably minor. The ESP oil was a semi-solid (high-viscosity liquid) at room temperature. Further, the relatively high ash content suggests this fraction would need to be filtered prior to upgrading though it may be possible to utilize this material with little or no further treatment in certain applications, e.g. as an asphalt cement or modifier following thermal treatment. Sulfur content was significantly lower than in the light oil fraction (2.11 wt%) whereas the nitrogen content of this less volatile fraction was significantly higher (1.38 wt%). It would appear that without additional treatment or filtration, this fraction represents a relatively low-value product due to the high ash and nitrogen content and relatively low H/C ratio.

6.2.3. Air-cooled heat-exchanger oil and reactor rinsings.

Analytical data for the oils collected in the air-cooled heat exchanger along with that of the oil rinsed from the reactor interior are shown in Table 6-3 and Table 6-4, respectively. The reactor rinsings appear to be similar to the ESP oils as indicated by their average H/C ratios (1.23 versus 1.24) as well as similar nitrogen and sulfur contents. On the other hand, the H-X oil appears to be much more aromatic as indicated by the low H/C ratio of 1.13. For both the H-X and rinsings oils, ash content is relatively high as might be anticipated considering the locations within the reactor from which they were obtained. The significant decline in ash content for the reactor rinsings following run 940518 is attributed to an increase in settling time for the CH₂Cl₂-rinse solution prior to decanting and evaporating the solvent.

It should also be noted that the relative amount of oil that collects on the reactor walls becomes less significant with increasing run time. This is due to the equilibrium that is established between vapor-phase and condensed-phase oil within the reactor once the reactor is thoroughly coated with a layer of heavy oil during the course of a run.

6.2.4. Composite oils.

Table 6-5 shows the analytical data for the composite oils that were prepared as described in section 6.1.1. For the five runs shown in Table 6-5, partitioning of carbon to liquid products averaged 33.8% and ranged from 28.0 to 38.8 wt% of the carbon in the feed shale. This may be compared to an average of 39.6 wt% of the feed-shale carbon that partitioned to oil products from tests previously conducted in the smaller 3" KENTORT reactor.¹

Table 6-1. Light oil properties (oil collected in the water-cooled heat exchanger).

LIGHT OILS									
RUN#	Weight	Feed C	Density	C	H	N	S	H/C	water
	(g)	(wt%)	(g/mL)	(wt%)	(wt%)	(wt%)	(wt%)	ratio-dry	(wt%-KF)
940511	1504.5	8.15	0.897	83.2	11.2	0.63	4.3	1.61	0.10
940518	2916.6	9.82	0.891	82.8	10.9	0.48	4.7	1.58	0.13
940607	1783.9	8.02	0.898	84.1	10.8	0.64	3.9	1.53	0.13
940614	2524.7	8.61	0.885	83.5	11.0	0.66	3.0	1.58	0.17
940622	1531.3	6.65	0.915	83.9	10.5	0.63	2.5	1.50	0.22
Average	2052.2	8.25	0.897	83.5	10.9	0.61	3.7	1.56	0.15

Table 6-2. ESP oil properties.

ESP OILS											
RUN#	Weight	Feed C	C	H	N	S	H/C	Water	Vol matter	Fixed C	HT-Ash
	(g)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	ratio-dry	(wt%-KF)	(wt%)	(wt%)	(wt%)
940511	1512.3	6.32	64.8	7.19	1.46	2.22	1.26	3.5	75.1	0.9	20.6
940518	4537.1	12.23	67.0	7.3	1.31	2.05	1.15	7.4	74.3	0.9	17.6
940607	1352.1	4.45	62.6	7.2	1.36	2.19	1.27	5.6	72.3	3.6	18.5
940614	4347.7	11.70	66.6	7.7	1.38	1.98	1.28	5.5	79.7	0.9	13.9
940622	3155.5	10.86	66.9	7.4	1.38	2.11	1.26	3.3	77.2	4.4	15.1
Average		9.11	65.6	7.4	1.38	2.11	1.24	5.1	75.7	2.1	17.1

Table 6-3. Air-cooled heat exchanger oil properties.

AIR											
RUN#	Weight	Feed C	C	H	N	S	H/C	Water	Vol matter	Fixed C	HT-Ash
	(g)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(dry)	(wt%-tga)	(wt%)	(wt%)	(wt%)
940511	311.5	1.34	66.8	7.97	1.36	2.83	1.22	10.7	71.5	5.8	12.0
940518	1051.2	2.85	67.9	7.41	1.46	3.10	1.14	8.9	71.9	4.7	14.5
940607	558.2	1.98	66.4	7.03	0.02	2.63	1.12	7.3	73.7	3.5	15.6
940614	1165.7	2.67	60.5	7.77	1.29	2.56	1.01	24.1	59.4	5.5	11.1
940622	682.2	2.63	74.7	7.63	1.38	2.33	1.16	3.6	82.9	3.3	10.2
Average		2.29	67.3	7.56	1.10	2.69	1.13	10.9	71.9	4.5	12.7

Table 6-4. Properties of the oil recovered from reactor interior.

Run#	Weight (g)	Feed C (wt%)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	H/C (dry)	Water (wt%-tga)	Vol matter (wt%)	Fixed C (wt%)	HT-Ash (wt%)
940511	2091.8	9.19	68.1	7.09	1.42	2.95	1.23	1.8	69.6	10.5	18.1
940518	3319.9	8.99	67.6	7.16	1.59	2.94	1.22	4.2	74.9	3.8	17.1
940607	2698.0	10.47	67.3	7.54	1.25	2.48	1.27	5.5	76.7	8.3	9.6
940614	2704.9	8.37	76.2	8.22	1.31	2.84	1.22	6.2	85.6	2.4	5.8
940622	2671.5	10.30	75.1	7.70	1.39	2.87	1.19	3.7	84.5	2.4	9.4
Average		9.46	70.8	7.54	1.39	2.81	1.23	4.3	78.3	5.5	12.0

As with the previously discussed oil fractions, variation in the analytical values between runs is reasonably minor. On average, the composite oils were comprised of approximately one-third light oil and two-thirds heavy oil, similar to results from the 3" reactor. These blending ratios are congruent with the average H/C and density values of 1.35 and 1.068 g/mL, respectively, both of which are intermediate to analogous values for the light oils and ESP oils from which the composite oils were generated. Analogous values of 1.37 (H/C) and 1.024 g/mL were previously reported for the composite oils recovered from the smaller 3" KENTORT reactor when operated in an integrated gasification/combustion mode.¹ Thus, the composite oils from the larger 6" unit were somewhat depleted in hydrogen and are a bit more dense than those from the 3" unit. The lower H/C ratio and higher density values are in agreement with the higher aromatic carbon fraction of 0.44 measured for the oils from the 6" unit versus 0.41 for the composite oils from the 3" test series.

The average molecular weight of the composite oils in this study was 303 amu compared to 370 amu for comparable oils from the 3" reactor. This perhaps suggests a significant increase in cracking reactions in the 6" unit. A presumed increase in cracking reactions would be consistent with the decrease in the proportion of carbon partitioning to oil products in the 6" reactor. We speculate that these additional product cracking reactions may stem from hot spots within the larger unit, more solids-hydrocarbon vapor contact in the larger reactor bed, and perhaps cracking reactions that continue after the product oils exit the reactor due to significantly greater levels of fines carryover (there was a substantial increase in ash content for composite oils from this test series, 12 wt% versus 1.5 wt% in the prior study). The increase in fines carryover is attributed in part to more severe conditions in the combustor resulting in more particle attrition as well as longer transport distances in the 6" versus 3" unit. The high ash content along with a relatively high metals content for the composite oils indicate a pretreatment step would be required before the total oil stream from the 6" reactor could be used as a refinery feedstock.

The average composite-oil values for pour point and viscosity were -27 °F and 100 cP (@40 °C) which is an improvement over comparable values of -4 °F and 170 cP for oils from the 3" test series. This difference is attributed to the lower average molecular weight and higher

Table 6-5. Composite oil properties.

Composite Oils						
RUN#	940511	940518	940607	940614	940622	Average
Feed C (wt%)	28.04	38.76	29.75	37.30	34.95	33.76
Composite ratios						
Light Oils (wt%)	38.6	30.8	41.2	37.5	30.6	35.7
ESP Oils (wt%)	61.4	69.2	58.8	62.5	69.4	64.3
C (wt%)	70.0	69.8	70.5	71.5	73.5	71.0
H (wt%)	8.1	8.1	8.2	8.5	8.6	8.3
N (wt%)	0.90	0.99	0.87	0.94	0.90	0.92
S (wt%)	3.05	2.99	2.55	2.52	2.51	2.72
H/C (dry)	1.36	1.36	1.33	1.35	1.34	1.35
Water (wt%-KF)	1.70	2.26	3.05	4.23	3.04	2.86
Vol matter (wt%)	85.6	83.4	84.9	85.7	85.8	85.1
Fixed C (wt%)	0.1	0.2	0.0	0.0	0.2	0.1
HT-Ash (wt%)	12.7	14.1	12.0	10.4	11.0	12.0
BTU/lb	15195	14690	15180	15390	15570	15205
Density (g/mL)	1.084	1.096	1.066	1.039	1.054	1.068
Aromatic C (Fract)	0.44	0.46	0.41	0.45	0.44	0.44
Pour Pt (F)	-30	-5	-45	-35	-20	-27
Viscos. (25C-cP)	195	550	95	95	175	222
Viscos. (40C-cP)	100	220	55	50	70	99
Conrad C (wt%)	23.0	27.3	21.2	12.1	20.7	20.9
Ave mol wt (amu)	313	288	305	315	295	303
As (ppm)	40	50	40	50	60	48
V (ppm)	10	20	10	20	20	16
Fe (ppm)	300	300	200	400	500	340
Ni (ppm)	50	50	40	60	80	56

aromatic content of the oils from the 6" reactor. Overall, it should be emphasized that in spite of the differences cited above, the composite oil properties were not radically different than those of the composite oils from the 3" reactor.

Finally, it should also be noted that inherent differences in the feed shale that was used in the 3" versus that used in the 6" test series cannot be ruled out as the reason, or at least part of the reason, for the observed differences in product properties between the two test series.

6.2.5. Gas analysis.

The composition of the gas stream following oil condensation is shown in Table 6-6. The values in this table have been corrected to a N₂- and O₂-free basis. Due to leakage of combustion gases (CO₂ in particular) from the combustor to the gasifier, inaccurately high readings of CO₂ in the pyrolysis-gasification product stream were measured (inaccurate in the sense that a portion of the CO₂ was not generated in the pyrolyzer or gasifier but rather in the

Table 6-6. Off-gas composition (Volume%) shown on a N₂-O₂-free basis (CO₂ levels were not measured but rather calculated from the assumption that CO₂ = 0.5 x H₂).

Run#	940511	940518	940607	940614	940622	Average
Methane	11.81	10.97	14.54	11.69	11.63	12.13
Ethene	1.62	1.48	1.90	1.51	1.47	1.60
Ethane	3.22	2.83	3.87	2.86	2.80	3.12
Propane	1.12	1.07	1.40	1.10	1.23	1.18
Propene	1.47	1.39	1.77	1.43	1.34	1.48
Isobutane	0.04	0.06	0.08	0.07	0.15	0.08
n-Butane	0.48	0.48	0.60	0.49	0.42	0.49
1-Butene	na	0.40	0.53	0.44	0.41	0.36
Isobutene	na	0.22	0.29	0.23	0.21	0.19
T-2-Butene	na	0.18	0.25	0.19	0.19	0.16
C-2-Butene	na	0.13	0.17	0.14	0.13	0.11
1,3-Butadiene	na	0.17	0.20	0.20	0.17	0.15
Isopentane	na	0.09	0.08	0.08	0.07	0.06
n-Pentane	0.15	0.31	0.37	0.32	0.28	0.28
1-Pentene	na	0.23	0.30	0.25	0.22	0.20
C6+ HC's	3.56	3.29	4.46	5.52	3.44	4.06
Total HC gases	23.47	23.30	30.82	26.52	24.15	25.65
Hydrogen	34.65	33.85	26.30	31.82	33.39	32.00
Carbon Monoxide	10.02	10.38	9.62	10.60	10.90	10.31
Carbon Dioxide	17.33	16.93	13.15	15.91	16.70	16.00
Hydrogen Sulfide	14.69	15.44	20.21	14.97	14.64	15.99
Total gas (vol%)	100.16	99.91	100.09	99.83	99.78	99.95

combustor). Because of this leakage, the values for CO₂ shown in Table 6-6 represent values that were calculated from the measured H₂ concentrations using the assumption that the CO₂ generated in the gasifier was equal to 1/2 the hydrogen generated (volume% basis). This assumption was verified by performing a 4-component balance of the combustor and gasifier product streams.

6.2.6. Water analysis

Table 6-7 shows analytical data for the process waters that were condensed in, as well as sampled from, the water-cooled heat exchanger. Process waters were gravity separated from the light oil that also condensed in the heat exchanger. The process waters and light oils were periodically drained from the settling vessel during the given run.

The amount (and perhaps nature) of fines that were carried from the gasification/pyrolysis reactors into the oil-collection train in the current test series was notably greater than for tests conducted in the 3" unit. This is attributed in large part to the higher combustion temperature used in the 6" test series. Higher combustion temperatures result in more complete carbon removal, greater attrition of the combusted particles, and additional mineralogic transformations (generally more extensive conversion to mineral oxides). Importantly, the higher combustion temperatures also result in greater disruption of the crystallinity of the inorganic matrix. This in turn facilitates the removal of inorganics from the reactor, either as vapor phase inorganics or as carryover fines.

One of the more significant differences between the 3" versus the 6" test-series results is in the pH of the process water. The average pH for the 3" integrated-reactor tests was 8.50 (basic) whereas the pH of the process waters from the 6" unit averaged 3.19 (acidic). This is a notable difference which would impact the partitioning of various anions, cations, metals, and polar hydrocarbons between the aqueous, oil, and gas phases. This pH difference is again believed to stem from the more extensive oxidation of minerals in the 6" test series, particularly of sulfides to sulfites and sulfates.

Comparison of the data in Table 6-7 with analogous data from the 3" test series indicates that both dissolved (1.06 vs. 0.37%) and suspended-solids (0.013 vs 0.0025%) content were higher for the runs in the 6" unit. On the other hand, trace metal concentrations for the tests conducted in the 6" unit were either consistently equal to or slightly greater than comparable values for the 3" test series.

Table 6-7. Process waters analyses.

Process waters									
		Susp.	Diss.						
RUN#	pH	Solids	Solids	C	S		Al	As	B
		(wt%)	(wt%)	(wt%)	(wt%)		(ppm)	(ppm)	(ppm)
940511	2.50	0.006	1.150	0.50	0.40		17.0	0.14	2.0
940518	2.06	0.037	1.000	0.42	0.50		12.0	0.13	2.0
940607	2.78	0.008	0.870	0.61	0.37		4.4	0.11	1.9
940614	3.03	0.009	1.780	0.73	0.43		6.8	0.27	2.5
940622	5.57	0.003	0.490	0.76	0.18		2.5	0.20	1.3
Average	3.19	0.013	1.058	0.60	0.37		8.5	0.17	1.9

RUN#	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
940511	0	41	0.009	0.01	0.64	0.06	30	6.5	2.5	0.46
940518	0	24	0.008	0	0.12	0.04	15	3.5	1.7	0.16
940607	0	67	0.005	0	0.40	0.01	19	2.7	1.2	0.22
940614	0	74	0.005	0	0.16	0.02	37	4.5	1.3	0.19
940622	0	98	0.006	0	0.04	0.01	9	3.0	1.8	0.14
Average		61	0.007	0.0	0.27	0.03	22	4.0	1.7	0.23

RUN#	Mo	Na	Ni	P	Pb	Se	Si	Ti	V	Zn
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
940511	0	2.5	0.42	1.85	0	0.12	6.2	0.05	0.19	0.26
940518	0.02	1.5	0.11	1.40	0	0.12	6.2	0.05	0.19	0.26
940607	0	1.7	0.23	0.75	0	0.09	2.3	0.01	0.05	0.09
940614	0.01	3.0	0.19	0.99	0	0.11	2.3	0.02	0.05	0.13
940622	0	1.5	0.07	0.50	0	0.17	2.5	0.01	0.05	0.05
Average	0.01	2.0	0.20	1.10	0	0.12	3.9	0.03	0.11	0.16

6.3. EVALUATION OF THE ASPHALT POTENTIAL OF EASTERN US SHALE OIL.

6.3.1. Introduction.

In the present era of plentiful and reasonably priced petroleum, commercial production of motor fuels from oil shale is viewed as a high risk venture at best. In other words, the prospects for near-term commercial development of Eastern oil shales strictly as a source of motor fuels is not promising. However, if a portion of the oil product, particularly a portion which is of little value as a refinery feedstock can be diverted to other uses with a higher market price, then the overall process economics may be substantially improved. The production of asphalt cement from shale oil has been advocated as just such an alternate use.^{2,3} The results of a scoping study directed at evaluating potential road-pavement applications for the oils derived from Eastern U.S. oil shales are presented in the following sections.

Coincidental to the advances in oil shale technology of the past decade has been a continuing decline in both the quality and availability of road asphalts. The decline in availability has led to the recycling of road asphalts (milling and reapplication) in many areas of the country. The decline in quality, attributed in part to advanced processing (e.g., fluid-cat crackers) which are used to recover more heating- or motor-fuel per barrel, has resulted in the marketing of asphalts which, on average, do not have the desirable properties or longevity as typical asphalts from 3-4 decades past. This general decline in quality accompanied by an increase in market price has created a potential niche market for shale oils, particularly since these materials often exhibit physical/chemical properties that suggest they may be a viable alternative to petroleum derived asphalts. Accordingly, a test program was implemented to evaluate KENTORT oils in three different paving applications; i.e., as an asphalt cement, an asphalt modifier, and an asphalt-recycling agent. A series of binder and mixture characterization procedures were included in order to better evaluate both short- and long-term performance potential of asphalts produced from or modified with Eastern shale oils (ESO).

The evaluation of the asphalt potential of Eastern shale oils is divided into two parts. In the first part, shale oils generated in a previous study using a 3" KENTORT prototype reactor were evaluated¹. Selected results from that study have been published in *Proceedings: 1991 Eastern Oil Shale Symposium*⁴, *Preprints of the American Chemical Society (Fuel Division)*⁵, and the journal *Fuel*.⁶ In addition to the authors of this report, other individuals that contributed to the initial study include K. Mahboub with the Kentucky Transportation Center; P. K. Oduroh and A. L. Simpson with the University of Kentucky Department of Civil Engineering; and R.E. Robertson and P.M. Harnsberger with the Western Research Institute, Laramie, Wyoming.

The results from the first part of this evaluation were promising with the exception that unmodified ESO showed an unacceptable rate of 'aging' or hardening which would ultimately lead to premature pavement failure if used directly as an asphalt cement. However, the potential for use as an asphalt modifier and particularly, as an asphalt-recycling agent were more encouraging. Accordingly, emphasis will be given to these latter applications in the first part of this report.

Due to the severity of the aging problem, a second investigation of a thermally-treated shale oil was undertaken using oils generated in the 6" reactor. Though this investigation is incomplete, preliminary results indicate that the aging problem has been resolved. Available results from this latter investigation are presented later in this chapter.

6.3.2 Evaluation of shale oils produced in the 3" reactor.

6.3.2.1. *Study samples.* Two samples of Eastern shale oil, generated in a 5 lb/hr KENTORT prototype unit, were selected for study. The first, referred to as the *hard* ESO, was a highly viscous material (3440 ps @60 °C) recovered in an electro-static precipitator and was examined without further treatment except for a mild distillation to remove excess water. The second, referenced as the *soft* ESO (8 ps @60 °C), was derived from a composite of the total oil product that was subjected to a vacuum distillation (160 torr and 200 °C pot temperature) prior to testing. Flash point measurements were obtained by Tag open cup according to ASTM D3143-83. Viscosity measurements were made with a Brookfield model HBT viscometer equipped with a Thermocell™ for temperature control.

These two oils were selected for study since it is believed that they represent the types of material that would be readily available and are the most likely to be utilized for asphalt production in a commercial operation. Both samples were derived from the Cleveland Member of the Ohio shale acquired from a freshly exposed outcrop in Rowan County, Ky. A detailed description of the oil shale sample and retort operation has been previously published.^{1,7}

6.3.2.2. *Binder Characterization.* The purpose of this portion of the study was to determine the physical properties of asphalt mixtures that contained ESO produced by a KENTORT II prototype. If Eastern shale oil is to be useful as an asphalt modifier, then the blend of asphalt and ESO must exhibit aging characteristics and rheological properties that are superior to the unmodified asphalt. Likewise, if ESO is to find application as an asphalt recycling agent, it must exhibit properties that are equivalent to or better than conventional agents. In an effort to determine if ESO could meet these criteria, the research was divided into two parts. The first part focused on evaluation of the hard ESO as an asphalt additive and the second on evaluation of the soft ESO as a softening agent for aged asphalt or aged-asphalt mix (pavement recycling). Both mixture characterization and binder characterization was performed for both phases. Researchers at the Western Research Institute (WRI) were responsible for binder characterization (asphalt and asphalt-ESO blends) whereas the binder-aggregate mixtures were evaluated at the Kentucky Transportation Center and the University of Kentucky Department of Civil Engineering.

Evaluation as an asphalt additive involved determining the rheological properties of an AC-20 asphalt (supplied by Ashland Oil, inc.), a 7 wt. % blend of hard ESO and AC-20 asphalt, and a neat sample of the hard ESO. The rheological properties of the three samples were also determined after they were subjected to an accelerated-aging procedure. Evaluation of ESO as an asphalt-recycling agent entailed measuring the viscosity of an asphalt extracted from a laboratory-aged pavement mixture, the soft ESO, and an AC-5 asphalt (representative of a commercial recycling agent). Elemental analysis of the four binders examined in this portion of the study are shown in Table 6-8.

Table 6-8 Elemental analysis data (wt%).

Binder	C	H	N	S	H/C
Hard ESO	83.6	8.2	0.6	2.2	1.2
Soft ESO	84.7	8.6	0.6	2.0	1.2
AC-20	85.2	10.0	0.4	4.3	1.2
AC-5	85.7	10.3	0.4	3.7	1.4

Two "recycle" blends, with a target viscosity of 10,000 poise at 60°C, were prepared by blending the laboratory-aged asphalt with 1) the soft ESO and 2) the AC-5 asphalt. Rheological properties of the two blends were then examined. The 10,000 poise target represents the maximum allowable

viscosity of an AC-20 asphalt after a thin-film oven test (ASTM D-3381) which is assumed to represent the viscosity of the asphalt in a freshly-produced mixture as it leaves the hot-mix plant.

Rheological Characterization. The materials used in the asphalt-modification study for stiffening purposes were the AC-20 asphalt and the hard-ESO sample. The materials examined in the recycling/rejuvenating study were an asphalt extracted from a laboratory-aged pavement mixture, the soft-ESO sample, and the AC-5. Researchers at the Texas Transportation Institute (TTI; Texas A&M University) extracted the asphalt binder from a laboratory-aged asphalt pavement mixture in accordance with newly developed protocols designed for minimizing procedure-related asphalt aging (developed as part of the Strategic Highway Research Program; SHRP). Prior to shipping binder samples to WRI, the viscosity of the soft-ESO sample was measured at 8 poise and the hard-ESO sample was measured at 3440 poise, both at 60 °C.

All sample blends were prepared by weighing 10 g of each material into glass vials and purging each vial with Ar. The vials were then placed into an aluminum heating block and heated in an oven at 150 °C for a total of three hours. Each hour, the vials were removed and mixed in a paint shaker for 5 minutes then returned to the heating oven.

Thin-film oven tests (TFO) were conducted according to ASTM D-1754 with the exception that sample size was reduced to 7.89 g and the pan size was reduced to 5.6 cm. This provides the same mass to surface area that is specified in the standard method.

Pressure-oxidation vessel (POV) aging experiments were conducted on cooled TFO samples. The vessels were pressurized to 300 psi with air and maintained at that pressure for the duration of the test. Sample temperature was maintained at 80 °C with a forced-draught oven. After six days, the POV's were removed from the oven, vented, opened, and stored in TFO-test pans.

Dynamic viscosity measurements were made on a Rheometrics RMS-605 mechanical spectrometer using a shear frequency range of 0.1 to 100 rad/sec at 25, 45, and 60°C. This permitted the two components of shear modulus, G' and G'' , to be determined. The storage modulus or the elastic component (G') quantifies the elastic-rebound capability of the material. The loss modulus or viscous component, G'' , is a measure of damping capacity. Higher G' values indicate good resistance to permanent deformation (rutting) but greater susceptibility to cracking failure. Higher G'' values indicate the reverse behavior. Since there is always a trade-

off between rutting performance and cracking performance, the term Tan Delta (ratio of G''/G') is used as a measure of the balance between damping and elastic properties. For a fresh asphalt, a Tan δ value higher than 3 indicates better than average resistance to cracking but less than average resistance to rutting.⁷ Values less than 3 indicate the opposite. It is important to note that these Tan δ ranges are not mechanistic criteria for pavement performance, but simply performance trend indices. To better quantify the propensity to changes in rheological properties with age, aging index values were calculated by dividing the aged viscosity by the unaged viscosity.

Asphalt binder modified with the hard ESO sample. The fresh AC-20 asphalt and the hard ESO were blended at a ratio of 13.25:1 (7 wt%). This ratio was selected since it represents the current state of practice with regard to polymer modified asphalts, as well as a set of polymer-modified-asphalt field projects in Kentucky with which future performance correlations are expected to be developed. The rheological properties at 25, 45, and 60 °C of the original materials and the blend were determined before and after aging and are shown in Table 6-9. The viscosity-temperature relationships for these three materials before aging are shown in Figure 6-1.

Prior to shipping the hard-ESO sample to WRI for testing, the viscosity was measured at 3440 p (60 °C) whereas a few weeks later at WRI, the viscosity for this same sample was measured at 19,390 p. Visual observations confirmed the increase in viscosity with time. After a few months of storage, the hard-ESO sample developed a thin layer of very brittle *skin* on its surface. This was not observed in the soft ESO or AC samples which were stored in a similar manner.

The cause for such a substantial increase in viscosity with time is unknown. However, it is believed that this material was still quite reactive following collection and distillation. Olefins, which are formed in high abundance during pyrolysis, are suspected as being, at least in part, responsible for this unusually high reactivity.

The original samples of hard ESO, the AC-20 asphalt, and the ESO/asphalt blend were subjected to the TFO test (ASTM D1754) followed by pressure oxidation for 144 h at 80°C and 300 psi air. These laboratory-aged samples were again subjected to rheological analysis at 25, 45, and 60°C. The results of these tests are shown in Table 6-9. The asphalt/ESO-blend aged more than either of the original materials as measured by an aging index (viscosity ratio) at all three temperatures. These viscosity-temperature plots are shown in Figure 6-2.

Figure 6-1. Viscosity-temperature relationship of unaged binders.

The high aging index of the asphalt/ESO-blend suggests that the hard-ESO sample remains highly reactive and continues to change over long periods of time. The large difference between the aging index of the AC-20 and that of the blend indicates that the hard ESO is not a favorable material for blending with petroleum asphalts.

It is interesting to note the substantial change in the $\tan \delta$ of the hard-ESO material over the temperature range shown in Table 6-9. In fact, at 25°C, the viscous or loss component (G'') was not measurable under dynamic loading, hence no $\tan \delta$ was reported. This is a clear indication of the highly temperature-susceptible nature of the hard ESO, a property that is not desirable in pavement materials. Therefore, the apparent improvement in rutting resistance for the blended sample over the AC-20 asphalt ($\tan \delta$ of 2.582 vs. 3.143 for the AC-20) will be short lived because of high-aging susceptibility. This is supported by analyses of the mixtures presented in the next section.

Figure 6-2. Viscosity-Temperature relationship for TFO-POV aged binders (144h, 80°C).

Aged-Asphalt-Binder Rejuvenation. The 60°C viscosities of the laboratory-aged and extracted asphalt, the soft ESO, and the AC-5 asphalt as described above were determined to be 5.98×10^6 , 15, and 515 poise, respectively. Three trial blends each of the laboratory-aged asphalt/soft ESO (Figure 6-3) and the aged asphalt/AC-5 (Figure 6-4) were prepared in an effort to produce samples whose viscosity would bracket the 10,000 poise target value. As previously stated, 10,000 poise represents the maximum viscosity specified for an AC-20 asphalt after the TFO test (ASTM D-3381). The viscosities for the various trial blends are shown in Table 6-10.

The straight line in each plot represents ASTM D-4887, which is a simplified approach for determining the concentration of the recycling agent, i.e., it assumes a linear viscosity-concentration relationship. Clearly, the trial blends in this study demonstrate that the relationship between concentration and viscosity is not linear.

Unfortunately, the trial blends did not bracket the target viscosity for either blend series. Nonetheless, from the trial blends data, the mixing ratios required to produce 10,000 poise blends were estimated to be 66% aged asphalt/34% soft ESO and 42% aged asphalt/58% AC-5 asphalt. The measured viscosity of the test blends prepared at these ratios are represented by the unfilled square symbols in Figure 6-3 and Figure 6-4, respectively. Note that the amount of soft ESO needed to achieve the target viscosity is considerably less than for the AC-5.

Nearly identical viscosity-temperature relationships are shown for the test blends in

Table 6-9 Rheological properties of unaged and aged AC-20 asphalt, hard ESO, and blends of hard ESO/AC-20 asphalt.

Binder	Temperature (°C)	Dynamic viscosity (poise)		Aged binder $\tan \delta^a$	Ageing index ^b
		Unaged	Aged		
AC-20 (not annealed)	60	3349	—	—	—
AC-20 (annealed)	60	2386	6.21×10^4	3.143	26.0
AC-20/7% hard ESO (annealed AC-20)	60	2389	2.93×10^5	2.582	122.6
Hard ESO	60	19 390	1.75×10^6	7.251	90.3
AC-20 (annealed)	45	3.98×10^4	9.54×10^5	2.287	24.0
AC-20/7% hard ESO (annealed AC-20)	45	2.52×10^4	4.44×10^6	2.085	176.2
Hard ESO	45	5.59×10^5	6.60×10^7	1.301	118.1
AC-20 (annealed)	25	2.31×10^6	4.18×10^7	1.116	18.1
AC-20/7% hard ESO (annealed AC-20)	25	1.97×10^6	1.54×10^8	0.956	78.2
Hard ESO	25	4.81×10^7	2.41×10^9	—	50.1

^a $\tan \delta$ = viscous modulus (G'')/elastic modulus (G')

^b Ageing index = aged viscosity/unaged viscosity

Figure 6-5. Likewise, $\tan \delta$ values were similar at all three temperatures with the AC-5/aged asphalt blend being slightly lower at 60°C and slightly higher at 25 and 45°C (Table 6-11). These results are favorable, indicating good asphalt rejuvenation potential for the soft ESO both in terms of adequate dispersal of the aged asphalt and the ability to provide an equivalent viscosity as the AC-5 with less sample. This ability to achieve the target viscosity with less sample stems not only from a lower viscosity for the soft ESO but to better softening characteristics compared to the AC-5 as well.

6.3.2.3. Mixture Characterization. The term mixture refers to a combination of asphalt and road aggregate. The mixture characterization program was designed so that the potential pavement performance of ESO-modified asphalts could be related to that of an asphalt modified with a more conventional material

Figure 6-3. Blending plot for extracted asphalt and soft ESO.

with known field performance. This was accomplished by on-site sampling of ~40 Kg of hot mix (containing no modifier) during construction of an asphalt overlay research project during September 1990 (Pulaski County, Ky.). For this project, several test strips were constructed from a single asphalt blended with different commercial modifier agents. The test strips were placed on a long term monitoring schedule and samples of each asphalt/modifier blend were returned to the laboratory for testing. So, by blending the ESO with the same hot mix and subjecting this asphalt/ESO blend to the same lab tests as the field samples, a more realistic assessment of pavement performance could be obtained.

The field-sampled hot mix was divided into two portions. The first portion was mixed with the hard ESO at the same proportions as the polymer modified mixtures. This was to compare the behavior of the hard-ESO-modified asphalt to the asphalts modified with commercial agents. The second portion was aged in a forced-draft oven at 80°C for two weeks prior to mixing with the soft ESO. This was in order to test the soft ESO as a pavement recycling agent. An additional 4 Kg of the aged mixture was set aside for extraction and binder characterization.

Mixture characterization included a series of mechanical response tests on compacted specimens (Marshall procedure; ASTM 1559) directed at evaluating the performance potential of the hard-ESO-modified asphalt mixture relative to the conventional polymer-modified asphalts (brands "A" through "D"). All statistical comparisons were conducted at a 95% level of confidence.

Tensile Strengths. Fatigue and durability of asphalt pavements are believed

Figure 6-4. Blending plot for extracted asphalt and AC-5 asphalt.

Figure 6-5. Viscosity-temperature relationship of extracted asphalt blends.

Table 6-10. Viscosity at 60°C for trial blends of extracted asphalt with soft ESO and AC-5 asphalt.

Binder	Dynamic visc. at 60°C (P)
Extracted asphalt	5.98x10 ⁶
60/40 wt% xtracted asph/soft ESO	3967
50/50 wt% xtracted asph/soft ESO	831
40/60 wt% xtracted asph/soft ESO	250
Soft ESO	15
40/60 wt% xtracted asph/soft ESO	7926
35/65 wt% xtracted asph/soft ESO	5415
30/70 wt% xtracted asph/soft ESO	3323
AC-5	515

to be related to tensile strength. It is customary to characterize tensile strength of pavement materials indirectly in accordance with ASTM-4123. The bars plotted in Figure 6-6 show that the hard-ESO blend has tensile-strength properties that are superior to the control mixture (unmodified, aged hot-mix) and are on par with two of the high-tensile-strength, polymer-modified asphalts. Taken alone, these results indicate desirable fatigue and durability performance potential for the hard-ESO blend. However, as the preceding

Table 6-11. Rheological Properties of Aged Asphalt Blended With Soft ESO and AC-5 Asphalt.

Binder	Dynamic Viscosity, 60°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	1.244 x 10 ⁴	6.112
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.376 x 10 ⁴	5.973
Binder	Dynamic Viscosity, 45°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	1.576 x 10 ⁵	2.513
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.627 x 10 ⁵	2.721
Binder	Dynamic Viscosity, 25°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	5.077 x 10 ⁶	1.582
42 wt.% Recovered Asphalt/58 wt.% AC-5	6.187 x 10 ⁶	1.738

Figure 6-6. Mixture tensile strengths.

sections suggest, the aging characteristics of a hard-ESO blend that has not been subjected to some sort of pre-aging treatment may lead to early pavement failure.

Moisture Damage Characterization. Asphalt-binder stripping from aggregate is a moisture-induced effect. The potential for this type of damage is often characterized in the laboratory in accordance with the Root-Tunnicliff test⁸ (Kentucky Department of Highways Test Method 64-428-85). This method produces a moisture-damage index (tensile-strength ratio) based upon the tensile strength of the mixture before and after a moisture-

Figure 6-7. Tensile strengths for modified pavement mixtures. *H₂O exposed*-after moisture susceptibility tests; *freeze-thaw*-after 100 freeze-thaw cycles. *Control*-unmodified pavement mixture.

conditioning procedure. Though not expressed in ratio form (tensile strengths before and after exposure are shown), the results of this test are represented by the sets of bars labelled fresh and H₂O exposed shown in Figure 6-7. The mean tensile-strength data (Figure 6-7), along with statistical analyses of repeat tests, indicate that the hard-ESO moisture-damage susceptibility compares favorably with the control mixture and was not significantly different from two of the polymer-modified mixtures (C and D). Nonetheless, the data also indicate that the hard-ESO-modified asphalt is somewhat susceptible to binder stripping.

Freeze-Thaw Damage. The potential susceptibility to freeze-thaw damage was characterized, again using tensile strength as an index parameter. Mixtures were subjected to 100 cycles of freeze and thaw (3 hours at -18°C, followed by 3 hours at +4°C). This procedure is similar to that used for Portland cement. It was employed in this study due to the lack of a standardized freeze-thaw procedure for asphaltic materials. Cross comparisons (Figure 6-7), along with statistical analyses of the values from repeat tests, revealed no statistically significant change in tensile strength after 100 cycles of freeze-thaw. Evidently, more freeze-thaw cycles would be necessary in order to induce significant mixture damage. The tensile-strength test results obtained for the fresh, moisture exposed, and freeze-thaw-tested pavement mixtures are shown in Table 6-12.

Rejuvenated Mixture Characterization. Asphalt aging/oxidation severely reduces the tensile-strength properties of an asphalt-aggregate mixture, which manifests itself as widespread ravelling and cracking in the pavement. Addition of soft ESO to the aged mixture resulted in a notable increase in tensile strength, comparable to that obtained by adding AC-5 asphalt (see Figure 6-8). However, addition of either soft ESO or AC-5 asphalt did not restore the tensile strength to the level prior to aging. This increase in tensile strength is typical and has led to a common practice of adding fresh hot-mix to the recycled mixture along with the rejuvenating agent. The mixture-rejuvenation analysis shows the soft ESO to have potential asphalt-recycling applications and merits further examination. This is an important point as asphalt recycling is experiencing steady growth and represents the market segment which provides the greatest potential for a return on investment which is sufficiently large to favorably impact oil-shale processing economics.

6.3.2.3. Summary of results for phase I. Two samples of eastern shale oil (ESO), a hard ESO and a soft ESO (referring to their viscosity), produced in a 3" Kentort II prototype reactor were evaluated for their potential use with paving asphalts. The hard-ESO material was evaluated as an asphalt additive or modifier and the soft ESO was evaluated as an asphalt-recycling agent to soften a laboratory-aged asphalt extracted from an asphalt-aggregate mix.

The hard ESO, added at 7 wt% to an AC-20 asphalt, showed unfavorable aging characteristics when the blend was subjected to a thin-film-oven test followed by pressure-oxidation (144 h; 80°C). The hard-ESO/AC-20 blend exhibited an aging index that ranged from 4.3-7.3 times greater than neat AC-20. These same blends were also found to be susceptible to moisture damage (moisture induced stripping of the binder from the aggregate). Although an improvement in tensile properties of the aged-asphalt mixture was achieved through addition of the hard ESO, this improvement, as well as any short-term improvement in Tan δ values, are likely to diminish rapidly with time as the samples continue to age.

Table 6-12. Tensile strength comparisons of unmodified (control), hard ESO-modified, and polymer-modified pavement mixtures. Results are for repeat tests on fresh, water exposed, and freeze-thaw tested samples.

Mixture	Untreated samples (psi)	Moisture Damage Index (%)	After 100 Freeze-Thaw Cycles (psi)
Control	236.0	61.4	201.4
	220.1	71.0	163.0
	186.9	85.7	250.5
	235.4	84.8	235.0
	257.3	80.6	265.4
			201.1
Mean->	227.1	76.7	219.4
Control + hard ESO	263.9	63.0	281.5
	257.9	82.6	320.9
	299.3	90.2	
	Mean->	273.7	78.6
Control + brand A	292.2	113.8	299.8
	258.1	94.5	334.4
	253.9	92.4	244.0
	263.1	70.7	323.7
			236.3
			267.8
Mean->	266.8	92.8	284.3
Control + brand B	287.0	89.3	240.2
	263.0	92.0	297.1
	260.0	106.3	262.5
	258.5	89.6	297.9
	266.9		295.8
			285.2
Mean->	267.1	94.3	279.8
Control + brand C	231.2	90.1	240.6
	217.8	98.3	201.2
	195.6	79.9	229.3
	173.0	92.2	222.1
	181.1	89.1	229.8
			229.6
Mean->	199.7	89.9	225.4
Control + brand D	196.1	88.9	210.2
	231.0	80.9	224.8
	235.9	89.7	234.2
	159.8	79.2	240.8
	199.1	86.9	230.4
			198.8
Mean->	204.4	85.1	223.2

Both soft ESO and AC-5 asphalt were used to soften a hardened asphalt extracted from a laboratory-aged pavement mixture. The rheological properties of the aged asphalt/soft-ESO blend were essentially the same as those of the aged asphalt/AC-5 blend as verified by analysis of the rejuvenated mixtures. The amount of ESO required to soften the aged asphalt was less than the amount of AC-5 due mostly to the lower viscosity of the soft ESO. However, the large negative deviation of the ESO blending curve suggests that even at equivalent viscosities, the soft ESO would exhibit more softening per unit weight than the AC-5 asphalt which is often used in such applications. Overall, the soft ESO appears to have potential application as an asphalt rejuvenating agent. Thus, this application has the potential to favorably impact plant economics assuming that the shale-oil aging problem can be satisfactorily resolved.

Figure 6-8. Rejuvenated asphalt tensile strengths.

One of the more important results from this phase of the asphalt evaluation was the demonstration that the ESO samples, particularly the hard ESO, were unstable or reactive for some time following preparation. For reasons discussed throughout this section, measurement and control of this phenomenon is an important step that must be addressed prior to further testing since a chemically and thermally stable material is necessary for paving applications. It is also suggested that further mixture studies are needed to fully characterize both short-term and long-term performance potential of ESO-modified/rejuvenated asphalts. Assuming the aging problem can be resolved, field trial projects are recommended for verification of laboratory test results.

6.3.3. Evaluation of the shale oils produced in the 6" reactor.

6.3.3.1. Introduction. Following the first phase of evaluation of the ESO samples for potential asphalt applications, it was clear that in spite of generally favorable properties of the ESO samples, the severe aging problem that was encountered would preclude further progress in this area. The highly-reactive nature of oils that are generated by pyrolysis is responsible for the continued hardening of the samples with time. In particular, it is believed that the relatively high olefin content of these materials is primarily responsible for the observed hardening (although oxidation of heteroatom containing species may contribute as well). Therefore, one of the primary objectives of the second phase of the evaluation was the elimination of this obstacle.

Several approaches were considered to suppress the ESO reactivity. These included 1) accelerated aging of the sample by a mild thermal treatment in an inert atmosphere; 2) aqueous extraction of the acidic and basic oil components; 3) *vulcanizing* or cross-linking the sample by heating with elemental sulfur to eliminate the reactive olefins; or 4) mild hydrogenation, also directed at olefin removal. Option #2 was rejected for both economic reasons as well as the fact that removal of the polar species would also likely eliminate many desirable asphalt properties. Option #3 was rejected due to commercial cost concerns. Thus by elimination, the final options were either mild-thermal treatment or mild hydrogenation. Of these, the mild thermal treatment appeared to be the more attractive both in terms of cost and simplicity. It was anticipated that such treatment would tend to accelerate the aging process by increasing the rate of reaction of the reactive species due to the elevated temperatures. Furthermore, it is believed such treatment should more selectively deplete those oil components most responsible for the aging problem than would a mild hydrogenation. That is, a mild thermal treatment should be more directly focused on removal of those components that lead to asphalt failure attributable to hardening by increasing the rate of their reaction.

6.3.3.2. Sample preparation. The sample selected for study was generated in the 6" KENTORT prototype during run #940518. The run was of 10 h duration and all systems behaved in an acceptable manner for the duration of the run. A 4.3-kg composite oil was prepared by blending aliquots of Light and ESP oils as described on page 2 of this chapter (section on composite oil preparation). The composite ratios used were the same as those shown in Table 6-5; 30.8 wt% Light oil and 69.2 wt% ESP oil.

After thoroughly blending the Light and ESP oils, the sample was placed into a 5-gal boiling flask that was connected to a reflux column and condensor. A 3' type K-thermocouple was routed into the distillation flask. The flask was blanketed with nitrogen, sealed except for the condensor outlet and heat was applied for a total of 8 days. Temperatures ranged from approximately 100-160°C from the top to the bottom of the liquid. Approximately 10 wt% of the sample was distilled from the flask during this interval. Unfortunately, the precise loss could not be determined due to failure to weigh the amount of sample that was periodically removed for viscosity measurements. The remaining sample was then transferred to a 5-L flask and placed onto a rotoevaporator. The sample was then placed under full house vacuum with the flask spinning in a water bath for six additional days. Over this interval, the bath temperature was gradually increased from 40 to 90°C. An additional weight loss of 181.7 g (~7 wt%) was measured during this interval. Finally, the sample was placed into a vacuum still and heated an additional three hours just below the temperature at which a vapor mist could be observed to form (vapors from cracking reactions). The vacuum-still pot temperature was not monitored but was estimated at 200°C based on the voltage applied. An additional 8.7-g (~0.4 wt%) loss was measured in this step. Obviously, no attempt was made to optimize the thermal treatment step in terms of temperature or time. Rather, the objective was simply to determine if a mild thermal treatment could produce a significant improvement in oil stability relative to the sample examined in the first phase of the evaluation.

6.3.3.3. Results. Since sample aging can best be followed by monitoring increases in viscosity, this parameter was selected as a means of determining if the thermal treatment successfully eliminated the aging problem. In the first phase of this evaluation described in preceding

sections, the viscosity of the hard-ESO sample was measured at the UK-CAER at 3,440 P. This sample was shipped to WRI for additional testing where a few weeks later the viscosity was found to be in excess of 19,000 p. In a similar manner, the sample described above, which was measured at 1,000 cp @60C at the UK-CAER, was also shipped to WRI for additional testing. Approximately 3-4 weeks later, the viscosity of this material was measured by WRI staff at 1,290 cp @60°C. This value is reasonably similar to that measured at the CAER considering that different viscometers were used and the 1,000-cp value measured at the CAER was near the lower viscosity range of the viscometer being used. After storage of the sample at room temperature for four additional weeks at WRI, a second measurement of viscosity of 1,300 cp @60°C was made. This represents < 0.1% increase in viscosity over the four week interval which is well within experimental error. This was a highly encouraging result as it appears that the rate of aging has been drastically reduced if not altogether eliminated.

Prior to shipping the thermally-treated sample to WRI, an agreement was attained with researchers at that center (Dr. Ray Robertson and Dr. Ken Thomas) to conduct a no-cost evaluation of the sample, but only if it could be shown that the aging problem had been contained or eliminated. Based on the results of the viscosity measurements at WRI, a decision was made that the ESO sample appeared to be sufficiently stable to proceed with the evaluation.

The next step was to vacuum distill the sample to meet the viscosity specifications for an AC-2.5 asphalt cement. This has been performed. At this time, the WRI staff intends to blend the distilled shale oil with three petroleum asphalts which are known to be susceptible to moisture damage and test these blends with three different aggregates. Tests will include moisture susceptibility and freeze-thaw evaluations directed at determining the short-term properties of the samples blended with ESO. In addition, thin-film oven and pressure oxidation tests will be performed to evaluate the long-term stability of the ESO/petroleum-asphalt blends.

As of this writing, evaluation of the stabilized-ESO sample is incomplete. It is anticipated that this evaluation will be completed and reported within the next six months. However, as part of the no-cost agreement, it was agreed that the results of this study would be the property of the WRI researchers and as such, it will be their responsibility to prepare a final report. It is suggested that individuals that may be interested in a copy of this report contact Dr. Ray Robertson or Dr. Ken Thomas of the Western Research Institute, Laramie, WY, (307) 721-2345 or (307) 721-2326.

6.3.3.4. *Summary.* Because evaluation of the thermally-stabilized sample of Eastern shale oil is incomplete, its potential useage as an asphalt cement, modifier, or recycling agent cannot be determined at this time. However, based on the results from the first phase of this evaluation coupled with the apparent elimination of the ESO aging problem, it is anticipated that ESO that has been subjected to accelerated aging will prove to be a suitable asphalt modifier and/or rejuvenating agent. Both of these applications are good from an economic stance since such agents command a market price that is often several times that of asphalt cement. Furthermore, the mild thermal treatment as applied to this sample has the potential advantage of being relatively inexpensive at a commercial scale relative to alternate treatment options. It also permits the higher value light-end components to be recovered for subsequent marketing as a chemical or refinery feedstock. Additional discussion of such applications is deferred until the

next chapter dealing with economic evaluation of the product suite from a KENTORT-based plant.

Acknowledgement. In addition to those individuals cited as co-investigators at the beginning of this section, the authors would like to express their appreciation to Mr. J. Button and Mr. S. Greer of TTI who extracted and recovered the aged asphalt, and to J.M. Wolf, F.A. Reid, and M. Harnberger of the WRI who conducted the blending and aging experiments in Phase I under subcontract to the UK-CAER. Mr. R. Pemberton of Ashland Oil is acknowledged for supplying the AC-5 asphalt binder. This work was supported in part by the Morgantown Energy Tech. Ctr., USDOE, under Coop. Agreement DE-FC21-90MC27286 through subcontract with the UK-CAER (such support does not constitute an endorsement by the USDOE of the views expressed in this article).

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7. ECONOMIC EVALUATION

7.1. EXAMINATION OF EASTERN US OIL SHALE BY-PRODUCTS AND BY-PRODUCT MARKETS

In an effort to identify those components or configurations that demonstrate the potential to improve process economics as well as to evaluate promising directions for future research, both established and potential oil shale by-product/co-product markets were examined. These include current or potential markets for trace elements, sulfur, cement, asphalt, bricks, fixed gases, specialty carbon fibers, adsorbent carbons, chemicals, and chemical feedstocks. The most recent data on market size and market price for these products is presented in this report where available. Market evaluations are, for the most part, based on the yields of by-products anticipated from an Eastern US oil shale using KENTORT fluidized-bed technology in a 7,500 t/d plant. Market evaluations, for the most part, are based on the yields of by-products anticipated from an Eastern US oil shale using KENTORT fluidized-bed technology in a 7,500 short-ton/day plant. For certain value-added products such as specialty fibers and adsorbent carbons, discussions are more general.

7.1.1. Introduction

Following the oil supply imbalances of the 1970's, oil shale research, particularly for the Eastern US Devonian deposits, has focused primarily on maximizing liquid hydrocarbon yields for transportation fuel production. However, various circumstances have eroded the ability of OPEC to dictate the price and supply for petroleum crude resulting in an abundance of low cost petroleum in the world market. Continued low prices and plentiful supplies for the foreseeable future will require that both researchers and government policy makers re-evaluate the merits of current research and reflect on the most appropriate direction for future investigations.

It is clear that under prevailing market conditions and short of an improbable governmental mandate, prospects for near-term development of a domestic oil shale industry are remote. From a long-term perspective, it is equally clear that the near-term economic climate should not compel us to abandon tangible gains made over the past two decades since many of the circumstances that fostered the renewed interest in oil shale in the 1970's still exist. Thus, it is important that research into alternate energy sources continue; but continue with some revision of the objectives and initiatives, so as to focus on and take advantage of the differences and opportunities inherent to oil shale development relative to petroleum. Specifically, the marketing or utilization of products and by-products that are either unavailable or more costly to produce from petroleum. In this context, this report has been prepared with the objectives of 1) estimating yields of known or potential oil-shale products and by-products; 2) surveying the domestic market size and price for same; and 3) exploring potential plant configurations or alliances with other industries that may enhance the commercial viability of oil shale.

As those familiar with the history of oil shale utilization are aware, the marketing of by-

products is not a novel strategy to commercial development. Nearly all previous oil shale ventures have relied in part on the sale of by-products.¹ These include asphalts (Austria, Russia), construction bricks (Sweden, Scotland, Estonia), cement (Germany, Russia, China, Estonia, USA), ammonia (Scotland), soil additives (Russia, Macedonia, Yugoslavia, Bulgaria, Hungary), town gas (Russia, Italy), lamp oil (Romania, Australia), rock-wool insulation (Russia, Estonia), chemicals (Estonia), and power generation (Russia, Spain, Israel, China, Germany).

7.1.2. Basis for by-product estimates

Product or by-product yields are highly dependent on the starting shale and the technology utilized; thus, both must be known or specified. Accordingly, three cores that had been extensively analyzed at the CAER, were used as a basis for estimating by-product yields. These cores, internally referenced as KP-5 and KP-6 from Fleming and DN-5 from Montgomery County, Kentucky, are reasonably representative of the deposits of Northeastern Kentucky, the region believed to be one of the more promising for commercial development in the Eastern US. For each core, averaging was applied to the entire Sunbury interval plus the Cleveland Member high-grade zone (hgz), an approximate 30-foot interval located immediately below the Sunbury. The weighted averages for the three cores were subsequently used in estimating yields for major/trace elements, cement production, etc. Data for individual gas and liquid components were taken directly from results of a previous study of the Cleveland hgz using KENTORT II technology.²

KENTORT II, developed specifically for the Eastern US shales, was selected as the processing technology. It should be noted that liquid and gas yields are process dependent and so the estimated values may vary several fold in a different technology or under different processing conditions. Table 7-1 summarizes estimated daily and annual data for a medium size 7,500 t/d KENTORT plant processing an Eastern US shale containing 11.8% carbon (from core averaging described above). The estimated liquid yield is 14 g/t with an assumed market price of \$18/bbl. This equates to ~\$6/t raw shale for the oil product. This \$6/t value is used throughout the manuscript as a convenient means to put by-product values, also expressed on a \$/t basis, in perspective.

7.1.3 Off-gases

Table 7-2 shows off-gas production rates from a previous study.² For each of the listed components, the domestic market for 1992 was quite large and thus unlikely to be affected by an influx of these components from a fledgling oil shale industry. The production values per ton (Table 7-2) were generated from average market price and production rates. Considering the added capital costs of gas purification and the fact that most plant configurations require combustion of gaseous hydrocarbons to meet thermal input requirements, it is unlikely that any of the components in Table 7-2 would substantially impact economics with the possible exception of hydrogen. Even here, if oil upgrading is part of the processing strategy, insufficient hydrogen would remain to justify the cost of recovery.

Table 7-1. Estimated daily and annual production using KENTORT II technology and an 11.8% C Eastern US oil shale.

	DAILY	ANNUAL	COMMENT
Oil Shale (sh tns)	7,500	2.6 Million	95% capacity
Shale Oil (bbl)	2,500	865,000	14.0 GPT
Oil Value	\$45,000	\$15.6 Million	@\$18/BBL

7.1.4. Liquid hydrocarbons

Following the approach used by Sinor,³ marketing the liquid product can follow one (or more) of three schemes; 1) selling the entire liquid product stream, 2) isolating and marketing individual components, or 3) marketing broad classes of components, e.g., asphalt, BTX, basic fractions, etc.

7.1.4.1. Entire Liquid Stream

As Sinor noted, the only market large enough to use or absorb the entire liquid stream would be the petroleum refining industry. However, transportation fuel production has been a primary focus of oil shale research since the 1970's when crude prices were often in excess of \$30/bbl. In today's market, \$30+/bbl shale oil simply cannot compete with \$15-18/bbl crude oil. Thus, operating an oil shale plant solely to produce motor fuels is not profitable in today's market and won't be considered further in this discussion.

Table 7-2. Marketable off-Gases

Gas Component	Production Rate ft ³ /tn(lbs/tn)	Domestic Sales	Domestic Price	Production Value/Ton (\$/tn)
¹ Hydrogen	130 (0.7#)	163 Biln ft ³	0.0037/ft ³	0.48
² Methane	125 (5.5#)	19.7 Biln ft ³	0.002/ft ³	0.25
³ Ethylene	16 (1.2#)	8.1 Biln kg	0.40/kg	0.23
⁴ Ethane	30 (2.5#)		0.46/kg	0.53
³ Propylene	14 (1.7#)	9.8 Biln kg	0.36/kg	0.28
³ Butene	10 (1.3#)	0.43 Biln kg	0.44/kg	0.26
^{5,6} Ammonia	(1#)	14.5 Miln tn	110/tn	0.05

¹1986 price

²Natural Gas Monthly-Sept. 1993

³Synthetic Organic Chemicals - ITC - 1992

⁴Chemical Marketing Reporter - July 1993

⁵Mineral Commodity Summary - 1993

⁶NH₃ from Susan Oh, 1989 EOSS

7.1.4.2. *Liquid Components*

It has been proposed that isolating individual liquid components with high market value can greatly enhance process economics. In one study, the market value of components that could feasibly be isolated from Western shale oils, e.g. olefins, phenols, etc., was estimated in the range of ~\$100/bbl,⁴ no doubt a reasonable figure. In addition, the generally greater levels of heteroatom containing, olefinic, and aromatic components in shale oil present a potential advantage for these liquids over petroleum crudes. However, there are two key considerations. The first, and most obvious is, the isolation cost. Such costs depend on factors such as starting concentration, chemical/physical properties of the component being isolated, and importantly, the required purity. It is estimated that the minimum cost of isolation and purification from a complex feed stream is on the order of \$1/lb.³ An elaborate separation scheme utilizing a combination of distillation, extraction, and chromatographic techniques must be demonstrated before a credible economic evaluation can be made.

A second consideration is the impact of even a single oil shale plant on the market price of a given liquid component. If the by-product market is adequately large to absorb additional production from a shale plant, then a minimal suppression of sale price can be anticipated. However, in a concise discussion of simple supply and demand economics, Sinor warns of the pitfalls of assuming the sale price of components with smaller markets would be unaffected by increased production capacity. A survey of market size and price for literally hundreds of organic chemicals showed that no chemical with an annual market in excess of 100 million pounds, was marketed for more than \$1/lb. With only one exception, no chemical marketed in excess of 1 million lbs/yr commanded a price greater than \$3.50/lb.³ Further, market size, price, and competition for various components would have to be evaluated on a component-by-component basis. This is not to say that on a small scale, sale prices of \$2-10/lb for certain chemicals could not be realized. Rather, one must simply exercise caution in blindly extrapolating profit margins to larger scale.

Nonetheless, there are numerous shale oil components which are absent or in low concentration in petroleum crudes, whose abundance, relative ease of isolation, and market size make them attractive candidates for isolation. These components are usually found in the light ends since, in general, at higher molecular weight, component quantities decrease, purification is more difficult, and isolation costs must be spread over a smaller quantity of product. Selected components that meet the criteria of large markets and reasonably inexpensive isolation costs are shown in Table 7-3. The only component that exhibits the potential to significantly enhance process economics is marketing of the C₆-C₁₀ alpha olefins, though the cumulative BTX value (\$56/ton) could have a favorable impact. These are not individual components but rather, in each case, five components. This means a cumulative expense for isolating five components would be incurred if marketed separately though it may be possible to market them as mixtures at a reduced price.

One area which is intentionally not evaluated in this report pertains to the isolation and marketing of various heteroatom containing species from shale oil (NSO compounds). These

Table 7-3. Liquid components

	KENTORT Production kg/ton	Domestic Market (Billion kg)	Average Sale Price-1992	Value/ ton
Cyclohexane	0.20	1.1	\$0.42/kg	\$0.08
Hexane	0.58	0.17	0.29/kg	0.17
Benzene	0.40	5.2	0.37/kg	0.15
Toluene	0.55	2.9	0.28/kg	0.15
Xylenes	1.0	2.9	0.26/kg	0.26
Ethylbenzene	0.23	4.0	0.43/kg	0.10
C6-C10	2.1	0.47	0.79/kg	1.66
Alpha Olefins				

Synthetic Organic Chemicals 1993-ITC

materials represent a significant fraction of the total oil product (up to 50% in some configurations) and include components such as phenols, cresols, amines, anilines, mercaptans, sulfides, thiophenes, etc. Even though the previous discussion of market limitations and high isolation costs would certainly apply to the marketing of such components, their market value is relatively high and this represents an area of potential advantage for shale oil relative to petroleum. The reason this area is not properly evaluated in this report is that estimating the market value for these components is not a trivial task as there are numerous and complex factors that must be considered, e.g., the number of components to be isolated, the selected purification scheme, the quantities of material to be isolated (highly process and resource dependent), the required purities, multiple markets or uses, and so forth. Such an area can only be reasonably addressed in a study dedicated solely to this one topic. However, such a study has previously been attempted for Western shale oils with the results from that work being generally applicable to the oils generated from the Eastern deposits. Our general conclusion following perusal of these studies is that, even though there exists a potential to improve the overall plant economics by this strategy, the magnitude of this improvement cannot be determined but is unlikely to be sufficiently large to offset the capital risks. That is, the enhanced sale price of isolated components appears to be sufficient to offset the cost of isolation using current-market prices. However, the increase in supply of many of these components that would result from oil-shale venture would likely result in suppression of the current market prices to an unknown extent. The reader is referred to these prior works for a more detailed discussion.⁵

7.1.4.3. Paving Asphalt Market

Sinor concluded in his study³ that converting the least volatile shale oil fraction to a paving asphalt or to an asphalt modifier is the most viable approach to small scale commercialization. This strategy is attractive for several reasons including 1) the least valuable heavy oils would be utilized, 2) the need to remove fines from and upgrade that portion of the oil product would be eliminated, and 3) residual oils derived from Eastern US shales have been shown to possess favorable properties as an asphalt recycling agent.⁶ This latter utilization, i.e.,

production of asphalt recycling agents, would benefit from the fact that the recycling segment of the asphalt market will likely experience continued growth, and such agents command higher prices than conventional asphalts. On the down side, a preliminary assessment revealed a severe aging problem for Eastern shale oils when attempting to utilize the heavy-oil fraction without prior treatment.⁶ It may be possible to alleviate this problem with either accelerated thermal aging or reaction with elemental sulfur (both to eliminate reactive olefins). Tests of accelerated thermal aging are in progress and are discussed in more detail in Chapter 6.

The July 1993 price for commercial grade AC-20 asphalt averaged \$109.35/ton. This equates to ~\$19/bbl, near the price of petroleum crude and insufficient to render an oil-shale venture profitable. To overcome this impediment, it has been proposed that shale oil be marketed as an asphalt modifier, a material that improves overall performance and sells for 2-3 times more than commercial asphalt.³ The production of asphalt modifier from Western shale oil using the SOMAT process⁷ has met with some success in a series of test strips and more recently, in a small scale commercial operation.⁸

A third concern is market limitation. The total U.S. paving asphalt market for 1992 was 23.3 million short tons. More importantly, due to prohibitive shipping costs, the regional market for KY, AL, TN, IN, and OH totaled 4 million short tons. Assuming ~2/3 of the total liquid product could be converted to an asphalt modifier, a 7,500 t/d plant would produce ~100,000 t/yr modifier. If the modifier is added to commercial asphalt at a level of 10 wt%, an unlikely regional market penetration of ~25% would be required. One solution is to construct a smaller plant (with the accompanying loss in economy of scale). In any case, it would appear that no more than 1-2 small plants could be supported by revenue from the asphalt market and production of paving asphalt is not a panacea for large scale commercial development. However, as previously advocated,³ the asphalt market could provide critical cash flow for a first generation facility as it progressed along the learning curve to higher efficiency. It is anticipated that tests currently being conducted* will determine if Eastern shale oils can be processed so as to exhibit acceptable properties as an asphalt modifier.

7.1.4.4. *Carbon Specialty Fibers*

Heteroatoms in shale oil, particularly nitrogen, have historically been viewed as detrimental to oil shale development due to high removal costs. However, recent work at the CAER in which shale oils were used as precursor material for producing carbon specialty fibers, suggests that the high heteroatom content of shale oil may offer a potential advantage.

Low strength, general purpose carbon fibers have been produced commercially for more than two decades from petroleum and coal-tar pitch. Their lower cost makes them more attractive than high performance PAN- (polyacrylonitrile) or mesophase pitch-based fibers for

* These tests are being conducted at the Western Research Institute in Laramie, Wyoming on oils generated in the KENTORT II reactor-see Chapter 6.

applications in which high tensile strength or stiffness are not required. In the past few years there has also been a growing interest in the production of activated carbon fibers from isotropic pitch fibers. Such fibers have novel properties that make them more attractive than other forms of activated carbon (powder, granular, or extrudate) for certain applications.⁹ They can be produced with high surface areas, narrow pore size distributions, and their small diameter essentially eliminates mass transfer limitations, i.e., faster rates of adsorption and desorption.

At present, world-wide commercial production is low (2,750 tons in 1992), and precursor materials have been confined to specific petroleum and coal-tar pitches. However, there is a tremendous potential for growth with cost being the main impediment to more widespread use. The cost of general purpose fibers is around \$20/lb, and higher still for activated fibers. The ability to produce both types of fiber with a range of properties, would expand the prospective applications and markets.

Recently, using an asphaltene fraction isolated from an Eastern shale oil as the starting material, it was shown that continuous filament isotropic carbon fibers can be successfully produced, and steam activated to produce high surface areas.¹⁰ Comparison with a commercial petroleum pitch shows that the oil shale precursor offers advantages in terms of simplicity of feedstock preparation, excellent spinnability, and more facile processing, all of which could reduce production costs. The activated shale-oil-based fibers also contained a much higher proportion of mesopores (2-50 nm diameter) and higher nitrogen content than petroleum-based fibers, which could lead to novel adsorptive properties. This was confirmed by a recent evaluation of the shale-oil-based fibers which demonstrated a high catalytic activity with respect to reduction of NO in the presence of NH₃ and for oxidation of SO₂ to H₂SO₄, both at ambient temperature.¹¹ Results from this study compared very favorably to similar tests with activated PAN-based fibers.

Though this field is in its infancy, fibers that exhibit such unusual properties represent a value-added product that could command a premium price, measured in the dollars per pound range. Thus, while the high nitrogen content of residual oil shale liquids can be detrimental to their upgrading to distillate fuels, it may be possible to use this characteristic to advantage in the production of value-added carbon materials. Since such utilization represents an area in which shale oils exhibit an apparent advantage over petroleum crude, further investigation is clearly warranted.

Figure 7-1. Production of activated carbon from oil shale.

7.1.5. Solids utilization

7.1.5.1. Major and Trace Elements

In the late 1970's and early 1980's, primarily in an attempt to develop domestic sources of uranium, a substantial effort was directed at studying the removal and marketing of major and trace elements from the Eastern Devonian Shales. Though extractive removal of one or more of these elements would require a significant capital investment, the market value for several of these elements was suitably high, e.g., up to 3 time the value of the oil product, to warrant serious investigation. Though the market for uranium has plummeted, other elements make this area worthy of a second look in the context of today's market.

Table 7-4 lists concentrations of the major inorganic elements in the Kentucky deposits calculated as described in the *Basis for Product Estimates* section. Column 3 lists the percentage of these elements that can be extracted with either H_2SO_4 or HCl following combustion at $750^\circ C$.^{12,13} Coupling raw shale concentration and the extractable portion yields the lbs/ton available for each element (col. 4). The fifth and seventh columns show the form in which the element may be marketed and the market price for that form. The last column shows value-per-ton of pure element if marketed in the form indicated. Market size depicts the total market on a pure element basis regardless of the marketed form. Analogous information for trace elements is shown in Table 7-5. A percent extractable figure was unavailable for many of the trace elements and so a conservative 50% extractable value was assumed. Isolation and recovery strategies for many of the elements in these tables have been demonstrated at the laboratory scale^{12,13} but no serious economic assessment has been reported. It should be noted that major element concentrations are reasonably consistent across the deposit but that trace element

Table 7-4. Major inorganic elements

Element	Raw Shale concn.	% extractable at 750C ¹	lbs/Ton	Form	Domestic Market (short ton)	Domestic Price (\$/sh tn)	Value/Ton Shale
² Al	6.7%	77	103	Al ₂ O ₃	5,400,000	\$192	\$18.70
² Ca	0.38%	96	7	CaCl ₂	378,000	142	1.45
³ Fe	4.1%	99	81	Fe ore	77,000,000	35	2.35
⁴ Fe				FeCl ₂ IG		200	18.40
⁴ K	2.9%	71	41	K ₂ SO ₄	540,000	180	8.25
⁴ Mg	0.68%	93	13	MgO		240	2.87
⁴ P	0.10%	92	1.8	tri-phosphate		135	1.10
³ S	3.1%	67	42	elem S	14,200,000	54	1.14
² Ti	0.40%	10	0.8	TiO ₂	1,250,000	1867	1.25

¹Gilliam, Canon, Ryan, and Watson-1981 EOSS.

²Current Industrial Reports, MA28A, Report on Inorg. Chem. for 1992

³Mineral Commodity Summary 1993, USEM

⁴Chemical Marketing Report, July 1993

Table 7-5. Trace Elements¹

Element	Raw Shale concn.	% extractable at 750C ²	lbs/Ton	Form	Domestic Market (short ton)	Domestic Price (\$/lb)	Value/Ton Shale
As ³	47	50	.047	As	24,000	\$0.29	\$0.01
Ba	497	50	.497	BaSO ₄	565,000	0.02	0.02
Cd	22	50	.022	Cd	3,700	1.00	0.02
Co	18	96	.035	Co	7,900	22.80	0.80
Cr	160	79	.253	Cr ₂ O ₃		5.50	2.03
Cr				Chromite ore	479,000	0.05	0.04
Mn	145	94	.273	MnO ₂	61,000	0.71	0.30
Mo	133	97	.258	Mo	19,000	2.30	0.59
Ni	149	95	.283	Ni	160,000	3.21	0.90
Pb	122	50	.122	Pb	1,360,000	0.36	0.04
Sb	32	50	.032	Sb	47,000	0.80	0.03
Se	27	50	.027	Se	560	5.15	0.14
Sr	105	75	.158	Sr	33,000	0.03	0.005
Th	10	50	.010	ThO ₂	60	28.90	0.29
V	803	92	1.478	V ₂ O ₅	4,200	2.60	6.85
Y	47	63	.059	Y ₂ O ₃	770-wld	67.00	2.00
Zn	581	84	.976	Zn	1,350,000	0.59	0.58
Zr	156	50	.156	Zr sponge	61,000	10.00	0.78

¹Market/Price Data from Minerals Commodity Summary USEM 1992

-except Cr (Chem. Marketing Report, 1993) and Mn (Current Industrial Reports, 1992)

²Gilliam, Canon, Ryon, and Watson, 1981 EOSS.

³Tian and Ehmann, 1984 EOSS

concentrations are much more variable both vertically and laterally. Therefore, it should be kept in mind that the values in Table 7-5 are merely averages.

There are several elements in Table 7-4 and Table 7-5 that appear to merit serious cost analysis. Sulfur is the element most likely to be marketed, not because of an exceptionally high value, but because in most process configurations, and particularly in the KENTORT reactor (due to steam gasification), up to 90% of the total sulfur in Eastern shales is liberated as H₂S. This necessitates designing for sulfur recovery regardless of its by-product value. Thus, sulfur production can, for the most part, be taken as a credit on operations. Other elements of potential benefit include Al, Fe, K, Mg, Co, Cr, and Ni, as well as V though significant marketing of the latter would likely suppress the market price. The cumulative value/ton for these elements if sold in the form shown (Table 7-4 and Table 7-5; excluding V) is approximately \$53/t (\$60/t including V). Recovery of these elements would be costly, both in terms of capital investment and operating expenses. However, with a cumulative potential market value approximately ten times that of the oil, extractive recovery of these elements has the potential to favorably impact economics and warrants further investigation.

7.1.5.2. *Residential/Construction Bricks*

In 1993, the domestic brick market was approximately 8 billion standard units (about 30 million tons) with annual sales of ~\$1.5 billion. The regional market (KY, IL, IN, TN, AL, and GA) was ~1.5 billion units.

Spent shale residues have historically been utilized for brick production.¹ Both the oil shale and brick plant stand to benefit from sharing costs associated with mining, crushing, and spent shale disposal. In addition, excess combustible gas from retorting can be used to help meet heating requirements in the brick plant. However, brick production requires a plastic clay as a feed material. With the exception of organic matter and pyrite, the clays used are otherwise often similar to those contained in the Eastern oil shale deposits. In at least one local plant, clays situated directly above the New Albany oil shale are currently being utilized. The underlying oil shale is deemed unsuitable due to significant amounts of carbon, which can result in swelling and black coring of the brick during firing, and pyrite, which can lead to swelling and elevated SO₂ emissions. Complicating matters, combustion of the shale to remove residual carbon and sulfur results in the loss of clay plasticity.

These factors suggest that Eastern oil shales are not suitable as clay substitutes in a commercial brick plant. However, due to the low porosity of many of the feed clays, calcined material or sand must often be added to enhance the brick porosity during firing. Such an application represents a potential, though smaller, end-use for the combusted shale. Porosity enhancers are typically added in the range of 10-20%. This places an upper limit of ~one million tons in the regional market. More realistically, this limit would be established by the capacity of the brick plant(s) near which the retort is located. Nonetheless, there are legitimate economic reasons to locate an oil shale plant in close proximity to a brick plant when the latter is in operation near an oil shale deposit (not uncommon in the Ohio Valley region).

7.1.5.3. *Portland Cement*

In a review of the history of oil shale cement, Knutson lists approximately 40 patents worldwide that specify the use of oil shale for cement production.¹⁴ The first patents were issued as early as 1918 with cement production beginning in the 1920's. Today, what Knutson terms 'relatively mature technologies' operate in Germany, Russia, and China. Several other countries, to a lesser extent, have also adopted this technology, e.g., the largest cement plant in North America, operated by the Lafarge Corporation in Alpena Michigan, uses 0.7 million tons of Antrim (Devonian) shale annually.¹⁵

In 1992, ~90 million tons of Portland cement was marketed domestically at an average price of \$64.20/short ton.¹⁶ Though specifics on the regional market were not obtained, a large portion of production capacity appears to be located east of the Mississippi river.

There are two reasons why oil shale is beneficial to cement production. Producing cement is an energy intensive process, generally requiring large amounts of coal and/or natural gas.

Table 7-6. Typical portland cement composition and potential contribution from oil shale residue.

	Portland Cement ¹	Contribution from shale ash (limestone/shale ash 2:1)
CaO	60-70%	0.2%
SiO ₂	20-24%	23%
Al ₂ O ₃	3-8%	5.4%
MgO	1-4%	0.5%
FeO ₂	2-4%	2.2%
SO ₃	3-11%	3.3%

¹Shultz, Lamont, Daniel, 1991 EOSS

Thus, the latent heat content of an oil shale, over 2000 btu/lb for the Sunbury and HGZ-Cleveland Member shales, can supply a significant portion of the required energy input.

The second reason is summarized in Table 7-6. The column headed 'Portland Cement' shows the acceptable ranges for the major oxides in cement.^{14,15} The last column shows the portion of these oxides that would be contributed by an Eastern US oil shale when mixed with limestone at 2:1 (limestone:shale). With the exception of Ca and Mg, which originate chiefly from the limestone, all of the major oxides can conceivably be obtained from the shale

matrix. Thus, not only can the oil shale provide a significant portion of the heat requirements, but the combusted residue can be fully utilized to offset constituents that otherwise must be added to the kiln, e.g., sand, gypsum, clay, and smelter slag.

7.1.5.4. Combined Cement and Oil Production?

The Rohrbach Cement works in Dotternhausen, Germany is one of the more tightly controlled and technically advanced cement plants in the world. This plant, in operation since 1939, utilizes around 350,000 t/y oil shale (about 210,000 t/y combusted residue) in the production of ~650,000 tons cement.¹⁷ About 80% of the total oil shale is combusted in a fluidized bed for power generation with the remainder routed to a kiln plant where it is combusted with sand, clay, and limestone to produce clinker. The combustor residue is mixed with the clinker in cement mills.

Locating a pyrolysis bed immediately upstream of the fluid-bed combustor in such a plant in which the pyrolysis unit is fluidized with steam, heated by recycled-combusted solids, and

operated at 650-750 °C (Figure 7-2) would offer several advantages. The most notable effect of the high pyrolysis temperature would be a reduction in oil yield to perhaps 30-50% of Fisher Assay. However, the liquid would be of significantly higher quality and thus command a higher sale price, perhaps being marketed as a chemical rather than refinery feedstock due to an abundance of 1-ring aromatics. Second, the heating value of carbon deposited as coke on the recycle solids

Figure 7-2. Schematic of combined oil shale/cement plant.

Table 7-7. Estimated production and market value from high temperature (~700 °C) fluidized bed pyrolysis

Hydrogen	500 ft ³ (4 fold increase)	\$1.80/t
Benzene	1 kg/t (2 fold increase)	0.40/t
Toluene	1 kg/t "	0.25/t
Xylenes	2 kg/t "	0.50/t
Light oils	3-4g/t (high quality)	1.50/t
Sulfur	Dependent on cement plant consumption	

would still be available for power generation since these solids would be routed to the combustor. Third, there would be a substantial increase in gas production, particularly H₂, with high-temperature steam fluidization. Hydrogen and hydrogen sulfide could either be removed for marketing or combusted in the cement kiln along with the other off-gas components.

Potentially marketable products from such a configuration are summarized in Table 7-7. Due to the high pyrolysis temperature, several components (aromatics and off-gases) would be produced at relatively high levels. The

cumulative H₂ and light oils value is estimated at \$4.50/t or ~75% of the value of the liquid product from a KENTORT II plant operating in a high-oil-yield mode.

More importantly, in this configuration, product sales need only show a profit on the additional pyrolysis bed and liquids-handling system, not on a full fledged oil shale plant that must support the costs of mining, crushing, solids disposal, and solids processing downstream of the pyrolyzer. It is estimated that a 1000 t/d retort and gas/oil handling system would cost ~\$9.4 million US. This figure was derived from a 1987 oil shale plant cost analysis,¹⁸ by dropping plant support systems unneeded in this configuration, e.g., combustor, shale disposal, hydrogen plant, hydrotreating, etc.; and downsizing the plant to 1000 t/d using the power factor method assuming a factor of 0.75. At \$4.50/bbl for the gas/oil product, such a plant would generate ~1.56 million dollars annually for a simple payback period of ~six±1.5 years. The one obvious drawback to this approach is the required merger of what are otherwise two unrelated industries, cement and liquid fuels/chemicals production.

7.1.5.5. Adsorbent Carbons

This final section on adsorbent carbon does not pertain to the Eastern US oil shale deposits. It is included since recent work at the CAER shows this to be a promising area for oil shales that meet the criteria of low ash and high carbon residue following pyrolysis, e.g., the Alpha Torbanite of Australia and Goynuk oil shale of Turkey. It is anticipated that the KENTORT reactor could be modified to process these or other similar high-carbon deposits.

Commercial carbons have surface areas in the range of 800-1500 m²/g and sell for ~\$500/ton. Carbons produced from the Goynuk shale have surface areas up to ~400 m²/g, yield ~150 lb/ton after activation, and exhibit reasonably good adsorption capacities.¹⁹ Adsorbent carbons have a variety of applications, the most important with respect to oil shale derived carbons probably being in the area of industrial emissions (scrubbing NO_x, SO₂, NH₃, H₂S, etc.) and removal of aqueous pollutants (phenols). The 1991 production capacity was 420,000 t/y with a projected growth rate of 4% annually through 1995.²⁰ This represents an opportunity for

and removal of aqueous pollutants (phenols). The 1991 production capacity was 420,000 t/y with a projected growth rate of 4% annually through 1995.²⁰ This represents an opportunity for increased revenue from an oil shale plant, perhaps several fold, with minimal additional investment. More work is needed, particularly on optimization, but initial results are highly encouraging.

7.1.6. Summary

By-product marketing, as has historically been the case, will likely play a critical role in any future oil shale development. Sulfur production is or was usually taken as a credit for most plants that were proposed or designed to process the Eastern U.S. deposits. This is because the cost of recovery and conversion to elemental sulfur is offset by the cost of scrubbing and disposal which are otherwise required.

Though further evaluation would be needed, depending on plant configuration, there appears to be a significant potential to improve retorting economics from sales of one or more by-products. These include Al, Fe, K, Co, Cr, Ni, V, H₂, BTX, alpha olefins, asphalt modifiers, specialty carbon fibers, chemicals (NSO components), adsorbent carbons, and cement. The latter three appear to have the most potential to impact commercial development.

ACKNOWLEDGMENTS

We wish to acknowledge the assistance of John Brown of General Shale, Inc., Kingsport, Tennessee, and M. Reidhammer with Rohrbach Zement, Dotternhausen, Germany in preparing this report.

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APPENDIX A. MASS TRANSFER MODEL FOR COKING OF OIL VAPORS IN A FLUIDIZED BED

The objective of this part of the research was to construct an intraparticle reaction/diffusion model within a simple fluidized bed model in order to gain a rough approximation to interparticle mass transport effects. While there are more sophisticated fluidized bed models available than the two-phase model which will be described here, it was determined that the simplest model would be sufficient for the purposes of this work. The main objective was to gain a sense of the mass transfer characteristics of the system and not to undertake extensive fundamental modeling. Of particular interest was the modeling of intraparticle mass transport limitations because of the large average size of the oil vapor molecules under consideration. Another objective of this effort was to determine what role transient mass transfer effects played during the initial stages of the coking kinetics experiments.

A.1 Approach

For the purposes of this study, the simplest possible fluidized bed model, which captures the essence of the mechanisms of a fluidized bed, was chosen. The bed is assumed to consist of a bubble phase and an emulsion phase, and the bubbles are considered to be spherical and of uniform size. The coking reaction is assumed to take place only within the pores of spherical particles. Only the initial rapid coke formation regime (first-order reaction without deactivation) is considered because the initial timeframe of the vapor-solid contact is of most interest. Simple binary counter diffusion is assumed within the particles. The system is considered to be in an unsteady state, and the concentration profile within the particles is coupled with the emulsion phase in the fluidized bed. A FORTRAN subroutine in the NAG library (D03PFG) was used to solve the system of parabolic partial differential equations.

A general two-phase fluidized bed model assuming first order, solid-catalyzed kinetics for the emulsion phase is given by Yates¹ (1983) as:

$$E_e \frac{\partial^2 C_e}{\partial z^2} - U_e \frac{\partial C_e}{\partial z} - K_{be}(C_e - C_b) - k_e C_e = \frac{\partial C_e}{\partial t} \quad (\text{A-1})$$

This equation is basically the convective-diffusion equation with chemical reaction. The third term in Equation A-1 represents the mass transfer rate between the emulsion and bubble phases. A similar equation describes the bubble phase, but in this case it is assumed that no chemical reaction takes place:

$$E_b \frac{\partial^2 C_b}{\partial z^2} - U_b \frac{\partial C_b}{\partial z} - K_{be}(C_b - C_e) = \frac{\partial C_b}{\partial t} \quad (\text{A-2})$$

For the purposes of the present study, however, Equation A-1 is not sufficient to explicitly describe reactions within a porous particle. By changing the reaction term to a mass transfer term from the emulsion phase to the particle, Equation A-1 becomes:

$$E_e \frac{\partial^2 C_e}{\partial z^2} - U_e \frac{\partial C_e}{\partial z} - K_{be}(C_e - C_b) - \frac{1 - \epsilon_{mf}}{\epsilon_{mf}} k_p a(C_e - C_r(R)) = \frac{\partial C_e}{\partial t} \quad (\text{A-3})$$

where $C_r(R)$ is the vapor concentration in the particle at the surface.

To account for the coking reaction which is assumed to take place only within the particle, the unsteady state diffusion equation for a sphere is needed. By adding an nth-order chemical reaction term this equation becomes:

$$D_{eff} \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) - S_p \rho_p k_r C_r^n = \theta \frac{\partial C_r}{\partial t} \quad (\text{A-4})$$

Equation A-4 prescribes binary counter diffusion and no convective mass flux.

Equations A-2 and A-3 can be solved as a coupled set of equations numerically, but a means of coupling Equation A-4 to Equations A-2 and A-3 is needed. By utilizing continuity at the particle surface, the following boundary condition for Equation A-4 is obtained:²

$$D_{eff} \left(\frac{\partial C_r}{\partial r} \right)_R = k_p (C_e - C_r(R)) \quad (\text{A-5})$$

The problem can then be completely characterized with the addition of standard boundary conditions. At the center of the particle the usual boundary condition is applied to Equation A-4:

$$\frac{\partial C_r}{\partial r} = 0 \quad \text{at } r=0 \quad (\text{A-6})$$

For the emulsion and bubble phases the following boundary conditions are assumed:

$$C_e = C_b = C_{in} \quad \text{at } z=0 \quad (\text{A-7})$$

$$\frac{\partial C_e}{\partial z} = \frac{\partial C_b}{\partial z} = 0 \quad \text{at } z=L \quad (\text{A-8})$$

While Equations A-2 to A-4 contain 2 space variables, the problem is not strictly two dimensional. Since the solids in a fluidized bed are well-mixed, the time-averaged concentration of oil vapor in the emulsion phase that the particle contacts is not a function of axial position. It is suggested, therefore, that C_e in Equation A-4 can be replaced by $C_{e,avg}$ which is the average concentration in the axial direction and is only a function of time. Equation A-5 is then written as:

$$D_{eff} \left(\frac{\partial C_r}{\partial r} \right)_R = k_p (C_{e,avg} - C_r(R)) \quad (A-9)$$

Similarly, $C_r(R)$ is not a function of axial position and is also only a function of time. Therefore, the parameters coupling Equations A-3, A-4, and A-7 are only functions of time and a simultaneous solution of Equations A-2 to A-4 in 2 space variables is not required.

A.2 Parameter Estimation

The difficulty in dealing with a fluidized bed reactor is made worse by the situation that the physical properties of the oil vapor must also be empirically estimated. The oil vapor was considered to have a molecular weight of 400 and a critical temperature of 823 K. A heavy oil was assumed because it is generally believed that the heaviest oil fractions participate to the greatest extent in the coking reactions.

The molecular diffusivity of oil vapor in the fluidizing gas (steam or nitrogen) was determined by the Lennard-Jones relationship:³

$$D_{12} = \frac{0.001858 T^{3/2} [(M_1 + M_2)/M_1 M_2]^{1/2}}{P \sigma_{12}^2 \Omega_D} \quad (A-10)$$

The Lennard-Jones force constants, ϵ and σ , were estimated for the oil vapor by the relationships:

$$\frac{\kappa T}{\epsilon} = 1.30 \frac{T}{T_c} \quad (A-11)$$

$$\sigma = 1.18 V_b^{1/3} \quad (A-12)$$

Tabulated values of ϵ and σ were obtained for nitrogen and steam.³ A geometric mean was used to determine ϵ_{12} and an arithmetic mean for σ_{12} . Once these values were obtained, the collision integral, Ω_D , was determined from published values.⁴ To aid computation, smooth

curves were fitted to the collision integral data as a function of $\kappa T/\epsilon_{12}$. Then effective molecular diffusivity was defined by:³

$$D_{12,eff} = \frac{D_{12}\theta}{\tau} \quad (A-13)$$

Knudsen diffusion prevails under conditions where pore-wall collisions are more frequent than molecular collisions. Since gases have low density at high temperatures, the possibility for significant Knudsen diffusion exists. The Knudsen diffusivity, D_K , was determined by the relationship:

$$D_K = 9700 r_e \sqrt{T/M} \quad (A-14)$$

The mean pore radius was defined by:

$$r_e = \frac{2\theta}{S_p \rho_p} \quad (A-15)$$

Similar to Equation A-13, the porosity and tortuosity of the solid was accounted for by the relation:

$$D_{K,eff} = \frac{D_K\theta}{\tau} \quad (A-16)$$

Finally, the overall effective diffusivity, D_{eff} , was determined as the combination of molecular diffusion and Knudsen diffusion by the relation:

$$\frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}} \quad (A-17)$$

What remains to be estimated are the fluidized bed parameters themselves. The determination of the minimum fluidization velocity, U_{mf} , is important because it specifies the velocity of gas passing through the emulsion phase. The following relations (Equations A-18 to A-20), presented by Yates,¹ were used to determine U_{mf} :

$$Re_{mf} = [(33.7)^2 + 0.0408 Ga]^{1/2} - 33.7 \quad (A-18)$$

$$\text{where } Re_{mf} = \frac{U_{mf} d_p \rho_g}{\mu} \quad (A-19)$$

$$\text{and } Ga = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad (A-20)$$

Based on the model of Davidson and Harrison the average bubble velocity was determined by the relationship as presented by Yates:¹

$$U_b = (U_o - U_{mf}) + 0.711 (g d_b)^{1/2} \quad (A-21)$$

This relationship assumes that the bubble diameter, d_b , is known, and for the purposes of this work, a value of 1 cm was assumed, based on observations from cold-flow modeling of similar fluidized bed systems.

While the model used in this work assumes only bubble and emulsion phases to exist, the exchange coefficient, K_{be} , was determined by including the cloud phase as an intermediate resistance in series as suggested by Kunii and Levenspiel.⁵ The bubble-to-cloud coefficient is given by:

$$K_{bc} = 4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{D^{1/2} g^{1/4}}{d_b^{5/4}} \right) \quad (A-22)$$

The cloud-to-emulsion coefficient was determined by:

$$K_{ce} = 6.78 \left(\frac{\epsilon_{mf} D_e U_b}{d_b^3} \right)^{1/2} \quad (A-23)$$

The bubble-to-emulsion coefficient is then derived by:

$$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}} \quad (A-24)$$

Using the emulsion phase gas velocity, the mass transfer coefficient to the particle, k_p ,

is determined by the relationship:

$$Sh = 2.0 + 0.6 Sc^{1/3} Re_{mf}^{1/2}$$

$$\text{where } Sc = \frac{\mu}{\rho_g D_{12}}$$

$$\text{and } Sh = \frac{k_p d_p Y}{\mu}$$
(A-25)

A.3 Numerical Results

To facilitate numerical solution to the problem, the variables were non-dimensionalized as follows:

$$C_e^* = \frac{C_e}{C_{in}} ; C_b^* = \frac{C_b}{C_{in}} ; C_r^* = \frac{C_r}{C_{in}}$$

$$Z^* = \frac{z}{L} ; R^* = \frac{r}{R}$$
(A-26)

The following initial conditions were used throughout the work:

$$C_e^* = 0 ; C_b^* = 1 ; C_r^* = 0 \quad \text{at } t = 0$$
(A-27)

The base case for the numerical solution to the model included no chemical reaction, nitrogen as the fluidizing gas and a temperature of 873 K. A mesh size of 41 was used for both the r- and z-directions. The same mass flowrate of fluidizing gas was used throughout the study. Axial dispersion coefficients, $E_c = E_b = 1 \text{ cm}^2/\text{s}$, were used and are low enough to be considered nearly plug flow, but large enough to perhaps dampen wiggles in the numerical solution. While many have assumed either plug flow or backmixed flow for the bubble and emulsion phases, it is more realistic to consider that the flow only approaches one of these ideal cases.

Figure A-1 shows that steady state conditions are achieved for each of the 3 phases within 1 second for the base case conditions. The solution is smooth for all of the "surfaces" with the exception of some wiggles which develop in the bubble phase solution at $Z^* = 0.8$ which are artifacts of the numerical solution due to the convection term. The wiggles disappear, however, at times greater than $t = 0.6 \text{ s}$. Using a coarser mesh of 21 grid points the wiggles were much more pronounced. The concentration in the bubble phase displays a minimum at approximately 0.2 s. This sort of behavior is expected because the bubble phase

"feeds" the emulsion and particle phases until the initial vapor concentration is achieved. A very small concentration gradient is initially evident across the particle which is not completely surprising since a relatively small particle size was tested, $d_p=0.08$ cm. The concentration of the emulsion phase follows closely the concentration in the particle which indicates that resistance into the emulsion phase is an influential parameter.

Lowering the temperature by 100 K to 773 K only reduced the effective diffusivity from $0.008 \text{ cm}^2/\text{s}$ to $0.007 \text{ cm}^2/\text{s}$. The data at 773 K was nearly indistinguishable from that at 873 K. Increasing the particle diameter to $d_p=0.12$ cm, however, significantly changed the transient response of the system (Figure A-2). The system achieved steady state more quickly than for the small particle, which was somewhat surprising. None of the mass transfer coefficients changed significantly with increased particle size, but the minimum fluidization velocity increased substantially. The velocity of gas through the emulsion phase, therefore, increased and the velocity of bubble gas decreased because the overall superficial velocity was held constant. This created greater mass transfer from the bubble phase to the emulsion phase and greatly increased the temporal response of the system. A more intuitive effect of particle size can be also observed, however. The initial concentration gradient across the particle radius is much steeper compared to the small particle size simulation. Due to the larger gradient for the emulsion phase, an imprint of the bubble phase response in the emulsion phase position-time surface is observable.

The effect of chemical reaction on the transient response of the system is similar to that without reaction except that lower concentrations are reached at steady state (Figure A-3). In addition, it appears that steady state is reached more slowly. The first-order kinetic rate constant was adjusted so that the conversion approximately matched the experimental results. Therefore, no conclusions can be drawn concerning the closeness of fit to experimental results. Since it was the objective to study the initial transient response of the system due to mass transfer, only a first-order reaction term without deactivation utilized. Simulation of the coking reaction created a steeper concentration gradient within the particle, so diffusional effects cannot be neglected even for small particle sizes. In the case of no reaction the wiggles in the bubble phase solution disappeared at steady state, but with chemical reaction present the wiggles survive.

The 0.08 cm particle size that was used as the base for the numerical simulations was at the upper end of the range that was used for most of the experiments. Increasing the particle size to 0.12 cm in the fluidized bed model shows that pore diffusion becomes influential. Figure A-4 shows that the conversion using the same kinetic rate constant dropped slightly and a larger concentration gradient of oil vapor within the particle was a result. Only one experiment was performed with larger size particles, and the coking rate was found to be lower.

A.4 Summary

These numerical simulations showed that the unsteady state experimental results cannot be attributed to mass transfer effects because steady state without including coking deactivation in the chemical reaction term was shown to be achieved within a second. The typical coking kinetics experiment, however, reached an apparent steady state within minutes rather than a second. In addition, more evidence was provided by the numerical simulations to indicate that pore diffusion was not a significant factor. However, for particles 1.2 mm diameter and greater, it appears that pore diffusion begins to become influential.

Figure A-1. Base case numerical solution of model. Temperature, 600°C; Fluidizing gas, nitrogen; Bed height, 7.6 cm; no chemical reaction. Units are dimensionless except for time.

Figure A-2. Numerical solution to model with $d_p=0.12$ cm and no chemical reaction.

Figure A-3. Numerical solution to model under base case conditions with chemical reaction and $d_p=0.08$ cm.

Figure A-4. Numerical solution under base case conditions with chemical reaction and $d_p=0.12$ cm.

A.5 Modeling Nomenclature

- C_b = concentration of oil vapor in bubble phase, mol/cm³
 C_e = concentration of oil vapor in emulsion phase, mol/cm³
 $C_{e,avg}$ = average conc. of oil. vapor in emulsion phase, mol/cm³
 C_{in} = inlet oil vapor concentration, mol/cm³
 C_r = concentration of oil vapor in particle phase, mol/cm³
 $C_r(R)$ = conc. of oil vapor at particle surface, mol/cm³
 d_p = particle diameter, cm
 D_{12} = molecular diffusivity of oil in fluidizing gas, cm²/s
 $D_{12,eff}$ = effective mol. diff. of oil in fluidizing gas, cm²/s
 D_{eff} = effective diffusivity of oil vapor in particle, cm²/s
 D_K = Knudsen diffusivity, cm²/s
 $D_{K,eff}$ = effective Knudsen diffusivity, cm²/s
 E_b = axial diffusion coefficient in bubble phase, cm²/s
 E_e = axial diffusion coefficient in emulsion phase, cm²/s
 E_o = activation energy of coking reaction, cal/mol
 g = gravitational constant, 980.665 cm/s²
 k_e = first order chemical reaction constant in emulsion, s⁻¹
 k_p = mass transfer coef. between emulsion and part. surf., s⁻¹
 k_r = n-th order reaction constant in particle,
 (cm³)ⁿ/(cm²)(mol)ⁿ⁻¹s
 K_{bc} = bubble-cloud mass transfer interchange coefficient, s⁻¹
 K_{be} = bubble-emulsion mass transfer interchange coefficient, s⁻¹
 K_{ce} = cloud-emulsion mass transfer interchange coefficient, s⁻¹
 L = axial length of fluidized bed, cm
 M_1 = molecular weight, amu
 n = order of coking reaction
 r = radial position in particle, cm
 r_e = mean effective radius of pore in solid particle, cm
 P = pressure, atm
 R = radius of particle, cm
 R = gas constant, 82.057 atm*cm³/mol*K, 1.9872 cal/mol*K
 Re_{mf} = particle Reynolds number at minimum fluidizing velocity
 S_p = surface area of particle, cm²/g
 t = time, s
 T = temperature, K
 T_c = critical temperature, K
 U_b = velocity of emulsion gas, cm/s
 U_e = velocity of bubble gas, cm/s
 U_{mf} = minimum superficial fluidization velocity, cm/s
 U_o = superficial gas velocity, cm/s
 V_b = molar volume of oil at normal boiling temperature, cm³/mol

z = axial position in fluidized bed, cm

Greek Letters

ε = Lennard-Jones force constant

ε_{mf} = void fraction in the emulsion phase

θ = void fraction within particle

κ = Boltzmann Constant, 1.3805×10^{-16} erg/K

μ = gas viscosity, g/cm*s

ρ_g = density of gas, g/cm³

ρ_p = density of particle, g/cm³

σ = Lennard-Jones force constant

τ = tortuosity of the porous solid

Ω = Lennard-Jones collision integral

Subscripts

1 = oil vapor

2 = fluidizing medium (steam or nitrogen)

A.6 References

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A.7 Program Code

```

C*****
C*****
C*
C* THIS PROGRAM IS INTENDED TO MODEL THE TRANSIENT COKING BEHAVIOR *
C* OF PROCESSED OIL SHALES AND SIMILAR MATERIALS WHEN SUBJECTED TO *
C* FRESHLY GENERATED SHALE OIL VAPORS IN A DUAL FLUIDIZED BED REACTOR *
C*
C*****
C*****
C*
C*
C* INPUT PARAMETERS
C*
C*****
C*
C* T - TEMPERATURE OF COKING BED, K
C* P - REACTOR PRESSURE, ATM
C* FLUMW - MOLECULAR WEIGHT OF FLUIDIZING GAS, AMU
C* OILMW - MOLECULAR WEIGHT OF SHALE OIL VAPOR, AMU
C* STEAM - IS STEAM FLUIDIZING GAS, 1=YES, 0=NO
C* TCOIL - CRITICAL TEMPERATURE OF SHALE OIL VAPOR, K
C* VBOIL - MOLAR VOLUME OF OIL AT NORMAL BOILING TEMP, CM3/MOL
C* EKFLU - LENNARD-JONES FORCE CONSTANT FOR FLUIDIZING GAS, K
C* SIGFLU - LENNARD-JONES CONSTANT FOR FLUIDIZING GAS, ANGSTROMS
C* THETAP - VOID FRACTION OF PORES IN PARTICLE, CM3/CM3
C* TORTP - PARTICLE TORTUOSITY, DIMENSIONLESS
C* SA - PARTICLE SURFACE AREA, CM2/G
C* AREA - EXTERNAL SA OF PARTICLE PER BED VOLUM, CM2/CM3
C* RHOP - PARTICLE BULK DENSITY, G/CM3
C* DP - MEAN PARTICLE DIAMETER, CM
C* DB - BUBBLE DIAMETER, CM
C* EMF - VOID FRACTION OF EMULSION, DIMENSIONLESS
C* XAREA - CROSS SECTIONAL AREA OF FLUIDIZED BED, CM2
C* FLOW - FLOWRATE OF FLUIDIZING GAS AT 273 K AND 1 ATM, CM3/S
C* EE - DIFFUSION COEFFICIENT IN EMULSION PHASE, CM2/S
C* EB - DIFFUSION COEFFICIENT IN BUBBLE PHASE, CM2/S
C* Y - LOGARITHMIC MEAN FRACTION OF NONDIFFUSING COMPONENT, DIM'LESS*
C* BEDLEN - BED HEIGHT, CM
C* FEEDRATE - SHALE FEEDRATE, G/S
C*
C*****
C*****
C*
C*
C* CONSTANTS
C*
C*****
C*
C* BOLTZ - BOLTZMANN CONSTANT, 1.3805E-16 ERG/K
C* RGAS - GAS CONSTANT, 82.057 (ATM*CM3)/(GMOL*K)
C* GRAV - ACCELERATION OF GRAVITY, 980.665 CM/S2
C*
C*****
C*****
C*
C*
C* DERIVED PARAMETERS
C*
C*****
C*
C* D12 - DIFFUSION COEFFICIENT FOR OIL IN FLUIDIZING GAS, CM2/S
C*

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C*      EKOIL - LENNARD-JONES FORCE CONSTANT FOR OIL, K      *
C*      SIGOIL - LENNARD-JONES SIZE PARAMETER FOR OIL VAPOR, ANGSTROMS *
C*      OMEGAD - LENNARD-JONES COLLISION INTEGRAL          *
C*      EP12 - LENNARD-JONES PARAMETER KT/E12 FOR OIL/FLUID. GAS PAIR *
C*      SIG12 - L-J SIZE PARAMETER FOR OIL/FLUIDIZING GAS PAIR *
C*      D12EFF - EFFECTIVE DIFFUSIVITY FOR OIL/GAS PAIR, CM2/S *
C*      REFF - EFFECTIVE PORE RADIUS, CM                    *
C*      DK - KNUDSEN DIFFUSIVITY, CM2/S                    *
C*      DKEFF - EFFECTIVE KNUDSEN DIFFUSIVITY, CM2/S        *
C*      DEFF - OVERALL EFFECTIVE DIFFUSIVITY, CM2/S         *
C*      RHOGAS - DENSITY OF FLUIDIZING GAS, G/CM3           *
C*      VISC - VISCOSITY OF FLUIDIZING GAS, G/CM*S          *
C*      REMF - REYNOLDS NUMBER AT MIN. FLUIDIZATION VELOCITY, DIM'LESS *
C*      UMF - MINIMUM SUPERFICIAL FLUIDIZING GAS VELOCITY, CM/S *
C*      UO - SUPERFICIAL GAS VELOCITY, CM/S                 *
C*      GA - GA NUMBER, DIMENSIONLESS                       *
C*      UB - BUBBLE VELOCITY, CM/S                          *
C*      BCBK - INTERCHANGE BETWEEN BUBBLE AND CLOUD, 1/S   *
C*      CEBK - INTERCHANGE BETWEEN CLOUD AND EMULSION, 1/S *
C*      BEBK - INTERCHANGE BETWEEN BUBBLE AND EMULSION, 1/S *
C*      SHM - SHERWOOD NUMBER AT UMF, DIMENSIONLESS         *
C*      SC - SCHMIDT NUMBER, DIMENSIONLESS                  *
C*      PARTK - MASS TRANSFER COEFFICIENT TO PARTICLE, CM/S *
C*      CIN - INLET OIL VAPOR CONCENTRATION, GMOL/CM3       *
C*                                                           *
C*****
C*****
C*                                                           *
C*      VARIABLES                                           *
C*                                                           *
C*****
C*                                                           *
C*      Z - AXIAL LENGTH, CM                                *
C*      R - RADIAL COORDINATE OF PARTICLE, CM               *
C*      CB - OIL VAPOR CONCENTRATION IN BUBBLE PHASE, G/CM3 *
C*      CE - OIL VAPOR CONCENTRATION IN EMULSION PHASE, G/CM3 *
C*      CS - CARBON CONCENTRATION ON SOLID, G/CM3           *
C*      CPART - OIL VAPOR CONCENTRATION INSIDE PARTICLE, G/CM3 *
C*                                                           *
C*****
C*****
C
C      MAIN PROGRAM
C
C      IMPLICIT REAL*8(A-H,O-Z)
C      IMPLICIT INTEGER(I-N)
C      PARAMETER (NR=11,IWKR=16*NR+50,NZ=11,IWKZ=16*NZ+50)
C      DIMENSION CE(NZ),WORKZ(IWKZ),ZVAL(NZ)
C      DIMENSION CP(NR),WORKR(IWKR),RVAL(NR)
C      INTRINSIC FLOAT
C      EXTERNAL D03PAF
C      COMMON /INDEX/ KOUNT
C      COMMON /BLKNAG/ DEFF,THETAP,SA,RATE,UMF,EMF,
+      PARTK,AREA,CPR,CAVG,EE,DP,RHOP,BEDLEN,CIN
C
C
C      INPUT PARAMETERS
C
C      T=873.
C      P=1.
C      FLUMW=28.
C      OILMW=400.
C      STEAM=0.0

```



```

TCOIL=823.
VBOIL=475.
EKFLU=71.4
SIGFLU=3.798
THETAP=.5
TORTP=2.
SA=1.2D5
DP=0.08
BEDLEN=7.6D0
FEEDRATE=0.2D0
AREA=3.14/2./DP
RHOP=2.3
DB=1.0
EMF=0.6
XAREA=33.4186
FLOW=750.0
EE=0.1
EB=0.0
Y=1.0
C
BOLTZ=1.3805D-16
RGAS=82.057
GRAV=980.665
C
C
C
ESTIMATION OF GASEOUS DIFFUSIVITY
C
SIGOIL=1.18*VBOIL**(1./3.)
EKOIL=TCOIL/1.3
SIG12=0.5*(SIGOIL+SIGFLU)
EP12=BOLTZ*T/DSQRT(EKOIL*BOLTZ*EKFLU)
IF (EP12 .LE. 4 .AND. EP12 .GE. 0.3) OMEGAD=EXP((1.758933-
+ .70481905*EP12)/(1. +1.8946479*EP12))
IF (EP12 .GT. 4 .AND. EP12 .LE. 400) OMEGAD=EXP(.052955551-
+ .15495455*LOG(EP12)+.61381956/EP12/EP12)
IF (EP12 .LT. 0.3) OMEGAD=2.662
IF (EP12 .GT. 400) OMEGAD=0.417
D12=0.001858*T**1.5*DSQRT((FLUMW+OILMW)/FLUMW/OILMW)/(P*SIG12*
+SIG12*OMEGAD)
D12EFF=D12*THETAP/TORTP
C
C
C
ESTIMATION OF KNUDSEN DIFFUSIVITY
C
REFF=2.*THETAP/(SA*RHOP)
DK=9700*REFF*DSQRT(T/OILMW)
DKEFF=DK*THETAP/TORTP
C
C
C
ESTIMATION OF OVERALL EFFECTIVE DIFFUSIVITY
C
DEFF=1./(1./DKEFF+1./D12EFF)
C
C
C
DETERMINATION OF VISCOSITY OF FLUIDIZING GAS AT REACTION TEMP.
C
IF (STEAM .NE. 1.0) VISC=1./(0.000471996-2.4028D-7*T)
ELSE VISC=-262.52381+3.857142857*T
VISC=1.0D-7*VISC
C
C
C
DETERMINE MINIMUM FLUIDIZATION VELOCITY
C
RHOGAS=P*FLUMW/RGAS/T

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GA=DP**3.*RHOGAS*(RHOP-RHOGAS)*GRAV/(VISC*VISC)
REMF=DSQRT(33.7*33.7+0.0408*GA)-33.7
UMF=VISC*REMF/(DP*RHOGAS)

C
C
C
C DETERMINE SUPERFICIAL GAS VELOCITY IN COKING BED
C
C U0=FLOW/XAREA*T/273.
C
C
C DETERMINE BUBBLE VELOCITY
C
C UB=U0-UMF+.711*DSQRT(GRAV*DB)
C
C
C DETERMINE BUBBLE-TO-CLOUD COEFFICIENT
C
C BCBK=4.5*UMF/DB+5.85*DSQRT(D12)*GRAV**.25/DB**1.25
C
C
C DETERMINE CLOUD-TO-EMULSION COEFFICIENT
C
C CEBK=6.78*DSQRT(EMF*D12*UB/DB**3.)
C
C
C OVERALL INTERCHANGE COEFFICIENT
C
C BEBK=1./(1./BCBK+1./CEBK)
C
C
C DETERMINE MASS TRANSFER COEFFICIENT TO PARTICLE
C
C SC=VISC/RHOP/D12
C SHM=2.+6*SC**(1./3.)*DSQRT(REMF)
C PARTK=SHM*D12/DP/Y
C
C
C CALCULATE THE COKING RATE CONSTANT
C
C RATE=2.0D6*DEXP(-19270.0/T)
C
C
C CALCULATE THE INLET OIL VAPOR CONCENTRATION
C
C CIN=FEEDRATE*0.08/OILMW/U0/XAREA
C
C
C PRINT INPUT CONDITIONS AND DERIVED PARAMETERS
C
C WRITE (9,91) T,SA,THETAP
C WRITE (9,93) D12EFF
C WRITE (9,95) DKEFF
C WRITE (9,97) DEFF
C WRITE (9,98) VISC,GA,REMF
C WRITE (9,99) UMF,U0
C WRITE (9,100) UB
C WRITE (9,101) BCBK,CEBK,BEBK
C WRITE (9,103) PARTK
C WRITE (9,104) CIN
C WRITE (9,105) SC,SHM
C
91 FORMAT (1X,'TEMP= ',F6.0,' SURF AREA= ',D10.4,' POROSITY= ',F8.3)
93 FORMAT (1X,'EFFECTIVE MOLECULAR DIFFUSIVITY= ',D10.4)
95 FORMAT (1X,'EFFECTIVE KNUDSEN DIFFUSIVITY= ',D10.4)
97 FORMAT (1X,'EFFECTIVE OVERALL DIFFUSIVITY= ',D10.4)
98 FORMAT (1X,'VISC= ',D10.4,' GA= ',D10.4,' REMF= ',D10.4)

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99  FORMAT (1X,'MINIMUM FLUIDIZING GAS VELOCITY= ',F6.2,
+      ' SUP GAS VEL= ',F6.2)
100  FORMAT (1X,'BUBBLE VELOCITY= ', F6.2)
101  FORMAT (1X,2D10.4,'BUBBLE-EMULSION INTERCHANGE COEFF= ',D10.4)
103  FORMAT (1X,'MASS TRANSFER COEFF= ',D10.4)
104  FORMAT (1X,'INLET OIL VAPOR CONCENTRATION= ',D10.4)
105  FORMAT (1X,'SCHMIDT= ',D10.4,' SHERWOOD= ',D10.4)
C*****
C*
C*  PERFORM NUMERICAL INTEGRATION
C*
C*****
C
C  PARAMETERS IN R DIRECTION
C
C      MR=1
C      AR=0.0D0
C      BR=1.0D0
C      DR=(BR-AR)/(NR-1)
C
C  INITIAL CONDITIONS AT T0 FOR CP
C
C      DO 10 I=1,NR
C          CP(I)=0.0D0
C          RVAL(I)=I*DR-DR
10  CONTINUE
C
C  PARAMETERS IN Z DIRECTION
C
C      MZ=0
C      AZ=0.0D0
C      BZ=1.0D0
C      DZ=(BZ-AZ)/(NZ-1)
C      CAVG=1.0D0
C
C  INITIAL CONDITIONS AT T0 FOR CE
C
C      DO 20 I=1,NZ
C          CE(I)=1.0D0
C          ZVAL(I)=I*DZ-DZ
20  CONTINUE
C
C      TFINAL=1.0D0
C      TINC=0.1D0
C      TOUT=0.0D0
25  TS=TOUT
C      TOUT=TINC+TS
C      TSZ=TS
C      TOUTZ=TOUT
C      ACC=1.0D-3
C      IND=0
C      IFAIL=-1
C      KOUNT=0
C
C      CALL D03PAF(MR,AR,BR,TS,TOUT,CP,NR,ACC,WORKR,IWKR,IND,IFAIL)
C
C      IF (IFAIL.NE. 0) GO TO 1000
C      CPR=CP(NR)
C      INDZ=0
C      IFAILZ=-1
C      KOUNT=1
C
C      CALL D03PAF(MZ,AZ,BZ,TSZ,TOUTZ,CE,NZ,ACC,WORKZ,IWKZ,INDZ,IFAILZ)

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C      IF (IFAILZ .NE. 0) GO TO 1000
      CAVG=0.0D0
      DO 30 I=1,NZ
        CAVG=CAVG+CE(I)
30     CONTINUE
      CAVG=CAVG/NZ
C
      WRITE (9,995) IFAIL,TOUT,IFAILZ,TOUTZ
      WRITE (9,996)
C
      WRITE (9,997) (I,RVAL(I),CP(I), I=1,NR)
      WRITE (9,998)
      WRITE (9,999) (I,ZVAL(I),CE(I), I=1,NZ)
      IF (TOUT .LT. TFINAL) GO TO 25
      GO TO 200
1000   CONTINUE
      WRITE (9,9990)
      WRITE (9,9991) IFAIL,TOUT,IFAILZ,TOUTZ,KOUNT
C
995    FORMAT('IFAIL=',1X,I5,2X,'TOUT=',1X,E10.1,1X,
+ 'IFAILZ=',1X,I5,2X,'TOUTZ=',1X,E10.1)
996    FORMAT(14X,'R',12X,'CP ')
997    FORMAT(I8,2E14.6)
998    FORMAT(14X,'Z',12X,'CE ')
999    FORMAT(I8,2E14.6)
9990   FORMAT('EARLY EXIT!!!!!!!!!!!!!!!!!!!!')
9991   FORMAT('IFAIL=',1X,I5,2X,'TOUT=',1X,E10.1,1X,
+ 'IFAILZ=',1X,I5,2X,'TOUTZ=',1X,E10.1,1X,'KOUNT=',1X,I5)
200    CONTINUE
      END
      SUBROUTINE PDEF(X,T,U,DUX,F,G)
      IMPLICIT REAL*8(A-H,O-Z)
      IMPLICIT INTEGER(I-N)
      COMMON /INDEX/ KOUNT
      COMMON /BLKNAG/ DEFF,THETAP,SA,RATE,UMF,EMF,
+ PARTK,AREA,CPR,CAVG,EE,DP,RHOP,BEDLEN,CIN
      IF (KOUNT .EQ. 1) GO TO 300
      F=8./X*DEFF*DUX/THETAP/DP/DP-SA*RATE*U*RHOP/THETAP
      G=4.*DEFF/THETAP/DP/DP
      RETURN
300    CONTINUE
      F=-UMF*DUX/BEDLEN-(1.0D0-EMF)/EMF*PARTK*AREA*(U-CPR)
      G=EE/BEDLEN/BEDLEN
      RETURN
      END
      SUBROUTINE BNDY (T,U,IBND,P,Q,R)
      IMPLICIT REAL*8 (A-H,O-Z)
      IMPLICIT INTEGER (I-N)
      COMMON /INDEX/ KOUNT
      COMMON /BLKNAG/ DEFF,THETAP,SA,RATE,UMF,EMF,
+ PARTK,AREA,CPR,CAVG,EE,DP,RHOP,BEDLEN,CIN
      IF (KOUNT .EQ. 1) GO TO 400
      P=0.0
      IF (IBND .EQ. 0) THEN
        Q=2.0*CIN/DP
        R=0.0
      ELSE
        Q=2*DEFF/DP
        R=PARTK*(CAVG-U)
      ENDIF
      RETURN
400    CONTINUE

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```

IF (IBND .EQ. 0) THEN
  P=1.0
  Q=0.0
  R=1.0
  ELSE
  P=0.0
  Q=CIN/BEDLEN
  R=0.0
  ENDIF
RETURN
END
TEMP= 873. SURF AREA= 0.1200D+06 POROSITY= 0.500
EFFECTIVE MOLECULAR DIFFUSIVITY= 0.2081D-01
EFFECTIVE KNUDSEN DIFFUSIVITY= 0.1298D-01
EFFECTIVE OVERALL DIFFUSIVITY= 0.7994D-02
VISC= 0.3813D-03 GA= 0.3103D+04 REMF= 0.1829D+01
MINIMUM FLUIDIZING GAS VELOCITY= 22.31 SUP GAS VEL= 71.77
BUBBLE VELOCITY= 71.73
0.1098D+030.1283D+02BUBBLE-EMULSION INTERCHANGE COEFF= 0.1149D+02
MASS TRANSFER COEFF= 0.2187D+01
INLET OIL VAPOR CONCENTRATION= 0.1668D-07
SCHMIDT= 0.1992D-02 SHERWOOD= 0.2102D+01
IFAIL= 0 TOUT= 0.1E+00 IFAILZ= 0 TOUTZ= 0.1E+00
      R      CP
1 0.000000E+00 0.588256E-01
2 0.100000E+00 0.630609E-01
3 0.200000E+00 0.694727E-01
4 0.300000E+00 0.818028E-01
5 0.400000E+00 0.101575E+00
6 0.500000E+00 0.131756E+00
7 0.600000E+00 0.177061E+00
8 0.700000E+00 0.244831E+00
9 0.800000E+00 0.346439E+00
10 0.900000E+00 0.499520E+00
11 0.100000E+01 0.731494E+00
      Z      CE
1 0.000000E+00 0.100000E+01
2 0.100000E+00 0.844549E+00
3 0.200000E+00 0.780567E+00
4 0.300000E+00 0.757064E+00
5 0.400000E+00 0.749693E+00
6 0.500000E+00 0.747695E+00
7 0.600000E+00 0.747222E+00
8 0.700000E+00 0.747125E+00
9 0.800000E+00 0.747107E+00
10 0.900000E+00 0.747104E+00
11 0.100000E+01 0.747104E+00
IFAIL= 0 TOUT= 0.2E+00 IFAILZ= 0 TOUTZ= 0.2E+00
      R      CP
1 0.000000E+00 0.462086E-01
2 0.100000E+00 0.495172E-01
3 0.200000E+00 0.545283E-01
4 0.300000E+00 0.641683E-01
5 0.400000E+00 0.796339E-01
6 0.500000E+00 0.103251E+00
7 0.600000E+00 0.138716E+00
8 0.700000E+00 0.191778E+00
9 0.800000E+00 0.271347E+00
10 0.900000E+00 0.391233E+00
11 0.100000E+01 0.572912E+00
      Z      CE
1 0.000000E+00 0.100000E+01
2 0.100000E+00 0.754739E+00

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3	0.200000E+00	0.650510E+00			
4	0.300000E+00	0.608888E+00			
5	0.400000E+00	0.592943E+00			
6	0.500000E+00	0.586968E+00			
7	0.600000E+00	0.584813E+00			
8	0.700000E+00	0.584075E+00			
9	0.800000E+00	0.583835E+00			
10	0.900000E+00	0.583765E+00			
11	0.100000E+01	0.583735E+00			
IFAIL=	0	TOUT=	0.3E+00	IFAILZ=	0
	R	CP		TOUTZ=	0.3E+00
1	0.000000E+00	0.379863E-01			
2	0.100000E+00	0.407276E-01			
3	0.200000E+00	0.448767E-01			
4	0.300000E+00	0.528546E-01			
5	0.400000E+00	0.656456E-01			
6	0.500000E+00	0.851684E-01			
7	0.600000E+00	0.114474E+00			
8	0.700000E+00	0.158310E+00			
9	0.800000E+00	0.224033E+00			
10	0.900000E+00	0.323048E+00			
11	0.100000E+01	0.473087E+00			
	Z	CE			
1	0.000000E+00	0.100000E+01			
2	0.100000E+00	0.697138E+00			
3	0.200000E+00	0.569222E+00			
4	0.300000E+00	0.516483E+00			
5	0.400000E+00	0.495059E+00			
6	0.500000E+00	0.486489E+00			
7	0.600000E+00	0.483108E+00			
8	0.700000E+00	0.481792E+00			
9	0.800000E+00	0.481281E+00			
10	0.900000E+00	0.481106E+00			
11	0.100000E+01	0.480990E+00			
IFAIL=	0	TOUT=	0.4E+00	IFAILZ=	0
	R	CP		TOUTZ=	0.4E+00
1	0.000000E+00	0.330997E-01			
2	0.100000E+00	0.354706E-01			
3	0.200000E+00	0.390613E-01			
4	0.300000E+00	0.459688E-01			
5	0.400000E+00	0.570503E-01			
6	0.500000E+00	0.739724E-01			
7	0.600000E+00	0.993831E-01			
8	0.700000E+00	0.137402E+00			
9	0.800000E+00	0.194413E+00			
10	0.900000E+00	0.280310E+00			
11	0.100000E+01	0.410481E+00			
	Z	CE			
1	0.000000E+00	0.100000E+01			
2	0.100000E+00	0.659244E+00			
3	0.200000E+00	0.515755E+00			
4	0.300000E+00	0.456101E+00			
5	0.400000E+00	0.431404E+00			
6	0.500000E+00	0.421253E+00			
7	0.600000E+00	0.417107E+00			
8	0.700000E+00	0.415427E+00			
9	0.800000E+00	0.414735E+00			
10	0.900000E+00	0.414495E+00			
11	0.100000E+01	0.414297E+00			
IFAIL=	0	TOUT=	0.5E+00	IFAILZ=	0
	R	CP		TOUTZ=	0.5E+00
1	0.000000E+00	0.295929E-01			
2	0.100000E+00	0.317328E-01			

3	0.200000E+00	0.349732E-01					
4	0.300000E+00	0.412060E-01					
5	0.400000E+00	0.512031E-01					
6	0.500000E+00	0.664655E-01					
7	0.600000E+00	0.893780E-01					
8	0.700000E+00	0.123650E+00					
9	0.800000E+00	0.175030E+00					
10	0.900000E+00	0.252429E+00					
11	0.100000E+01	0.369703E+00					
	Z	CE					
1	0.000000E+00	0.100000E+01					
2	0.100000E+00	0.635156E+00					
3	0.200000E+00	0.481745E+00					
4	0.300000E+00	0.417489E+00					
5	0.400000E+00	0.390620E+00					
6	0.500000E+00	0.379449E+00					
7	0.600000E+00	0.374820E+00					
8	0.700000E+00	0.372915E+00					
9	0.800000E+00	0.372108E+00					
10	0.900000E+00	0.371831E+00					
11	0.100000E+01	0.371577E+00					
IFAIL=	0	TOUT=	0.6E+00	IFAILZ=	0	TOUTZ=	0.6E+00
	R	CP					
1	0.000000E+00	0.277178E-01					
2	0.100000E+00	0.297025E-01					
3	0.200000E+00	0.327085E-01					
4	0.300000E+00	0.384911E-01					
5	0.400000E+00	0.477681E-01					
6	0.500000E+00	0.619347E-01					
7	0.600000E+00	0.832076E-01					
8	0.700000E+00	0.115036E+00					
9	0.800000E+00	0.162764E+00					
10	0.900000E+00	0.234676E+00					
11	0.100000E+01	0.343652E+00					
	Z	CE					
1	0.000000E+00	0.100000E+01					
2	0.100000E+00	0.620402E+00					
3	0.200000E+00	0.460673E+00					
4	0.300000E+00	0.393395E+00					
5	0.400000E+00	0.365125E+00					
6	0.500000E+00	0.353298E+00					
7	0.600000E+00	0.348357E+00					
8	0.700000E+00	0.346306E+00					
9	0.800000E+00	0.345426E+00					
10	0.900000E+00	0.345125E+00					
11	0.100000E+01	0.344836E+00					
IFAIL=	0	TOUT=	0.7E+00	IFAILZ=	0	TOUTZ=	0.7E+00
	R	CP					
1	0.000000E+00	0.264020E-01					
2	0.100000E+00	0.282927E-01					
3	0.200000E+00	0.311562E-01					
4	0.300000E+00	0.366649E-01					
5	0.400000E+00	0.455025E-01					
6	0.500000E+00	0.589984E-01					
7	0.600000E+00	0.792641E-01					
8	0.700000E+00	0.109585E+00					
9	0.800000E+00	0.155053E+00					
10	0.900000E+00	0.223559E+00					
11	0.100000E+01	0.327375E+00					
	Z	CE					
1	0.000000E+00	0.100000E+01					
2	0.100000E+00	0.611780E+00					
3	0.200000E+00	0.447850E+00					

4	0.300000E+00	0.378666E+00			
5	0.400000E+00	0.349534E+00			
6	0.500000E+00	0.337298E+00			
7	0.600000E+00	0.332158E+00			
8	0.700000E+00	0.330013E+00			
9	0.800000E+00	0.329085E+00			
10	0.900000E+00	0.328769E+00			
11	0.100000E+01	0.328457E+00			
IFAIL=	0	TOUT= 0.8E+00	IFAILZ=	0	TOUTZ= 0.8E+00
	R	CP			
1	0.000000E+00	0.254204E-01			
2	0.100000E+00	0.272593E-01			
3	0.200000E+00	0.300436E-01			
4	0.300000E+00	0.353980E-01			
5	0.400000E+00	0.439844E-01			
6	0.500000E+00	0.570907E-01			
7	0.600000E+00	0.767632E-01			
8	0.700000E+00	0.106187E+00			
9	0.800000E+00	0.150297E+00			
10	0.900000E+00	0.216745E+00			
11	0.100000E+01	0.317429E+00			
	Z	CE			
1	0.000000E+00	0.100000E+01			
2	0.100000E+00	0.606372E+00			
3	0.200000E+00	0.439856E+00			
4	0.300000E+00	0.369522E+00			
5	0.400000E+00	0.339867E+00			
6	0.500000E+00	0.327377E+00			
7	0.600000E+00	0.322112E+00			
8	0.700000E+00	0.319908E+00			
9	0.800000E+00	0.318949E+00			
10	0.900000E+00	0.318623E+00			
11	0.100000E+01	0.318297E+00			
IFAIL=	0	TOUT= 0.9E+00	IFAILZ=	0	TOUTZ= 0.9E+00
	R	CP			
1	0.000000E+00	0.251338E-01			
2	0.100000E+00	0.269307E-01			
3	0.200000E+00	0.296523E-01			
4	0.300000E+00	0.348879E-01			
5	0.400000E+00	0.432881E-01			
6	0.500000E+00	0.561174E-01			
7	0.600000E+00	0.753810E-01			
8	0.700000E+00	0.104214E+00			
9	0.800000E+00	0.147427E+00			
10	0.900000E+00	0.212598E+00			
11	0.100000E+01	0.311216E+00			
	Z	CE			
1	0.000000E+00	0.100000E+01			
2	0.100000E+00	0.602709E+00			
3	0.200000E+00	0.434627E+00			
4	0.300000E+00	0.363604E+00			
5	0.400000E+00	0.333622E+00			
6	0.500000E+00	0.320973E+00			
7	0.600000E+00	0.315630E+00			
8	0.700000E+00	0.313390E+00			
9	0.800000E+00	0.312413E+00			
10	0.900000E+00	0.312081E+00			
11	0.100000E+01	0.311746E+00			
IFAIL=	0	TOUT= 0.1E+01	IFAILZ=	0	TOUTZ= 0.1E+01
	R	CP			
1	0.000000E+00	0.252358E-01			
2	0.100000E+00	0.269835E-01			
3	0.200000E+00	0.296374E-01			

4	0.300000E+00	0.347533E-01
5	0.400000E+00	0.429843E-01
6	0.500000E+00	0.555860E-01
7	0.600000E+00	0.745497E-01
8	0.700000E+00	0.102959E+00
9	0.800000E+00	0.145603E+00
10	0.900000E+00	0.209864E+00
11	0.100000E+01	0.307321E+00
	Z	CE
1	0.000000E+00	0.100000E+01
2	0.100000E+00	0.600327E+00
3	0.200000E+00	0.431292E+00
4	0.300000E+00	0.359839E+00
5	0.400000E+00	0.329648E+00
6	0.500000E+00	0.316898E+00
7	0.600000E+00	0.311507E+00
8	0.700000E+00	0.309245E+00
9	0.800000E+00	0.308256E+00
10	0.900000E+00	0.307921E+00
11	0.100000E+01	0.307580E+00

This cover stock is 30% post-consumer waste
and 30% pre-consumer waste, and is recyclable.