**The Development of an Integrated Multistage
Fluid Bed Retorting Process**

**Annual Report
September 1990 - September 1991**

**S. Carter
A. Vego
D. Taulbee
J. Stehn**

January 1992

Work Performed Under Cooperative Agreement: DE-FC21-90MC27286

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

By
University of Kentucky
Center for Applied Energy Research
Lexington, Kentucky

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EB

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

**The Development of an Integrated Multistage
Fluid Bed Retorting Process**

**Annual Report
September 1990 - September 1991**

**S. Carter
A. Vego
D. Taulbee
J. Stehn**

Work Performed Under Cooperative Agreement: DE-FC21-90MC27286

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433**

January 1992

ABSTRACT

This report summarizes the progress made on the development of an integrated multistage fluidized bed retorting process (KENTORT II) during the period of September 28, 1990 through September 30, 1991 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 is to design and test the KENTORT II process at the 50-lb/hr scale. The work performed during this year involved projects that will contribute physical and chemical data for the final design of the 50-lb/hr retort.

A cold-flow model of the 50-lb/hr retort was built and tested. The unit demonstrated stable operation and proper fluidization of all beds. Good control of solid recirculation up to the maximum design rate for each loop (200 and 500 lb/hr, respectively) was achieved simultaneously. Basically, the cold-flow model is completely operational and translation of the cold-flow design parameters to the design of the retort is ready to begin. In another aspect of the program, a study of the cracking and coking kinetics of shale oil vapors passed over processed shales was initiated. The addition of a mass spectrometer to the system to monitor total carbon, nitrogen and sulfur evolution in real-time was successful. Coking activities of processed shales were ranked as follows: combusted shale > gasified shale > pyrolyzed shale. Arrangements for conducting an evaluation of KENTORT-derived oil for asphalt applications were finalized and testing was initiated.

ACKNOWLEDGMENT

The work described herein was performed at the University of Kentucky Center for Applied Energy Research under Cooperative Agreement DE-FC21-90MC27286 with the Laramie Project Office of the Morgantown Energy Technology Center (METC), U.S. Department of Energy.

TABLE OF CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	v
EXECUTIVE SUMMARY	1
INTRODUCTION AND BACKGROUND	2
OBJECTIVES	4
COLD-FLOW MODELING	5
Introduction	5
Experimental	5
Apparatus	5
Procedure	9
Results and Discussion	9
Fine-Grained Solids	9
Coarse-Grained Solids	11
Blend of Coarse- and Fine-Grained Solids	13
Summary and Conclusions	13
CRACKING AND COKING KINETICS	14
Approach	14
Method Development	14
Introduction	14
Apparatus	15
Procedure	17
Measures of Carbon Uptake	18
Measurement of Carbon Deposition in Real-Time	19
Baseline Noise	20
Comparison of Carbon Uptake Measurement Methods	22
Coking Activity of Processed Shale and Related Minerals	24
Introduction	24
Materials	24
Results and Discussion	26
Conclusions	29
ASPHALT APPLICATIONS STUDIES	30
REFERENCES	32

LIST OF FIGURES

Figure 1.	Diagram of the 50-lb/hr cold-flow model.	6
Figure 2.	J-valve with liftpipe.	8
Figure 3.	Mass flowrate vs. pressure drop in pneumatic liftpipe.	8
Figure 4.	Types of pipe exits studied.	11
Figure 5.	Schematic diagram of the fluidized bed coking and cracking kinetics apparatus.	16
Figure 6.	QMS response to shale oil vapor exposure to combusted oil shale at 803 K for 15 minutes. a) CO_2/Ar ratio, and b) NO_2/Ar ratio.	19
Figure 7.	QMS response to shale oil vapor exposure to Ottawa sand at 853 K for 5 minutes. a) CO_2/Ar ratio, and b) absolute Ar intensity.	21
Figure 8.	Least-squares curve and line fit to the QMS CO_2/Ar data in Figure 6.	22
Figure 9.	Comparison of the two methods for determining carbon deposition for all substrates tested. The raw shale feedrate was 12 g/minute and substrate charge was approximately 100 g.	23
Figure 10.	Comparison of the two methods for determining carbon deposition for gasified shale, ∇ , and illite, $\square$	23
Figure 11.	Carbon deposition as measured by ultimate analysis under constant pyrolysis conditions for combusted, gasified, and pyrolyzed oil shales. The temperature of the coking bed is indicated.	26
Figure 12.	Carbon deposition as measured by ultimate analysis under constant pyrolysis conditions for kaolinite, illite, and Ottawa sand. The temperature of the coking bed is indicated.	27
Figure 13.	Carbon deposition at 933 K and 15 minutes solid residence time as a function of pore volume (neglecting micro-pores). Solids with initial carbon of less than 2%, $\circ$; solids with initial carbon of 7 to 10%, ∇ . . .	29

LIST OF TABLES

Table 1.	Average Operating Conditions for the Cold-Flow Model.	10
Table 2.	Ultimate Analyses (As-Received Basis) of the Raw Oil Shale and Coking Substrates (wt%).	25
Table 3.	Surface Area (m^2/g) and Pore Volume (cm^3/g) of Coking Substrates as Determined by N_2 Adsorption (micro) and Hg Porosimetry (macro and meso).	25

EXECUTIVE SUMMARY

The cold-flow model of the 50-lb/hr reactor was built, and following modification, has demonstrated stable operation and has achieved all of its targeted design parameters. The most important of which are the solid recycle rates to the pyrolyzer and the combustor, 200 and 500 lb/hr, respectively. Three particle size ranges (20x60 mesh, 8x20 mesh, and 8x60 mesh) were investigated and all performed satisfactorily in the system. In short, all aspects of the system work flawlessly, and the final design and construction of the 50-lb/hr retort is now ready to begin.

A method for evaluating the cracking and coking kinetics of shale oil vapors in a fluidized bed was developed. Carbon deposition is determined as a function of solid exposure time by two methods. The first method involves post-run analysis of the processed substrates. The second method provides real-time data by on-line measurement of vapor-phase carbon, nitrogen, and sulfur evolution with a mass spectrometer. Pyrolyzed, gasified, and combusted shales were studied as coking substrates, as were the principal silicate minerals in eastern U.S. Devonian shales. The coking activity of these materials were ranked as: kaolinite > combusted shale > illite > gasified shale > pyrolyzed shale > quartz. The effects of temperature were small indicating that pore diffusion plays a role in the rate of carbon deposition. It appears that the rate of carbon uptake is also influenced by the carbon content of the substrate.

The final strategy for evaluating KENTORT shale oil for asphalt applications was decided. The more viscous of the two oil samples (distilled ESP oil) is being tested as an asphalt modifier, and the less viscous sample (distilled composite oil) is being evaluated as an asphalt recycling agent. Testing of these materials was initiated late in the year, and these results will be available in the next Quarterly Technical Progress Report.

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. This enhancement varies according to shale type, but for most shales of the world it can be significant, and the oil shales contained in the U.S. are not exceptions. 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 (short solid residence time), 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, and an intermediate gasification stage was included in the KENTORT II design to utilize this excess carbon for synthesis gas production. 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 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 remaining carbon 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, but because of the small size of the unit, questions relative to scale-up remain. The most critical issue is the effect that scale-up will have on solid-recycle induced cracking and coking losses in the pyrolysis zone. A study of the kinetics of cracking and coking over various process solids has begun, and it is expected to contribute data for the design of the 50-lb/hr retort.

At the time of this writing, the program is still at an early stage, so the current focus is the generation of chemical and physical data to complete the design of the 50-lb/hr retort. This report will describe the efforts toward the testing of a full-scale, cold-flow of the 50-lb/hr retort, and the progress of the aforementioned cracking and coking kinetics study. The study of asphaltic applications for the heavy oil fraction from the KENTORT II process is also described.

OBJECTIVES

The primary objective of this program is to perform the research necessary to design, construct and test 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 Prototype Unit

- 1.1 - Cold-Flow Modeling of the Reactor
- 1.2 - Mini-Plant Investigation of Solids Recycle (Cracking and Coking Kinetics)
- 1.3 - Final Design and Construction of the KENTORT II Prototype Unit

Task 2 - Operation of the Prototype Unit

- 2.1 - Reactor and System Shakedown
- 2.2 - Prototype Operational Runs

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 Materials and Products for Utilization and Environmental Characteristics
 - 3.2.1- Characterization of KENTORT II Products for Asphalt Application
 - 3.2.2- Characterization of Nitrogen and Mineralogic Transformations in the KENTORT II Process
- 3.3 - Economic Evaluations

Efforts were directed toward subtasks 1.1, 1.2, and 3.2.1 during this reporting period. The objective of subtask 1.1 is to operate a full-scale cold-flow model of the 50-lb/hr unit so that the design of items such as distributor plates and standpipes can be tested before implementation. The objective of subtask 1.2 is to gain a better understanding of the kinetics of cracking and coking of shale oil vapor over recycled shale in the KENTORT II process. With this knowledge, the design and operation of the solid-recycle loop to the pyrolyzer may be adjusted to minimize oil losses. Once the results from subtasks 1.1 and 1.2 are available, the final design of the 50-lb/hr retort may be completed. The objective of subtask 3.2.1 is to examine the possible uses of KENTORT II-derived oil for asphalt applications.

COLD-FLOW MODELING

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,⁸ a full-scale cold-flow model has been built to verify the preliminary design of the 50-lb/hr retort.

An area of particular concern is the solid recycle loop between the gasification and pyrolysis zones. The most uncertain aspect of this recycle loop is 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 5-lb/hr 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 has been 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.

Experimental

Apparatus. The cold-flow model, Figure 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

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

are separated by gas distributors which are sandwiched between flanges. The total height of the unit is about 20 feet.

Due to the smaller diameter of the pyrolysis zone, the fluidizing gas velocity will be 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 actual retort 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 has a bleed-off tube mounted near the top of the gasification zone. By bleeding off some of the air from the gasifier before it enters the pyrolyzer, the gas velocity within the pyrolysis zone can be lowered. An orifice flowmeter measures the gas flowrate through the bleed-off tube.

The pyrolysis and the gasification zones each have a vertical baffle which splits the zones into two equally sized beds. The purpose of the baffles is 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 penetrate the gas distributors of the pyrolysis, gasification and combustion zones. These pipes provide passage for solids to flow from the upper to the lower sections of the unit. The standpipes also control the bed heights of each zone, where the height of the pipes are 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 2, which control the solid recirculation rates to the pyrolysis and the combustion zones, are connected to the angled standpipes extending from the gasification section. The J-valves deliver shale to vertical lift pipes which serve as pneumatic conveyers for the solids.

The liftgas velocity is held constant at 20 ft/s in each of the liftpipes. The pressure drop across the liftpipes is measured, and by using previously developed pressure drop correlations versus mass flowrate, Figure 3, the recirculation rates are determined. The

Figure 2. J-valve with liftpipe.

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

required capacity of the two recirculation loops has been determined from the anticipated range of temperatures to be studied in the 50-lb/hr retort.

A screwfeeder is used to meter the shale into the pyrolysis zone at a rate of 50 lb/hr. Solids leave the system through the exit port in the cooling zone, which also serves to control the bed height, and are collected in a sealed bin.

Procedure. The air blower is started and the air flowrate to each side of the system is 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 are 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 are larger than the particles, so these beds drain into the cooling zone when not fluidized.

The pressure difference between the gasification and the combustion zones is adjusted to zero. Aeration gas is then introduced to the J-valves to start the recirculation of solids. The screwfeeder motor is turned on, and solids are metered into the pyrolysis zone. Once proper bed levels are attained, the exit port in the cooling zone is 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 are 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.

Results and Discussion

Fine-Grained Solids. The fine-grained particles, 20x60 mesh retorted oil shale, showed very smooth flow and fluidization behavior. However, some adjustments to the original design had to be done to meet the specifications.

The recirculation loop for the pyrolysis zone was shown to work flawlessly. It 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 transports solids from the gasification to the combustion zone, needs an estimated 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 now be balanced while the required recirculation rate was achieved (see Table 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

Table 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

exit port 2 (see Figure 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 has been found that the pressure drop across the beds, measured in inches of water column, is roughly equivalent to the dense bed height in inches. As can be seen from Table 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.¹¹

Coarse-Grained Solids. The coarse-grained raw shale, 8x20 mesh, has 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 is 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 standpipe with its corresponding dipleg, also called a downcomer, is a crucial element in a circulation system for solids.^{12, 13, 14} 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.

Figure 4. Types of pipe exits studied.

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 is attached to the bottom end of the standpipe to make a restriction for the 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 needs 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 is well below what is needed to ensure stick-slip flow.¹³

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 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 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.

Summary and Conclusions

A full-scale cold-flow model of the 50-lb/hr KENTORT II reactor has been built and tested. The cold-flow model has been 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.

Following modifications, it has been demonstrated that the operation of the unit is 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 have been demonstrated to work flawlessly, and final design and construction of the 50-lb/hr retort is now ready to begin.

CRACKING AND COKING KINETICS

Approach

The objective of this task is to further our understanding of the chemistry and kinetics associated with solids-recycle retorting. A valved fluidized bed, designed to permit rapid exposure and isolation of fluidized solids to shale oil vapors, was utilized for this study. This technique allows a wide range of solid-recycle ratios to be simulated and permits the accurate control of the exposure time and temperature of the solids. The kinetics of coke deposition are determined by ultimate analysis of the solids before and after vapor contact. In addition, total carbon, nitrogen, and sulfur evolution are monitored in real-time with a mass spectrometer. Gasified and combusted shales are the primary substrates of interest, but other materials such as naturally occurring minerals have been tested. Once the kinetics portion of the study is completed, the reactor will be operated in a manner to simulate continuous solid-recycle conditions in order to collect sufficient products to conduct complete material balances and oil analyses.

Method Development

Introduction. Several workers have developed techniques to investigate heterogeneous cracking and coking of shale oil vapor, but all these methods lack the ability to deliver a representative shale oil vapor to the bed of solids at a steady rate. Levy et al.¹⁵ continuously injected Fischer assay shale oil into a reactor where the shale oil was first vaporized and then passed through a bed of solids. A disadvantage of this approach is that the vaporized shale oil does not necessarily have the same characteristics as the freshly generated shale oil vapors from pyrolysis. This is especially true for shale oils that contain large amounts of non-volatile residual material. Another approach, by Coburn et al.,¹⁶ entails the generation of a pulse of shale oil vapor in a fluidized bed pyrolyzer followed by passage of the vapor through a packed bed of solids. While this technique lends itself well to kinetic measurements, it suffers because the pyrolysis products differ in nature and concentration as a function of time. Rubel et al.¹⁷ utilized a technique where a packed bed pyrolyzer was in series with a packed bed of solids within the same furnace, subjecting the pyrolyzing shale and the solid substrate to the same heating profile. While this technique is excellent for comparative studies, its transient nature is not appropriate for kinetic measurements, nor does it readily simulate fluidized bed conditions.

The following sections describe a technique where shale oil vapors are generated in a fluidized bed pyrolyzer and are subsequently sent to another fluidized bed where secondary coking and cracking reactions are measured. Since the pyrolyzate is transferred quickly (within 1 s) and without condensation, non-catalyzed secondary reactions are minimized, and product loss reactions are thought to closely simulate those in a circulating solids fluidized bed reactor. At least four modes of operation are possible with this system, but only the coking kinetics mode will be discussed in detail. A

second mode of operation utilizes model compounds instead of shale oil vapor as the reactants. A third mode utilizes the continuous feed of solid substrate in order to collect significant quantities of product for subsequent study. Additionally, a fourth mode will involve continuous substrate feed with model compounds as reactants.

Apparatus. The apparatus consists of two vertically aligned fluidized beds (7.6-cm internal diameter) which share a common fluidizing medium and which are heated externally by two dual-zone (each zone independently controlled) electrical resistance furnaces (see Figure 5). The fluidizing gas, nitrogen in this study, is preheated in a separate furnace and introduced into the plenum chamber beneath the lower fluidized bed. Raw oil shale is metered by a nitrogen-purged screwfeeder into the lower fluidized bed operating at 803 K. The level of solids in the bed is held constant by a standpipe through which the pyrolyzed oil shale is removed from the reactor. The lower fluidized bed contains a baffle to narrow the residence time distribution of the solids.

In the upper portion of the apparatus, a vertical baffle divides the pipe into two unequal sections; one covers 73% of the cross sectional area and the other 27%. The larger section contains a fluidized bed of solids, and the smaller section provides a bypass-path for the fluidizing stream. The temperature of the upper fluidized bed is controlled independently from the pyrolysis bed. A semi-butterfly valve beneath the baffled section is used to select which of the routes the upward flowing vapors and gases will follow. A gas injection port is located on each side of the baffle so that gas-flow is maintained within each side of the reactor regardless of the butterfly valve position. The flow of balancing gas is important for four reasons: 1) the total flow of gas in the reactor remains constant regardless of the position of the semi-butterfly valve; 2) the upper bed always remains fluidized; 3) the balancing gas acts as a seal for the semi-butterfly valve which is not completely leak-free; and 4) the balancing gas may be different than the fluidizing gas and may serve as a pretreatment gas for the substrate. Switching the balancing gas is coordinated by a three-way valve connected in tandem with the semi-butterfly valve through a pneumatic valve actuator. Therefore, diverting the fluidizing gas occurs simultaneously with the change in injection point of the balancing gas. A purge gas (He or Ar) is introduced into the seal assembly of the semi-butterfly valve to both inhibit coke formation and serve as a tracer gas. This tracer gas facilitates mass spectrometer analyses by correcting for pressure surges, changing flowrates, and instrumental fluctuations.

Drains for the solids in the upper bed are located adjacent to the gas distributor and 5 cm and 10 cm above the distributor. In the kinetic mode of operation, the lowest port is used to drain the solids, and purge gas is flowed upward through the tube to prevent solids from exiting the bed prematurely. Processed solids are collected in a flask that has been evacuated and filled with an inert gas to prevent oxidation of the hot substrate. In the mode where solids are continuously fed to the upper bed, the bed height is maintained by one of the two angled standpipes located above the distributor (not shown in Figure 5).

Figure 5. Schematic diagram of the fluidized bed coking and cracking kinetics apparatus.

The balancing gas and the pyrolysis/fluidization stream are joined in the uppermost portion of the reactor and then sent to two insulated cyclones in series to remove entrained fines. Most of this gas stream is cooled, cleaned and vented, but a portion is sampled at approximately 773 K at the outlet of the second cyclone and drawn through a combustion tube. Oxygen is metered into the heated tube downstream of the sampling location, and to ensure thorough combustion, the majority of the tube is filled with a Pt/Al₂O₃ catalyst. The temperature of the combustion tube is maintained at approximately 873 K. The gases/vapors are withdrawn in a direction opposite to the main flow, so only very small particles can break away from the main fluid streamlines and enter the sampling tube.

Following combustion, a 0.3 mm fused silica capillary maintained at 550 K withdraws a small sample of the combustion gases. The combustion gases are 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 permits 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 include 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 (HC-to ensure adequate combustor performance). All selected masses were sampled at approximately 1.5 second intervals.

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

Once proper system operation has been verified, a weighed aliquot of substrate is loaded into the upper fluidized bed and allowed to reach thermal steady state. The heat-up time can vary from three to ten minutes depending on the solid being tested. The pressure drop across the bed is monitored because it is a direct indication of the mass of solids in the bed, and provides an on-line measure of the entrainment of particles from the bed. After conditions have again stabilized, QMS data collection is initiated. After at least 100 scans of the 9 selected masses have been collected, the semi-butterfly valve is rotated so that the upper bed of solids is fluidized by the gases and vapors from the lower bed (i.e. "fluidize" position). When the selected time interval has elapsed (5 to 15 minutes is typical), the valve is returned to the bypass position and the bed of solids is

immediately drained from the bed by halting the flow of purge gas to the drain pipe. Ten minutes are allowed for solids to completely drain from the reactor; most exit within one to two minutes. The solid receiver flask is removed and replaced with an empty one, which is then evacuated and purged with nitrogen before the procedure is repeated.

The batch of processed solids is weighed, and ultimate analyses are performed on each sample by standard methods. Surface area and pore volume measurements by Hg porosimetry and N₂ adsorption are 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, could be observed with minimal interference from variations in the measurement conditions that typically occur over the course of a run. These uncontrolled measurement variations include 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 a carefully metered tracer gas, it would be impractical to resolve elemental changes due to coking from those due to measurement variations.

Measures of Carbon Uptake. There are two independent measures of carbon deposition available in the kinetics mode of operation. One measure is obtained simply through elemental analysis of the coked substrate in comparison to the original substrate. An advantage of this method is that ultimate analysis is a reliable technique with well known standard errors. A disadvantage of post-run analysis of the solids is that numerous runs are 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 or short solid residence time, the analytical scatter of the ultimate analysis becomes significant. Therefore, a complementary measure of carbon deposition was wanted which could provide an on-line determination of coke formation and which would be more sensitive at low conversion.

Since only coke formation is of interest in this 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) for similar studies,^{3, 6, 18} but the response of the FID becomes increasingly nonlinear as the size of the hydrocarbon increases. In addition, the FID is not sensitive to heteroatoms. Because of these limitations, the combustion/QMS approach was adopted as described in the previous section. If combustion is complete, there should be no linearity problem in the range studied, and by monitoring the combusted pyrolysis products with a QMS, total N and S deposition can potentially be measured as well as C.

Measurement of Carbon Deposition in Real-Time. A typical coking sequence is illustrated by the CO_2/Ar ratio in Figure 6a. For all experiments, the ion of interest is normalized by the tracer gas in order to account for differences in sampling flowrates during the course of a run. Initially, helium was used as the tracer gas. However, it appeared to be skewing the response time due to its high rate of diffusion into the QMS, so the tracer gas was switched to argon. With the semi-butterfly valve in the bypass position, the CO_2/Ar ratio initially remains constant. Following the turn of the valve to the fluidize position, the ratio immediately drops to a minimum value before it gradually returns to an apparent asymptotic value. The initial plunge in the CO_2/Ar ratio is apparently due to the rapid transfer of oil vapor into the pores and subsequent adsorption onto the solids. The ratio then rises as the composition inside the pores nears the extraparticle concentration. Finally, when the valve is returned to the bypass position, the original baseline is restored. Similar response is observed for the NO_2/Ar ratio, and in most cases, the curves mirror the CO_2/Ar response almost exactly (Figure

Figure 6. QMS response to shale oil vapor exposure to combusted oil shale at 803 K for 15 minutes. a) CO_2/Ar ratio, and b) NO_2/Ar ratio.

6b). 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. Many of the SO_2/Ar response curves contained large baseline shifts that could not be explained by substrate exposure, and were unusable.

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. 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 7 illustrates that a reduction in the CO_2/Ar ratio can only be due to deposition onto the solids in the upper bed. Ottawa sand, which has little potential to induce coke formation, was used as the bed material, and no evidence of shale oil conversion is observable. Also shown in Figure 7 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 CO_2/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.

Baseline Noise. Obvious from Figures 6 and 7 is a large amount of baseline noise. Of the nine ion intensities monitored, the four that exhibit the most noise are 12(C), 44(CO_2), 46(NO_2), and 64(SO_2), and all originate primarily from pyrolysis of the oil shale. Other m/e signals such as 32(O_2), 28(N_2) and 40(Ar) were relatively more stable and represent gases that are 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 is 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 to reduce the pulsating nature of the feed. As a consequence, periodic oscillations in QMS response could no longer be discerned relative to screwfeeder speed. However, the feedrate of particles still exhibited relatively large fluctuations over short time intervals and still accounts for a portion of the observed noise. The chaotic nature of fluidized beds must also be considered as a significant source of noise. Another potential source of noise, although probably much less significant than the other two, is 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

Figure 7. QMS response to shale oil vapor exposure to Ottawa sand at 853 K for 5 minutes. a) CO_2/Ar ratio, and b) absolute Ar intensity.

entrainment presents greater problems than just the nuisance factor associated with dust accumulation in downstream equipment. The residual organic material on fine particles reaching the combustion tube rapidly combusts and produces oxides which generate spikes in the QMS response and create another source of noise. Special efforts made to exclude fines from the tube included adding a second cyclone and the reverse sampling tube to the apparatus. This served to significantly reduce, but not eliminate, fines entrainment.

In the coking kinetics apparatus, fines can 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 appears that the majority of the entrained solids originate from the coking bed. The mass of solid substrate lost from the bed following a coking sequence is roughly comparable to the amount of solids collected in the cyclones. The loss of solids by entrainment can be determined during operation by monitoring the pressure drop across the upper bed. In most cases, the majority of the solid loss occurs during the preheating period of the substrate, so there is little loss while the shale oil vapors are in contact with the tested substrate. Accordingly, the mass of each batch of substrate 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.

Although the baseline noise in the QMS data is 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 was 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. Because of the high noise levels, integration was not done directly, but a least-squares curve was fitted to the data and the area between the fitted curve and a least-squares line fitted to the baseline data was determined (see Figure 8). The 2-parameter functional form (excluding the intercept) that best fit the response curves for all runs was a decaying exponential form (Eq. 1).

$$C_{solid} = a + b(1 - \exp(-ct)) \quad (1)$$

No particular significance is placed on the form of the fitted equation because the purpose was to most accurately integrate the area under the curve. Modeling the data is planned for the future. The area under the QMS curve was related to the increase in carbon content of the substrate through a proportionality constant. 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.

Comparison of Carbon Uptake Measurement Methods. The QMS-determined carbon uptake data is compared with the data as determined by post-run analysis in Figure 9. While there is a significant amount of scatter, the data occur about the equity

Figure 8. Least-squares curve and line fit to the QMS CO_2/Ar data in Figure 6.

Figure 9. Comparison of the two methods for determining carbon deposition for all substrates tested. The raw shale feedrate was 12 g/minute and substrate charge was approximately 100 g.

line as would be expected. The scatter or deviation, however, was more pronounced for some substrates than others. For example, gasified oil shale, which contained approximately 7% carbon before the coking treatment, deviated more from the unity line than the illite sample which contained less than 1.5% C (Figure 10). For the gasified shale, the QMS data indicated more extensive coke deposition than the ultimate analysis. The likely reason for this phenomenon is that during preheating, especially at temperatures above 873 K, pyrolysis of the residual organic matter in the substrate may occur which will measurably lower the starting carbon content of the substrate and result in lower carbon deposition reported by post-run analysis. To a lesser extent, trace oxygen impurities in the fluidization gas may lead to analogous results.

Figure 10. Comparison of the two methods for determining carbon deposition for gasified shale, ∇ , and illite, $\square$.

Coking Activity of Processed Shale and Related Minerals

Introduction. 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.^{19, 20, 21, 22} Our interest in this area has been primarily focused on the coke inducing 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 and 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.

Materials. The master sample of oil shale utilized in this study was from the Cleveland Member of the Ohio Shale from northeastern Kentucky, USA (see raw shale analysis in Table 2). The shale was prepared to a size distribution of $-841\mu\text{m} +250\mu\text{m}$. This shale sample was used both for the production of shale oil vapors in the apparatus and as the starting material for the generation of pyrolyzed, gasified, and combusted shales, respectively. The production of the processed shales was performed 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. It is emphasized, however, that each type of processed shale was produced under a distinct set of conditions, and was not obtained by simply sampling the solids from operation of the KENTORT II process. By doing so, a complex mixture of solids, which had been subjected to various residence times in each of the zones, would have been obtained. The pyrolyzed shale was produced at 803K with nitrogen as the fluidizing gas; the gasified shale was produced at 1073K using steam; the combusted shale was generated in air at 973K. Ultimate analyses of these materials are given in Table 2.

The mineralogy of Devonian oil shales is reasonably consistent. The silicate fraction of the shale is composed primarily of illite, which constitutes about 2/3 of the minerals, followed by quartz (~20%) and the clay minerals, chlorite (~10%) and kaolinite (~5%).^{23, 24} Therefore, naturally occurring kaolinite, illite, and quartz samples were also tested as coking substrates. Pure chlorite is not amenable to fluidized bed processing and was not tested. Kaolin taken 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 distribution of $-841\mu\text{m} +250\mu\text{m}$. The quartz sample was unmodified Ottawa sand ($-841\mu\text{m} +600\mu\text{m}$). No other treatment was performed on these samples prior to testing. The surface area and porosity characteristics of all the coking substrates are listed in Table 3.

Table 2. Ultimate Analyses (As-Received Basis) of the Raw Oil Shale and Coking Substrates (wt%).

	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
Gasified Shale	7.3	0.2	0.6	0.4	91.0
Combusted Shale	1.6	0.2	0.7	0.2	95.9
Kaolin (kaolinite)	<0.1	1.6	0.6	<0.1	85.0
Huron Shale (illite)	0.2	0.6	0.6	1.4	92.9
Ottawa Sand (quartz)	<0.1	<0.1	0.3	<0.1	99.6

Table 3. Surface Area (m²/g) and Pore Volume (cm³/g) of Coking Substrates as Determined by N₂ Adsorption (micro) and Hg Porosimetry (macro and meso).

Pore Diameter	Surface Area (Pore Volume)			Total
	> 50 nm macro	2-50 nm meso	< 2 nm micro	
Pyrolyzed Shale	2.1 (0.125)	11.3 (0.030)	0.1 (0.000)	13.5 (0.155)
Gasified Shale	2.5 (0.164)	9.2 (0.024)	15.8 (0.034)	27.5 (0.221)
Combusted Shale	3.6 (0.230)	9.1 (0.032)	12.0 (0.058)	24.7 (0.319)
Kaolinite	8.2 (0.188)	13.9 (0.105)	1.1 (0.001)	23.2 (0.294)
Illite	1.0 (0.044)	8.1 (0.030)	0.8 (0.000)	9.9 (0.074)
Ottawa Sand	0.0 (0.000)	1.0 (0.001)	0.0 (0.001)	1.0 (0.002)

Results and Discussion. The method of operation in these tests accounts for the loss of hydrocarbons (oil and gas) due to deposition (coking) onto the tested substrates, but it does not reflect the effects of the substrates on cracking reactions (mainly vapor products). Future experiments are planned in which the substrate is fed continuously to the reactor so that the altered pyrolysis products can be collected and analyzed. In this continuous mode of operation the effects of substrate type on cracking reactions will be discernable.

The formation of coke on each of the substrates generally followed a power function relationship with time (see Figure 11). This is in general agreement with the classic work of Voorhies²⁵ and the logarithmic relationship given by Dumez and Froment.²⁶ The combusted oil shale displayed the highest coking activity relative to the gasified and pyrolyzed shales, Figure 11. The higher activity of combusted shale compared to pyrolyzed shale has been observed by several workers,^{19,20,21,22} and recently Rubel et al.¹⁷ reported that gasified shale had less reactivity than combusted shale. The reactivities of the processed shales in the present study are consistent with the hypothesis that carbon coverage of mineral surfaces retards additional carbon deposition.

Figure 11. Carbon deposition as measured by ultimate analysis under constant pyrolysis conditions for combusted, gasified, and pyrolyzed oil shales. The temperature of the coking bed is indicated.

Besides carbon content, the processed shales were different in surface area and pore volume characteristics which also appeared to affect their activity toward coke formation. Naturally occurring minerals, which are both low in carbon and represent a significant portion of the mineral matrix in eastern U.S. Devonian shales, were tested to facilitate the discernment of surface area effects without interference from high initial carbon content. The kaolinite sample displayed higher coking activity than illite, and coke deposition onto the Ottawa sand was barely detectable, Figure 12. These results are all consistent with the surface area and porosity data given in Table 3. The kaolinite has the most total surface area and pore volume compared to illite while the sand has basically no surface area or porosity. It is not clear from this data, however, which combination of surface-related parameters is responsible for the increased activity.

Since surface area and pore volume are not necessarily related from one solid to the next, they must be treated separately because they contribute differently to the process of carbon deposition. Surface area and the activity of the surface area are important because they affect the rate at which vapor inside the pores is adsorbed onto the surface. Total pore volume and the pore diameter distribution are important because they affect the rate of pore diffusion. It is assumed that surface area and pore

Figure 12. Carbon deposition as measured by ultimate analysis under constant pyrolysis conditions for kaolinite, illite, and Ottawa sand. The temperature of the coking bed is indicated.

volume associated with micro-pores (<2 nm dia.) are inaccessible to the large molecules which are mainly responsible for coke formation in the current study. It is expected, however, that a portion of the meso-pore surface area (2-50 nm dia.) and all of the macro-pore surface area (>50 nm dia.) are accessible to the largest hydrocarbons.

To illustrate that total surface area alone is not an appropriate measure of coking activity, consider that the carbon deposition onto gasified shale is much lower than combusted shale, but the total surface area of gasified shale is greater. When micro-pore surface area is neglected, the surface area of the combusted shale becomes slightly greater, but not enough to account for the difference in carbon uptake. The high initial carbon content of the gasified shale is the likely cause of this difference in activity. As another example, the total surface areas of the kaolinite and combusted shale are similar, as are the amounts of carbon deposition, which indicates that total surface area may be a good indicator of coking activity when the substrates have equivalent initial carbon contents. The assumption, however, that micro pores cannot provide access for coking, lowers significantly the value assigned as the available surface area for the combusted shale. The sum of the macro- and meso-pore surface areas of the kaolinite in this study is 74% greater than the combusted shale, but carbon deposition is only about 20% greater under otherwise similar conditions. Therefore, even with similar starting carbon content, available surface area is not the sole comparative measure of coking activity.

Pore volume, which has a large influence on the rate of gaseous diffusion in particles, is another important factor to consider. Carbon deposition appears to be related to pore volume (neglecting micro-pore volume) when the initial carbon content of the substrate is taken into account, Figure 13. The substrates with low initial carbon content, except for sand, displayed greater affinity for carbon deposition compared to the pyrolyzed and gasified shales. The effect of temperature on carbon deposition was small for all substrates, Figures 11 and 12, which provides more evidence that pore diffusion must substantially influence the coking rates for these materials.

For solid-recycle retorts, the small temperature effect on carbon deposition has important consequences. The same quantity of heat can be transferred by either recirculating high-temperature solids at a low rate or low-temperature solids at a high rate or some combination in between. Thus, to limit coke formation, it appears from these results that the former scenario is preferred because it reduces the substrate/vapor ratio while incurring only small temperature-related oil losses.

The result that gasified shale has lower coking activity than combusted shale is especially important for the KENTORT II process which recycles materials from the gasification zone to the pyrolysis zone. Combusted shale is also contained in the recycled solids, however, and the question arises concerning the effects of the gasification environment on the coking activity of combusted shale. Rubel et al.¹⁷ have indicated that steam treatment of combusted shale lowers its coking activity, but it is unclear what role steam played to produce this result. Instead of utilizing pure N₂ as the balancing gas for

Figure 13. Carbon deposition at 933 K and 15 minutes solid residence time as a function of pore volume (neglecting micro-pores). Solids with initial carbon of less than 2%, ○; solids with initial carbon of 7 to 10%, ▽.

the upper section of the reactor, steam (30% by volume) was blended with N₂ during the preheating period for a few runs in the present study. No significant effects were observed, but this may have been a result of the steam treatment being too mild. Runs will be performed where a more severely steam-treated combusted shale is studied.

Conclusions

The rate of carbon uptake declined as greater amounts of carbon were deposited onto the solids with time. The initial carbon content of the solid was also found to reduce the rate of coking. The data appears to suggest that once the mineral surfaces are covered by char, the subsequent adsorption and coking of oil vapor is slowed significantly. The relationship of pore volume (excluding micro-pores) to carbon deposition and the small temperature effect on coke uptake implicates pore diffusion as a rate influencing step as well. The following rank of coking activity was observed: kaolinite > combusted shale > illite > gasified shale > pyrolyzed shale > sand. The study of steam-treated combusted shale was inconclusive in the current study, but the steam-deactivation of combusted shale, as shown by other studies, and the lower activity of gasified shale indicates that the KENTORT II process is configured to minimize coking losses due to the recycle of processed shale to the pyrolysis zone.

ASPHALT APPLICATIONS STUDIES

The purpose of the task is to determine the feasibility of KENTORT II-derived eastern shale oil (ESO) for paving applications. During this period, the final strategy for the study was decided, and testing was initiated. Arrangements were made with the Kentucky Transportation Center (KTC) to evaluate the properties of binder-aggregate mixtures and the Western Research Institute (WRI) to evaluate the properties of binder (asphalt and asphalt-ESO blends). The Texas Transportation Institute has extracted and recovered aged asphalt for the study. The two ESO samples under examination were produced in the 3-inch diameter, 5-lb/hr KENTORT II reactor operated in the integrated gasification/combustion mode. Much of the testing has been completed, and a comprehensive summary of the work will be available in the next Quarterly Technical Progress Report. What follows is a brief outline of the evaluation strategy which is being employed.

Two oil streams, produced in the 5-lb/hr KENTORT prototype unit, were selected for study. The first, referred to as the 'hard' ESO, was a highly viscous material (3440 P @60° C) recovered in the electrostatic precipitator (ESP) from a series of runs in the 3-inch prototype. The second, referenced as the 'soft' ESO (8 P @60° C), was derived by blending portions of the total oil product from a similar series of runs and then subjecting the blend to a vacuum distillation prior to testing. These two oils were deliberately selected for study since it is believed they represent the types of material that would be readily available and most likely to be utilized for asphalt production in a commercial operation. Both samples were derived from the Cleveland Member of the Ohio shale as described before.

A test program was implemented to evaluate KENTORT oils in three different paving applications: asphalt cement, asphalt modifier, and asphalt recycling agent. Early results indicated that the latter two applications should be the focus of the work since rapid hardening of neat ESO seemed to exclude using this material directly as an asphalt cement. The testing program included a series of binder and mixture characterization procedures for evaluation of both short- and long-term performance potential.

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 centered 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 and aged asphalt mix (pavement recycling).

Evaluation as an asphalt additive involved rheological characterization of an AC-20 asphalt, a 7 wt. % blend of hard ESO and AC-20 asphalt, and neat hard ESO.

The rheological properties of the three samples were then remeasured and compared after they were subjected to an accelerated aging procedure. Part of the evaluation of ESO as an asphalt recycling agent entailed measuring the viscosity of an asphalt extracted from a laboratory-aged pavement mixture (see below), the soft ESO, and an AC-5 asphalt (representative of a commercial recycling agent). Two 'recycle' blends were then prepared by blending the laboratory-aged asphalt with 1) the soft ESO and 2) with the AC-5 asphalt for comparison. Rheological properties of the two blends were examined and compared in order to evaluate the recycling qualities of the soft ESO relative to those of a commercial agent.

The final test series was aimed at evaluating an asphalt mixture modified with ESO. 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 more conventionally modified asphalts 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.). During this project, several test strips were constructed from a single petroleum-derived 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 laboratory 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 was mixed with the hard ESO at the same proportions as the polymer modified mixtures in order to compare the behavior of the hard ESO modified asphalt to the asphalt 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 to test the soft ESO as a pavement recycling agent. Mixture characterization included a series of mechanical response tests on compacted specimens (Marshall procedure). Tests of tensile strength, resistance to moisture damage, and resistance to freeze-thaw damage were conducted on all ESO modified materials as well as on selected 'control' samples.

REFERENCES

1. Rubel, A.M., M.J. Margolis, J.K. Haley, and B.H. Davis, *1983 Eastern Oil Shale Symposium Proceedings*, 1983, IMMR83/089, University of Kentucky, Lexington, Ky.
2. Margolis, M.J., *1981 Eastern Oil Shale Symposium Proceedings*, 1981, University of Kentucky, IMMR82/066, Lexington, KY.
3. Richardson, J.H., E.B. Huss, L.L. Ott, J.E. Clarkson, M.O. Bishop, L.J. Gregory, and C.J. Morris, Lawrence Livermore National Laboratory, UCID-19548, 1982.
4. Ahmed, M.M., D.W. Parker, and D.H. Archer, *1982 Eastern Oil Shale Symposium Proceedings*, 1982, University of Kentucky, IMMR82/075, Lexington, KY.
5. Rubel, A.M. and S.D. Carter, *Preprints Div. Pet. Chem.*, ACS, 1984, 29, 202-208 (1).
6. Wallman, P.H., Tamm, P.W., and Spars, B.G., *ACS Symp. Ser. 163*, 1981, 93.
7. Bissel E.R., Burnham, A.K., and Braun, R.L., *I and EC Proc. Des. Dev.*, 1985, 24, 381.
8. Carter, S.D., Rubel, A.M., Robl, T.L., and Taulbee, D.N., 'The Development of the KENTORT II Process for Eastern U.S. Oil Shale,' 1990, Final Report for work performed under Contract No.: DE-FC21-86LC11086, DOE/LC/11086-2860.
9. Carter, S.D. and D.N. Taulbee, *Fuel Processing Technology*, 1985, 11, 251-272.
10. Robl, T.L., K. Cisler, G. Thomas, and D.W. Koppenaal, *1985 Eastern Oil Shale Symposium Proceedings*, 1985, University of Kentucky, KCERL/85-147, Lexington, Ky.
11. D. Kunii and O. Levenspiel, *Fluidization Engineering*, John Wiley & Sons, Inc., 1984.
12. L.S. Leung and P.J. Jones, "Coexistence of Fluidized Solids Flow and Packed Bed Flow in Standpipes," *Fluidization*, Cambridge University Press, 1978.
13. M.R. Judd and P.D. Dixon, "The Flow of Fine, Dense Solids Down a Vertical Standpipe," *Fluidization: Application to Coal Conversion Processes*, AIChE Symposium Series, No.176, Vol. 74, 1978.
14. D. Kunii and O. Levenspiel, *Fluidization Engineering*, Second Edition, Butterworth-Heinemann, 1991.
15. Levy, J.H., Mallon, R.G., and Wall, G.C., 'Proc. 3rd Australian Workshop on Oil Shale,' Lucas Heights, NSW, 1986, p. 133.
16. Coburn, T.T., Taylor, R.W., Morris, C.J., and Duval, C., 'Proc. of Int. Conf. on Oil Shale and Shale Oil,' Beijing, China, 1988, Colorado School of Mines Press.

17. Rubel, A.M., Rimmer, S.M., Keogh, R., Robl, T.L., Carter, S.D., and Derbyshire, F.J., *Fuel*, 1991, 70, 1352.
18. Carter, S.D., ACS Div. of Pet. Chem. Preprints, 1987, 32 (1), 133.
19. Coburn, T.T., *Proc. 1988 Eastern Oil Shale Symp.*, 1989, University of Kentucky, p. 325.
20. Dung, N.V., Wall, G.C. and Kastl. G., *Fuel*, 1987, 66, 372.
21. Wall, G.C. and Udaja, P., *Fuel*, 1988, 67, 1340.
22. Udaja, P., Duffy, G.J., and Chensee, M.D., *Fuel*, 1990, 69, 1150.
23. Robl, T.L., Rubel, A.M., and Barnhisel, R.I., *Proc. 1989 Eastern Oil Shale Symposium*, 1990, University of Kentucky, IMMR88-101, 212-218.
24. Hosterman, J.W. and Whitlow, S.I., U.S. Geol. Sur., 1981, Open File Rep. No. 81-585, 178 p.
25. Voorhies, Jr., A., *Ind. Eng. Chem.*, 1945, 37 (4), 318.
26. Dumez, F.J. and Froment, G.F., *Ind. Eng. Chem. Process Des. Dev.*, 1976, 15 (2), 291.

**DATE
FILMED**

8 / 20 / 92