The Development of an Integrated Multistaged Fluid Bed Retorting Process

**Annual Report
October 1991 - September 1992**

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December 1992

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
Center for Applied Energy Research
Lexington, Kentucky**

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ABSTRACT

This report summarizes the progress made on the development of an integrated multistage fluidized bed retorting process (KENTORT II) during the period of October 1, 1991 through September 30, 1992 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 completed this year involved several different areas. Basic studies of the cracking and coking kinetics of shale oil vapors were carried out in fluidized and fixed bed reactors using both freshly generated shale oil vapors and model compounds. The design and fabrication of the 50-lb/hr KENTORT II reactor was completed and installation of the process components was initiated. The raw oil shale sample (Cleveland Member from Montgomery County, Kentucky) for the program was mined, prepared, characterized and stored. A preliminary study of KENTORT II-derived oil for possible paving applications was completed, and it was concluded that the shale exhibits acceptable properties as an asphalt recycling agent.

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EXECUTIVE SUMMARY

A major objective of the program is the study of solid-induced secondary coking and cracking reactions. Much of this work has involved a valved, fluidized bed reactor to study the coking kinetics of freshly generated shale oil vapors in a fluidized bed of solids. Experiments were performed to examine the effects of surface area, initial carbon content and steam treatment on coking activity. From the data that has been collected to-date, it appears that the coking activity of the tested substrates can be explained in terms of porosity (surface area and pore volume) and the initial carbon content of the solid. In addition, a mathematical model was implemented to characterize the important mass transfer effects of the system. This model will be eventually broadened to become a general fluidized bed coking model.

In addition to the fluidized bed experiment, two additional techniques were utilized to investigate coking and cracking under high-pressure conditions and with model compounds. First, the two-stage hydrolysis reactor at the University of Strathclyde, Glasgow, Scotland, was used to study the coking tendency of shale oil vapors under a wide range of pyrolysis and hydrolysis conditions. This work enabled us to examine secondary reactions under high pressure conditions (up to 150 bar) which were previously unavailable. Second, the development of a fixed bed reactor system was initiated at the CAER to study the coking and cracking characteristics of model compounds. A fixed bed apparatus was necessary because the conversion of model compounds was too low in the fluidized bed apparatus.

The design and fabrication of the 50-lb/hr KENTORT II retort was completed and installation of the reactor and auxiliary equipment was initiated. Testing and shakedown of the unit is scheduled for early 1993.

A homogeneous oil shale sample was specially mined for the retorting tests to be carried in this program. The shale that was chosen was from the high-grade zone of the Devonian Cleveland Member of the Ohio Shale in Montgomery County, Kentucky. The shale was mined and then 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 transported to the CAER where the shale was double-screened, analyzed and stored.

A preliminary study of KENTORT II-derived oil for possible paving applications was completed using oil generated in the 3-inch diameter prototype. Following distillation, samples of heavy end materials were subjected to a battery of tests aimed at evaluating their potential utilization as an asphalt cement, additive, or recycling agent. Due to the unusually rapid aging characteristics of the shale oil, emphasis was placed on the latter applications. Preliminary tests used to evaluate the potential utilization of Eastern shale oil as an asphalt recycling agent were generally favorable in that these materials exhibit acceptable dispersant and rejuvenation properties.

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, 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 (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 issues are the effects that scale-up will have on the physical operation of the system and the potential for larger solid-recycle induced cracking and coking losses in the pyrolysis zone. To reduce the risks of scale-up, a cold-flow model of the unit was built and tested. The important

features of the successfully operated cold-flow model were then incorporated into the designs of the reactor vessels which were completed this year.

Another consideration is the effect of scale-up on the magnitude of solid-recycle induced cracking and coking losses in the pyrolysis zone. A study of the kinetics of cracking and coking over various process solids in a fluidized bed reactor was continued, and the development of a fluidized bed coking model was initiated. Additional studies involving both secondary reactions at high pressure and model compound coking and cracking have been performed. In total, the basic coking and cracking studies are intended to provide a guide in the selection of operating parameters for the 50-lb/hr retort which will either maximize oil yield or improve oil quality.

The scaled-up retort provides the opportunity to conduct tests on larger quantities of oil products. One of the potentially attractive options for the heavy fraction of the shale oil is for use in asphaltic applications. Asphalt and asphalt additives typically command attractive prices, while the production cost for asphaltic materials would be low compared to upgrading the heavy shale oil fraction to transportation fuel. In order to best select the tests which will be performed on a large scale, a preliminary bench-scale test of heavy KENTORT II-derived shale oil was performed.

OBJECTIVES

The primary objective of this program is 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 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 Tasks 1 and 3 during the year. The objective of subtask 1.1 was 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 could 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 and/or affect oil quality for the particular application of interest. Sufficient information has been generated from subtasks 1.1 and 1.2 to finalize the design and fabrication of the 50-lb/hr reactor, subtask 1.3.

The objective of Task 2 is to operate and test the 50-lb/hr KENTORT II oil shale retort using eastern U.S. Devonian oil shale. This task is scheduled to begin next year.

Broadly, the objective of Task 3 is to acquire and study the raw material and products associated with the KENTORT II process. The mining and initial characterization of the raw oil shale sample for the project was completed and represents

subtask 3.1. The objective of subtask 3.2.1 is to examine the potential utilization of a KENTORT II electrostatic precipitator (ESP) oil and a vacuum distillation bottom of the total product oil for use as an asphalt cement, additive, or recycling agent. Subtasks 3.2.2 and 3.3 are scheduled for later in the study.

CRACKING AND COKING KINETICS

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.^{11,12,13,14} 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.

It has been previously reported that the rate of carbon deposition is largely influenced by the type of processing that the oil shale has been exposed to. From this early work it appeared that pore volume and the initial carbon content of the shale affected the coking properties the most.¹⁵ The greater the porosity and the lower the carbon content, the greater the rate of carbon deposition that was observed. The coking activities of the three main categories of shales were ranked as: combusted > gasified > pyrolyzed. For these materials, the initial carbon content was the most influential coking indicator since the porosity characteristics were not dissimilar.

An area that has not been addressed is the state of the mineral matter and its effect on the coke producing tendency of the solids. Steam and oxygen at high temperature have the potential to alter the surface characteristics of minerals, and experiments were also performed to investigate any possible mineralogical effects on carbon deposition.

Approach

Three different techniques have been utilized to further our understanding of the chemistry and kinetics associated with solids-recycle retorting. The first system is a valved fluidized bed which is designed to permit rapid exposure and isolation of fluidized solids to shale oil vapors. 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. 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.

The second system used for the cracking and coking study is the two-stage hydropyrolysis reactor at the University of Strathclyde, Glasgow, Scotland. This reactor enabled us to examine secondary reactions under high pressure conditions (up to 150 bar) which are unattainable in our existing equipment. By examining coking and cracking under a wide range of pressures, the basic rate controlling phenomena may be more easily discerned. In addition, hydrotreating catalysts could be used in the second stage to enable a precursory examination of the upgradability of the shale oils.

Thirdly, the development of a fixed bed reactor system was initiated at the CAER to study the coking and cracking characteristics of model compounds. A fixed bed apparatus was necessary because the conversion of model compounds was too low in the fluidized bed apparatus.

To complement the experimental work, a model has been developed to evaluate the diffusional limitations and to characterize the transient mass transfer behavior of porous solids in an isothermal fluidized bed. This model represents the beginnings of a comprehensive fluidized bed coking model.

Fluidized Bed Model

Model Development. Due to the complexity that is to be eventually added to the coking model, 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 constant size. The coking reaction (nth order) only takes place within the pores of the particles which are considered to be spherical. Only a first-order reaction was chosen for the present study because the intent of the model at this time is to identify the important mass transport parameters of the system. Certainly, a chemical reaction term that considers deactivation will eventually be added. Simple binary counter diffusion is assumed within the particles. The problem is considered to be 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 Yates¹⁶ as:

$$E_e \frac{\partial^2 C_e}{\partial z^2} - U_e \frac{\partial C_e}{\partial z} - K_{be}(C_e - C_b) - k_e C_e - \frac{\partial C_e}{\partial t} \quad (1)$$

This equation is basically the convective-diffusion equation with chemical reaction. In addition, the third term in Eq. 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:

$$E_b \frac{\partial^2 C_b}{\partial z^2} - U_b \frac{\partial C_b}{\partial z} - K_{be}(C_b - C_e) - \frac{\partial C_b}{\partial t} \quad (2)$$

For the purposes of the present study, however, Eq. 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, Eq. 1 becomes:

$$E_e \frac{\partial^2 C_e}{\partial z^2} - U_e \frac{\partial C_e}{\partial z} - K_{be}(C_e - C_b) - \frac{1 - \epsilon_{mf}}{\epsilon_{mf}} k_p a (C_e - C_r(R)) - \frac{\partial C_e}{\partial t} \quad (3)$$

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:

$$D_{eff} \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) - S_p \rho_p k_r C_r^n - \theta \frac{\partial C_r}{\partial t} \quad (4)$$

Equation 4 prescribes binary counter diffusion and no convective mass flux, which are assumptions that must eventually be shown to be proper.

Equations 2 and 3 can be solved as a coupled set of equations either analytically, if enough terms are neglected, or numerically. A means of coupling Eq. 4 to Eqs. 2 and 3 is needed, however. By utilizing continuity at the particle surface, the following boundary condition for Eq. 4 is obtained:¹⁷

$$D_{eff} \left(\frac{\partial C_r}{\partial r} \right)_R = k_p (C_e - C_r(R)) \quad (5)$$

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 Eq. 4:

$$\frac{\partial C_r}{\partial r} = 0 \quad \text{at } r=0 \quad (6)$$

For the emulsion and bubble phases the following boundary conditions are assumed:

$$C_e = C_b = C_{in} \quad \text{at } z=0 \quad (7)$$

$$\frac{\partial C_e}{\partial z} = \frac{\partial C_b}{\partial z} = 0 \quad \text{at } z=L \quad (8)$$

While Eqs. 2-4 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 Eq. 5 can be replaced by $C_{e,avg}$ which is the average concentration in the axial direction and is only a function of time. Equation 5 is then written as:

$$D_{eff} \left(\frac{\partial C_r}{\partial r} \right)_R - k_p (C_{e,avg} - C_r(R)) \quad (9)$$

Similarly, $C_r(R)$ is not a function of axial position and is also only a function of time. Therefore, the parameters coupling Eqs. 3, 4, and 9 are only functions of time and a simultaneous solution of Eqs. 2-4 in 2 space variables is not required.

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:¹⁸

$$D_{12} = \frac{0.001858 T^{3/2} [(M_1 + M_2)/M_1 M_2]^{1/2}}{P \sigma_{12}^2 \Omega_D} \quad (10)$$

The Lennard-Jones force constants, ϵ and σ , were estimated for the oil vapor by the relationships:

$$\frac{\kappa T}{\epsilon} = 1.30 \frac{T}{T_c} \quad (11)$$

$$\sigma = 1.18 V_b^{1/3} \quad (12)$$

Tabulated values of ϵ and σ were obtained for nitrogen and steam.¹⁸ 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.¹⁹ To aid computation, smooth curves were fitted to the collision integral data as a function of T/ϵ_{12} . Since we are interested in diffusion that occurs in porous solids, an effective molecular diffusivity was defined by:¹⁸

$$D_{12,eff} = \frac{D_{12} \theta}{\tau} \quad (13)$$

Knudsen diffusion prevails under conditions where pore-wall collisions are more frequent than molecular collisions. Since gas has low density at high temperatures, the possibility for significant Knudsen diffusion exists. The Knudsen diffusivity, D_K , was determined by the relationship:

$$D_K = 9700 r_e \sqrt{T/M} \quad (14)$$

The mean pore radius was defined by:

$$r_e = \frac{2\theta}{S_p \rho_p} \quad (15)$$

Similar to Eq. 13, the porosity and tortuosity of the solid was accounted for by the relation:

$$D_{K,eff} = \frac{D_K \theta}{\tau} \quad (16)$$

Finally, the overall effective diffusivity, D_{eff} , was determined as the combination of molecular diffusion and Knudsen diffusion by the relation:

$$\frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}} \quad (17)$$

The remaining parameters that need to be estimated are all fluidized bed parameters. 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 (Eqs. 18-20), presented by Yates,¹⁶ were used to determine U_{mf} :

$$Re_{mf} = [(33.7)^2 + 0.0408 Ga]^{1/2} - 33.7 \quad (18)$$

$$\text{where } Re_{mf} = \frac{U_{mf} d_p \rho_g}{\mu} \quad (19)$$

$$\text{and } Ga = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad (20)$$

Based on the model of Davidson and Harrison the average bubble velocity was determined by the relationship as presented by Yates:¹⁶

$$U_b = (U_o - U_{mf}) + 0.711(gd_b)^{1/2} \quad (21)$$

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.

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.²⁰ The bubble-to-cloud coefficient is given by:

$$K_{bc} = 4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{D^{1/2} g^{1/4}}{d_b^{5/4}} \right) \quad (22)$$

The cloud-to-emulsion coefficient was determined by:

$$K_{ce} = 6.78 \left(\frac{\epsilon_{mf} D_e U_b}{d_b^3} \right)^{1/2} \quad (23)$$

The bubble-to-emulsion coefficient is then derived by:

$$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}} \quad (24)$$

Using the emulsion phase gas velocity, the mass transfer coefficient to the particle, k_p , is determined by the relationship:

$$\begin{aligned} Sh &= 2.0 + 0.6 Sc^{1/3} Re_{mf}^{1/2} \\ \text{where } Sc &= \frac{\mu}{\rho_g D_{12}} \\ \text{and } Sh &= \frac{k_p d_p Y}{\mu} \end{aligned} \quad (25)$$

The activation energy used for the coking rate constant was taken from Wallman et al.²¹ ($E_o = 38293$ cal/mol) and the frequency factor was adjusted to agree with the conversion observed from the experiments.

Numerical Results. To facilitate numerical solution to the problem, the variables were non-dimensionalized as follows:

$$\begin{aligned} C_e^* &= \frac{C_e}{C_{in}} ; & C_b^* &= \frac{C_b}{C_{in}} ; & C_r^* &= \frac{C_r}{C_{in}} \\ Z^* &= \frac{z}{L} ; & R^* &= \frac{r}{R} \end{aligned} \quad (26)$$

The following initial conditions were used throughout the work:

$$C_e^* = 0 ; C_b^* = 1 ; C_r^* = 0 \quad \text{at} \quad t = 0 \quad (27)$$

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, $E_e = E_b = 1 \text{ cm}^2/\text{s}$, 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 flow only approaches one of these ideal cases.

Figure 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 evident across the particle which is not completely surprising since a relatively small particle size is tested, $d_p = 0.08 \text{ cm}$. 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 is nearly indistinguishable from that at 873 K. Increasing the particle diameter to $d_p = 0.12 \text{ cm}$, however, significantly changed the transient response of the system (Figure 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

Figure 1. Base case numerical solution of model. Temperature, 873K; Fluidizing gas, nitrogen; Bed height, 7.6 cm; no chemical reaction. Units are dimensionless except for time.

$L = 7.6 \text{ cm}$

Temperature = 873 K

Fluidizing Gas = Nitrogen

Figure 2. Numerical solution to model with $d_p = 0.12 \text{ cm}$.

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 concentration gradient across the particle radius is much steeper, at least initially, compared to the small particle size simulation. Due to the larger gradient for the emulsion phase, an imprint of the bubble phase response 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 3). In addition, it appears that steady state is reached more slowly. The frequency factor was adjusted so that the conversion approximately matched the experimental results. Therefore, no conclusions should be drawn concerning the closeness of fit to experimental results. A simple first order chemical reaction was used, and this was sufficient for the purposes of this work. Since it was the objective to study the transient response of the system due to mass transfer, complicated chemical reaction deactivation models were not attempted. This is, however, the objective of future work with this model. Chemical reaction created a steeper concentration gradient within the particle, so diffusional effects cannot be neglected even for the small particle size. 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.

Results from a test case utilizing steam as the fluidizing gas are basically indistinguishable from the base case results, so no other test cases were attempted for steam.

Comparisons of the computer model to the experimental results are difficult because a proper expression for the rate and deactivation of the coking reactions was not utilized. An important conclusion which may be made, however, is that the unsteady state experimental results cannot be attributed to mass transfer effects. A typical experiment reaches an apparent steady state within minutes rather than a second. The deactivation of the solid particles is the only explanation for the temporal response of the experiments.

Figure 3. Numerical solution to model under base case conditions with chemical reaction.

Fluidized Bed Coking Experiments

Apparatus. A detailed description of the apparatus and method development was reported in the latest annual report, but an abbreviated summary will be included here for the reader's convenience.¹⁵ 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 4). The fluidizing gas 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. 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.

In the kinetic mode of operation, a port nearly flush with the distributor plate 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.

The gas stream leaving the upper portion of the reactor 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 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 rapid rate (approx. 1.5 s per scan). 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).

Figure 4. Schematic diagram of the fluidized bed coking and cracking kinetics apparatus.

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 steady state operation has been attained, a weighed aliquot of substrate is loaded into the upper fluidized bed and allowed to reach thermal steady state. 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. For consistency, this will be the measure of carbon deposition used throughout the remainder of the report. Surface area and pore volume measurements by Hg porosimetry and N₂ adsorption are performed on selected solid specimens.

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 1). 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. 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. In addition, portions of the pyrolyzed and gasified shales were low-temperature ashed to remove carbon without affecting the mineral matrix. Finally, a sample of the combusted shale was steam treated at 730°C in the fluidized bed reactor. Ultimate analyses of these materials are given in Table 1.

Table 1. 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
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

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%).^{22,23} 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. Two kaolin samples (fine- and coarse-grained) were 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 ($-841\mu\text{m} +600\mu\text{m}$). A portion of the low-carbon shale ('illite') was heat treated to 600°C in air. The surface area and porosity characteristics of all the coking substrates are listed in Table 2.

Table 2. Surface Area (m^2/g) and Pore Volume (cm^3/g) of Coking Substrates as Determined by Hg Porosimetry (macro and meso).

Pore Diameter	Surface Area (Pore Volume)		
	> 50 nm macro	2-50 nm meso	Total
Pyrolyzed Shale	2.1 (0.125)	11.3 (0.030)	13.4 (0.155)
Pyrolyzed-LTA	2.4 (0.147)	7.3 (0.025)	9.69 (0.173)
Gasified Shale	2.5 (0.164)	9.2 (0.024)	11.6 (0.188)
Gasified-LTA			
Combusted Shale	3.6 (0.230)	9.1 (0.031)	12.7 (0.261)
Combusted-Steamed	4.0 (0.252)	6.2 (0.026)	10.3 (0.279)
Kaolinite-Fine	8.3 (0.190)	13.9 (0.106)	21.7 (0.296)
Kaolinite-Coarse	6.8 (0.346)	3.7 (0.022)	10.5 (0.368)
Illite	1.0 (0.044)	8.1 (0.030)	9.1 (0.074)
Illite-Heat Treated	1.8 (0.080)	7.6 (0.023)	9.3 (0.103)
Ottawa Sand	0.0 (0.000)	1.0 (0.001)	1.0 (0.001)

Experimental Results. Results from numerical modeling of mass transfer phenomena indicated that pore diffusion may not be as important as we had originally thought. The testing of a coarse-grained sample of kaolinite this quarter provided valuable insights into separating the effects of pore volume and surface area. While the chemical compositions of the fine- and coarse-grained kaolins are essentially identical, the porosity and surface areas are very different. We consider only meso- and macro-pores as being important to the carbon deposition process because the molecules most likely responsible for the majority of the coking are too large to fit into micro-pores (<2 nm dia.). Therefore, the porosity measurements reported here do not include micro-pore volume or surface area. The fine-grained kaolinite has twice the surface area but only 80% of the pore volume of the coarse-grained material. The fine-grained kaolinite consistently displayed greater carbon deposition compared to the coarse-grained which suggests that surface area played a more significant role than pore volume. This result urged us to more closely evaluate surface area as a coking indicator.

When considering only substrates that have a 'low' initial carbon content, an increase in carbon deposition as a function of surface area is observed (Figure 5). Low-carbon substrates are distinguished from high-carbon substrates because it appears that carbon coverage hinders additional carbon deposition. The amount of carbon deposition for the lowest surface area materials, illite and heat-treated illite, in Figure 5 is somewhat lower than the other substrates because the pore volumes are approximately 50% of the

Figure 5. Carbon deposition onto low-carbon content substrates as a function of meso- and macro-surface area. 10 minutes solid residence time; 12 g/minute raw shale feedrate; 75 g charge of substrate.

other materials. The surface area relationship in Figure 5 also holds for the gasified and pyrolyzed shale samples which had been subjected to a low-temperature ash (LTA) procedure. The total carbon content for these samples was high, 3.26 and 6.47 wt%, respectively, but it appears that the carbon coverage which is most significant to the carbon deposition process was removed by LTA. The LTA samples, therefore, performed like materials which contained essentially no carbon.

The initial carbon content of the substrate strongly affects the amount of carbon deposition (see Figure 6). Only combusted, gasified, and pyrolyzed shales were considered in this plot so that pore structure and surface area were as similar as possible. The LTA samples, especially the pyrolyzed shale, do not strictly adhere to this relationship which, again, indicates that the total carbon content is not always indicative of the nature of the carbon coverage experienced by the shale oil vapors in the pores of the solids.

To this point, no mention has been made of the activity of the bare mineral surface itself. Among the various un-pretreated substrates, no differences in coking activity were discernable when surface area, carbon content, and pore volume were accounted for. Several different pretreatment procedures were undertaken this quarter to determine whether a difference in chemical activity of the substrate could affect the rate of carbon deposition. Acid-washed and base-washed samples of combusted and gasified shales displayed the same rate of carbon deposition as the un-pretreated parent materials. The value of this test is uncertain, however, because only a low concentration of acid or base could be used in the washing procedure without destroying the physical integrity of the substrates. A portion of the illite sample was heat-treated in air at 600°C to investigate the effect of oxygen on the mineral matrix without the presence of carbon. The heat-treatment did not significantly change the porosity characteristics of the substrate and the carbon uptake was essentially the same as the un-pretreated illite.

Steam has long been regarded as a coke reducing agent during the processing of hydrocarbons. Rubel et al.²⁴ have indicated that steam treatment of combusted shale lowers its coking activity, but it is unclear what role steam played to produce this result.

Figure 6. The effect of initial carbon content of the substrate on subsequent carbon deposition.

We wanted to investigate the effects of steam as a pretreating agent and as an inhibitor during exposure of shale oil vapors to the substrate. One method of pretreating with steam was to blend steam (30% by volume) with N_2 during the preheating period. No significant effects were observed, however, and a more severe pretreatment method was later utilized to more thoroughly evaluate the effects of steam pretreatment. Here, a portion of the combusted shale sample was processed in the fluidized bed reactor at 700°C with steam used for fluidization. It was determined that a slight reduction in coking activity was achieved from this steam treatment, but as discussed previously this appears to be attributable to a reduction in surface area (see Figures 5 and 7). In another series of runs, steam was used for fluidization to search for any effects during oil vapor exposure, but no effects were discernable (Figure 7).

Secondary Reactions in a Two-Stage Hydropyrolysis Reactor

Apparatus and Procedure. The reactor consisted of high-pressure tubing (0.79 cm I.D.) which was configured for both one- and two-stage operation (see Figure 8). 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

Figure 7. Effects of steam on the coking activity of combusted oil shale.

Figure 8. Schematic diagram of the two-stage fixed-bed hydropyrolysis reactor.

transformer, the shale was heated 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 the heating of 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 soak 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 soak periods. The gas flowrate was measured downstream of the pressure let down valve, and a representative sample was collected for analysis of C_1 - C_4 by gas chromatography. Following each run, the cold trap was weighed and rinsed with toluene to recover the liquids. Dean-Stark analysis was performed on the toluene wash to determine moisture content and the oil content by-difference. Other tests done on the oils include size exclusion chromatography and ^1H -NMR. In some cases a neat oil product was recovered so that certain tests (i.e. elemental analysis) would be facilitated. It should be noted, however, that this was not

possible in all cases because of the small amount of liquids produced. 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.

A series of single-stage tests was performed to provide baseline data for the two-stage runs. Approximately 15 g of raw oil shale was loaded into the reactor for the single-stage tests which resulted 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 included nitrogen sweep at 1 and 50 bar pressure and hydrogen at 50 bar. 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.

For two-stage tests a smaller charge of raw shale (10 g, 19 cm depth) was used because of space limitations within the reactor for the first stage (33-cm heated length). Approximately 5 g of substrate made up the second stage which resulted in bed heights of 13 cm and 15 cm for the combusted shale and hydrotreating catalyst, respectively. The heated length of the second zone was 46 cm and was maintained at 520°C and 400°C for the combusted shale and catalyst, respectively. Two-stage tests included nitrogen sweep at 1 and 150 bar and hydrogen sweep at 50, 100, and 150 bar for each substrate. In addition, a "single-stage" run was performed in the two-stage configuration because no comparable run at 150 bar H₂ pressure was performed in the single-stage setup.

Materials. The master sample of oil shale utilized in these studies was from the Cleveland Member of the Ohio Shale from northeastern Kentucky, USA (see raw shale analysis in Table 3). The shale was prepared to a size distribution of -250 μ m +150 μ m. This shale sample was used both for the production of shale oil vapors in the first stage and as the starting material for the generation of the combusted shale which was used in the second stage. The combusted shale was generated in air at 973K in a 7.6-cm diameter fluidized bed reactor. A commercially available Ni/Mo γ -alumina catalyst was precalcined at 400°C for 12 hours prior to use as a second stage material.

Table 3. Ultimate Analyses (As-Received Basis) of the Raw and Combusted Cleveland Oil Shale (wt%).

	C	H	N	S	Ash
Raw Shale	16.0	1.9	0.8	1.9	74.1
Combusted Shale	1.4	0.2	0.6	0.2	97.0

Results and Discussion. Since product analyses were not complete at this writing, a comprehensive presentation of the results and conclusions of the study will not be attempted here. Instead, the discussion will primarily focus on total hydrocarbon evolution from the first stage and subsequent coke deposition in the second stage. Information on substrate-catalyzed cracking reactions will be summarized later when all results are available for interpretation.

Mass transfer limitations were small for these experiments because of the rapid particle heat-up and the sweep gas through the bed, so carbon conversion to volatile products was higher than Fischer assay for the nitrogen-swept runs at 1 bar total pressure (see Table 4). Utilization of 50-bar N₂ sweep gas resulted in slightly lower carbon conversion. As anticipated, 50-bar H₂ pressure increased significantly the conversion to volatile products (approx. 73%) at 10 minutes solid residence time. These results are slightly lower than those reported by IGT who generally utilizes 30 minutes solid residence time.²⁵ The increased conversion at the longer residence times is most likely attributable to extra hydrocarbon gas production. It is emphasized, however, that the purpose of this study was not the study of hydropyrolysis, *per se*, but it was the study of secondary reactions, and by nature of the apparatus, hydropyrolysis was a necessary element of the investigation.

Carbon deposition onto the combusted shale in 1 bar nitrogen accounted for 4% of the carbon in the raw shale. Under otherwise similar conditions, carbon deposition on the combusted shale was slightly lower at a pressure of 150 bar, but when considering standard analytical error, the amounts of carbon can be considered essentially equal. Nevertheless, a zeroth-order reaction rate mechanism in terms of oil vapor partial pressure for char formation is indicated under these conditions. When the Ni/Mo catalyst was used as the 2nd-stage substrate, nearly 17% of the carbon originally present in the raw shale was deposited onto the catalyst. This is consistent with the hypothesis that carbon deposition is controlled by the available surface area of the substrate since the catalyst has a total BET surface area of 180 m²/g compared to 20 m²/g for the combusted shale.

Hydrogen partial pressures of 50 and 150 bar effectively reduced carbon deposition onto the combusted shale to near zero. Under otherwise equivalent conditions, however, substantial carbon deposition occurred on the catalyst, even at 150 bar H₂ partial pressure. This result appears to indicate that high rates of coke formation may occur when crude shale oils from high-yield processes are catalytically upgraded. This is an area which deserves much more attention since coke formation during upgrading is equivalent to the loss of oil yield during the pyrolysis process itself.

The determination of oil yield was probably the most uncertain measurement from this set of experiments, as it is for almost all pyrolysis procedures. Oil trapping inefficiency and the measurement of the amount of water co-collected with the oil mainly contributed to the uncertainty in oil yield determinations. Eastern oil shales form an

Table 4. Run Conditions and Selected Results from the Two-Stage Hydropyrolysis Reactor.

Run	Sweep Gas	2nd Stage Substrate	Press., Bar	No. of Stages	Gas Vel., m/s	2nd Stage Temp., K	1st Stage C Conv.(%)	Alkene/Alkane Ratios		
								C2	C3	C4
2	N2		1	1	0.99		50.22	na	na	na
3	N2		1	1	1.98		53.35	na	na	na
7	N2		1	1	1.98		51.73	0.489	1.015	0.882
4	N2		53	1	0.19		49.10	na	na	na
5	H2		51	1	0.19		71.75	na	na	na
6	H2		51	1	0.19		73.41	0.326	0.701	0.702
18	H2	none	150	2	0.07	793	75.58	0.354	0.612	0.000
14	N2	NiMo	1	2	2.47	793	51.73	0.524	1.141	0.992
10	N2	Comb Shale	1	2	2.47	793	49.50	0.518	1.134	0.995
19	N2	Comb Shale	150	2	0.07	793	47.51	0.382	0.944	nd
9	H2	Comb Shale	49	2	0.30	793	73.18	0.441	0.748	nd
17	H2	Comb Shale	150	2	0.07	793	81.12	0.209	0.475	nd
12	H2	NiMo	48	2	0.31	673	69.32	0.112	0.278	nd
13	H2	NiMo	100	2	0.15	673	80.97	0.064	0.205	nd
15	H2	NiMo	150	2	0.07	673	79.75	0.000	0.000	0.000

Run	Sweep Gas	2nd Stage Substrate	Press., Bar	Carbon Distribution (wt% C/wt% C in r.s.)				C Balance (%)
				Char	2nd Stage	Oil	Gas	
2	N2		1	0.498		0.195	na	69.31
3	N2		1	0.467		0.412	na	87.83
7	N2		1	0.483		0.389	0.050	92.15
4	N2		53	0.509		0.322	na	83.11
5	H2		51	0.283		0.685	na	96.75
6	H2		51	0.266		0.677	0.159	110.23
18	H2	none	150	0.244	na	0.608	0.076	92.87
14	N2	NiMo	1	0.483	0.168	0.273	0.048	97.17
10	N2	Comb Shale	1	0.505	0.038	0.266	0.048	85.83
19	N2	Comb Shale	150	0.525	0.023	0.157	0.058	76.27
9	H2	Comb Shale	49	0.268	0.007	0.509	0.144	92.81
17	H2	Comb Shale	150	0.189	0.000	0.669	0.034	89.23
12	H2	NiMo	48	0.307	0.117	0.465	0.109	99.75
13	H2	NiMo	100	0.190	0.143	0.546	0.154	103.36
15	H2	NiMo	150	0.202	0.150	0.509	0.056	91.65

aerosol, especially when sweep gas is used, that is particularly difficult to trap, and the dry-ice-cooled trap was not sufficient to completely collect the oil in this study. Light oil and water were present in the glass wool in the outlet of the trap following each run which suggests that some liquids were escaping. In most cases the water content of the

toluene wash from the trap was too low to be detected by the Dean-Stark method, so it was assumed that the raw shale produced 4 wt% water which was collected in the trap. Inferences from relatively small changes in oil yield should, therefore, be considered carefully.

Oil yields generally followed the trends suggested from the carbon contents of the first and second-stage solids. The highest oil yields were obtained under high H_2 partial pressure and no second-stage substrate. Combusted shale in the second stage did not seriously affect oil yield, as opposed to the upgrading catalyst, which significantly lowered the measured oil yield. The lowest oil yields were obtained in N_2 -swept runs when catalyst was present in the second stage or the total pressure was high.

As anticipated, the hydrogenation of the primary pyrolysis products increased at higher H_2 partial pressures when the upgrading catalyst was utilized in the second stage. This was clearly demonstrated by the alkene/alkane ratios of light gases (C_2 - C_4) which decreased with increasing H_2 partial pressure until disappearing to zero at 150 bar. Hydrogenation was visually apparent for the oil which had passed through the catalyst at 150-bar H_2 partial pressure; it was light in color, was nearly transparent, and did not change in appearance with time. Oils produced from tests without the upgrading catalyst became more aromatic (as determined by 1H NMR) at either increased H_2 partial pressure or exposure to combusted shale.

The gas yields were erratic, especially between high- and low-pressure runs, and this appears to be due to a systematic sampling error. The apparatus was designed for high-pressure operation, so a relatively large sweep-gas flowrate, measured at ambient conditions, is required for a fast 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, it was not sufficient to displace air contamination in the relatively large gas sampling system, and the samples from the low-pressure runs probably became diluted with room air. Unfortunately, confirmation of this was not available because only the analysis of hydrocarbon gases by GC was performed. While the absolute gas yields are questionable, the alkene/alkane ratios are still valid and provide useful indications of the relative extent of cracking, coking, and hydrogenation reactions.

Summary. This brief study has provided useful information that will complement the fluidized-bed coking kinetics study because of the ability to examine coking under high-pressure conditions. Since high pressures did not significantly enhance carbon deposition, it appears that the coke formation rate is largely influenced by the rate of the surface reaction.

Another important facet of this work was the study of the upgrading behavior of the shale oil vapors. The oils produced in the two-stage mode were significantly upgraded as displayed by the nearly clear liquid that was produced. Of course, the

extent of upgrading needs to be quantitatively determined, but the results are, nevertheless, encouraging. Coke formation on the upgrading catalyst was relatively high, even at high H_2 partial pressure, so more work in this area is needed.

Hydrocarbon Cracking Study

Introduction. Before exiting the reactor, liquid products generated during oil shale pyrolysis in the KENTORT II reactor are exposed to hot pyrolyzed, gasified, and combusted shale surfaces. Such exposure catalyzes secondary cracking and coking reactions resulting in both hydrocarbon loss and a shift to a lower average molecular weight product. Since coking reactions have a detrimental effect on process economics (and must be understood in order to be suppressed via design considerations), coking reactions and kinetics have been the topic of a previous study.

Though not as immediately detrimental to plant economics, cracking reactions within the reactor are also of concern in any systematic attempt at process optimization. For simplicity, cracking reactions are defined as reactions in which a molecule is cleaved to produce two or more smaller components with little or no carbon deposition in the initial step. Cleavage reactions result in production of stable gases and lower molecular weight liquids as well as unstable free radical intermediates. These latter tend to rapidly interact with other HC's or radical intermediates to produce a suite of products including H_2 , olefins, cyclic alkenes, aromatics, and coke. Thus, cracking reactions have a profound effect on product quality and yield, both good (lower average molecular weight and viscosity) and bad (eventual coke production). By improving our understanding of the rates and mechanisms for these catalyzed reactions, it is hoped that the processing conditions, particularly management of the heat transfer solids, can be optimized to produce a superior product.

In an approach similar to that of the coking kinetics research reported in previous quarters, an apparatus is being constructed to facilitate the study of hydrocarbon cracking reactions. This effort will attempt to measure the rate and, time permitting, identify the cracking pathways and mechanisms as a function of substrate, hydrocarbon type, and temperature.

Experimental. A simplified schematic of the apparatus is shown in Figure 9. Nitrogen gas is metered to two parallel carrier lines which are routed to a heated valve oven. One of the carrier lines (termed the balancing gas) serves to maintain a constant total flow through the system regardless of valve position. The other, (termed the hydrocarbon line) carries both the model compound and metered Ar (used as a tracer gas). The model compound is introduced to the HC line via a Waters Assoc. model 6000 liquid chromatography pump, typically at 0.1-0.2 mL/min, and is vaporized prior to mixing with the N_2 -Ar blend.

Both carrier lines are heat traced and routed to a 3" diameter furnace operating at a selected target temperature. The two carrier lines pass through either a bypass reactor or a substrate reactor before being combined and routed to the inlet of a VG model EGA 300MM quadrupole mass spectrometer (QMS). The bypass and substrate tube reactors are 9" X 3/8" OD stainless steel. The bypass bed will be packed with an

Figure 9. Schematic of model compound cracking reactor

inert material, i.e., Ottawa sand. The substrate bed will be packed for most tests with either pyrolyzed, gasified, or combusted shale to simulate the solid surfaces to which vapor phase hydrocarbons are exposed in an integrated KENTORT II reactor. In addition, limited cracking tests will be conducted using kaolinite and illite substrates for comparison to the previously reported coking studies.

For most tests, the QMS will be operated in the multiple ion monitoring (MIM) mode. This permits the measurement of up to 16 selected masses at approximate 1 second intervals. For these tests, the masses for Ar, N₂, and the molecular ion of the study hydrocarbon, among others, will be selected. In addition, a log histogram run will be made from 0 amu to the molecular mass for each substrate/model compound combination.

In the initial tests, the model compounds studied will include a series of n-alkanes, n-1-alkenes, a set of aromatics and alkylated aromatics as well as a cyclic aliphatic and a cyclic alkene. These compounds were selected since they are representative of the major

hydrocarbon components produced from Eastern shale oil in the KENTORT II process. Time permitting, similar tests will be conducted on selected heteroatom components.

The reactor beds will be operated between 300 and 650°C to study both adsorption and cracking. A typical cracking sequence will entail establishing thermal equilibrium in the reactor beds under inert gas flow, initiating model compound flow across the bypass bed, starting QMS data collection to establish a response baseline, actuating the switching valve so that the HC stream is routed through the substrate bed for a selected time interval, and returning the switching valve to the bypass position to re-establish baseline. The drop in response of the molecular ion during the substrate exposure segment is a direct indicator of product cracking. Exposed substrates will also be analyzed for carbon content to determine the amount of coking that accompanies the measured cracking.

In a second series of experiments, the reacted product will be collected for GC-MS analysis. This should help clarify whether the reaction mechanism and path varies as a function of substrate or exposure time, that is, does the initial reaction differ between substrates or within a given substrate before and after coke deposition.

Conclusions

In short, from a preliminary evaluation of the data, it appears that the only effective pretreatment method for reducing the coking activity of the shale is to reduce the surface area and porosity of the substrate. Basically, substrate reactivity is mainly governed by the surface area of the mineral matrix and the extent of carbon coverage on the accessible pores. The results of the mathematical model of the experimental system indicated that diffusion limitations were not as pronounced as we had originally thought, but are still significant, especially at larger particle sizes. The transient nature of carbon deposition cannot be attributed to mass transfer effects.

DESIGN OF 50-LB/HR KENTORT II RETORT

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 10). All beds are designed to operate in the bubbling mode, and cold-flow studies have shown that a gas velocity of about 3 ft/s provides proper fluidization for an 8 x 60 mesh particle size range.²⁶

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. Air, 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 or eliminated completely.

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. The spent shale bin may be changed during a run to permit lengthy periods of operation. Fines recovered from the pyrolysis cyclone during a previous run are loaded into a hopper with a 50-lb capacity and are metered into an air lift into the combustor by a screwfeeder.

Figure 10. Schematic diagram of the 50-lb/hr KENTORT II process.

Reactor Design and Fabrication

During the previous year, a full-scale cold-flow model of the 50-lb/hr reactor was built and tested. It was demonstrated that the operation of the unit was stable for three selected particle size distributions (8 x 20, 20 x 60, and 8 x 60 mesh) at a design throughput rate of 50 lb/hr. The design of the 50-lb/hr retort was then obtained from the final configuration of the cold-flow model 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. Late in the fiscal year, our machining subcontractor completed fabrication of the reactor, and the unit was secured into the scaffolding. Installation of auxiliary systems and instrumentation is scheduled for the early part of next year, and shakedown procedures will immediately follow. 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 retort⁸ 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 5-lb/hr retort, 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 at the 5-lb/hr scale, this measure of corrosion protection was adopted for the 50-lb/hr retort. The base metal used for some of the internals of the 5-lb/hr reactor, 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 5-lb/hr reactor, 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 appears to most closely meet all of our requirements, however, is 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.²⁷ This material will be used for the shell of the reactor vessel.

Seals Between Reactor Sections. The sections of the KENTORT II unit are separated by gas distributors which are sandwiched between standard ANSI 150-lb flanges. The selection of the type of device to seal the sections of the reactor is, 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 may be unsuitable for the highest temperature flanges, it will be 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 11) were obtained for testing purposes. The C-rings consist of a limiting plate and a spring-energized seal. The

Figure 11. Spring energized c-ring.

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 are reusable after thermal cycling. The C-rings were, therefore, selected for use in the 50-lb/hr retort.

Since the C-rings cannot be aluminized, protection against corrosion was an important consideration. If the seal is directly exposed to the shale particles, especially in the gasification zone, the potential for corrosion is increased. By using an extension ring to mount the gas distributor above the C-ring (see Figure 12), the seal becomes isolated from the solids. Since the C-ring is at the bottom of the fluidized bed, the concentration of corrosive gases is low and sulfidation is not expected to be a problem.

Reactor Assembly. Figure 13 shows an assembly view of the main body of the KENTORT II system. The gasification and combustion sections are each mounted at the same level above the floor (10 feet) so that thermal expansion will have a minimal effect on the connecting pipes between the sections. Expansion joints are still required, however, for connection to downstream equipment and connections between sections. The scaffold which supports the reactor system is constructed of eight 4 x 4-inch, 22 feet-long columns which are tied together with channel-type bars.

Figure 12. Gas distributor mount.

Figure 13. Assembly view of KENTORT II reactor.

Figure 14. Cross-section of KENTORT II reactor.

The main reactor sections are sealed with the aforementioned spring energized C-rings. The inlet and outlet ports for the solid recirculation loops which link the pyrolysis, gasification, and combustion zones will also be 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 consist of 1/2-inch schedule 40 pipe with 150-lb flanges. The temperature of these flanges will be below 525°C, so Grafoil gaskets can be used. All ports extend approximately 5 inches from the vessel wall so that a 4-inch layer of insulation can be installed without restricting access to the ports. High-temperature electrical heating elements will be placed beneath the layer of insulation surrounding the pyrolysis and combustion zones to compensate for heat loss and to aid the preheating of the system.

Pyrolyzer Design. The pyrolysis section is 6-feet tall and consists of 6-inch schedule 40 pipe. A modified 8-inch 150-lb flange for mating with the gasifier is connected to the bottom of the pipe (see Figure 15). A 46-inch tall baffle splits the pyrolysis zone into two equally sized beds to narrow the residence time distribution of the solids. Raw shale is introduced above the bed through an angled 1-inch pipe on one side of the baffle, and shale exits the zone through a downcomer, which is attached to the distributor, on the other side of the baffle. There are 12 ports along the vertical axis (6 on each side of the baffle) which will accommodate a combined thermowell and pressure tap assembly.

The recirculation inlet to the pyrolysis zone is a 1-inch pipe (Fig. 15, section A-A), which is connected directly to the lift pipe from the gasifier. It is placed 3.5 inches above the gas distributor. This position was successfully tested on the cold-flow model and is incorporated into the final design.

The fluidizing gas and product vapors leave the pyrolysis zone through a 2-inch pipe at the top of the vessel (Fig. 15, section A-A) and enter a cyclone that separates 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 has been modified so that fines collected in the cyclone from a previous run are loaded into a sealed bin and are fed into the combustor at a rate that is not necessarily related to the rate of fines entrainment from the pyrolyzer. This new arrangement allows the accurate determination of fines carry-over which is another important benefit.

Gasifier Design. The gasification zone is 6-feet high and is constructed of 8-inch schedule 40 pipe with 150-lb flanges at each end. The gasification zone has 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, is placed 15 inches above the distributor and cut at a 60° angle (see Figure 16, section A-A). This was observed from cold-flow studies²⁶ 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, is available for feeding raw shale during start-up and during periods of upset when the dipleg of the downcomer which feeds the gasifier becomes uncovered. Six 1/2-inch ports on each side of the baffle are available for temperature and pressure readings.

A 46-inch tall baffle is 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 are used to mount the unit to the scaffold.

Cooling Zone Design. Because the cooling zone is designed to operate between 350-500°C, a slightly smaller inside diameter is required compared to the pyrolyzer, so a 6-inch schedule 80 pipe has been specified as the vessel shell. A concentric reducer is used to ensure a smooth transition between this zone and the gasification zone (see Figure 17). The reducer eliminates any dead space around the edges of the gasifier distributor. A 1-inch pipe is used as the outlet port for the spent shale (Fig. 17, section A-A). This pipe, which also controls the bed height, is mounted at a 30 degree angle from the vessel wall. The cooling zone is 3-feet tall and the bed height is 15 inches.

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

Combustor Design. The combustor consists of 6-inch schedule 40 pipe, and has been slightly modified from the cold-flow design. The height has been 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 5-lb/hr unit because of a very short freeboard section in the combustion zone. Additionally, a taller freeboard should reduce entrainment of non-fine particles.

Pyrolyzed fines and shale from the gasification zone are injected pneumatically into the combustor bed through 1.5-inch pipes which are placed 3.5 inches above the distributor (see Figures 10 and 18). Gases and entrained solids exit the combustor

Figure 15. Pyrolyzer.

Figure 17. Cooling zone.

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through a horizontal 1.5-inch pipe at the top which is 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 serves as the combustor base. The standpipe which controls the depth of the combustion bed extends through the gas distributor and through the outlet port at the bottom of the plenum chamber. This configuration makes 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 mount the combustor to the scaffold. The combustor is covered with 4 inches of high temperature insulation to minimize heat losses. A propane burner will be used to preheat the fluidizing air during start-up and during steady state operation, if necessary.

Summary

During the year, the design of the KENTORT II reactor was completed and blueprints for manufacturing were developed. Construction materials were selected, and pipes and flanges for fabrication of the main body of the unit were procured. A spring energized metallic C-ring was tested and was found to perform adequately as a seal for the different sections of the unit. Fabrication of the 50-lb/hr retort was completed by our subcontractor and was installed in the supporting scaffold. System installation and shakedown procedures are scheduled for early in the next fiscal year.

MINING 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 19, Table 5). 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.²⁸

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.²⁹ There may be a slight trend toward lower

Figure 19. Cumulative size distribution of KENTORT II run of mine feedstock.

Table 5. 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

carbon values with decreasing size (Table 5). However, the standard deviation for the carbon was 0.4 or 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.

Sample preparation plans for the next quarter will include air drying the sample and screening out the +8 mesh and -60 mesh material. The fine fraction will be stored separately. It will be used for blending with the 8x60 mesh materials (2.4 x 0.25 mm). This approach will allow fines content of the feedstock to be treated as a variable in the experimental design of the runs.

ASPHALT APPLICATIONS STUDIES

Introduction

This report describes the results of a scoping study directed at evaluating the potential road paving applications of oils derived from the eastern U.S. oil shale deposits that were produced in a KENTORT II prototype reactor.^{8,30} In the present era of plentiful and reasonably priced petroleum, commercial production of motor fuels from oil shale is viewed as high risk by those capable of financially supporting such a venture. Thus, the prospects for near-term commercial oil shale development aimed strictly at the transportation fuel sector is not promising. Development of alternative oil shale products that can exploit niche markets and thereby, enhance process economics, are viewed as an important step in stimulating commercial oil shale development.

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 primarily to advanced processing (e.g., fluid-cat crackers) used to recover more heating or motor fuel per barrel, has resulted in asphalts which do not have the desirable properties or longevity as asphalts from 3-4 decades past. Though this is bad news for motorists, this situation has created a potential niche market for shale oils,^{31,32} 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. The study included a series of binder and mixture characterization procedures for evaluation of both short- and long-term performance potential.

Details of the test methods along with preliminary results are described elsewhere^{33,34} and so only a brief description of test methods is given here. The conclusion from this earlier work was that unmodified Eastern shale oil (ESO) showed an unacceptable rate of 'aging' or hardening which would ultimately lead to 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 showed more promise. Accordingly, these latter applications are the focus of this report.

Methods and Results

Study Samples. Two oil streams, produced in a 5-lb/hr KENTORT prototype unit, were selected for study. The first was a highly viscous material (3440 P @60° C) recovered in an electrostatic precipitator and is referred to as the 'hard' ESO. The second, referenced as the 'soft' ESO (8 P @60° C), was derived from a composite of the total oil product that was subjected to a vacuum distillation prior to testing. These two oils were deliberately selected for study since it is believed they represent the types of materials 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 acquired from a freshly exposed outcrop in Rowan County, Ky. A detailed description of the oil shale sample and retort operation is given elsewhere.^{8,30}

Binder Characterization. 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 and aged asphalt mix (pavement recycling).

Evaluation as an asphalt additive involved determining the rheological properties 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 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). 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) with the AC-5 asphalt. Rheological properties of the two blends were then examined.

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 from which the two components of shear modulus, G' and G'' , were 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 Delta value higher than 3 indicates better than average resistance to cracking but less than average resistance to rutting.³⁵ Values less than 3 indicate the opposite.

Aged Asphalt Binder Rejuvenation. The 60°C viscosities of the laboratory-aged asphalt, the soft Eastern shale oil, 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 and the aged asphalt/AC-5 were prepared in an effort to produce samples whose viscosity would bracket the 10,000 poise target value (see Figures 20 and 21). 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 P 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 shown by the unfilled square symbols in Figures 20 and 21. The amount of soft ESO needed to achieve the target viscosity is considerably less than for the AC-5 due mainly to the lower viscosity of the ESO. However, the greater negative deviation in the ESO/aged asphalt curves suggests that even if the AC5 and ESO were of the same viscosity, less ESO would be required to produce an equivalent viscosity blend.

Figure 20. Viscosity of blends from aged asphalt/soft ESO blends. ●-trial blends; □-blend used for mechanical testing.

Figure 21. Viscosity of blends from aged asphalt/AC-5 blends. ●-trial blends; □-blend used for mechanical testing.

Figure 22. Viscosity-temperature plots. □-soft ESO/aged asphalt (34%/66%); ■-AC-5/aged asphalt (58%/42%).

Nearly identical viscosity-temperature relationships are shown for the test blends in Figure 22. 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). These results indicate good asphalt rejuvenation potential for the soft ESO both in terms of dispersal of the aged asphalt and the ability to provide an equivalent viscosity as the AC-5 with less sample.

Table 6. 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	1.244×10^4	6.112
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.376×10^4	5.973
Binder	Dynamic Viscosity, 45°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	1.576×10^5	2.513
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.627×10^5	2.721
Binder	Dynamic Viscosity, 25°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	5.077×10^6	1.582
42 wt.% Recovered Asphalt/58 wt.% AC-5	6.187×10^6	1.738

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 a more conventionally modified asphalt with a 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. Thus, 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 modified field mixtures. This was to compare the behavior of the hard ESO-modified asphalt to the same 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 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 95% level of confidence.

Tensile Strength Characterization. Fatigue and durability response of asphalt pavements are believed to be related to tensile strength. Since it is difficult to make in-situ tensile strength measurements, it is customary to characterize tensile strength of pavement materials indirectly in accordance with ASTM-4123. Figure 23 shows 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 blend ESO. However, previously reported results suggest that 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.^{14,15}

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 test.³⁶ The mean tensile strength data shown in Figure 23, along with statistical analyses of the data, indicates that the hard ESO moisture damage susceptibility compares favorably with the control mixture and was not significantly different than at least two of the polymer modified mixtures. Nonetheless, the data show that hard ESO modified asphalt is somewhat susceptible to binder stripping, as were the comparable modified mixtures.

Figure 23. Tensile strength data for series of modified pavement mixtures. Samples were tested following preparation, moisture susceptibility analysis, and 100 freeze-thaw cycles. Control is pavement mixture without added modifier.

Freeze-Thaw Damage Characterization. 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 $+4^{\circ}\text{C}$). Cross comparisons (Figure 23), along with statistical data analyses, 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 differences.

Rejuvenated Mixture Characterization. Asphalt aging/oxidation severely reduces the tensile strength properties of an asphalt-aggregate mixture as demonstrated by the substantial decline in tensile strength of the aged control sample plotted in Figure 24. Addition of soft ESO to the aged mixture resulted in a notable increase in tensile strength, comparable to that from adding AC-5 asphalt. However, ESO addition did not restore the tensile strength to the level prior to aging. This phenomenon is not untypical and has led to a common practice of adding fresh hot mix to the recycled mixture along

Figure 24. Tensile strength test series for fresh pavement mix, aged mix, and mix rejuvenated with either soft ESO or AC-5.

with the rejuvenating agent. Nonetheless, the mixture rejuvenation analysis shows the soft ESO to have potential asphalt recycling applications and merits further examination.

Summary

Two samples of Eastern shale oil (ESO), one a hard ESO and the other a soft ESO, produced in the KENTORT II process, were evaluated for potential use in the paving industry. The hard ESO material was evaluated as an asphalt additive and the soft ESO was evaluated as an asphalt recycling agent to soften both an aged asphalt and an aged asphalt-aggregate mix.

The hard ESO added at 7 wt% to an AC-20 asphalt showed some susceptibility to moisture damage, though in most cases, no worse than shown by the same asphalt modified with commercial polymers. An improvement in tensile properties of the aged asphalt mixture was achieved through addition of the hard ESO, however, in time, this effect is likely to be offset by pavement cracking due to previously reported aging characteristics.^{5,6}

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. This finding was verified by mixture rejuvenation analysis. 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 equal viscosity, the soft ESO would exhibit more softening per unit weight. Overall, the soft ESO appears to have potential application as an asphalt rejuvenating agent.

Recommendations

Previously reported results indicate that the hard ESO was unstable or reactive for some time following preparation. 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. Therefore, the logical next step is to devise a method to pre-age these oils since they otherwise exhibited favorable asphalt qualities. Further mixture studies could then be conducted to fully characterize both short-term and long-term performance potential of ESO modified/rejuvenated asphalts. Field trial projects are recommended for verification of laboratory test results.

NOMENCLATURE

- A = preexponential factor for 1st-order coking reaction, s^{-1}
 C_b = concentration of oil vapor in bubble phase, mol/cm^3
 C_e = concentration of oil vapor in emulsion phase, mol/cm^3
 $C_{e,avg}$ = average conc. of oil. vapor in emulsion phase, mol/cm^3
 C_{in} = inlet oil vapor concentration, mol/cm^3
 C_r = concentration of oil vapor in particle phase, mol/cm^3
 $C_r(R)$ = conc. of oil vapor at particle surface, mol/cm^3
 d_p = particle diameter, cm
 D_{12} = molecular diffusivity of oil in fluidizing gas, cm^2/s
 $D_{12,eff}$ = effective mol. diff. of oil in fluidizing gas, cm^2/s
 D_{eff} = effective diffusivity of oil vapor in particle, cm^2/s
 D_K = Knudsen diffusivity, cm^2/s
 $D_{K,eff}$ = effective Knudsen diffusivity, cm^2/s
 E_b = axial diffusion coefficient in bubble phase, cm^2/s
 E_e = axial diffusion coefficient in emulsion phase, cm^2/s
 E_o = activation energy of coking reaction, cal/mol
 g = gravitational constant, $980.665\ cm/s^2$
 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,
 $(cm^3)^n/(cm^2)(mol)^{n-1}s$
 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, $82.057\ atm\cdot cm^3/mol\cdot K$, $1.9872\ cal/mol\cdot K$
 Re_{mf} = particle Reynolds number at minimum fluidizing velocity
 S_p = surface area of particle, cm^2/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, cm^3/mol

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 = 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)

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This cover stock is 30% post-consumer waste
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