

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

**Annual Report
October 1, 1992 - September 30, 1993**

**S. Carter
D. Taulbee
A. Vego
J. Stehn
Y. Fei
T. Robl
F. Derbyshire**

November 1993

Work Performed Under Cooperative Agreement 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

MASTER

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University of Kentucky
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3572 Iron Works Pike
Lexington, Kentucky 40511**

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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, 1992 through September 30, 1993 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 PDU was assembled, instrumented and tested during this fiscal year. Along with the major activity of commissioning the 50-lb/hr retort, work was also completed in other areas. Basic studies of the cracking and coking kinetics of model compounds in a fixed bed reactor were continued. Additionally, as part of the effort to investigate niche market applications for KENTORT II-derived products, a study of the synthesis of carbon fibers from the heavy fraction of KENTORT II shale oil was initiated.

ACKNOWLEDGMENTS

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EXECUTIVE SUMMARY

The commissioning of the 50-lb/hr KENTORT II retort was completed this fiscal year. The retort was found to be functional when nitrogen was used for fluidization. To be completely operational, however, steam must be used for fluidization. Once the problems with steam delivery are solved a test matrix consisting of 20 10-hour steady-state runs will proceed next fiscal year.

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. In addition, a fixed bed reactor system was used this year to study the coking and cracking characteristics of model compounds. A fixed bed system was used because the conversion of model compounds was too low in the fluidized bed apparatus. In this study, selected hydrocarbons ranging from benzene to n-decane were passed across pyrolyzed, gasified, or combusted oil shale particles at temperatures between 270°C and 650°C. The reactor was shown to provide a rapid means of measuring hydrocarbon reaction kinetics. The reactivities of the substrates studied were ranked in the following order: gasified shale > combusted ≥ pyrolyzed.

Heavy shale oil produced from the 5-lb/hr KENTORT II prototype was used as the starting material for a study of the synthesis of carbon fibers. This project fits into our objective of exploring and developing niche markets for the various products from the KENTORT II process. A benzene-soluble, hexane-insoluble fraction of the shale oil was processed by melt spinning, oxidative stabilization, carbonization, and activation to produce carbon fibers and activated carbon fibers. Carbon fibers were successfully produced, and one sample which was steam activated yielded a surface area of 960 m²/g. The shale oil fibers have a high nitrogen content which may provide unusual adsorptive or catalytic 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 H₂S prior to combustion creates a relatively concentrated stream of H₂S which is easier to scrub than a dilute stream of SO₂ from combustion. The H₂S 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. One of the most critical issues are the effects that scale-up will have on the extent of solid-recycle induced cracking and coking losses in the pyrolysis zone. The study of secondary coking and cracking reactions of model compounds has been initiated to more fully understand these phenomena. By having basic data which is directly applicable for the materials and conditions of the KENTORT II system, we will have a reliable guide for 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. Another option which deserves attention is the production of adsorbent or activated carbons from the heavy shale oil fractions. It would be a tremendous economic advantage to recover a high value product from the heavy ends without costly hydrotreating. By producing a high value material, the economy of scale for an oil shale plant would be lowered, and it would be much easier to get an industry off the ground in the near term.

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, 2, and 3 during the year. 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, and the model compound study falls in this category. 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. Task 2.2 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 study of the synthesis of carbon fibers falls under this task.

CRACKING OF MODEL COMPOUNDS OVER SHALE PARTICLES

Introduction

In the KENTORT II reactor, pyrolysis heat is provided by recycling hot gasified or combusted shale particles to the pyrolysis zone. Thus, of particular interest are those reactions that can be attributed to the recycling of hot solids and which impact oil yield, i.e., cracking and coking reactions. Within limits, the detrimental effect of recycling hot solids to the retort can be minimized by varying the relative proportion of gasified versus combusted particles or by selecting the optimum recycle rate/particle temperature, i.e., fewer high temperature vs. more low temperature particles.

A previous study^{11,12} focused on the kinetics of shale oil coking as a function of substrate type and temperature using gasified, combusted, and pyrolyzed shales. In a similar manner, the current study will focus on product adsorption and cracking. However, unlike the coking study which utilized freshly generated shale oil, the measurement of adsorption and cracking kinetics in the system described here dictated the use of model compounds.

Experimental

Reactor System. A simplified schematic of the reactor system is shown in Figure 1. High purity N₂ is introduced to a heated valve oven (275 °C) at 100 psig, split into parallel carrier lines and routed through a pair of metering valves. From the metering valves to the reactor, all carrier/transfer lines are constructed of 1/16" x 0.03" 304 ss.

One of the carrier lines, termed the bypass line, is routed through a switching valve, an 18" heat traced transfer line, a 48" preheater coil, and into one of the parallel tube reactors positioned in a 2" x 15" Lindberg tube furnace. In the initial "bypass" mode, this line is routed through the substrate-packed reactor (substrate reactor).

High purity Ar is introduced at 100 psig and metered to the parallel HC carrier line just downstream from the N₂ metering valve. A Waters model 6000A LC pump is used to dispense the liquid hydrocarbon (HC) which first passes through a restriction coil to maintain pump back pressure (and thus constant flow), then into the valve oven where it passes through a downward spiraling volatilization/surge suppressor coil before connecting to the HC carrier line. The HC line parallels the bypass line to the reactor furnace where, in the initial valve position, it passes through the sand-packed bypass reactor.

After passing through the parallel reactors, both lines are combined and continuously sampled just inside the reactor furnace by a heated capillary connected to the inlet of a VG/Fisons Sensorlab 300D quadrupole mass spectrometer (QMS). The QMS may be operated in either a log histogram mode which monitors all mass intensities at 1-amu resolution from zero to a selected upper limit (usually just above the molecular ion of the model compound) or in a selected ion monitoring (SIM) mode which records up to 16

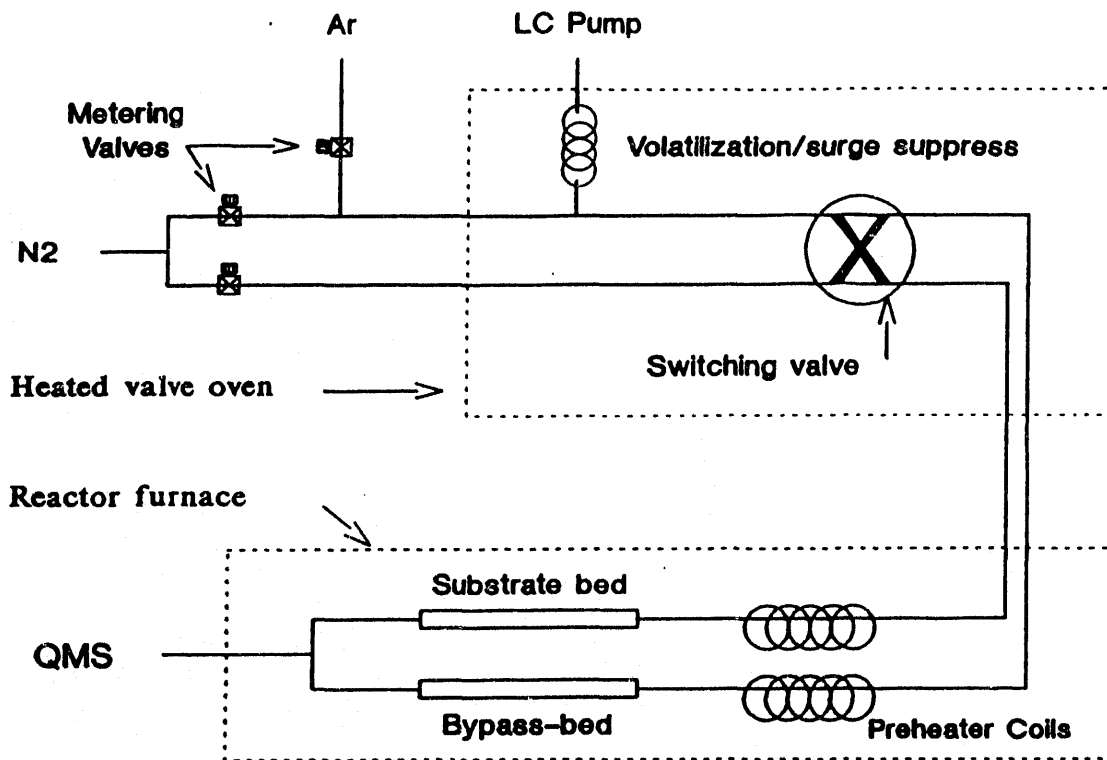


Figure 1. Adsorption/cracking reactor schematic.

selected ion intensities at approximately 1 second intervals. The latter is the preferred operating mode due to a more rapid sampling rate but with the trade-off that not all ion intensities are monitored.

The tube reactors are constructed of 9" x 3/8" -o.d. (1/4" i.d.) 316 ss. One of the reactors, the bypass, is packed with 6 gm of sand while the second, the substrate reactor, is packed with 4 gm of one of the substrates listed in Table 1. Quartz wool is used to hold the solids in place. Substrates are centered in the reactor tubes with an approximate 2" void on each end. A type K thermocouple is placed into each reactor tube, 2.5" from the entrance to the bypass tube and 4" from the entry to the substrate tube. The substrate was removed following each run, crushed, and submitted for elemental analysis. The bypass sand was replaced after each 650°C run (or when the model compound or study substrate was changed).

Study Substrates. The three substrates examined in this study (Table 1) originated from the CL₃-003 master sample taken from Fleming County, Ky.^{11,13,14} These materials represent the three types of solids present in the pyrolysis section of the KENTORT II reactor to which the vapor phase shale oil is exposed. All three substrates were prepared in a fluid-bed reactor using N₂, steam, or air as the fluidizing medium (Table 1). All three substrates were screened to 20 x 60 mesh. The Ottawa sand was screened to 20 x 30 mesh.

Table 1. Study Substrates. Substrates dry-screened to 20x60 mesh.

<u>Substrate</u>	<u>Origin</u>	<u>Reactor Load (g)</u>	<u>Preparation/comment</u>
Pyrolyzed Shale	Cleveland oil shale	4 g	530°C in N ₂ /10 min
Gasified Shale	Cleveland oil shale	4 g	800°C in Steam/20 min
Combusted Shale	Cleveland oil shale	4 g	700°C in air/10 min
Sand	Ottawa, Canada	6 g	20 X 30 mesh

Run Conditions and Procedure. A nominal model compound flow of either 0.1 or 0.2- mL/min was used for all runs. A total gas flow of 150 mL/min (ambient temperature) was maintained through each reactor. This flow was comprised solely of N₂ in the bypass line. For the HC carrier line, Ar tracer gas flow was set to 50 mL/min; the volume of the gas phase model compound was calculated assuming ideal gas behavior; the cumulative flow was adjusted to 150 mL/min with high purity N₂.

Run preparation entailed packing 4 gm of substrate into the substrate reactor and 6 gm of sand into the bypass reactor, setting the Lindberg furnace controller to the target temperature with the reactors in place, and initiating carrier gas and model compound flow. QMS data collection was initiated following a minimum 2-minute equilibration at temperature. The substrate thermocouple reading was manually maintained within 2°C of the target temperature for the duration of the run. After a minimum of 100 data points were collected in the SIM mode (or at least 2 minutes in the log histogram mode), the valve was rotated so that the HC carrier passed through the substrate reactor (make-up line is simultaneously switched to the bypass reactor). Following the selected exposure time, the valve was returned to the initial position and the QMS baseline reestablished. Control runs were made by packing both the bypass and substrate reactor tubes with sand to ensure acceptable system operation.

Data Management. Following data collection, the QMS data files are imported to a spreadsheet where the model compound's molecular ion (and/or selected cracking product) intensity is ratioed to the Ar intensity. These ratios are then exported to a curve-fitting software routine (Sigma Plot) where a linear equation was fitted to the data points collected in the bypass mode (before and after HC/substrate exposure). A function containing both linear

and decaying exponential terms (Eq. 1) was fitted to the molecular ion/Ar ratio obtained during substrate exposure:

$$y = -ae^{-bt} + ct + d \quad (1)$$

The difference in the integrated area between the linear and exponential equations over the substrate exposure interval represents either product loss due to cracking/coking reactions for the high temperature runs ($\sim > 500$ °C), to HC adsorption for low temperature runs ($\sim < 400$ °C), or to a combination of these at the mid temperature ($\sim 400-500$ °C). Further, since the HC flow is known, HC loss can be expressed on an absolute basis, i.e., gms HC/gm substrate

Results and Discussion

A typical run sequence in which cyclohexene was passed through gasified shale at 500 °C is shown graphically in Figure 2a. The response as plotted shows the ion intensity for the molecular ion of cyclohexene ratioed to the Ar ion intensity. Data are displayed as ratios instead of absolute intensities in order to correct for changing conditions during a run, e.g., QMS drift, pressure fluctuations, etc. The first segment represents QMS response in the initial valve position (bypass mode) in which the model compound is flowing through the sand-packed bypass bed. The second segment shows QMS response with the valve switched so that the model compound passes through the substrate reactor. The third segment shows the return to bypass mode at which time the QMS baseline is reestablished.

There is no measurable desorption in the data of Figure 2a following return to bypass suggesting that all product loss is attributable to cracking or coking losses. Evidence that this loss is due in large part to cracking reactions can be found in Figure 2b, which shows a substantial increase in the mass 42 (largely propene) to mass 82 (cyclohexene) ratio during exposure.

The high initial HC loss followed by a gradual decline to constant response was characteristic of the high temperature runs (Figure 3). Generally, substrate reactivity followed the order of gasified $>$ combusted \geq pyrolyzed. Also, cyclic aliphatics were found to be more susceptible to induced reaction than were straight chain aliphatics with aromatics generally exhibiting the greatest stability. As of this writing, carbon analysis of the substrates is incomplete and thus product loss due to coking versus cracking cannot yet be differentiated. However, it is believed that cracking reactions (i.e., thermal cleavage with little or no coke deposition) are much more prevalent for aliphatics (particularly cyclic aliphatics) than aromatics which more likely undergo a higher proportion of coking reactions in the initial interaction. To help differentiate between cracking and coking losses, future runs are planned in which the total product stream will be combusted with the resulting CO_2 and H_2O products monitored with the QMS. It is anticipated that this approach will unambiguously determine coking losses with cracking losses determined by difference.

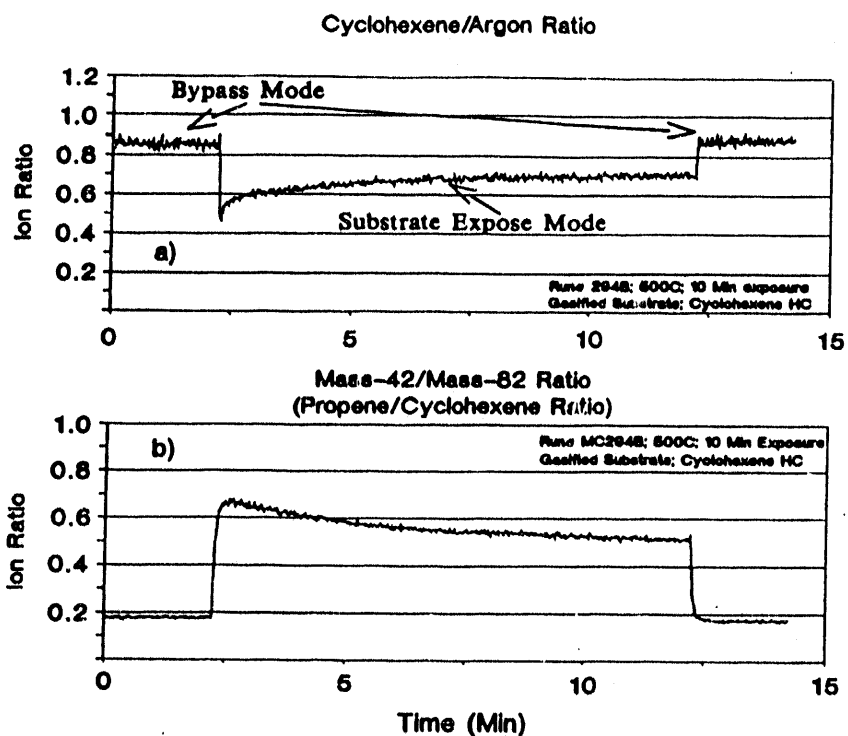


Figure 2. Gasified Shale, 500°C, 10 min. exposure, 10 vol% cyclohexane in Ar/N₂ carrier. a) Cyclohexene/Ar (82/20) ion ratios, b) Mass 42/mass 82 (largely Propene).

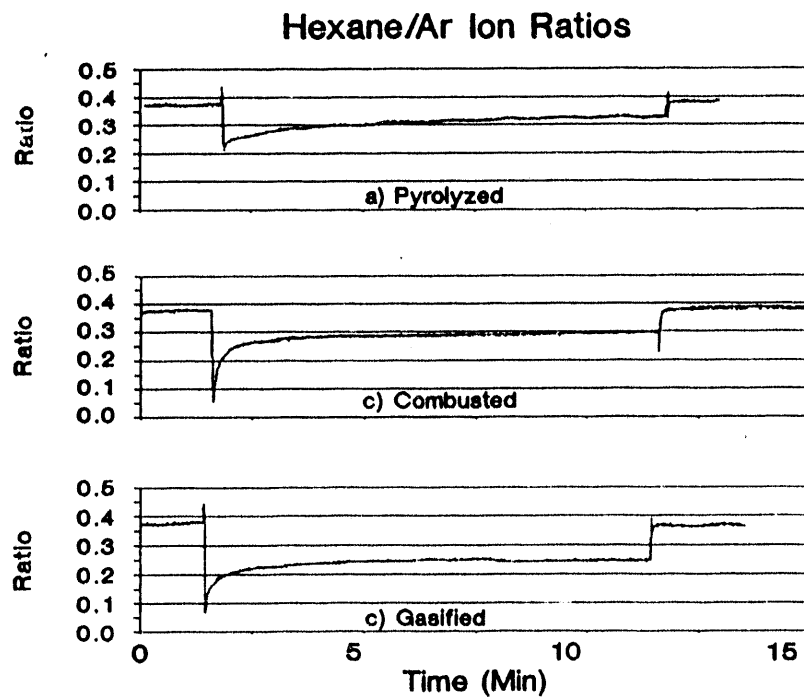


Figure 3. Hexane/Ar ratios for 650°C, 10 min. exposure, 10 vol% hexane in Ar/N₂ carrier. a) pyrolyzed, b) combusted, and c) gasified shale.

Figure 4 shows a similar cyclohexene/Ar ion intensity plot at a lower temperature of 300 °C. HC loss in this run is attributed solely to adsorption since 1) the QMS response during the bypass mode and the latter portion of the expose mode are equivalent and 2) the desorption curve following return to bypass is equal in magnitude to the HC loss observed in the initial stages of substrate exposure. Generally, adsorption capacity followed the order of gasified >> combusted \geq pyrolyzed shale. Adsorption was so extensive for many of the low temperature gasified shale runs that QMS response dropped off scale resulting in a delay in data collection of up to 2 minutes in some instances.

Summary

The reactor system described in this manuscript provides a rapid means of measuring HC reaction kinetics. The system is flexible in that direct comparisons of solid substrate reactivities may be compared over a wide temperature range with a variety of hydrocarbons. Though not discussed, fixed gases are also amenable to adsorption/desorption studies by this technique. Future plans include: 1) examination of the liquid products and ultimate analysis of the solid substrates following exposure in order to help elucidate reaction mechanisms and differentiate between predominantly cracking versus predominantly coking reactions and 2) examining mixtures of two or more hydrocarbons to determine differential adsorption/desorption kinetics.

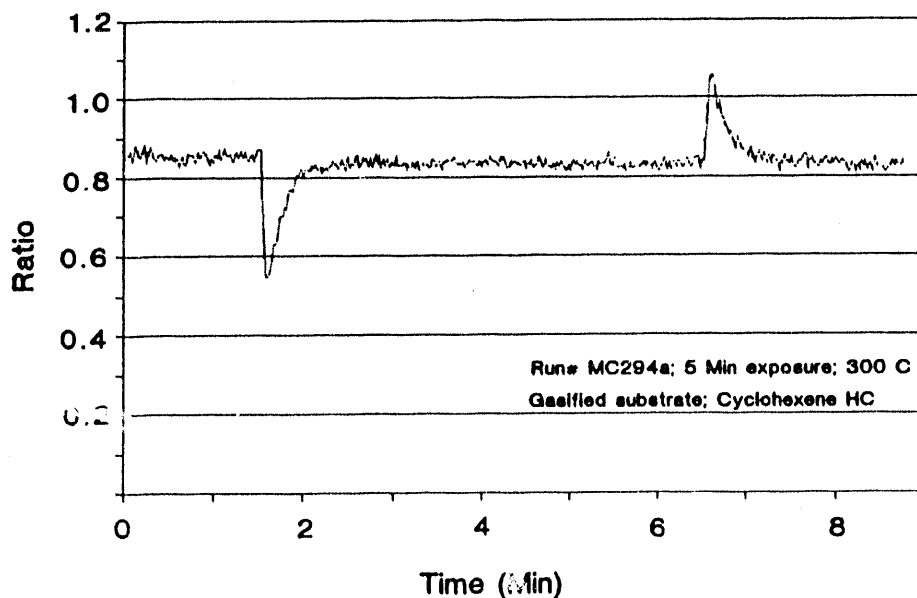


Figure 4. Cyclohexene/Ar ion intensity during gasified shale run at 300°C, 5 minute exposure. Otherwise, same conditions as Figure 2.

CONSTRUCTION AND SHAKEDOWN OF 50-LB/HR KENTORT II PDU

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 5). 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.¹⁵

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.

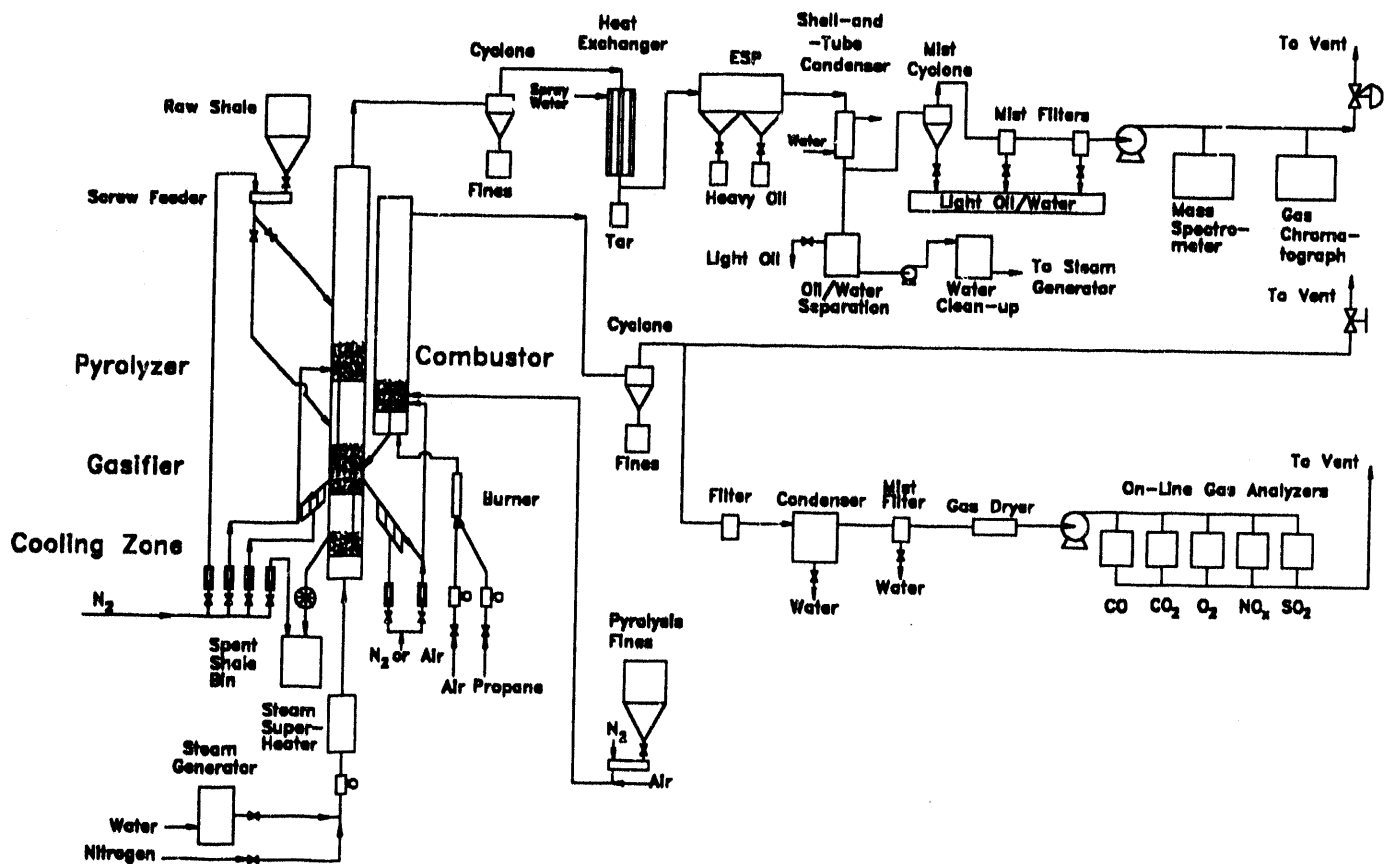


Figure 5. Schematic diagram of the 50-lb/hr KENTORT II process.

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

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

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

Construction Activities

During the last quarter of the previous annual reporting period, our machining subcontractor completed fabrication of the main reactor. The retort was set permanently into place early in this fiscal year, and then the fabrication and installation of ancillary equipment, utilities, and instrumentation was completed. The most significant pieces of equipment which were custom-fabricated and installed this year include:

- o aerated J-valves
- o electrostatic-precipitator housing
- o oil and water collection system
- o pyrolysis-gas heat exchanger
- o raw shale feed hopper
- o retort internals (distributor plates, downcomers, etc.)
- o screwfeeder
- o spent shale bin
- o steam superheater

In addition to these items, the cyclones and the start-up burner were installed. All necessary process fluids (air, nitrogen, steam, and water) were connected to the retort. Installation of the instrumentation, process control, and computerized data acquisition systems were completed.

Retort internals which are exposed to temperatures above 700°C were aluminized, as was the combustor cyclone. The entire reactor was covered with 4 inches of alumina silicate insulation, and heating tapes were installed beneath the insulation around the cooling, gasification, and pyrolysis zones. The heating tapes are designed to compensate for heat losses and facilitate the heat-up process.

By the beginning of the fourth quarter, the KENTORT II 50-lb/hr PDU was completely functional and instrumented. All of the equipment shown in Figure 5 is now installed with the exception of the pyrolysis-fines feeding system.

Retort Shakedown

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

associated with the start-up of the 50-lb/hr PDU can be roughly termed cold-flow and hot-flow testing, respectively.

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

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

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

Fines generation during cold-flow testing was not excessive. Approximately 11% of the feed was recovered in the pyrolysis cyclone (10% carryover was the design basis). Most of these collected fines were fed into the retort as undersized material clinging to particles in the 20 x 60 mesh range. Minimal attrition of the particles can be expected at room temperature as demonstrated by the small amounts collected in the combustion cyclone. Since the gasifier and pyrolyzer are the feed points for shale into the retort, any fines which are fed to the system will be entrained before circulation to the combustor. Small quantities of fines were found in the pyrolyzer heat exchanger and in the electrostatic precipitator. It is difficult to determine at this time whether these quantities are excessive. Only under actual pyrolysis conditions will it be apparent whether entrained fines will hamper oil collection, especially in the electrostatic precipitator (ESP).

Hot-Flow Testing. Nitrogen was used for fluidization of the cooling, gasification, and pyrolysis (CGP) zones during the hot-flow tests. This was done for convenience because condensation of steam in undesirable areas of the system would cause unnecessary difficulties during this early phase of testing. The nitrogen was heated by the steam superheater to approximately 500°C which, in turn, heated the CGP zones during the start-up process. The maximum temperature of the nitrogen from the superheater was achieved within three hours when starting from room temperature (see Figure 6). The electrical heating tapes surrounding the cooling and pyrolysis zones also provided some energy during start-up. The heat tapes for the pyrolyzer provide enough energy to make it hotter than the gasifier during this portion of the heat-up process (see Figure 6).

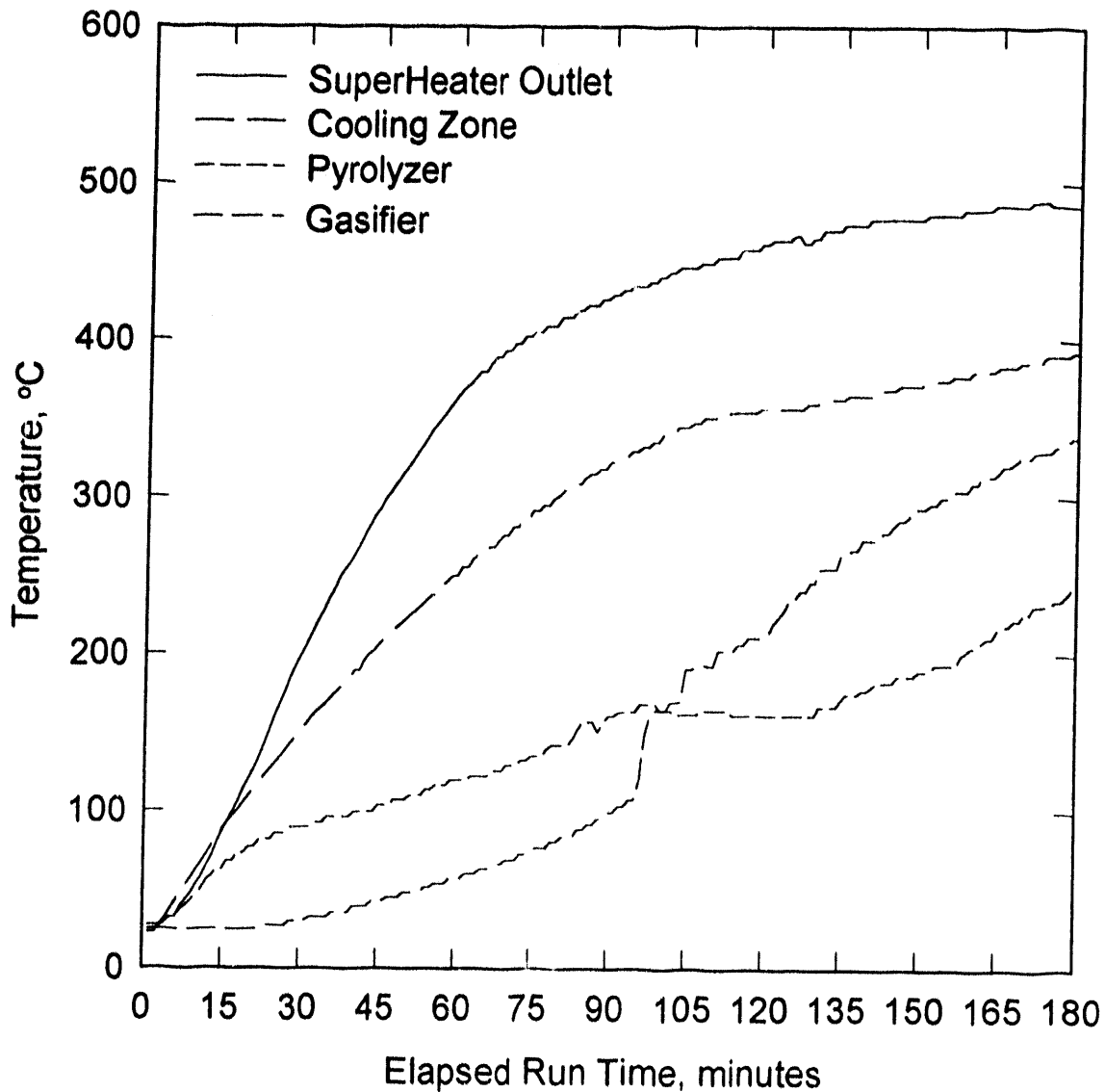


Figure 6. Heat-up profiles of the cooling, gasification, and pyrolysis zones from run KT930902 as a result of heated nitrogen from the steam superheater.

Start-up heat for the combustor was provided by a propane burner which was in line with the fluidizing air. Early in the start-up process, no solids were recycled to the combustor so that the temperature would be quickly elevated. Typically, the combustor temperature reached 800°C within one hour (see Figure 7). To avoid over heating the combustor and to heat the remainder of the system, the next step in the start-up procedure was to initiate the recirculation of shale between the combustor and the gasifier. This caused an initial drop in the combustor temperature (Fig. 7), but it caused a corresponding increase in the rate at which the gasification zone was heated. The burner provided approximately 40,000 Btu/hr of gross energy input while the superheater contributed approximately 20,000 Btu/hr of gross heat.

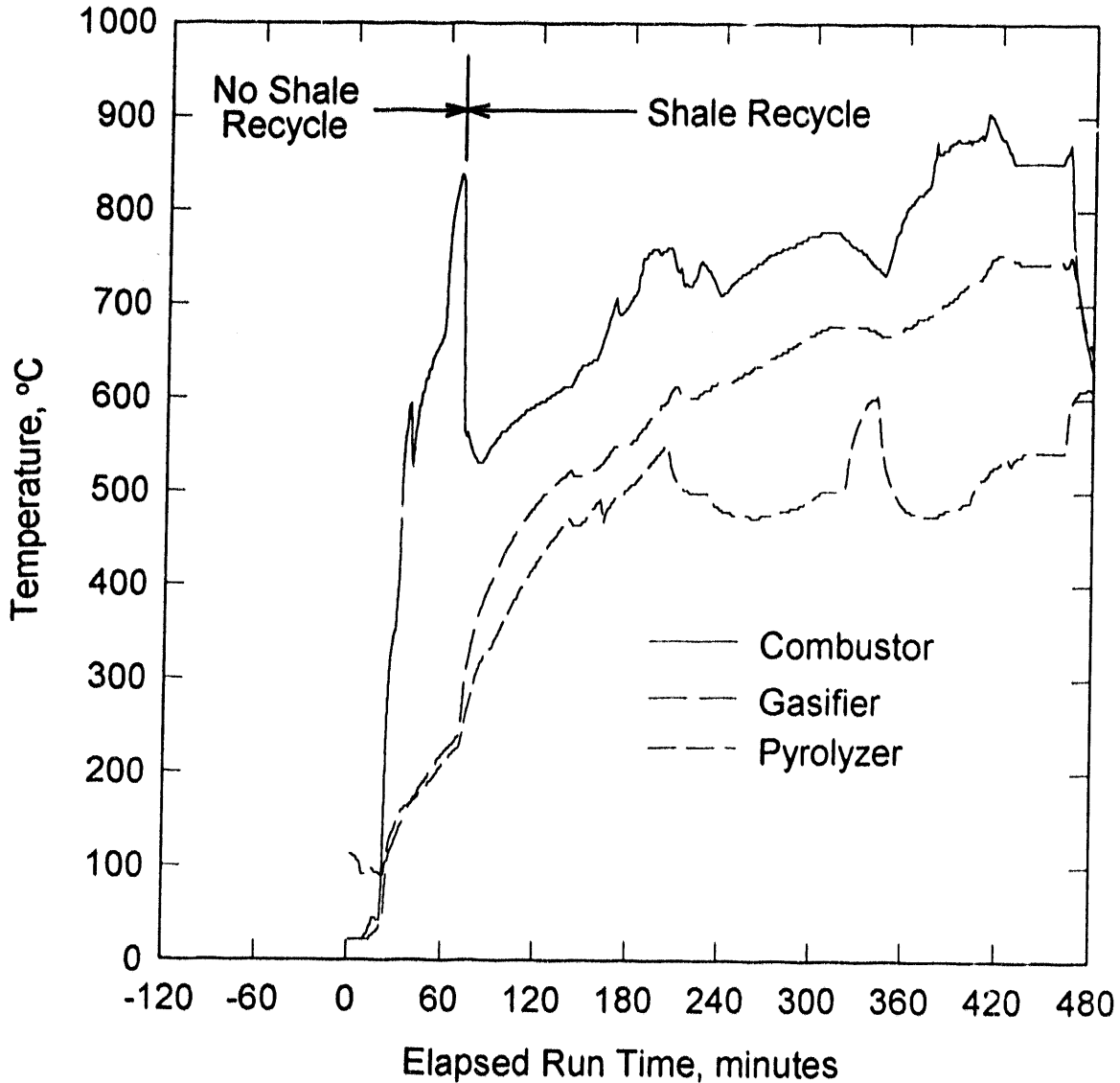


Figure 7. Temperature profiles for the combustor, gasifier, and pyrolyzer from run KT930920 illustrating the effect of shale recycle between the combustor and gasifier on the heat-up rate of the system.

The 100% greater energy input by the propane burner is appropriately reflected by the more rapid heat-up rate of the gasifier during the period of solids-recycle between the combustor and gasifier compared to the period when heat was only supplied by the steam superheater.

Three major shakedown runs were completed during the last month of the fiscal year (see synopses in Table 2), and the successes outweighed the setbacks. The most significant

Table 2. Run Synopses

Run	Highlights
KT930902	<ul style="list-style-type: none"> o From a cold start, the run lasted approximately 8 hours which included about 3 hours where the temperatures of the 4 beds were at near steady state. o The propane burner raised the temperature of the combustor to 650°C before it ceased operation following the initiation of solid recycle between the combustor and gasifier. o The combustor sustained temperatures ranging from 700 to 780°C without the aid of the start-up burner. o Shale was fed to and withdrawn from the retort continuously to provide enough carbon to sustain combustion. o The pressure in the gasifier could not be sufficiently adjusted downward so that it was the same as in the combustor at the balance point. This hindered the operation of the unit, and was at least partly responsible for a process upset that caused termination of the run. o The temperature of the ESP was too low (less than 120°C) to permit operation with steam, so nitrogen fluidization was used for the duration of the test. o Some oil was produced and collected, but because of the relatively short duration of the steady state period and the inability to operate with steam, the amount of oil collected was not meaningful.
KT930920	<ul style="list-style-type: none"> o Combustion flue gas analyzers were placed on line. o A higher-pressure source of propane was used to fuel the burner, and it operated flawlessly. o Pyrolyzed shale was periodically fed to the system in order to provide carbon for fuel yet not produce oil. o Design temperatures for each of the zones were achieved: Pyrolyzer (500-600°C), Gasifier (750°C), and Combustor (850°C). o Pressure balance between the combustor and gasifier could not be achieved. o The ESP temperature was still too low to permit steam fluidization.
KT930927	<ul style="list-style-type: none"> o No shale was fed to the system in order to test the capabilities of the start-up heaters without aid from carbon in the shale. o Proper pressure balance between the gasifier and the combustor was maintained. o The temperatures attained for each of the zones were: Pyrolyzer (600°C), Gasifier (725°C) and Combustor (775°C). o Additional insulation was not sufficient to raise the outlet temperature of the ESP above 100°C.

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

- o The problem with the burner was solved by using a source of propane which was higher in pressure. In the original configuration, the burner would cease operation whenever the back pressure in the burner increased. This generally occurred when the proper bed height in the combustor was attained.
- o The problem of pressure balancing the combustor and gasifier was solved by installing a gate valve at the outlet for the combustion flue gases. It was found that independent adjustment of back pressure at each of the gas stream outlets was necessary in order to properly pressure balance the retort.
- o Excessive heat losses from the pyrolyzer to the inlet of the heat exchanger caused the inlet temperature of the ESP to be much lower than expected. In addition, heat losses from the ESP itself were also quite large. Much additional insulation was installed from the pyrolyzer to the heat exchanger, and electrical heating pads were installed on the ESP to eliminate the large heat losses so that the temperature in the ESP will remain well above 100°C. While testing of these improvements was not completed during this reporting period, it was known at the time of this writing that these efforts were successful.

Summary and Future Plans

The 50-lb/hr PDU has been shown to be functional when nitrogen is used to fluidize the CGP zones. To be considered completely operational, however, steam must be used for fluidization. Steam is crucial to the KENTORT II PDU for two reasons. First, steam is a necessary reactant for the gasification zone, and, second, the oil collection system was designed around the use of steam. Shakedown runs using steam for fluidization are planned for the first month of the next fiscal year. Once the system can successfully operate with steam, an experimental matrix will be initiated. The yield and composition of oil and gas products will be evaluated as a function of the gasification temperature and the rate and temperature of shale being recycled to the pyrolyzer.

CARBON FIBERS FROM RESIDUAL SHALE OIL

Introduction

Oil shale is one of the world's largest, albeit unused, fossil fuel reserves, and an important source of liquid fuels and chemicals. One of the disadvantages of shale oil liquids is their high nitrogen content, which causes difficulties in their upgrading to premium quality products.¹⁶ To accentuate the problem, the nitrogen-containing species tend to be concentrated in the higher boiling fractions.¹⁷ A more attractive use for the heavy liquids may be as precursors for the synthesis of added-value advanced carbon materials. The ability to generate valuable by-products could enhance the economics of oil shale retorting.

Carbon fibers (CF) and activated carbon fibers (ACF) are commercially produced from polyacrylonitrile (PAN) and petroleum and coal-tar pitches. The PAN-based fibers have very high strength, so they command a higher price than pitch-based ones. Other factors that contribute to the price are the high raw material cost, and low yield.¹⁸ Pitch-based fibers can be formed, by directly processing the precursor, to produce moderate strength isotropic carbon fibers, or after heat treatment to induce mesophase formation, when the fibers can have high modulus, and high thermal and electrical conductivity.¹⁹

Activated carbon fibers produced from PAN have several unique properties,²⁰ including the ability to adsorb NO_x , SO_x , and vitamin B12,^{21,22} and where there may be novel metal-support interactions.²³ This may be related to their nitrogen content, which can lead to the presence of basic functional groups on the adsorptive surface. For similar reasons, it is considered that carbon fibers and activated carbon fibers produced from oil shale residues might exhibit unusual properties that are not possessed by fibers from petroleum or coal-tar pitches. Accordingly, a program of work has been initiated to study the synthesis of carbon fibers from residual shale oil liquids.

Experimental

A shale oil residue (SOR), produced in the KENTORT II process,¹⁴ was used as the starting material. The asphaltene fraction, SOR-AS, (hexane insoluble, benzene soluble) was separated as follows. The hexane fraction of the shale oil residue was removed by extraction with boiling hexane.²⁴ The hexane insoluble fraction was then Soxhlet extracted with benzene, and the benzene was removed from the extract by rotary evaporation. A petroleum-derived isotropic precursor pitch (PP) was selected for comparison.

Continuous single filament carbon fibers were produced from the shale oil asphaltenes and the petroleum pitch by melt spinning, using a spinneret (capacity about 8 g, nozzle diameter 0.3mm) that is operated under nitrogen pressure. The shale oil and petroleum precursors were spun under 150-300 kPa pressure at about 240 and 300°C, respectively. The resulting fibers were then chopped into 15-20 mm lengths and stabilized by oxidation in air for 90 minutes at 180 and 230 °C for the shale oil and petroleum pitch fibers, respectively.

The stabilized fibers were carbonized in nitrogen at 850°C for 30 minutes. Carbon fibers were activated at 850°C for 60 minutes in 50 vol% steam or carbon dioxide, in nitrogen. The sequence of process steps for the preparation of CF and ACF is shown in Figure 8.

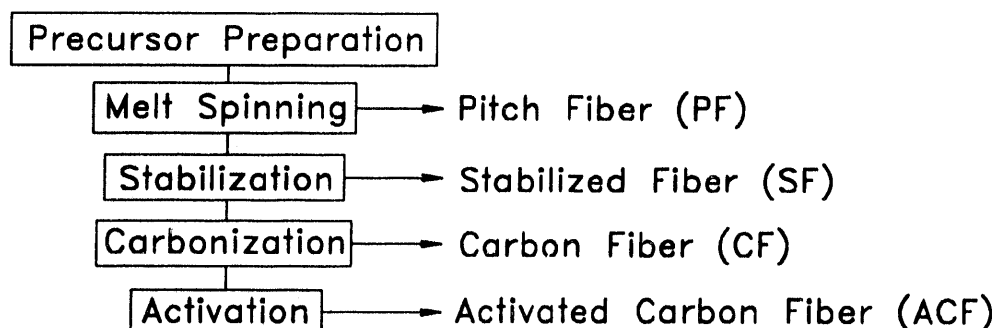


Figure 8. Flowsheet of the preparation of carbon fibers and activated carbon fibers.

The morphology of the CF and ACF was studied at magnifications of up to $\times 10^4$ by SEM (Hitachi S-2700). The BET surface area of ACF was measured by nitrogen adsorption at 77K, using a Quantachrome Autosorb 6.

Results and Discussion

Carbon Precursors. Analyses of the shale oil residue, its asphaltene fraction, and the petroleum pitch are shown in Table 3. The asphaltenes represent about 20 wt% of the original residue. It can be seen that the slightly higher nitrogen content of the residue (compared to the petroleum pitch) is considerably concentrated in the asphaltene fraction. The sulfur contents of the three materials are similar, but the petroleum pitch has a somewhat lower ash content. The shale oil asphaltene fraction has a softening point of 183°C, which is lower than that of the petroleum pitch, consistent with its higher hydrogen content.

Table 3. Analyses of Precursor Materials.

Sample*	Elemental Analysis (wt%)				Atomic Ratio		Ash (wt%)	Softening Point(°C)
	C	H	N	S	H/C	N/C		
PP	92.9	4.6	0.3	2.0	0.6	0.3	0.2	258
SOR	83.2	9.6	0.5	1.8	1.4	0.5	0.8	<25
SOR-AS	81.0	6.6	2.5	2.0	1.0	2.7	1.0	183

* PP, petroleum-derived isotropic pitch; SOR, shale oil residue; SOR-AS, asphaltenes: hexane insoluble, benzene soluble.

Carbon Fibers. Carbon fibers were successfully produced from the shale oil asphaltene fraction. SEM micrographs of the carbonized fibers are shown in Figure 7. Small particles (100-500nm) were observed on fiber surfaces; their origin is tentatively ascribed to the ash components in the precursor.

The form of the fibers was clearly retained after carbonization, indicating that the conditions chosen for stabilization were sufficient. The stabilization temperature of 180°C used here is much lower than those for conventional isotropic or mesophase pitches.²⁵ This suggests that the precursor has a very high oxidation reactivity.

While the freshly spun fibers has similar diameters for both precursors, the diameter of the shale oil carbonized fibers was smaller (in the range of 5-12 µm) than that of petroleum-derived ones (6-15 µm), as shown in Table 4. The greater degree of contraction of the shale oil fibers reflects their lower carbonization yield (50% versus 71%), or higher volatile matter content.

Table 4. Carbonization of two kinds of green fibers.

Sample Code	Precursor Type	Yield (wt%)*	Diameter of CF (mm)
CF-P1	PP	71	6-15
CF-S1	SOR-AS	50	5-12

* carbonized at 850°C for 30 min; yield as % of green fibers.

Activated Carbon Fibers. The morphology of ACF derived from petroleum pitch and shale oil asphaltenes, and produced by activation of the respective carbonized fibers is shown in Figures 8 and 9. Ridges are apparent on the surfaces of the petroleum fibers, and they tend to follow the fiber circumference. Despite this, the surface appears relatively smooth and there are no evident cracks or pores. With the shale oil fibers, an irregular distribution of small pits or pores have developed over the fiber surfaces. In addition, particles can be observed on the surfaces of some of the pore walls. It may be that some of the ash components can have a catalytic influence on the activation or gasification of the fibers, and are instrumental in the generation of these features. The SEM micrographs also suggest that there are some differences in the internal morphology of the two types of fiber.

As shown in Table 4, under similar conditions, the shale oil carbon fibers experienced much greater burn-off during steam activation than the petroleum pitch fibers. This finding also indicates that the former are more reactive to reactions with oxidizing gases, whether due to certain inherent aspects of their composition and structure, or to the catalytic effect of ash constituents. Predictably, activation in carbon dioxide, which is known to be a slower reaction, caused lower burn-off than steam under the same conditions. Despite the different

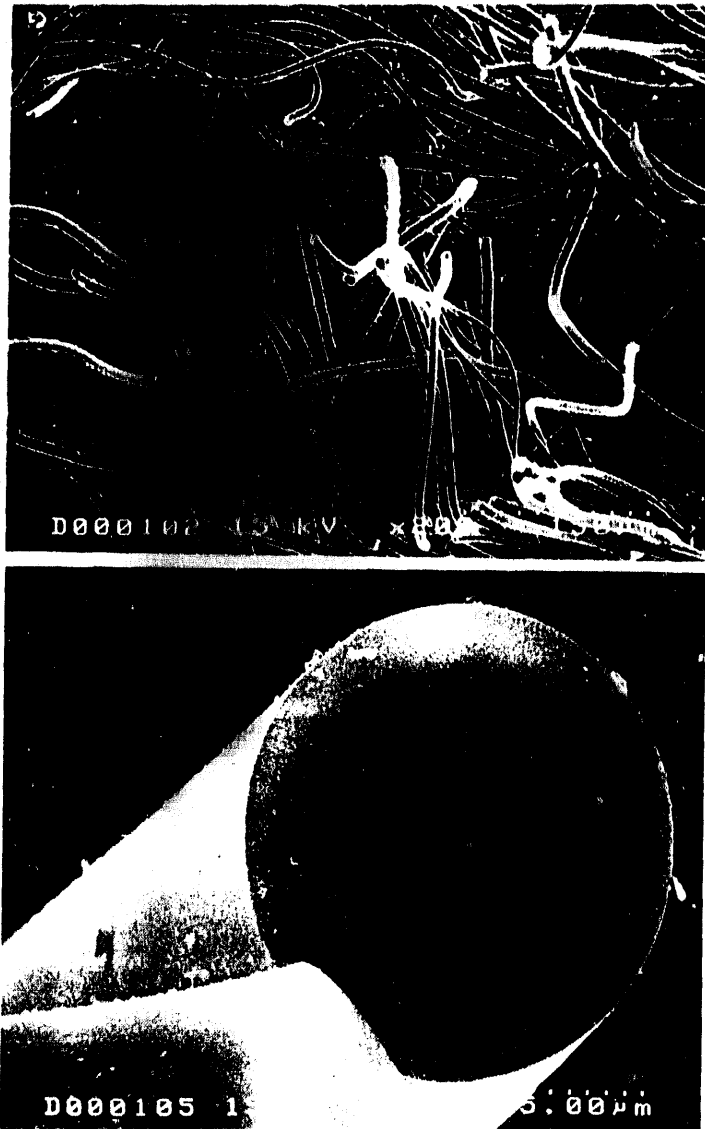


Figure 9. SEM micrographs of carbon fibers produced from shale oil.

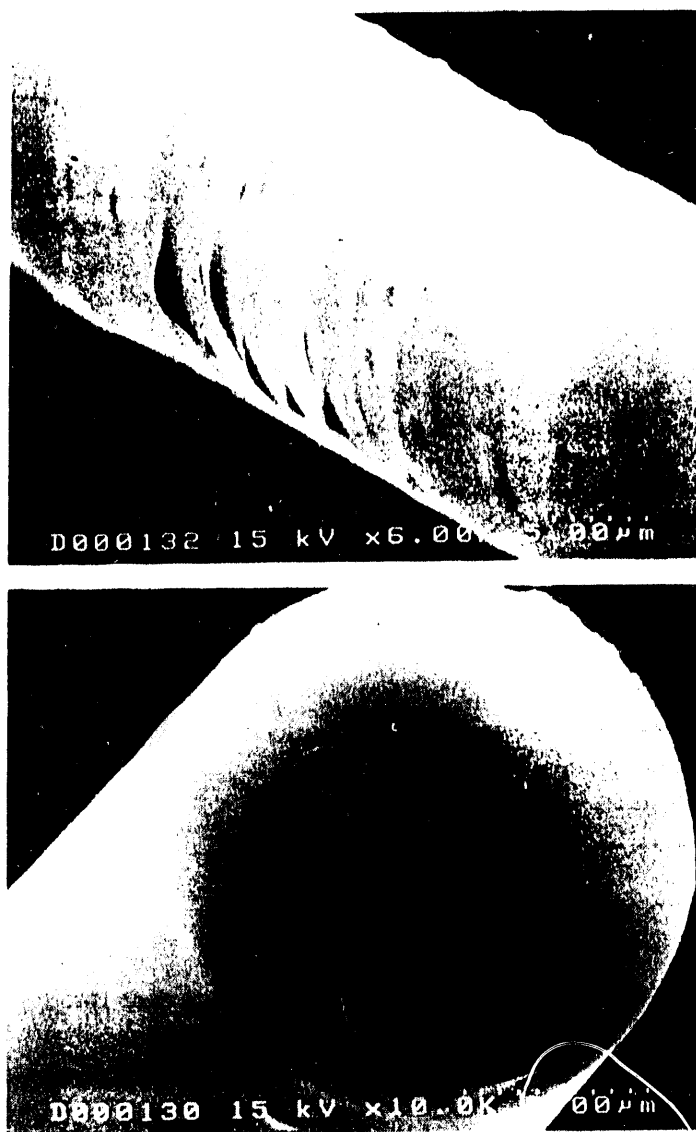


Figure 10. SEM micrographs of activated carbon fibers from petroleum pitch by steam activation.



Figure 11. SEM micrographs of activated carbon fibers from shale oil by steam activation.

Table 5. Activation of petroleum and shale-oil-derived carbon fibers.

Sample Code	Precursor Type	Activating Agents	Burn-off (wt%)*	Dia. of CF (mm)	Surface Area (m ² /g)
AF-P1	PP	H ₂ O/N ₂ (50:50)	38	4-12	978
AF-S1	SOR-AS	H ₂ O/N ₂ (50:50)	63	3-10	960
AF-S2	SOR-AS	CO ₂ /N ₂ (50:50)	49	3-10	566

* carbonized at 850°C for 30 min; yield as % of green fibers.

degrees of burn-off, the steam-activated fibers from pitch and shale oil have similar BET surface areas. There may be significant differences in their pore size distributions, although this has yet to be determined, as does the dependence of pore structure on burn-off.

Nitrogen Content. The changes in nitrogen content (N/C atomic ratio) during carbonization and activation for both kinds of precursor are shown in Figure 12. For petroleum pitch, the nitrogen content increased upon carbonization and then remained at a similar level through steam activation. As already noted, the N/C ratio was much higher in the shale oil asphaltenes. It was slightly reduced upon carbonization, and then increased upon activation: the N/C ratio for activated carbon fibers was about 0.03.

Summary

Preliminary studies have been made of the feasibility of producing carbon fibers from high boiling shale oil liquids. Single filament carbon fibers and activated carbon fibers have been produced successfully from an asphaltene fraction of shale oil residuum, by spinning, oxidative stabilization, carbonization, and activation. Comparisons were made with fibers derived from a petroleum pitch.

The yield of the shale oil carbonized fibers was around 50% while that for the petroleum pitch was about 70%. Differences in yield are attributed to the different volatile contents of the precursors.

Activated carbon fibers were obtained by steam activation of the carbonized fibers at 850°C. A BET surface area of around 960 m²/g was obtained at 63% burn-off for the shale oil fibers. A similar surface area was obtained for the petroleum pitch based fiber after reaction under the same conditions but with only 38% burn-off. The greater reactivity of the shale oil fibers may be due to their inherent structure, the catalytic effect of ash constituents,

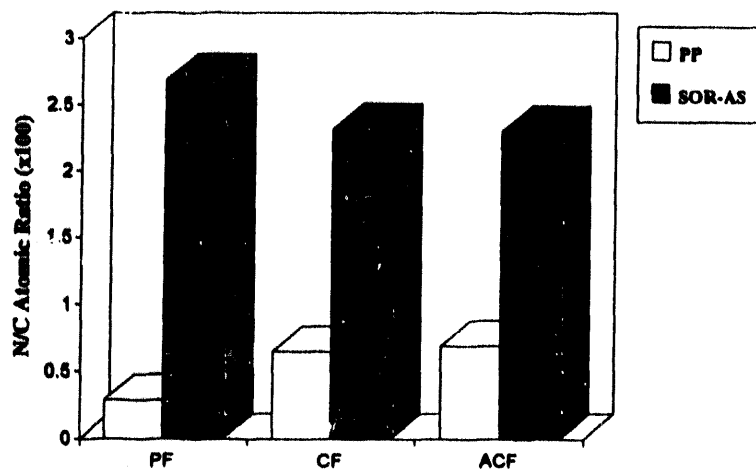


Figure 12. Changes in nitrogen content during the preparation of carbon fibers and activated carbon fibers from shale oil (SOR-AS) and petroleum precursors (PP).

or both; some evidence for catalysis is provided by microscopic observations. High reactivity of green fibers is also indicated by the low reaction temperature required for oxidative stabilization. The high nitrogen content of the activated shale oil fibers may provide unusual adsorptive or catalytic properties.

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