Conf-931156--39

DOE/MC/27286-94/C0281

Oil and Gas Yields From Devonian Oil Shale in the 50-lb/hr KENTORT II
Process Demonstration Unit: Initial Results

Authors:

R.L. Robl
S.D. Carter
D.N. Taulbee

Contractor:

Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511

Contract Number:

DE-FC21-90MC27286

Conference Title:

Fuels Technology Contractors Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

November 16-18, 1993

Conference Sponsor:

U.S. Department of Energy, Morgantown Energy Technology Center

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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

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

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

Oil and Gas Yields from Devonian Oil Shale in the 50-lb/hr KENTORT II Process Demonstration Unit: Initial Results

CONTRACT INFORMATION

Cooperative Agreement DE-FC21-90MC27286

Contractor Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511
(606) 257-0265
(606) 257-0302 (FAX)

Contractor Project Manager Thomas L. Robl

Principal Investigators Scott D. Carter
Darrell N. Taulbee

METC Project Manager J. Keith Westhusing

Period of Performance September 28, 1990 to March 27, 1994

Schedule and Milestones

FY93-94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Retort Shakedown	_____											
Retort Test Matrix		_____										
Product Characterization			_____									
Economic Evaluations						_____						

OBJECTIVES

The broad 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. Many of our objectives have already been realized. The retort has been successfully constructed and the

shakedown phase is essentially complete. In addition, much of the coking and cracking kinetics experiments have been completed which will provide important information for the operation of the retort. We are now entering the testing phase for the retort which has the following objectives:

- o Determine any relationships between the retorting conditions and the yield and characteristics of the products, and compare the results to those from the bench-scale shale oil cracking and coking experiments.
- o Study and develop alternative applications for the products from the KENTORT II process. In particular, asphalt performance tests will be conducted on the heavy fraction of oil produced during the testing phase.

BACKGROUND INFORMATION

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. 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. 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.

PROJECT DESCRIPTION

The project is divided into three main tasks. The tasks which are yet to be completed are 2.2, 3.2, and 3.3. The task list for the entire project is 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

RESULTS--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 1) 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.¹¹

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

rev. 10-12-93

Figure 1. Schematic Diagram of the 50-lb/hr KENTORT II Process

zone is baffled to narrow the particle residence time distribution. The design conditions for the pyrolyzer are: temperature, 500-550°C; raw shale feedrate, 50 lb/hr; mean shale residence time, 3 minutes; bed depth, 12 inches; maximum solid recirculation rate, 200 lb/hr.

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

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

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

bed to provide additional fuel. Air is used for fluidization in the combustor.

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

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

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

and superheater is reduced 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 FY91-92 our machining subcontractor completed fabrication of the main reactor. The retort was set permanently into place early in FY92-93, 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 during FY92-93 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 last quarter of FY92-93, the KENTORT II 50-lb/hr PDU was completely functional and instrumented. All of the equipment shown in Figure 1 is now installed with the exception of the pyrolysis-fines feeding system.

Retort Shakedown and Procedure Development

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 2). 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 2).

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

Figure 2. Heat-up profiles of the cooling, gasification, and pyrolysis zones from run KT930902 as a result of heated nitrogen from the steam superheater

combustor so that the temperature would be quickly elevated. Typically, the combustor temperature reached 800°C within one hour (see Figure 3). 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. 3), but it caused a corresponding increase in the rate at which the

gasification zone was heated. The burner provided approximately 50,000 Btu/hr of gross energy input while the superheater contributed approximately 20,000 Btu/hr of gross heat. The 150% 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.

Figure 3. 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 rates

Three major shakedown runs were completed during the last month of FY92-93 (see synopses in Table 1), and the successes outweighed the setbacks. The most significant findings were that the system displayed stable operating tendencies and that the design temperatures and shale recycle rates were achieved for each zone. The problems that were encountered had nothing to do with the retort itself as they were all associated with ancillary pieces of equipment. A brief

description of each 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

Table 1. 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.
	<p>occurred when the proper bed height in the combustor was attained.</p> <ul style="list-style-type: none"> 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.

SUMMARY AND FUTURE WORK

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 FY93-94. 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.

REFERENCES

1. Rubel, A.M., M.J. Margolis, J.K. Haley, and B.H. Davis, *1983 Eastern Oil Shale Symposium Proceedings*, 1983,

IMMR83/089, University of Kentucky, Lexington, Ky.

2. Margolis, M.J., *1981 Eastern Oil Shale Symposium Proceedings*, 1981, University of Kentucky, IMMR82/066, Lexington, KY.
3. Richardson, J.H., E.B. Huss, L.L. Ott, J.E. Clarkson, M.O. Bishop, L.J. Gregory, and C.J. Morris, Lawrence Livermore National Laboratory, UCID-19548, 1982.
4. Ahmed, M.M., D.W. Parker, and D.H. Archer, *1982 Eastern Oil Shale Symposium Proceedings*, 1982, University of Kentucky, IMMR82/075, Lexington, KY.
5. Rubel, A.M. and S.D. Carter, *Preprints Div. Pet. Chem.*, ACS, 1984, 29, 202-208 (1).
6. Wallman, P.H., Tamm, P.W., and Spars, B.G., *ACS Symp. Ser. 163*, 1981, 93.
7. Bissel E.R., Burnham, A.K., and Braun, R.L., *I and EC Proc. Des. Dev.*, 1985, 24, 381.
8. Carter, S.D., Rubel, A.M., Robl, T.L., and Taulbee, D.N., 'The Development of the KENTORT II Process for Eastern U.S. Oil Shale,' 1990, Final Report for work performed under Contract No.: DE-FC21-86LC11086, DOE/LC/11086-2860.
9. Carter, S.D. and D.N. Taulbee, *Fuel Processing Technology*, 1985, 11, 251-272.
10. Robl, T.L., K. Cisler, G. Thomas, and D.W. Koppenaal, *1985 Eastern Oil Shale Symposium Proceedings*, 1985, University of Kentucky, KCERL/85-147, Lexington, Ky.
11. Vego, A., Carter, S.D., Stehn, J.L., and Neathery, J.K., *1991 Eastern Oil Shale Symposium Proceedings*, 1991, University of Kentucky, in press, Lexington, KY.

DATE

FILMED

4 / 4 / 94
tb / tr / tr

END