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

**Quarterly Report
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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, 1993 through December 31, 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. Retort shake-down tests were performed this quarter, and during one of these tests, oil was generated for the first time in the 50-lb/hr system. Minor equipment problems were also identified and a remediation plan was implemented.

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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 provides few benefits and can make the system more complicated than necessary.

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 serious 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 scaled-up retort will also provide the opportunity to conduct tests on larger quantities of oil products. Investigation of the production of new materials from the shale oil which will have higher value at lower cost than transportation fuels is a main focus of the program.

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. We are now at a transition between Tasks 2.1 and 2.2.

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

50-LB/HR KENTORT II SHAKE-DOWN RUNS

Procedure

Several shake-down runs were conducted during the quarter with the objective of developing start-up procedures which begin with the retort at room temperature and end with the unit at steady, design conditions while raw shale is fed continuously. The start-up procedure involves three different periods: 1) preheating, 2) switch-to-steam and 3) start-shale-feed. Refer to Figure 1 for the flow diagram of the system.

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

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

3) Start-Shale-Feed. The start of shale feed to the pyrolyzer basically represents the beginning of the steady state period because temperatures, bed heights, and flowrates should be already near their specified levels. However, some operating adjustments are required shortly after the feeding commences. Fine tuning of the temperature in the pyrolyzer is done by adjusting the shale-recycle rate to the pyrolyzer. The flowrate of propane to the burner must be decreased because the level of carbon in the

Figure 1.

Schematic diagram of the 50-lb/hr KENTORT II PDU

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combustor begins to increase. The recycle rate between the combustor and gasifier may also need to be adjusted to change those temperatures. In general, the preparation for the start of feed to the pyrolyzer is done so that this transition period is as short as possible.

Results

There were four shake-down runs conducted this quarter that lasted for more than 8 hours each. Following each of these runs, either procedural adjustments or equipment modifications were made to improve the start-up procedure. One prematurely terminated run will also be described because it uncovered a serious, but easily correctable, problem with the system.

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

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

KT931021. Following approximately 3 hours of preheating, a section of pipe between the propane burner and the combustor plenum burst due to high-temperature oxidative fatigue. Plumbing constraints during construction dictated that the burner be situated at a 90° angle with the inlet pipe to the combustor plenum. The elbow-fitting and the pipe section immediately downstream became an area of intense heat impact due to the

turbulence induced by the bend and was the sight of the failure. Examination of the plenum chamber itself showed signs of oxidative scaling, inside and out. It was determined that modifications to the burner configuration and the plenum chamber were needed, not only to solve the materials problem, but also to make the heating of the combustor more efficient. These planned changes will be described in a following section. Rather than making any major changes immediately we chose to quickly replace the damaged section of pipe as a temporary measure so that we could complete the shake-down process. The reasoning for this was that more problems could become apparent during subsequent shake-down runs, and modifications could then be performed all at once during an extended down-time period.

KT931029. During this run, the preheating period was completed without incident, the switchover to steam was smooth, and the start of raw shale feed was successful. This was the first time that the system had gone through all steps of the start-up procedure. Steam flow was maintained for 51 minutes during the shale-feed period, but the steam generator was not even able to sustain lowered steam rates, so N₂ fluidization was restored for the remainder of the run. Raw shale feed was continued for an hour following the switch to N₂ because it was first time that the system had successfully fed raw oil shale under prime oil generating conditions, and we wanted to assess the performance of the oil collection system. Oil and small amounts of water drained continuously from the ESP, and light oil was collected in the receiver for the shell-and-tube condenser according to design. While relatively little oil was collected during this period, the basic functionality of the system was demonstrated. The robustness of the oil collection system during prolonged periods of operation still needs to be confirmed, however. Although the conditions during the two-hour raw-shale-feed period fluctuated somewhat, the average temperatures of all beds were at or near their design levels (see Table 1). Therefore, the conditions were believed to be good enough to report the yield of oil produced during this period with some degree of confidence (see Table 2).

Much more ESP oil was recovered during the clean-up process than was drained from the unit during the run due its shortness. It is expected that once the internals of the ESP become coated, the oil will drain from the unit steadily without additional hold up. The collection of light oil in the shell-and-tube condenser receiver most likely occurred during the portion of the run when steam was used for fluidization. Much fine oil mist was visible in the exhaust during the nitrogen-fluidization phase because the mist filters were not then in use. Therefore, the quantity of oil reported for the shell-and-tube condenser can probably be doubled as steam was only in use about half the time. This being the case, the oil yield as reported in Table 2 can be increased to 5.2 wt% which is slightly greater than the Fischer assay value of 5.0%. The compositions of each of the two gas streams were measured during the run and were generally in line with what was expected (see Table 3). The combustion gas composition was the average of on-line measurements, and the gasifier/pyrolysis gas composition was determined chromatographically from one sample taken during the steady-state period. While the gas measurements are fine for qualitative purposes, we do not feel that enough samples were taken by the gas chromatograph for the results to be viewed quantitatively.

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

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

Table 2. Oil generated during two-hour steady-state period of run KT921029. Oil weights are corrected for solids and moisture content.

Location	Yield, wt% of Raw Shale
ESP Collectors	0.49
ESP Hold-up	2.89
Shell-and-Tube Condenser	0.77
C ₆ + Vapor	0.31
Total	4.46

Table 3. Gas compositions from run KT931029 during the two-hour steady-state period

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

A high concentration of SO_2 from the combustor was observed which is attributable to the low conversion of pyrite to magnetite in the gasifier because of its relatively low temperature. The average carbon monoxide concentration was high in the combustor flue gas because at times there was a rich fuel/air ratio in the burner which starved the combustor of oxygen. When the propane flow was reduced so that it served only to preheat the fluidizing air, enough oxygen remained so that the carbon in the shale particles would readily combust. Under these conditions excess oxygen became present in the flue gas, CO was reduced, and the combustor temperature increased. Therefore, a rich fuel/air mixture in the burner worsened the operation of the combustor when there was an adequate level of carbon in the solids. It is estimated that 25% of the CO_2 in the combustion flue gas was from the propane gas and the balance was from the carbon in the oil shale. The combustor can sustain operation without aid from the propane burner, but the temperature gradually decreases to an unacceptably low level because of the cool fluidizing air.

A slight pressure differential between the gasifier and combustor caused the CO_2 content in the gasification/pyrolysis gas stream to be relatively high. Otherwise, the relative amounts of these gases are what we would predict for fluidized bed pyrolysis. The pressure imbalance was not detrimental to the generation of oil because the combustion flue gas generally contained little or no oxygen during the oil-producing period. The combustor was operated under oxygen-starved conditions for much of the run which meant that the combustion flue gases which were leaking into the gasifier and pyrolyzer did not contain oxygen that could oxidize the freshly generated shale oil vapors.

In summary, this run demonstrated the functionality of all parts of the 50-lb/hr KENTORT II system and showed that the product yields are generally similar to what we have found in the smaller integrated unit. It is emphasized, however, that only after several carbon-balanced runs will we be able to determine precisely the oil yield potential of the system. The information from this run suggests that oil yield is roughly equivalent to Fischer assay. The shortcomings of the system left to be resolved after the run were the low capacity of the steam generator and the low temperature of the gasification zone. In an attempt to increase its capacity to at least 50 lb/hr (the design capacity is 86 lb/hr), the steam generator was thoroughly cleaned and one partially clogged pipe was cleared. The low gasification temperature was felt to be related mainly to heat losses from the burner/combustor-plenum configuration so this problem was set aside until the scheduled modification down time.

KT931104. The objective of this run was to sustain steam fluidization for at least a 3-to-4-hour period. Once again, the steam generator was not able to sustain its target rate of 50 lb/hr, so fluidization by N_2 was restored. Because of the large effort involved with performing a run we elected to continue operation with N_2 just to gain more experience with the unit. Raw shale was fed continuously for three hours but little or no oil generation was apparent. A major reason for this was that the pyrolysis temperature was rather low (450-500°C), but it was not low enough to explain almost a complete lack of oil generation. Another, and more significant factor, was that much leakage of combustion flue gas into the gasifier and subsequently into the pyrolyzer was occurring. This was confirmed by high CO_2

concentrations in the pyrolysis/gasification gas stream. While this was also the case for run KT931029, the oxygen content of the flue gas was much higher for this run and apparently oxidized much of the oil that was generated in the pyrolyzer. In addition, there were portions of the run when the pyrolysis bed was poorly fluidized as indicated by a non-uniform axial temperature distribution in the bed region. Poor fluidization occurred in the pyrolyzer when the pressure differential between the combustor and gasifier was adjusted so that there was no flow of combustion gases into the gasifier. Therefore, at no time during this run were the conditions favorable for oil generation.

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

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

System Modifications

Burner/Plenum Configuration. As described earlier, a catastrophic failure of the piping between the propane burner and the combustor plenum occurred due to high-temperature oxidation of the metal at the elbow joint. The elbow joint was not only susceptible to high-temperature oxidative scaling, it was also a major source of heat loss. Elimination of the elbow joint was an essential modification. We found that it will be possible to direct the gases from the burner straight into the plenum by mounting the burner horizontally. In this configuration, the distance between the burner and the plenum is shortened and much heat loss minimized. Inspection of the plenum chamber itself showed scaling inside and out. To prevent additional corrosion we elected to aluminize the plenum chamber so that the oxidative resistance of the metal would be improved. To further protect the plenum chamber, its entire inside surface was coated with a castable ceramic (SiO_2). The ceramic layer will not only protect the metal it will also reduce heat losses from the plenum. We will also install a ceramic-sheathed R-type thermocouple in the plenum chamber so that we can adjust the flow of propane to achieve the plenum temperature that will permit the most efficient operation of the combustor.

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

Gasifier Standpipe. To increase the height of the gasifier bed we will increase the height of the gasifier standpipe to 30 inches. A 30-inch long pipe will be aluminized and will be fitted over the existing 15-inch pipe.

Steam Generator. Steam is produced by electrodes that pass electric current directly through the water in the main vessel of the steam generator. The rate of steam generation is directly related to the current flow through the water. A pressure regulator controls the level of water in contact with the electrodes, and therefore, the rate of electric current. We have found that this regulating process is facilitated at higher generator pressures. Since the generator was being fed directly by city water, we were limited to the line pressure which is 70 psig. This pressure was not adequate to achieve the main chamber water level that was needed to create the amount of steam that we required. Therefore, a water holding tank and a feed-water pump will be installed so that we can operate the steam generator above 100 psig. Once this is performed, it is anticipated that we will no longer have problems with steam generating capacity.

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