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Technical Report

The Development of the KENTORT II Process for Eastern U.S. Oil Shale

Progress Report for the Period of
January 1, 1989 - March 31, 1989

Prepared by

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For

U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Laramie Project Office
Laramie, Wyoming

Work Performed Under
Cooperative Agreement No: DE-FC21-86LC11086

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ABSTRACT

This report summarizes the progress made on the development of the KENTORT II process during the period of January 1, 1989 through March 31, 1989. The KENTORT II development program was conducted during this period under Cooperative Agreement No. DE-FC21-86LC11086 between the University of Kentucky Center for Applied Energy Research and the Laramie Project Office of the Morgantown Energy Technology Center, U.S. Department of Energy. The purpose of this program is to develop on a small scale a process to improve efficiency, process economics, and resolve environmental problems involved in the utilization of eastern U.S. oil shale as an energy source and chemical feedstock. The process includes fluidized bed sections of pyrolysis, gasification, and combustion with combined solid/gas heat transfer among the stages.

A test matrix evaluating the use of gasified shale as the heat carrier to the pyrolysis zone was continued in the 5-lb/hr, integrated reactor system. The main objective of this part of the study was to determine the effects on oil yield when the solid recycle ratio and temperature were varied for a given pyrolyzer heat load. The runs utilizing the highest solid temperatures and the lowest solid recycle rates produced slightly lower oil yields. Apparently the temperature effect was great enough to override the reduced concentration of hot particles in the bed. Findings from a preliminary coking model showed a similar relationship for the conditions studied. The gasification section was not affected by the recirculation of solids as carbon gasification and sulfur removal were similar to non-recycle runs.

ACKNOWLEDGMENT

The work described herein was performed at the University of Kentucky Center for Applied Energy Research under Cooperative Agreement DE-FC21-86LC11086 with the Laramie Project Office of the Morgantown Energy Technology Center (METC), U.S. Department of Energy.

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EXECUTIVE SUMMARY

This report describes technical progress from January 1, 1989 to March 31, 1989 on the KENTORT II process for eastern U.S. oil shales. This program was conducted under Cooperative Agreement No. DE-FC21-86LC11086 between the University of Kentucky Center for Applied Energy Research and the Laramie Project Office of the Morgantown Energy Technology Center, U.S. Department of Energy. KENTORT II is a multiple fluidized bed process designed to optimally utilize eastern U.S. shale as an energy source and chemical feedstock while reducing potential environmental problems. The process includes separate, but contiguous, stages of pyrolysis, gasification, and combustion with combined solid and gas heat transfer among the zones.

The goal of the program is to demonstrate and test the KENTORT II process concept in a 5-lb/hr integrated reactor system. The program is divided into two tasks:

- The development and integration of fluidized bed oil shale char gasification technology with fluidized bed pyrolysis technology.
- The development of an oil shale char combustion technology and integration with the pyrolysis and gasification stages.

Furthermore, each task contains two main subtasks:

- Fundamental chemical and kinetic investigation of each process (i.e., gasification or combustion).
- Application to the development and testing of the 5-lb/hr integrated reactor system.

The work completed during this quarter involved the operation of the integrated pyrolysis-gasification reactor system in the solid-recycle mode of operation. Of great importance to the development of the KENTORT II process is the abatement of oil yield losses caused by direct, solid-solid heat transfer in the pyrolyzer. Recirculating hot shale is the most straightforward method of transferring heat to the pyrolysis zone, but it has the potential to significantly reduce oil yields due to coking.

The primary objectives for the quarter were to evaluate the effects of recycle solid temperature and recirculation ratio on oil yield and composition in the 5-lb/hr integrated reactor, and investigate methods of reducing oil yield losses. The raw shale feedrate was increased to the limits of the system to most realistically simulate large-scale conditions where a greater proportion of heat would be carried by solids. A similar raw shale feedrate (i.e., pyrolyzer heat load) was utilized for the

runs being studied, dictating that the temperature and recycle rate of the gasified solids were interrelated.

The gasification section was not affected by the recycle of solids as carbon gasification and sulfur removal proceeded similarly to the non-recycle studies. The runs utilizing the highest solid temperatures had the lowest solid recycle rates and produced the lowest oil yields. Apparently the temperature effect was great enough to override the reduced concentration of hot particles in the bed. With recycle solid temperatures under 760°C oil yields of up to 115% of Fischer assay were observed, and under all solid recycle conditions studied, oil yields above Fischer assay were obtained. It appears possible to control oil yield losses by adjusting the combination of solid recycle ratio and temperature for a given pyrolysis heat load.

INTRODUCTION AND BACKGROUND

It has been shown (1,2,3,4,5) that fluidized bed pyrolysis of eastern U.S. oil shale can enhance oil yields up to 50% above Fischer assay. In addition, fluidized bed technology has the advantages of rapid pyrolysis kinetics (short solid residence time), total use of mined shale, thermal efficiency, and produces a spent shale which has good compaction characteristics. The CAER has investigated fluidized bed pyrolysis of eastern U.S. oil shales for the past several years, and emphasis has recently been broadened to include the development of a commercial retorting concept based on fluidized bed pyrolysis.

While fluidized bed pyrolysis significantly increases carbon conversion to liquid products, approximately 40% of the original carbon remains in the spent shale. This material is ideal for combustion in an integrated process step since it has already been heated to at least 500°C and is of no value once removed from the process. Additionally, it is a good material for use as a heat carrier because of its small size, relatively low rates of decrepitation, and high heat capacity. Therefore, char combustion and the use of char as a heat transfer medium are integral features of the KENTORT II process.

Since only a portion of the carbon in the char from pyrolysis is required by the combustor to heat the pyrolyzer, an intermediate gasification stage was included in the KENTORT II design to utilize this excess carbon. In addition to the production of synthesis gas, a gasification stage desulfurizes the shale. 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 clean-up than a dilute stream of SO_2 from a combustor. The additional H_2S also serves as feedstock for elemental sulfur production. Environmentally, the gasification process removes up to 90% of the original sulfur which greatly reduces the potential for acid drainage conditions in the disposal area. (6,7)

The main thrust of this program is the study and development of gasification and combustion methods for eastern U.S. oil shale and integration of these steps with existing fluidized bed pyrolysis technology. The demonstration and testing of the KENTORT II process concept will be performed in a 5-lb/hr integrated reactor system. The program is divided into two major areas:

- The development and integration of fluidized bed oil shale char gasification technology with fluidized bed pyrolysis technology.
- The development of oil shale combustion technology and integration with pyrolysis and gasification stages.

Furthermore, each task contains two main subtasks:

- Fundamental chemical and kinetic investigations of char gasification and combustion processes are being performed in a 1.5-inch diameter, single-stage fluidized bed reactor system.
- Integral operation of gasification and combustion zones with a fluidized bed pyrolyzer is being performed in a 3-inch diameter reactor system with a nominal shale throughput of 5-lb/hr.

OBJECTIVES

Of great importance to the development of the KENTORT II process is the abatement of oil yield losses caused by direct, solid-solid heat transfer in the pyrolyzer. It is not practical to transfer heat to the pyrolysis zone of the KENTORT II process exclusively with hot gases at the commercial scale. This is due to the relatively low heat capacity of gases and the cross sectional area and superficial gas velocity limitations of fluidized beds. Recirculating hot shale is the most straightforward method of transferring heat to the pyrolysis zone, but it has the potential to significantly reduce oil yields due to coking. Therefore, the primary objectives of this phase are to evaluate the effects of recycle solid temperature and recirculation ratio on oil yield and composition in the 5-lb/hr integrated reactor, and investigate methods of reducing oil yield losses.

METHODOLOGY

Apparatus. The integrated pyrolysis-gasification reactor system was configured as shown in Figure 1 for this phase of operation. Net process heat for the reactor system was provided through a combination of superheated steam and external heat to the gasification section. The pyrolysis zone was heated by a combination of hot gases and recirculating hot char from the gasification section. The liquid collection system was developed from similar systems used in the past for pyrolysis studies.(6) The main features of the system include: 1) an electrostatic precipitator which traps the majority of the oil from its aerosol suspension, 2) condensers and filters which collect water and light oil, and 3) on-line gas analysis capable of quantitating vapor phase C_5+ materials.

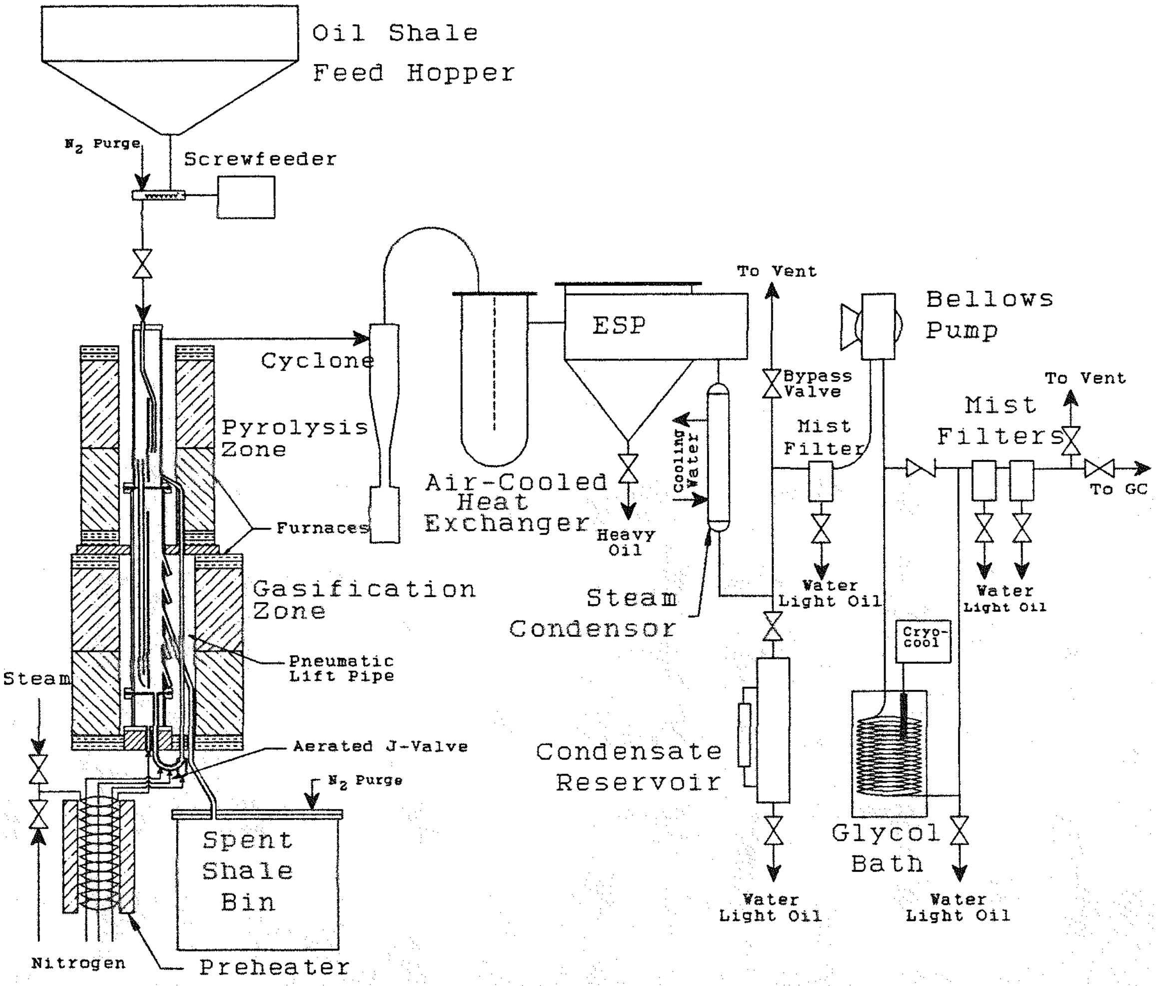

Figure 1. Simplified flow diagram of the integrated pyrolysis-gasification reactor system.

Oil Shale Sample. Oil shale from the Cleveland Member of the Ohio Shale is being used in the KENTORT II study based upon the judgment that it represents one of the shale types in the eastern U.S. that has the highest probability for initial commercial development. Detailed description of the characterization and acquisition of this master sample has been reported previously.(8) The shale was crushed, ground, and screened to a size distribution of 20x60 mesh, yielding five 55-gallon drums of material. The drums were purged with argon and sealed to prevent unnecessary oxidation. The average analysis of the sample is shown in Table 1.

Table 1. KENTORT II Master Sample Characteristics.

		Modified Fischer Assay*	
Carbon	16.7 wt%	Oil	17.7 gal/ton
Hydrogen	2.0 wt%	Oil	7.0 wt%
Nitrogen	0.7 wt%	Water	4.2 wt%
Sulfur	1.7 wt%	Gas+Loss	2.6 wt%
Ash	74.5 wt%		

* Modified Fischer Assay developed at CAER for Eastern shale.

Procedure. The reactor system was brought to operating temperature with flowing nitrogen to properly distribute heat throughout the system. Following the preheating period the nitrogen flow was replaced with steam, and the system temperatures and pressures were allowed to stabilize. Subsequently, raw shale was fed to the reactor by screwfeeder to initiate the run and final system adjustments were made. During the run there was sufficient steam condensation to require periodic drainage from the system. On-line gas samples were taken every 35 minutes for gas chromatography. Otherwise, conditions were maintained as constant as practicable and recorded by a computerized data acquisition system for the duration of the run, typically 2 to 5 hours.

Following the termination of shale feed, the steam flow was continued for 10 minutes which was followed by an overnight cooling period with flowing nitrogen. Liquids were drained from the various traps in the system when the flow of steam was halted. The collection of solid samples and the quantitation of liquids held up in the system were performed on the following day when cool. Heavy oils adhering to vessels in the system were rinsed with CH_2Cl_2 and recovered by distillation. Any solids encountered during this process were filtered from the washings. Solids recovered in the spent shale bin and cyclone were weighed, and sampled for ultimate analyses. The recovered oil fractions were analyzed both separately and also as combined according to production ratios.

Test Matrix. A test series (Table 2) to evaluate the effects of char recirculation as a method of heat transfer between the gasification and pyrolysis zones was performed. This report will concentrate on runs (KEN#31-36) in which the same raw shale throughput was utilized thereby fixing the heat load on the pyrolyzer. The independent variable for these runs was the gasification temperature which, in turn, determined the necessary solid recirculation rate. The shale recycle ratios were determined by performing a heat balance around the pyrolyzer. The enthalpy relations for eastern U.S. oil shale, as derived by Camp, were applied to the specific characteristics of the oil shale sample used in this study.(9) It was assumed that no net heat loss occurred through the walls of the pyrolyzer because of heat compensation from the external furnace. The temperatures of the gas and the solids in the pyrolyzer were assumed to be equal and were obtained from thermocouples immersed in the bed. As discussed in the previous report the average of the gasifier and lift pipe temperature readings are used for the temperature of the recycled shale.(10)

Table 2. Average Run Conditions for the 5-lb/hr Integrated Pyrolysis-Gasification Reactor.

Throughput	48 g/minute raw shale
Pressure	0 psig ± 5 inches water column
Temperature	
Pyrolyzer	529-537°C, 5 min. avg. solid holding time
Gasifier	760-839°C, 17 " " " "
Solid Recycle	1.5-2.2:1 gasified shale:raw shale (w/w)
Recycle Temp.	724-792°C
Fluidizing Gas	27.5-31.2 g/minute steam

RESULTS AND DISCUSSION

Heat Transfer Characteristics. The average solid recycle temperature was lower than the gasifier temperature due to heat loss from the lift pipe feeder. However, the two temperatures were directly proportional (Figure 2), and under truly adiabatic conditions would be identical. The inverse coupling between solid temperature and recycle ratio was caused by the similar pyrolysis heat load that was utilized for each run (Figure 2). The gasifier temperature for each run determined the rate of solid recirculation required to achieve the pyrolysis temperature (~530°C). Because of the small diameter of the reactor a significant amount of heat was transferred to the pyrolyzer by steam and product gases from the gasifier. As the gasification temperature was increased a greater proportion of pyrolysis heat was provided by gases (Figure 3).

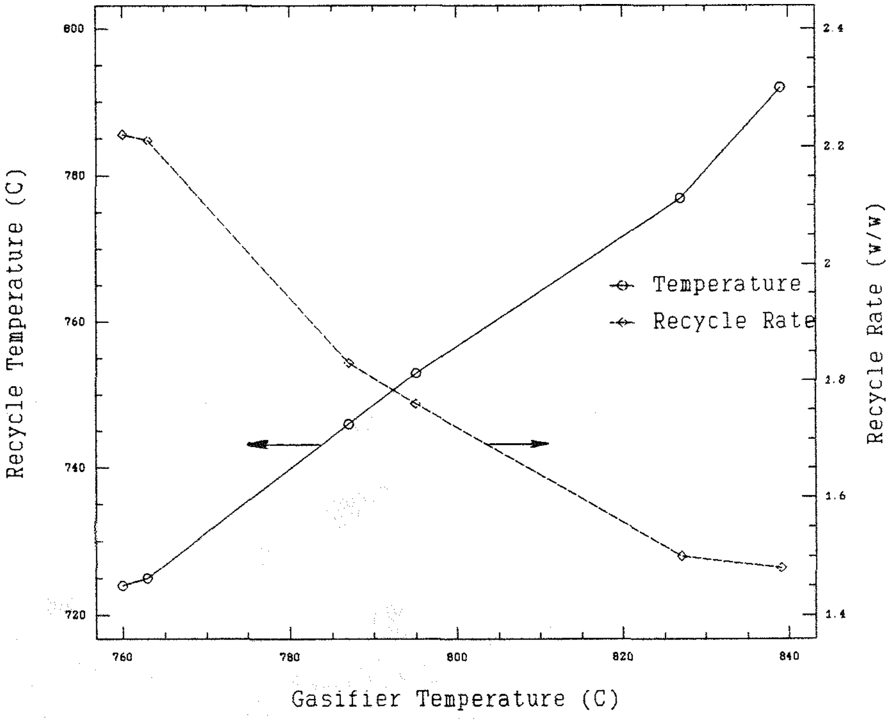

Figure 2. Relationship of gasifier temperature to the average solid recycle temperature and recycle ratio.

Product Distribution. The portion of carbon remaining in the shale following integral pyrolysis/gasification declined with increasing gasifier temperature which is attributable to the steam/carbon reaction (Figure 4). The associated increase in the production of carbon oxides was closely correlated to the decrease in carbon content of the processed solids. The total

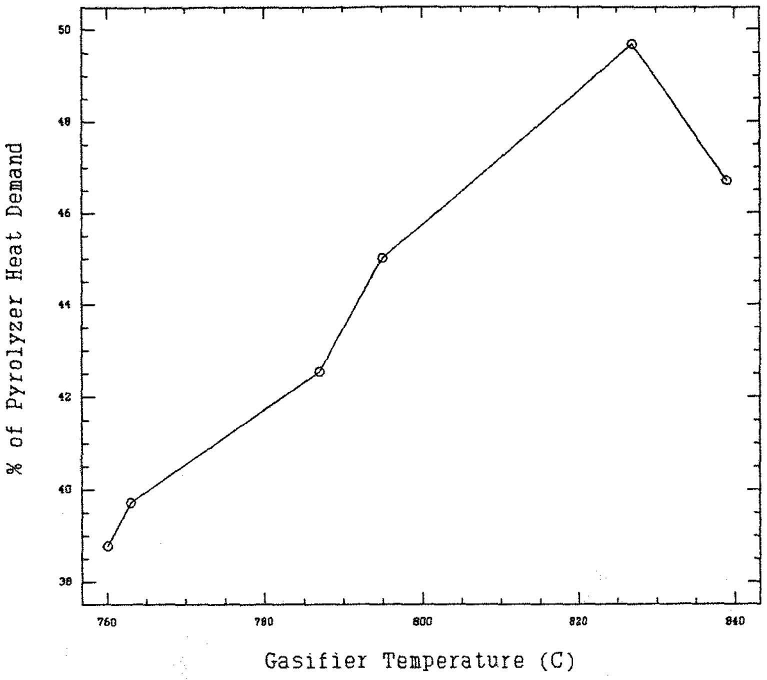

Figure 3. Amount of heat provided to the pyrolyzer by steam and product gases from the gasifier.

carbon distributed to the spent shale and CO_x was relatively constant among the runs, and represents the carbon which is not volatilized during the pyrolysis step.

Hydrocarbon gas production (C_1-C_4) remained essentially constant throughout the test series. Most of the hydrocarbons were produced in the pyrolyzer, but it appears from comparison to previous studies (6) that additional methane was produced in the gasifier. This is attributed to further charring reactions which occur at significantly higher gasification temperatures. Since the products of pyrolysis and gasification are combined, it is difficult to distinguish between the reactions occurring in each zone. This especially hampers our study of solid-recycle pyrolysis since coking and cracking indicators such as methane and hydrogen can also be produced in appreciable amounts in the gasifier.

Nearly 2% of the total carbon was measured in the condensed steam, and this value was essentially constant for these runs. The balance of the raw shale carbon was measured as C_5+ components.

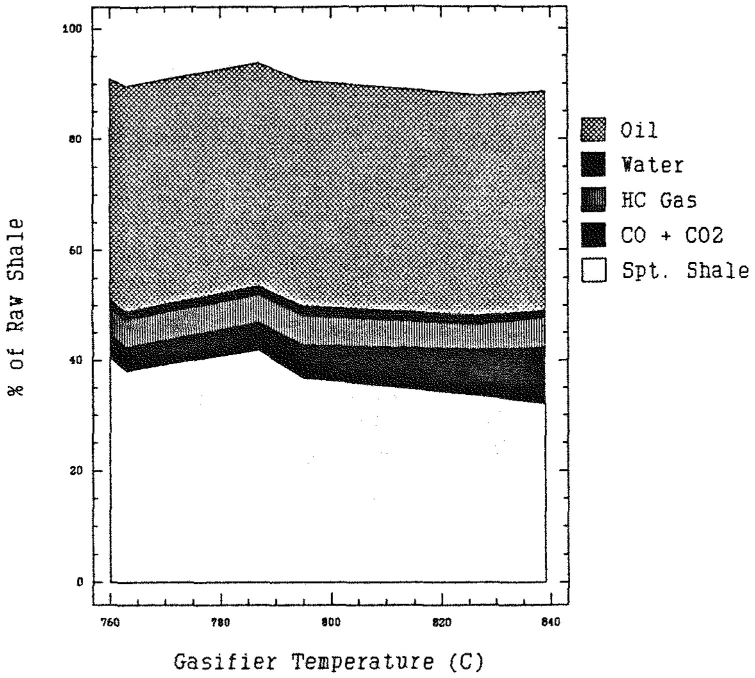

Figure 4. Distribution of carbon in the products of pyrolysis and gasification.

Overall carbon balances averaged 90% which were lower than previously obtained in similar equipment configurations. All vapor phase components were measured during steady-state portions of each run, so gases or vapors generated during heat-up or shutdown periods were not included in the carbon balance calculation. At least an hour of flowing steam is required for system conditions to stabilize, during which time a relatively large amount of carbon in the spent shale from the previous run is gasified. A constant amount of spent shale is retained in the reactor between runs to simplify procedures. Since this carbon was not measured in the spent shale or the steady state gas samples, carbon balances were underestimated. To determine the amount of gasification that can occur during non-steady periods, the reactor was charged with spent shale and cycled through a typical heat-up and cool-down sequence. From this experiment it is estimated that at least 2% of the overall carbon balance can be attributed to non-steady state gasification. Additionally, evaporation of oil held up in the system and outgassing from the gasified shale during the cooldown period are expected to account for some of the carbon balance discrepancy. It is believed, however, that the majority of the oil is recovered and that most of the carbon losses are due to non-steady state vapor phase losses during start-up and shutdown.

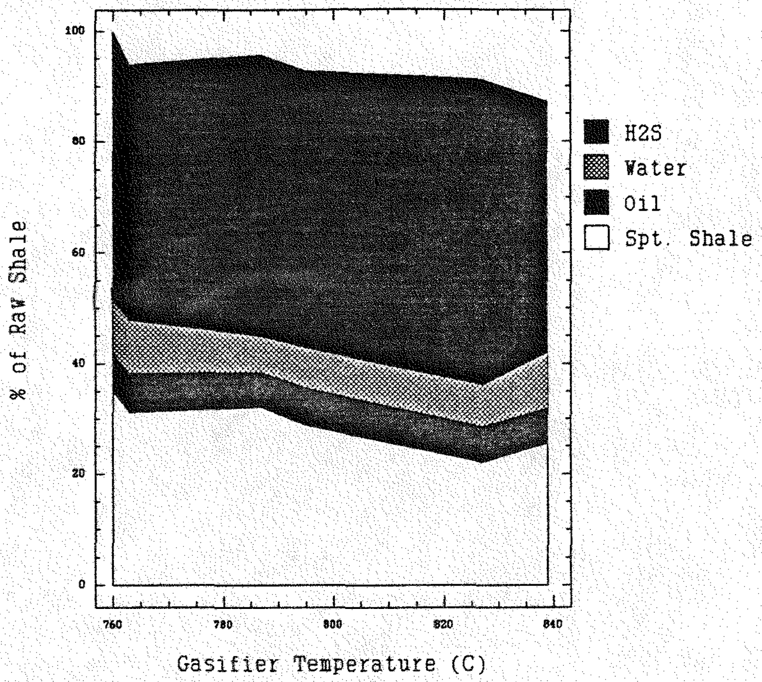

Figure 5. Distribution of sulfur in the products of pyrolysis and gasification.

Sulfur was removed from the shale primarily in the form of H_2S accounting for 45 to 55% of the total balance (Figure 5). Smaller amounts were distributed to the aqueous phase (6-10%) and into the oil (6-7%). The sulfur content of the spent shale decreased slightly with increasing gasifier temperature. This relationship is consistent with previous gasification studies, so it does not appear that solid recirculation affects sulfur removal.

Oil Yield. The mean carbon conversion to oil for non-recycle runs was 45.9%, compared to 35.6% for Fischer assay.(10) The heat of pyrolysis for these runs was provided by a combination of hot gases from the gasification section and external heat through the walls of the reactor. Under these conditions coking losses are minimal, but are not completely absent since oil vapors must pass through the pyrolysis zone with the potential to react with shale surfaces or the hot walls of the reactor. A situation in which all oil vapor/solid contact is eliminated could be defined as the level of zero coking, but this is not practical. The gas-heating mode of operation provides the lowest realistic level of oil coking in a fluidized bed pyrolyzer, so we define it as the baseline carbon conversion to oil, F_{A0}. The fractional oil loss, X_A, due to vapor phase coking is defined as:

$$X_A = (F_{A0} - F_A)/F_{A0}$$

where F_A is carbon conversion to oil in the solid-recycle mode.

In the previous quarterly report (10) it was reported that as the recycle ratio was increased, for a given solid temperature, the oil yield decreased due to the increase in hot, coking sites. In that portion of the study higher solid recycle ratios at a given temperature reflected a higher heat demand on the pyrolyzer. However, each run in the current test matrix had an equivalent pyrolysis heat load so similar isotherms cannot be drawn. Instead, recycle solid temperature was used to plot the data since it was correlated with recycle rate. Coking appeared to increase slightly at increased recycle shale temperature (i.e., lower recycle ratio), but this trend was observed within a relatively narrow range of oil yield losses (11-14%) making it difficult to derive confident conclusions about the relationship (Figure 6). While a single parameter is sufficient to characterize the run conditions for these tests, it does not necessarily reflect the actual effects of recycle rate and temperature on oil yield.

Since these relationships are such important considerations for a solid-recycle system, a model is being developed to

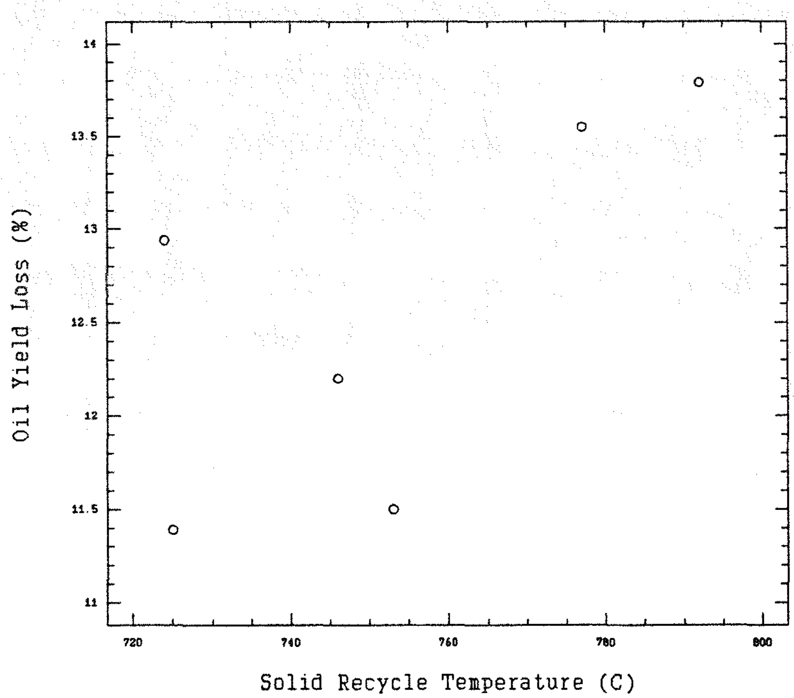

Figure 6. Oil yield reduction due to the recirculation of gasified shale to the pyrolysis zone.

parallel the experimental findings. Preliminary findings from the model indicate that an increase in coking should be expected at higher solid temperatures in the range that was studied. This is not unreasonable since a linear increase in coking rate is expected with recycle rate while an exponential increase in coking rate is expected with a rise in temperature. The temperature range of the this study needs to be extended somewhat to confirm the results of the preliminary model, but there are limitations for the combinations of temperature and recycle rate that can be used. For example, it appears that operation at a low recycle temperature is least detrimental to oil yield, but it may not be feasible to operate the gasifier below 700°C because of reduced sulfur removal. Similarly, an extremely low recycle rate would require a high recycle temperature, forcing the combustor temperature to be excessive.

CONCLUSIONS

The recycle of hot, gasified shale to transfer heat to the pyrolysis zone resulted in no significant differences in carbon gasification or sulfur removal compared to non-recycle studies. Oil yield reduction in the solid-recycle mode of operation is related to the solid-recycle ratio and temperature, and for the conditions studied, the temperature effect appeared to dominate oil yield losses. For a given pyrolyzer heat demand, it appears possible to reduce oil yield losses by adjusting the combination of solid recycle ratio and temperature.

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