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OSTI**SUMMARY OF LABORATORY SIMULATION STUDIES OF THE ROPE™ PROCESS****DISCLAIMER**

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SUMMARY

The Western Research Institute is currently developing a process for the recovery of distillable liquid products from alternate fossil fuel sources such as tar sand and oil shale. The fundamental processing concept is based on recycling a fraction of the produced oil back into the reactor to be mixed with the raw resource. This concept is termed the recycle oil pyrolysis and extraction (ROPETM) process. The conversion of the alternate resource to a liquid fuel is performed in two stages. The first pyrolysis stage is performed at moderate temperatures (325-420°C [617-788°F]) in the presence of product oil recycle. The second stage is performed at higher temperatures (450-540°C [842-1004°F]) in the absence of product oil.

Previous research has been performed in a 2-inch process development unit (PDU), and a 6-inch bench-scale unit (BSU). The large-scale experiments have provided data for engineering development of the concept and evaluation of the end-use potential of the liquid products. The research presented in this report is an account of the studies conducted in a laboratory simulation reactor. This effort was undertaken to provide a description of the fundamental mechanisms controlling the overall process.

The experiments reported here were performed using Asphalt Ridge tar sand in an all-glass laboratory simulation reactor. Several components of the ROPE concept were simulated during the course of this research. These areas include (1) simulation of each of the three principal zones of the reactor (tar sand preheat, recycle oil pyrolysis, and recycle oil drying zones), (2) the recycling of SAE 50 weight oil to an equivalent of steady-state operation, (3) evaluation of the potential catalytic effects of the sand matrix, and (4) evaluation of the chemistry of the pyrolysis of model polymers as it applies to the ROPE concept.

The tar sand preheat (pretreatment) zone functions as a region for solubilization of the raw tar sand. The soluble fraction of the tar sand bitumen goes into solution in the recycle oil within five minutes. This is much less time than the residence time of the material in this zone; therefore, solubilization of the bitumen is a process that is not rate-limiting. The results suggest that pyrolysis is not initiated in this zone. The products that are collected from this zone are formed in other parts of the reactor, carried by recycle oil to this zone, and are only collected from this zone. The distillate is produced by distillation of the lower boiling material in the recycle oil because Asphalt Ridge tar sand does not contain bitumen fractions that will vaporize at the temperature of this zone.

The recycle oil pyrolysis zone of the reactor functions as the initial region for pyrolysis of recycle oil and tar sand bitumen. The degree of pyrolysis increases, as expected, with increasing temperature. Char production is observed from the pyrolytic reaction, but gas production is not observed. Model-compound studies performed during this research suggest that hydrogen transfer from hydroaromatic species to the bitumen pyrolysis reactions occurs in this zone of the process.

The recycle oil drying zone accelerates the pyrolytic reactions and produces additional char as well as distillate. The material balances suggest that the gas production may be increased in this zone; however, the design of the experimental apparatus did not allow for the gas production to be measured.

Steady-state operation of the PDU has not been well defined and has been questioned by critics of the ROPE concept. The research conducted to evaluate the continued recycling of SAE 50 weight oil was directed at evaluating the approach to steady state and the composition of the heavy oil at steady state. The research has shown that steady state can not be easily achieved at an operating temperature of 375°C (707°F) because the reaction rate is too slow to bring about the changes in the heavy oil necessary to reach this condition. Steady state can not be achieved at an operating temperature of 425°C (797°F) because the recovery of heavy oil is significantly less than the initial heavy oil inventory and the recycle needs can not be met to sustain the process.

Steady-state operation has been demonstrated at an operating temperature of 400°C (752°F). The condition was achieved after 10 cycles of the heavy oil, and is equivalent to approximately 8 hours of operation in the PDU. This finding agrees well with the previous estimate of the time required to reach steady-state operation from evaluation of the PDU experiments.

The possible catalytic effects of the sand matrix were also evaluated, and it was determined that the sand matrix does not have significant catalytic effect. These results mean that the process energy requirements, and operation and construction costs could be reduced by disengaging the majority of the solids from the liquids before the material enters the pyrolysis zones of the reactor.

Polyethylene, polypropylene, and polystyrene were selected as model polymers to study thermal decomposition of organic materials in a heavy oil environment. The results from this part of the investigation have shown that the heavy oil acts as a diluent to minimize reactions that are the reverse of the pyrolytic reactions. The reverse reaction is the reaction pathway that will lead to coke production and decreases in liquid product yield. The diluent effect of the heavy oil is one of the fundamental processes that allows the ROPE concept to produce liquid product yields comparable to those obtained by Fischer assay.

INTRODUCTION

The Western Research Institute (WRI) is currently developing a process for the recovery of distillable liquid products from alternate fossil fuel sources such as tar sand and oil shale. The fundamental processing concept is based on the recycling of a fraction of the produced oil back into the reactor with the raw resource. This concept is termed the recycle oil pyrolysis and extraction (ROPETM) process. The conversion of the solid resource to a liquid fuel is performed in two stages. The first pyrolysis stage is performed at moderate temperatures (325-420°C [617-788°F]) in the presence of produced oil recycle. The second stage is performed at higher temperatures (450-540°C [842-1004°F]) in the absence of produced oil recycle. Research has been performed in a 2-inch process development unit (PDU), a 6-inch bench-scale unit (BSU), and in the laboratory simulation reactor.

The research using the PDU and BSU investigated the recovery of liquid products from tar sands, eastern oil shale, and western oil shale. These investigations have been directed at solving engineering problems involved in developing a commercial process and demonstrating the potential market value of the liquid products. The results from these investigations have been published as project milestone reports to the U.S. Department of Energy and as the proceedings of technical meetings (Cha et al. 1986, 1988, 1990). The PDU investigations, because of the large scale and complexity of the reactor systems, did not provide data that can be used to determine precisely which fundamental mechanisms occur during resource conversion. For this reason, a basic understanding of the factors that control the process could not be developed.

The research described in this report represents the results of laboratory scale research to supply fundamental information that has not been obtained from the experiments performed at the PDU and BSU levels. The effort of this research has been of an exploratory nature and it has been conducted in small-scale reactors so that the predominant mechanisms that control the conversions during processing can be determined. The objective of the research is to determine what chemical mechanisms control the process.

ROPE PROCESS DESCRIPTION

The design and operation of the PDU is described in detail by Cha et al. (1986, 1988), but it will be summarized here. The PDU can be divided into five processing zones. The four zones are identified as (1) tar sand feed zone, (2) tar sand preheat zone, (3) recycle oil pyrolysis zone, (4) recycle oil drying zone, and (5) spent solids collection. Figure 1 shows a schematic of one of the earlier versions of the PDU. We chose to illustrate this particular version because the individual zones are more easily identified than they are in the more recent schematics of the PDU.

The tar sand feed zone is the first inclined screw in the reactor and serves as a conveyor to supply the raw tar sand to the reactor. This zone operates near ambient temperature.

The tar sand preheat zone is the second inclined screw (Figure 1) region of the reactor. This zone of the reactor is operated between 204 and 260°C (400 and 500°F), and the material entering this zone has a residence time of 15 to 25 minutes. In this zone, raw tar sand is fed into the reactor with the recycle oil that is produced from the other processing zones. The recycle oil mixes with the tar sand and extracts the bitumen that is soluble in the recycle oil. Volatile material in the recycle oil and the extracted bitumen are removed from the reactor by distillation processes at the operating temperature. The recovered product (knock-out 1 distillate) is not recycled back into the reactor. The bitumen-recycle oil solution and the sand that may be coated with insoluble bitumen pass into the recycle oil pyrolysis zone for further processing.

The recycle oil pyrolysis zone (Figure 1) initiates the pyrolysis of the recycle oil, soluble bitumen, and the insoluble bitumen adhering to the sand. This zone of the reactor is operated between 325 and 420°C (617 and 788°F) and the residence time of the material is between 30 and 45 minutes. The solution of recycle oil and bitumen is removed from the reactor for recycle as the solid material enters this zone. The recycle oil is injected into the reactor farther downstream and is recycled counter current. Pyrolysis of the recycle oil, the soluble bitumen, and the insoluble bitumen adhering to the sand occurs in this zone of the reactor. The pyrolysis products that are volatile at the operating temperatures are recovered and collected at knock-out 2. The nonvolatile material is recycled as heavy oil and is renewed with recycle oil and bitumen solution from the tar sand preheat zone. The solids pass into the recycle oil drying zone for further processing.

The recycle oil drying zone is the fourth reactor screw. This region of the reactor is operated between 450 and 540°C (842 and 1004°F). The residence time of the material in this zone varies between 30 and 45 minutes. This zone acts as a disengaging area for the nonvolatile heavy oil and the solid material (sand with adhering insoluble bitumen). The temperature of the zone increases as the distance into the zone increases, and this assists in removing the oil by volatilization and decreasing viscosity of the heavy oil. At these relatively high temperatures, pyrolysis of the heavy oil, solubilized bitumen, and insoluble bitumen occur. The volatile products from this zone are collected at knock-out 3. The solid material, after being stripped of heavy oil, enters the spent solids collection. In a commercial process, the spent sand that is coated with the residual char enters a residual char combustion zone (not shown in Figure 1). The residual carbon-containing material may be combusted to produce clean sand, gaseous combustion products, and heat for use by the process.

EXPERIMENTAL

Resource Preparation And Verification

Approximately 9 kg (20 lb) of Asphalt Ridge tar sand was obtained from WRI storage. The tar sand sample was stored in a steel drum under a nitrogen atmosphere. The surface layer of raw sand was removed and discarded to ensure the sample taken for study was not oxidized. The following approach was used to obtain the most representative samples possible and to verify the uniformity of the samples used for the experiments. The 9 kg (20 lb) of tar sand was frozen with solid carbon dioxide and crushed in the presence of additional solid carbon dioxide in a jaw crusher chilled with solid carbon dioxide. The crushed tar sand material was placed in a 18.9 L (5 gal) container with additional solid carbon dioxide and sealed. The container was tumbled for 30 minutes to mix the contents.

The mixed tar sand material was sampled to provide aliquots of approximately 200 g each. The samples were stored in sealed containers, under a nitrogen blanket at -4°C (25°F). Two samples were selected at random for analysis to determine the variability of the sampling procedure. Each sample was analyzed to determine the bitumen saturation and elemental composition of the bitumen.

Before each experiment, a sample of raw tar sand was selected from storage. The sample was carefully ground using a mortar and pestle to produce a 100 g-sample with a particle size distribution of 0.16 to 0.32 cm (0.063 to 0.125 inch). The prepared sample was kept chilled with solid carbon dioxide until it was introduced into the reaction vessel.

The recycle oil used for the initial experiments to define the function of each reactor zone was obtained from previous Asphalt Ridge tar sand experiments conducted in the 2-inch PDU. The recycle oil was a mixture of the material collected in knock-outs 2 and 3. A 1938.1-g (4.3-lb) sample was obtained, bottled in glass, blanketed with nitrogen, and stored at 4°C (39°F) until used. Before the experimental program was initiated, the recycle oil was spiked at the 1% level with model compounds and analyzed to verify the concentration of the model compounds. The recycle oil was further characterized to determine elemental composition, and distillation profile.

The heavy recycle oil used for the experiments to evaluate the continued recycling of SAE 50 weight oil and the pyrolysis of model polymers was the same SAE 50 weight oil used in previous PDU experiments. The heavy recycle oil used for the experiments to investigate potential catalytic effects of the sand matrix was a composite heavy oil prepared by mixing the heavy recycle oil remaining from the experiments to evaluate the recycling of SAE 50 weight oil.

Laboratory Simulation Reactor

Three configurations of the laboratory simulation reactor were used for this investigation. Three configurations of the reactor were required to simulate various areas and operating modes of the 2-inch PDU. The following section will discuss the configurations of the laboratory simulation reactor used for this research.

The tar sand preheat zone was investigated with the reactor shown schematically in Figure 2. The reactor consists of a glass reaction vessel (500 mL, three-neck round bottom flask) with a Claisen distillation head attached to the vertical neck of the flask. A water-cooled condenser 30 inches (76.2 cm) in length is attached to the Claisen head for the addition of the raw tar sand. The distillate is collected through a conventional water-cooled condenser and collected in a four position cow. The temperature of the distillate is measured by a thermometer mounted in the Claisen head.

Figure 2. Schematic Diagram of the Laboratory Simulation Reactor Used to Model the Tar Sand Pretreatment and Recycle Oil Pyrolysis Zones

A sampling port is attached to one of the angle necks of the flask. The sampling port is designed to allow the removal of sand and oil samples from the reactor without admitting air to the reactor. The sampling port consists of a ground glass joint blown onto a stopcock valve. A 0.25- to 0.125-inch Swagelok reducing union is attached to the glass stem on the stopcock side of the reactor. This arrangement allows for a 0.125-inch-diameter needle attached to a 50-mL syringe to be introduced into the reaction vessel through the stopcock to remove samples during the experiments. A gas-tight seal using a graphite ferrule is made between the needle and the reducing union.

Samples were collected from the reactor by inserting the needle attached to the syringe into the reducing union and tightening the fitting around the needle. The stopcock was opened, and the needle was pushed into the reactor. The sample was withdrawn by suction from the syringe. The needle was removed from the reactor by reversing this procedure. Both sand and heavy oil samples were collected through this port using this procedure without allowing air to enter the reactor or allowing volatile products to escape.

The reaction vessel was heated using a pair of heating mantles that were manually controlled to $\pm 5^{\circ}\text{C}$ ($\pm 9^{\circ}\text{F}$) of the set-point temperature using variable resistance controllers. The temperature of the reactor was monitored with thermocouples. Two thermocouples were placed against the outer glass wall of the reaction vessel such that one thermocouple monitored the temperature of the lower mantle and the other thermocouple monitored the temperature of the upper mantle.

Possible gaseous-product evolution was monitored using a positive displacement device. The vacuum port of the distillation receiver was connected to a stainless steel tube passing through a single-hole rubber stopper. The stopper was fitted to a 1000-mL vacuum filtration flask filled with water to the level of the vacuum port. The stainless steel tube was adjusted so that the end of the tube was at the bottom of the filtration flask. A rubber hose was connected to the vacuum port of the filtration flask and the other end emptied into a 1000-mL graduated cylinder. As gas was produced in the closed system, water was displaced from the filtration flask to the graduated cylinder, and the volume of water displaced was measured. The volume of gas produced was calculated from the volume of water measured.

The laboratory simulation reactor was operated in the tar sand preheat mode by first adding 100 g of the recycle oil and assembling the reactor. The reactor was purged with nitrogen gas to expel residual air, and the reactor was brought to the desired experimental temperature. After the temperature stabilized at the desired set point, 75 g of the raw tar sand was added. The experiment clock was started when the temperature returned to the set point. The experiment was stopped, and the reactor was quenched when 25 minutes had elapsed on the experimental clock.

The reaction vessel was sampled periodically during each experiment. A heavy oil sample was collected when the temperature stabilized at the set point temperature. A second sample consisting of the heavy oil and

the solid material was taken when the reactor returned to the set point temperature after addition of the tar sand. Additional samples consisting of the heavy oil and the solid material were collected during the course of the experiment. Each time a sample was taken from the reactor, the position of the cow was changed so the distillate samples would correspond in time to the heavy oil-sand samples taken from the reaction vessel.

The same configuration of the laboratory simulation reactor that was used to investigate the tar sand preheat zone was used to investigate the recycle oil pyrolysis zone because the physics of the two zones is the same, and only the operating temperatures and residence times differ between the two zones. The reactor was operated in the same manner as in the tar sand preheat zone investigations, except that the set-point temperatures and experiment durations were increased to represent the operating conditions of the recycle oil pyrolysis zone. The temperatures studied were 350, 375, 400, and 425°C (662, 707, 752, and 797°F). The experiments were conducted for 45 minutes.

A diagram of the configuration of the laboratory simulation reactor used to conduct the recycle oil drying experiments is shown in Figure 3. This version is similar to that which was used to investigate the previous two processing zones except that a liquid dispensing funnel was mounted at the top of the vertical condenser.

Figure 3. Schematic Diagram of the Laboratory Simulation Reactor Used to Model the Recycle Oil Pyrolysis Zone

The experiments to investigate the recycle oil drying zone were conducted differently than the experiments studying the previous two processing zones. The spent sand collected at the end of the four experiments investigating the recycle oil pyrolysis zone was composited.

In addition, the heavy oil remaining in the reactor at the end of the recycle oil pyrolysis zone experiments was composited. A 50-g sample of the spent sand was added to the reaction vessel, and 15 g of the composited heavy oil was mixed with the spent sand. The reactor was assembled and 50 mL of the recycle oil was charged through the addition funnel.

The reactor was purged with nitrogen to remove residual air, and the temperature was raised to the set point. A sample of the contents of the reactor was taken, and the recycle oil was added at a rate of 25 mL per minute. When the temperature of the reactor returned to the set point, a sample of the reactor contents was taken, and the experimental clock was started. The reactor was sampled periodically until the end of the experiment, when the reactor was quenched. The position of the cow was changed each time a sample was taken from the reactor so that a distillate sample that corresponded to each reactor sample was available.

The configuration of the laboratory simulation reactor used to study the recycling of SAE 50 weight oil to steady state, the potential catalytic effects of the sand matrix, and pyrolysis of model polymers is shown in Figure 4. The reactor was operated in a mode to simulate the recycle oil pyrolysis zone because this zone represents the area of the process where the highest residence time for the heavy recycle oil is observed. The reactor consists of a glass reaction vessel (500-mL, round-bottom flask) with a Claisen distillation head attached to the vertical neck of the flask. The distillate is condensed through a conventional water-cooled condenser and collected. The temperature of the distillate is measured by a thermometer mounted in the Claisen head. The contents of the reactor are stirred by a motor-driven stirring shaft fitted with a single-blade paddle.

The reaction vessel was heated using a pair of heating mantles that were manually controlled to $\pm 5^{\circ}\text{C}$ ($\pm 9^{\circ}\text{F}$) of the set-point temperature using variable resistance controllers. The temperature of the reactor was monitored with thermocouples. Two thermocouples were placed against the outer glass wall of the reaction vessel such that one thermocouple monitored the temperature of the lower mantle and the other thermocouple monitored the temperature of the upper mantle. Possible gaseous-product evolution was monitored using the same positive displacement device used in other versions of the reactor.

The laboratory simulation reactor was operated by adding 100 g of the recycle oil and 100 g of tar sand or the desired weight of model polymer, and assembling the reactor. The reactor was purged with nitrogen gas to expel residual air, and the reactor was brought to the desired experimental temperature. The experiment clock was started when the temperature reached the set point. The experiment was stopped, and the reactor was quenched when the reaction had proceeded for the desired time period.

Figure 4. Schematic Diagram of the Laboratory Simulation Reactor Used to Study Different Processing Problems

Model-Compound Studies

The chemistry of complex systems is difficult to study because there are a large number of compounds present in the material and because the concentration of the individual species is typically low. Model compounds were used to investigate the chemistry of the processes that occur during the recovery of distillable products. Five model compounds were selected for the part of the study investigating the three major processing zones. These compounds represent the four major classes of hydrocarbons detected in products from previous PDU tests (1) n-octadecane (alkane), (2) phenanthrene (aromatic), (3) anthracene (aromatic), (4) 9,10-dihydroanthracene (hydroaromatic), and (5) perhydrofluorene (cycloalkane). The recycle oil was prepared by making a solution of all of the model compounds (except anthracene) in the recycle oil. The solution was prepared so that each selected model compound was present in the solution at approximately the 1-wt % level. The solution was analyzed using mass spectrometric techniques to establish the absolute concentration of each compound.

The recycle oil spiked with the model compounds was used as the recycle oil for the experiments investigating the three reactor zones. The distribution of the model compounds in the products and the changes in the concentration of the model compounds in the reactor were used to evaluate potential chemical mechanisms that occur during processing. The concentration of each model compound in the products was determined using mass spectrometric techniques that are discussed in the analytical section.

Three model compounds were selected for that part of the study investigating the recycling of the SAE 50 weight oil to a steady state. The three model compounds are (1) n-octadecane (alkane), (2) phenanthrene (aromatic), and (3) anthracene (aromatic). The two aromatic compounds were selected as model compounds because their similar structures and gas chromatographic retention times facilitate model-compound analysis. The heavy oil for these experiments was prepared by making a solution of the model compounds in the SAE 50 weight oil. The solution was prepared so that the concentration of each model compound in the solution was approximately 1 wt %.

The SAE 50 weight oil, spiked with the model compounds was used as the recycle oil for the experiments investigating the effects of continued recycling during the approach to steady state. The changes in the concentration of the model compounds in the heavy oil was used to evaluate the approach to a condition that approximates steady state during processing. The concentration of each model compound in the product heavy oil was determined using mass spectrometric techniques.

Model Polymers

Three polymer resins were selected for investigating the pyrolysis of model polymeric systems. The three polymeric resins selected were polyethylene, polypropylene, and polystyrene. The polymer resins were purchased from chemical supply companies and used as received.

Bitumen Extraction

Two samples of the raw tar sand were randomly selected from the 200-g samples to evaluate the sampling procedure and to determine the variability of the samples. A 100-g sample was extracted for 24 hours with toluene in a Soxhlet extractor. The toluene extraction was followed by a 24-hour pyridine extraction. The solvent was removed from each extract by thin-film evaporation, and the bitumen content was determined gravimetrically. The toluene extracts were subjected to elemental analysis. The extracted sand was subjected to residual organic carbon analysis by combustion.

Analytical Procedures

This section describes the preparation and preservation procedures used for samples generated during this research, and the analytical methods used for analysis of the samples. Some analyses such as viscosity and specific gravity were not performed on the samples generated during these experiments, because the scale of these experiments was too small to produce the quantity of sample required for these analyses.

Sample Preparation

Three types of samples were collected from all of the experiments: (1) distillate product, (2) heavy oil, and (3) spent sand. The material in the reactor at the end of each experiment was composed of heavy oil and spent sand, which had to be separated. The heavy oil was washed from the spent sand with a toluene rinse and filtered to separate the liquid from the solids. The toluene was removed from the heavy oil by thin-film evaporation.

Sample Preservation

After preparation, the liquid samples (distillate products and heavy oils) were preserved by storing them in glass containers with TeflonTM lid liners under a nitrogen gas atmosphere at 4°C (39°F). The spent sand samples were stored in glass containers with Teflon lid liners under a nitrogen gas atmosphere at room temperature.

Elemental Analyses

Elemental analyses were performed on selected samples of distillate and heavy oil using standard WRI analytical methods. The elements that were quantitated include carbon, hydrogen, nitrogen, and sulfur. Oxygen content of the samples was estimated by difference.

Residual Char by Combustion

The residual char (organic material) that remained on the spent sand was determined by combustion of the organic material. The spent sand was first dried at 110°C (230°F) for 24 hours to remove absorbed water and then weighed. The dried samples were combusted at 455°C (850°F) for 24 hours to burn off the organic material. The combusted sand was weighed. The weight percentage of char was determined as the weight loss by combustion of the spent sand sample.

Model-Compound Determinations

The model compounds were quantitated in the heavy oils using a classical total ionization approach based on gas chromatograph/mass spectrometric (GC/MS) analysis of the samples. The area response of each model compound was measured from the reconstructed ion current chromatogram. The percentage ionization of this area to the total ionization area was calculated.

Saturate, Aromatic, Resin, and Asphaltene Determinations

A class separation to determine the concentration of saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA) was performed on all of the heavy recycle oils generated during the experiments conducted to evaluate the effect of recycling SAE 50 weight oil. This separation was conducted by first precipitating the asphaltenes from the heavy oil in normal pentane (1 g heavy oil to 40 mL pentane). The remaining classes of compounds were separated by elution over active alumina. Twenty grams of active alumina were charged to a

0.95- x 40.6-cm (0.375- x 16-inch) column. A sample of the deasphalted heavy oil (0.25 g) was added to the top of the column and 2 cm of alumina placed on top of the sample to prevent disturbing the sample when solvent is added. The saturated hydrocarbons were eluted with 60 mL of hexane. The aromatic hydrocarbons were eluted with 30 mL of toluene. The resin fraction was recovered by passing 30 mL of toluene/methanol (9:1 vol) over the column followed by 30 mL of methylene chloride. The solvents were removed by evaporation of the solvent with a nitrogen purge. The weights of each fraction were determined and the results reported as weight percentages.

Gas Chromatography-Mass Spectrometric Analyses

Distillate samples from pyrolysis of the model polymers were subjected to analysis by gas chromatography-mass spectrometry (GC/MS) to identify the major components in these products. The chromatographic separation was performed on an open tubular, fused silica column (0.03 mm id. by 25 m long) coated with cross-linked methyl silicone. The gas chromatograph was temperature programmed from 20 to 200°C (68 to 392°F) at a rate of 3°C/min (5.4°F). The mass spectra were recorded over a mass range of 50 to 450 amu at an accelerating voltage of 2 kV and ionization voltage of 70 volts.

The components eluting from the gas chromatograph were identified by library search matches of the mass spectra recorded for each component. Relative concentrations of each component were determined as the area percentage of the ionization of each component based on the total ionization of the sample. This procedure assumes unit sensitivity on a weight basis for each compound, but provides a reasonable approximation of the volume percentage of each component.

RESULTS AND DISCUSSION

Definition of Products

The ROPE concept has been evaluated at the PDU and BSU levels, and several reports have been prepared discussing the concept from the PDU-scale reactor operation. The products generated during the PDU and BSU studies reflect the product slate that is expected from a commercial unit. The products obtained from the simulation studies need to be defined to prevent confusion with the products that have been discussed in reports of the PDU and BSU experiments. The following definitions are used to define the product slate from the laboratory simulation studies.

Heavy Oil is the liquid product that remains in the reaction vessel at the end of an experiment regardless of experimental temperature.

Distillate is the liquid product that is produced as vapor at the experimental temperature and condensed to the liquid phase.

Spent Sand is the sand remaining in the reactor that is free of toluene-soluble organic material. The spent sand is reclaimed from the experiment by rinsing the sand and heavy oil sample with toluene to remove the heavy oil.

Char is the organic residue on the spent sand that is not toluene soluble but can be removed by combustion at 454°C (850°F).

Bitumen Extraction

Two randomly selected samples of the raw tar sand were analyzed to determine the composition and oil saturation of the bitumen and to determine the variability of the method used to sample the raw tar sand. Each sample of tar sand was serially extracted with toluene and pyridine to recover the bitumen. The toluene extract, which represents the largest quantity of organic material, was analyzed to determine the elemental composition.

The results of the analyses of the two tar sand samples are listed in Table 1. (Tables are presented in the Appendix.) The total bitumen content (toluene-plus-pyridine extracts) of the two samples was 13.3 wt % of the tar sand. The toluene extract represented 13.1 and 13.2 wt % of the tar sand, and the pyridine extract represented 0.2 and 0.1 wt %. The recoveries of the organic materials from the raw tar sand are comparable, and the sampling procedure appears to provide uniform samples.

Evaluation of the elemental composition of the toluene extracts (Table 1) shows that there are no significant differences in the elemental compositions. Therefore, the samples and the sampling procedure are adequate for this project.

Evaluation of the PDU Reactor Zones

Fourteen experiments were performed to evaluate the three major processing zones of the ROPE concept. The majority of the samples collected during these experiments were analyzed, and the data were evaluated for this report. Some of these data do not provide information helpful in understanding the chemical and physical processes that control the process. However, these data do provide a data base for estimating the properties of the different reactants and products. The data not pertaining to understanding of the concept are not discussed in this report but are provided in tabular form in an earlier report (Guffey and Hunter 1989).

Material Balance Closures

Material balances were performed on each of the experiments performed during this study. The material balances are useful in accounting for the materials consumed or produced during an experiment, and they also provide a quantitative measure of the quality of each experiment by measuring the gain or loss of material. The material balances for each of the experiments (including duplicates) are listed in Tables 2 through 4.

The material balances are arranged in the three tables according to the reactor zone studied in each set of experiments. The material balances for the experiments investigating the tar sand preheat and the recycle oil pyrolysis zones (Tables 2 and 3) have closures between 98.8 and 100.7%. These closures are considered to be well within the experimental error of the experiments and indicate that there is accountability for the materials introduced into the reactor.

The material balances for the experiments investigating the recycle oil drying zone are listed in Table 4. The material balance closures for these experiments range from 90.9 to 100.0%. The experiment performed at 400°C (752°F) has a closure of 90.9%. This closure is too low to be acceptable for the accountability of the material in this experiment. Therefore, a duplicate experiment was performed at this temperature. The data collected from the duplicate experiment was used to evaluate this zone at 400°C (752°F).

Elemental Balance Closures

Elemental balances were performed on four elements (carbon, hydrogen, nitrogen, and sulfur) to determine the validity of using these results to evaluate the experiments. The closures for the elemental balances for the experiments investigating the three processing zones are listed in Tables 5 through 7. Examination of these results show that the closures for carbon and hydrogen are good. The closures range from 98.3 to 103.9 wt % for carbon and 96.2 to 105.3 wt % for hydrogen. These closures are in the range where good accountability of the two elements has occurred; therefore, the results can be used to evaluate the processing zones.

The ranges of the elemental balance closures for nitrogen and sulfur are wide. This suggests that the accountability of these two elements is not good. These results can not be used to evaluate the processing zones investigated during these studies. The probable reason for the poor closure of the elemental balances for nitrogen and sulfur is the high detection limit of the analytical methods for the analysis of solids. Poor estimation of the concentration of these elements in solid samples, which represent a large weight fraction of the material for each experiment, will cause large errors in the calculation of the recovered weights of these elements. These errors are reflected in the poor elemental balance closures for these elements.

Liquid Product Yields

The objective of the ROPE processing concept is to produce a distillable liquid product from the processing of tar sand bitumen. The distillate yield from bitumen conversion by the ROPE simulation experiments discussed in this report is difficult to distinguish from liquid products arising from distillation of light ends of the recycle oil and from pyrolysis of the recycle oil itself. The quantity and evolution profile of distillate derived from pyrolysis of the tar sand bitumen are important to understanding the production of distillable liquid products. An estimate of the distillation profile was made by

comparing the distillate production from a distillation of the recycle oil with the distillate production from each of the experiments investigating the tar sand preheat and recycle oil drying zones.

This comparison is shown graphically in Figure 5. The total distillate production from each of the ROPE simulation experiments is plotted as a function of the experimental temperature. The distillate production from the distillation experiment at the temperatures corresponding to the ROPE simulation experiments is also plotted as a function of the experimental temperatures.

Examination of the comparison shows that there is little difference between the distillate production from the distillation experiment and the ROPE simulation experiments over the temperature range of 200 to 375°C (392 to 707°F). The one data point above 375°C (707°F) shows a significant increase in the distillate production during the ROPE simulation experiments. This suggests that distillate production from pyrolysis of tar sand bitumen does not occur at temperatures below 375°C (707°F). This is an important consideration in the operation of a commercial process because the pyrolysis portion of the system must be operated at temperatures in excess of 375°C (707°F).

Figure 5. Comparison of Distillate Production from the ROPE Simulation Experiments and a Distillation of the Recycle Oil

Hydrogen-to-Carbon Atomic Ratios

Hydrogen-to-carbon (H/C) atomic ratios are a convenient method for comparing the hydrogen deficiency among a series of samples. This approach was used to evaluate the quality and changes in the distillate oils produced from the ROPE simulation experiments. The H/C atomic ratios for the distillates produced during the experiments investigating the recycle oil pyrolysis and recycle oil drying zones are listed in Tables 8 and 9, respectively. The H/C atomic ratios for the experiments conducted to investigate the tar sand preheat zone are not presented in this section because, as was discussed in the proceeding section, distillate is not produced from the tar sand bitumen at temperatures below 375°C (707°F). The tar sand preheat zone operates at temperatures below 300°C (572°F), and the distillate collected during these experiments is from distillation of the recycle oil and not from pyrolysis of the tar sand bitumen.

The data listed in Tables 8 and 9 show some variation. However, whether this variation is the result of changes in the composition of the distillate oils through changes in the processing conditions or the variation is normal for the population is unknown. These data were subjected to two-way analysis of variance (ANOVA) to determine if there are any differences among the data with respect to experiment temperature or the time into the experiments. The results of the two-way ANOVA are listed in Tables 10 and 11.

Examination of the results in Tables 10 and 11 shows that the F_{ratio} is less than the value of $F_{0.05}$ for both the rows and columns evaluated for the recycle oil drying and recycle oil pyrolysis zones. Because the F values are such, the null hypothesis is accepted. These results show that the variation among the H/C atomic ratios is random variation of the population and not the result of the experimental conditions investigated. The fact that the H/C atomic ratios do not vary with the experimental temperature or the time into the experiments suggests that the process produces a stable distillate composition and that this parameter is probably not adequate for monitoring the approach to steady-state of larger scale processing units.

The H/C atomic ratios of the heavy oils were also selected as a parameter to follow changes in the composition of the heavy oils produced during the recycle oil pyrolysis and recycle oil drying zone experiments. The heavy oils produced from the tar sand preheat zone were not considered for this evaluation because pyrolysis does not occur in this region of the process, and changes in the H/C atomic ratios will reflect only the changes caused by distillation of the lower boiling material in the heavy oil. The H/C atomic ratios for the heavy oils produced during the experiments investigating the recycle oil pyrolysis and recycle oil drying zones are listed in Tables 12 and 13. The data in these tables exhibit variations that may be caused by changes in the experimental conditions or may reflect normal variation of the population. Two-way ANOVA was applied to these data to determine the source of variance.

The results of the two-way ANOVA are listed in Tables 14 and 15 for the analysis of the heavy oil H/C atomic ratio data from the experiments investigating the recycle oil pyrolysis and recycle oil drying zones, respectively. Comparison of the F_{ratio} values with the $F_{0.05}$ values for the H/C atomic ratios for the heavy oils produced during investigations of the recycle oil pyrolysis zone (Table 14) shows that the null hypothesis can be rejected for both the rows and columns, and the differences in these data are caused by changes in experimental temperature and time into the experiment. The null hypotheses must be accepted for the H/C atomic ratios for the heavy oils produced during the investigations of the recycle oil drying zone (Table 15). This suggests that the differences in these data are normal variations of the population.

The changes in the H/C atomic ratios for the heavy oils produced during the recycle oil pyrolysis investigations (Table 12) show a decrease in the ratios with an increase in the time into each experiment. There is also a trend of decreasing H/C atomic ratios with increasing experimental temperature for the heavy oil samples collected after the tar sand was added to the reactor. The observed decreases in the H/C atomic ratios are indications that hydrogen is being transferred from the heavy oil to the distillate or gaseous products. This is significant because the H/C atomic ratios for the distillate products do not show a statistically significant change with respect to changes in experimental conditions.

These observations are important for two reasons. First, it is suggested that there may be a chemical mechanism for the transfer of hydrogen from the heavy oil to radicals produced during pyrolysis. Second, it is also suggested that hydrogen will be depleted from the heavy oil and that the availability of hydrogen will limit the production of distillate.

The indication that a chemical mechanism can be identified for the transfer of hydrogen from the heavy oil to the distillate opens an area of study that can be used to monitor and control the process. A chemical mechanism that can be identified for the transfer of hydrogen can be controlled through kinetics or equilibrium considerations to optimize the yield of distillate. The chemical mechanism to explain the transfer of hydrogen identified through this research will be more fully discussed in the section discussing the model-compound studies.

The transfer of hydrogen from the heavy oil for the production of the distillate, through reaction of the hydrogen with pyrolysis-produced radicals can limit the yield and usefulness of the process. In a continuous recycle process, it may be possible to deplete the transferable hydrogen from the heavy oil during the production of distillate product. If the transferable hydrogen is depleted from the heavy oil in a continuous recycle process, then the production of distillate would be limited by a decreasing concentration of transferable hydrogen, and the radicals produced by pyrolysis would tend to form coke in place of distillable liquid product.

The null hypothesis was accepted for the two-way ANOVA of the H/C atomic ratios of the heavy oils produced during the experiments investigating the recycle oil drying zone (Table 15). This suggests that at a probability level of 0.05 there is no significant variation among the values. These results suggest that hydrogen is not transferred to the distillate products in this region of the reactor. This is interesting because at the higher temperatures in this zone, we expect faster reaction rates and a greater variation in the difference in the H/C atomic ratios compared with those observed for the heavy oils produced for the recycle oil pyrolysis zone simulations. These are not observed, and their absence suggests a different chemical mechanism. Since hydrogen is not transferred to the distillate product the heavy oil may follow a different reaction pathway to produce coke and gas.

Coke Production

The quantity of char or coke deposited on the spent sand at the end of each experiment is a measurement of the quantity of material lost to the reactor system. If this material were not deposited on the spent sand, it could be used for production of distillate product or recycled back to the reactor as recycle oil. Therefore, evaluation of this parameter is a useful approach for studying the chemistry of the process. Figure 6 shows a graphical representation of the coke production as a function of experiment temperature. Only the coke production data for the recycle oil pyrolysis and recycle oil drying zones are shown in this figure. The data for the tar sand preheat zone was not included because the coke production in these experiments was

Figure 6. Coke Buildup on Spent Sand as a Function of Temperature

comparable to the residual organic material remaining on the sand after the bitumen was solvent extracted. This level of material on the sand is residual and suggests that coke production as well as distillate production does not occur in this zone of the reactor.

Examination of these results shows that each of the reactor zones has distinct curves for the production of coke and both curves increase with experiment temperature. The production of coke is higher in the recycle oil drying zone than it is in the recycle oil pyrolysis zone. These data reinforce the hydrogen-transfer limitations discussed for the heavy oils of the recycle oil drying zone. The lack of hydrogen transfer in this zone leads to the production of coke. The higher experimental temperatures used in the recycle oil drying zone will also increase the reaction rate for production of coke. The increased reaction rate is reflected in the higher production of coke shown in the data.

Model-Compound Studies and Hydrogen Transfer

The chemistry of complex systems is difficult to study because of the large number of compounds present and because the concentration of the individual species is often low. Model compounds were used to investigate the chemistry of the processes that occur during the recovery of distillable products. Five model compounds representing the four major classes of hydrocarbons observed in products from previous PDU and BSU tests were selected for this study. The five compounds selected for analysis include: (1) n-octadecane (alkane), (2) phenanthrene (aromatic), (3) anthracene (aromatic), (4) 9,10-dihydroanthracene (hydroaromatic), and (5) perhydrofluorene (cycloalkane). The recycle oil was prepared by making a solution of all of the model compounds (except anthracene) in the recycle oil at approximately the 1-wt % level. The solution was analyzed using mass spectrometric techniques to establish the absolute concentration of each compound.

The recycle oil, spiked with the model compounds, was used as the recycle oil for the experiments investigating the three major processing zones. The distribution of the model compounds in the products and the increases and decreases of the concentrations of the model compounds in the reactor were used to evaluate the chemical mechanisms that occur during processing. The concentrations of the model compounds in the products were determined using mass spectrometric techniques.

Evaluation of the model compound recovery data has shown that there are no obvious trends in the data except for anthracene and 9,10-dihydroanthracene (Guffey and Hunter 1989). The sum of the recoveries of these two species do show some interesting trends. These data are listed in Table 16. The recovery of 9,10-dihydroanthracene shows a general decrease in recovery with increase in experimental temperature, and the recovery of the sum of 9,10-dihydroanthracene plus anthracene appears to remain relatively constant over the same temperature range. One-way ANOVA (Table 17) was performed on the data in Table 16 to determine if there is statistical significance for the variation observed in the data. The null hypothesis is rejected for these data, and the variation in these data is not random at a probability of 0.05.

The decrease in the recovery of 9,10-dihydroanthracene over the temperature range suggests that this compound may be consumed in reactions that occur in the process. The relatively constant recovery of the sum of 9,10-dihydroanthracene plus anthracene at approximately 100% over the same temperature range suggests that the 9,10-dihydroanthracene is releasing hydrogen to produce one mole of hydrogen and one mole of anthracene. The conversion of 9,10-dihydroanthracene to anthracene is a potential hydrogen-transfer mechanism in this process.

Table 18 lists similar recovery data for an experiment that was performed with only the recycle oil (the distillation experiment). This experiment was performed by heating the oil over the temperature range used in the ROPE process and the distillate product collected. Examination of these data shows that there is variation in the recoveries for 9,10-dihydroanthracene and 9,10-dihydroanthracene plus anthracene. One-way ANOVA was performed on these data to determine if the variation was significant at a probability of 0.05. The results of this analysis are listed in Table 19. The null hypothesis is accepted, and these data vary as expected for the population at a probability of 0.05. These results suggest there is not an apparent conversion of 9,10-dihydroanthracene to anthracene during the distillation experiment. This means that hydrogen transfer does not occur and that tar sand bitumen is necessary for hydrogen transfer.

The above results lead us to believe that hydrogen release from a hydroaromatic species (9,10-dihydroanthracene) occurs during the pyrolysis of tar sand bitumen in the ROPE process. The results do not define a mechanism for hydrogen release in the process. If the hydrogen is released as molecular hydrogen (H_2), then the hydrogen is not available for reaction with pyrolysis intermediates and is lost to the process as hydrogen gas. The hydrogen is lost because the temperatures and pressures of this reactor system are significantly below those used for noncatalytic hydrogenation. However, if the hydrogen is released through a reaction sequence in which the release is actually an atomic hydrogen transfer to a reaction center, then the hydrogen can be retained in the reaction products.

McMillen et al. (1988) investigated the transfer of hydrogen in coal liquefaction processes. They propose a mechanism that explains the transfer of hydrogen from a hydroaromatic species to the pyrolysis reaction center through an aromatic hydrocarbon intermediate. This mechanism, as it applies to the ROPE concept, is shown schematically in Figure 7. Examination of this mechanism shows that the hydroaromatic compound reacts with an aromatic hydrocarbon producing two cyclohexdienyl radicals. The cyclohexdienyl radicals act as the actual hydrogen-transfer agent in the pyrolysis reaction. Each cyclohexdienyl radical transfers a hydrogen to the tar sand bitumen pyrolysis reaction center that in turn releases the hydrocarbon fragment. This forms an unstable intermediate that disassociates to yield the hydrocarbon fragment (containing the transferred hydrogen) and the remainder of the tar sand bitumen molecule.

Figure 7. Hydrogen Transfer Chemistry from Model-Compounds Studies in the ROPE Simulation Experiments (from McMillen et al. 1988)

This mechanism for hydrogen transfer explains the data for the recovery of 9,10-dihydroanthracene plus anthracene in the model-compound studies. The recovery of 9,10-dihydroanthracene decreases with increasing experiment temperature, whereas the recovery of the sum of the two species remains relatively constant near 100%. In the model-compound studies, hydrogen is transferred from 9,10-dihydroanthracene to an aromatic species creating two radicals. One of these radicals is produced from the 9,10-dihydroanthracene. When this radical transfers hydrogen to the pyrolysis reaction center, anthracene is produced. The overall reaction appears as 9,10-dihydroanthracene releasing hydrogen to produce anthracene. This is the reaction sequence suggested by the model-compound recovery data.

These results show that hydrogen transfer through radical intermediates is possible in the ROPE concept; these results do not prove that it is a driving force in the system. If tar sand bitumen contains a significant concentration of hydroaromatic-like structures, then this form of hydrogen transfer will be important to the production of liquid products. If the hydrogen source is hydroaromatic structures in the bitumen, then recycling the heavy oil will not effect the production of distillate by limiting the hydrogen that is available for transfer. The hydrogen source will be continuously renewed with the addition of tar sand bitumen to the reactor.

Recycling SAE 50 Weight Oil and Steady State

The objective of the experiments discussed in this section was to evaluate the recycling of SAE 50 weight oil to a composition that would be equivalent to steady state in the PDU. Steady state, as it applies to the ROPE process, is defined as the condition where the composition of the reactants entering the reaction system and the composition of the products leaving the reaction system do not change as a function of time.

The reactants entering the recycle oil pyrolysis zone of the process are the raw tar sand and the heavy recycle oil. We can assume that the composition of the tar sand is relatively constant as shown from the analysis of duplicate samples discussed in a preceding section. The heavy recycle oil is the reactant that we expect to change in chemical composition as a function of time, particularly when SAE 50 weight oil is used as the initial heavy oil. The SAE 50 weight oil is a substitute for the recycle oil and will undoubtedly undergo pyrolytic reactions in the process. The composition of the heavy oil must reach a constant composition before steady-state operation can be achieved.

Produced gas, distillate, heavy oil, and spent sand are the products that will leave the reaction system. Previous research shows that there is little change in the elemental composition of the spent sand as a function of temperature or residence time (Guffey and Hunter 1989). Experiments conducted in the PDU demonstrated that the gas composition, determined by gas chromatography, remains relatively constant for the duration of the tests (Cha et al. 1986, 1988). Therefore, the composition of these products can be considered constant with respect to time during the approach to steady state. This leaves the distillate and heavy recycle oil as the products that can undergo significant change as the process approaches steady-state operation. The compositional changes of these products were monitored during these experiments to evaluate the approach to a steady-state equivalent.

Simulation of the PDU as it approaches steady state is not an easy task to conduct in the laboratory simulation reactor. The laboratory simulation reactor is a batch reactor used to simulate a dynamic process. In addition, the question of steady-state operation of the PDU has not been resolved. The problem with using a batch reactor to simulate a dynamic process was approached by assuming that if we began the experiments at a given temperature with SAE 50 weight oil and continued recycling the heavy oil from one experiment to the next (at constant temperature), then a dynamic process could be approximated with a series of batch-reactor processes.

Operation of the PDU at steady state has not been well defined in previous research. Thus, this research addressed defining the approach to steady state in the PDU using the laboratory simulation reactor. Several chemical and physical parameters were selected that have the potential to monitor the approach to a condition in the laboratory simulation reactor that is equivalent to steady-state operation in the PDU. We made the assumption that when a steady-state equivalent is reached, the trend in the chemical indicators should remain at a

remain at a constant value (within experimental error). The selected parameters were monitored in the heavy oils and distillates produced during this series of experiments. The following sections discuss the results obtained from the experiments conducted at 375, 400, and 425°C (707, 752, and 797°F).

Material Balance Closures

Material balances were determined for each of the experiments performed during this phase of the study. The material balances for each of the experiments are listed in Tables 20 through 22. The material balances are arranged in these three tables according to the experimental temperature used in each series of experiments.

The material balances for the experiments investigating the recycling of SAE 50 weight oil at 375°C (707°F) have closures between 92.7 and 101.1% (Table 20). The experiments were halted after the ninth iteration because the results (discussed in detail below) showed that a condition equivalent to steady state could not be reached in a reasonable number of cycles of the heavy oil. All of the closures except experiment 8 (92.7%) are within the experimental error of the laboratory simulation reactor. The low recovery for experiment 8 can not be explained. It was not possible to duplicate this experiment, because the experiments were conducted by using the heavy oil recovered from the previous experiment as the initial heavy oil for the next experiment.

The material balances for the experiments conducted at 400°C (752°F) are listed in Table 21. A total of fourteen experiments were conducted at this temperature. The experiments were halted after the fourteenth experiment because the results (discussed in detail below) showed that a condition equivalent to steady state had been reached. The experiments conducted at this temperature have material balance closures between 93.2 and 100.7%. Experiment 8 had the only material balance (93.2%) below the level considered to be within the experimental error of the laboratory simulation reactor. Examination of the material balance data from this experiment shows that the cause of the low material balance closure is from the heavy oil recovered from the experiment. The weight of the heavy oil was checked when this error was identified, and it was found to be the correct weight. We have interpreted this to mean that the error was in the weight determination of the heavy oil charged to the reactor. This error should not have a large affect on the results of this study because this only changes the heavy oil-to-bitumen ratio from 8:1, used in the remainder of the experiments, to 6.3:1. An error of this type will add a higher percentage of bitumen to the organic material charged to the experiment and cause a slight increase in the rate of progress to a condition that is equivalent to steady state.

The material balances for the experiments conducted at 425°C (797°F) are listed in Table 22. A total of eight experiments were conducted at this temperature. The experiments were halted after the eighth experiment because the results (to be discussed in detail below) showed that this temperature did not produce sufficient heavy oil to sustain the process. The mass of tar sand charged to the reactor was increased

during these experiments in an attempt to increase the production of heavy oil so that a sufficient number of experiments could be performed to establish a steady-state equivalent at this temperature. This attempt was not successful as is shown by the results in Table 22. All of the material balance closures for the experiments conducted at this temperature are between 98.9% and 100.6%. These material balance closures are within the experimental error expected from experiments conducted in the laboratory simulation reactor.

Organic Product Distribution

Steady state is defined as the reactants and products from a process exhibiting constant composition with time. Relatively constant mass production of the products is also important for the ROPE process because the heavy oil is recycled through the system. Failure of the reactor to produce a constant mass of heavy recycle oil that is equal to or in excess of the initial inventory will not allow the process to continue to a steady state. The recoveries of heavy oil for the experiments conducted at each of the three temperatures are listed in Table 23. The recoveries are based on the initial charge of heavy oil for each experiment and are reported as weight percentages.

Examination of the results from the experiments conducted at 375 and 400°C (707 and 752°F) shows that the heavy oil recovered from the majority of the experiments was greater than 100%. The exceptions include experiment 8 at each of these temperatures and experiments 12 and 14 at 400°C (752°F). Experiment 8 at each of these temperatures did not have acceptable material balance closures and the heavy oil recoveries did not represent a trend in the data. Experiments 12 and 14 at 400°C (752°F) had severe bumping problems that caused heavy oil to be carried over to the distillate receivers, thus, reducing the recovery of heavy oil. Examination of these results, with consideration of the above discussed exceptions, shows that it is possible to produce sufficient heavy oil to sustain the recycle needs of the process. Therefore, it should be possible to achieve an equivalent to steady-state operation at 375 and 400°C (707 and 752°F). Further analysis of the data from these experiments is necessary to determine if a condition equivalent to steady state can be achieved.

Examination of the results from the experiments conducted at 425°C (797°F) shows that the recoveries of heavy oil from most of the experiments are less than 100%. The three experiments having heavy recycle oil recoveries greater than 100% are exceptions from the observed trend. The process will not be able to sustain itself in a recycle mode of operation at this temperature because the heavy recycle oil recoveries are less than 100%. Operation at steady state has little meaning for developing the process if the process can not sustain itself with heavy recycle oil, and further evaluation of the experiments in terms of achieving a condition equivalent to steady state are meaningless. For this reason, the experiments at 425°C (797°F) were discontinued after eight experiments, and we assumed that a condition equivalent to steady state could not be achieved.

The distribution of the organic products for the experiments conducted at 375, 400, and 425°C (707, 752, and 797°F) are listed in Tables 24, 25, and 26, respectively. The organic products are defined as distillate, heavy oil, coke, and produced gas. The results reported in these tables are listed based on the organic mass charged to the reactor. The results from the experiments conducted at 375°C (707°F) show that little distillate and no gas were produced at this temperature. We interpreted this as an indication that the reaction rate of the pyrolytic reactions at this temperature is significantly lower than the reaction rate at the two higher temperatures. The reaction rate is too low to produce a heavy recycle oil that approaches steady-state conditions in a reasonable amount of time (10 cycles of the heavy oil). For this reason, the experiments were terminated after nine cycles of the heavy oil.

The experiments conducted at 425°C (797°F) produced the highest quantity of distillate, but the amounts of coke and gas production are comparable to the amounts produced at 400°C (752°F). This suggests that operation of the process at 425°C (797°F) is most beneficial because this temperature produces the highest percentage yield of the desired product (distillate). The significance of the high distillate yield is offset by the fact that when the system is operated at this temperature it can not sustain itself by producing enough heavy oil for recycle. Further examination of the results in Tables 23 through 26 show that 400°C (752°F) is the optimum temperature. Operation of the system at 400°C (752°F) produces a high yield of distillate and provides a high enough recovery of heavy oil to sustain the recycle needs of the process.

Examination of the distillate yields from the series of experiments conducted at the three different temperatures illustrates an important point. The distillate production exhibits an approximate cyclic pattern with respect to the number of cycles of the heavy oil (time in the PDU or BSU reactors). The cyclic nature of the distillate production may be an artifact of the way in which these experiments were conducted in the batch mode or the cycling of the distillate production may be real and have implications for a continuous process. If the cyclic distillate production is not an artifact, then it may be indicative of an induction period in the reaction system where a precursor has to be formed to a threshold level before the reaction will proceed to form the distillate. The reaction to produce the distillate drops the concentration of the precursor to a level below the threshold, and the reaction slows until that threshold is reached again. This is an area that should be further investigated for the development of this process. If the mechanism for the formation of the precursor can be identified, it may be possible to control its formation in a different portion of the reactor. This can stabilize the production rate and improve the distillate yield.

Chromatographic Separation of the Heavy Oils

The produced heavy oils were separated chromatographically (SARA separation) into four fractions (saturates, aromatics, resins, and asphaltenes) on active alumina. These analyses were performed to monitor the compound-class distributions of the heavy oils as a function

of the number of times the heavy oil was cycled through the laboratory simulation reactor. The objective of these analyses was to determine if the approach to a steady-state equivalent effected the distribution of the compound classes present in heavy oil and if these data could be used to define and measure the steady-state equivalent.

The asphaltene concentrations (based on the total organic charge to the reactor) in the heavy oils produced from these experiments are listed in Table 27. There is a definite trend in the results for the experiments at the three temperatures. The asphaltene concentration increases as a function of the number of times the heavy oil was cycled. The asphaltene concentrations at 375°C (707°F) are low compared with the concentrations at the other two temperatures. These are additional data that support the belief that the reaction rate at this temperature is too low to reach a steady-state equivalent in a reasonable amount of time. An equivalent to steady state was not achieved during these experiments based on the concentration and trends in the concentration of the asphaltenes.

The asphaltene concentrations in the heavy oils produced at 400°C (752°F) show a significant increase as a function of the number of times the heavy oil is recycled. Careful evaluation of the concentration changes shows that it becomes relatively constant after 10 cycles of the heavy oil. After the tenth cycle, the heavy oil asphaltene concentration varies randomly from approximately 12 to 18%. The values are not absolutely constant at an equivalent of steady state, but the data show a cycle similar to that observed for the distillate production.

The asphaltene concentrations in the heavy oils produced at 425°C (797°F) also show an increase as a function of the number of times the heavy oil is recycled. Evaluation of these results shows that the asphaltene concentration reaches a relatively constant value and begins to cycle after six uses of the heavy oil. We interpreted this as an equivalent of steady state. The experiments could not produce sufficient heavy oil to sustain the recycle for the process; therefore, these results have little significance to evaluation of steady-state operation of the PDU.

The distributions of compound classes (saturate, aromatic, and resin fractions) in the heavy oils produced from the experiments performed at 375, 400, and 425°C (707, 752, and 797°F) are listed in Tables 28, 29, and 30, respectively. The chromatographic separation used to generate these fractions was performed on the maltene fraction (heavy oil after the asphaltenes were precipitated), and the results are reported as the weight percentage of each fraction based on the mass of the maltenes. The solvent was removed from the individual fraction with a nitrogen gas stream, which causes some loss of material by entrainment, and the material balances are normally less than 100 wt %. Examination of these results shows that the saturate fractions are the chromatographic fractions with the highest concentration in the experiments at all temperatures. In general, the aromatic fractions are present at higher concentrations than the resin fractions. Unfortunately, there are no detectable trends in the distribution of these classes of compounds as a function of the number of times the heavy oil is recycled.

Elemental Compositions

The elemental composition of selected samples of the produced distillates and heavy oils were determined and used as an aid in evaluating an equivalent to steady state. The elemental composition of selected distillate samples from the experiments performed at 400 and 425°C (752 and 797°F) are listed in Tables 31 and 32, respectively. Elemental compositions were not determined for distillate samples from the experiments conducted at 375°C (707°F) because there was not sufficient distillate produced to provide samples for the analyses.

The elemental compositions of the distillate samples (Table 31) produced at 400°C (752°F) show that the nitrogen concentration remains at 0.0% (or below the detection limit) until the heavy oil has been recycled nine times. The nitrogen concentration then reaches a relatively constant value for the remainder of the samples. The sulfur concentration drops to 0.0% (or below the detection limit) after seven cycles of the heavy oil. These trends parallel the trends observed for the asphaltene concentration in that a constant value is reached for these parameters after several cycles of the heavy oil. The hydrogen-to-carbon atomic ratios for the distillates show a trend of decreasing values through 11 cycles of the heavy oil. After 11 cycles, the value remains relatively constant. These trends are indicative of the compositional behavior expected at a steady-state equivalent.

The nitrogen concentration (Table 32) of the distillate samples produced at 425°C (797°F) show a trend similar to that observed for the distillates at 400°C (752°F). The concentration increases to a constant value (0.1%) after the fourth cycle of the heavy oil. The number of cycles required to reach the constant value is lower than was measured for the distillates produced at 400°C (752°F). This suggests that the reaction rate at this temperature is significantly higher than the rate at the other temperatures. Sulfur was not detected in these samples; we believe this shows that the system is extremely reactive at this temperature. The H/C atomic ratios are basically constant for all of the distillates analyzed at this temperature. The results from the elemental analyses of these samples show that an equivalent to steady state was probably achieved early in this series of experiments. However, this has little significance because reactions at this temperature can not produce sufficient heavy oil to meet the recycle needs of the process.

The elemental compositions of selected heavy oil samples produced at 375°C (707°F) are listed in Table 33. The nitrogen concentration shows a steady increase, and the H/C atomic ratios show a constant decrease as a function of the number of times the heavy oil is recycled. These results suggest that an equivalent of steady state has not been achieved after nine cycles of the heavy oil. This is not surprising because the reaction rate at this temperature is too slow to reach a steady-state equivalent in a reasonable number of heavy oil recycles.

The elemental composition of selected heavy oil samples produced at 400°C (752°F) are listed in Table 34. The nitrogen concentrations of these samples show a decrease as a function of the number of cycles of the heavy oil until the eleventh cycle. After the eleventh cycle, the nitrogen concentration becomes relatively constant. This suggests that the system has achieved a condition equivalent to steady state. The H/C atomic ratios do not show the same trend. The H/C atomic ratios show a constant decrease as a function of the number of cycles of the heavy oil and suggests that an equivalent to steady state has not been achieved. Although the H/C atomic ratios do not indicate a steady-state equivalent, the system may have still reached the desired condition. Previous research shows that the H/C ratios of the heavy oil are not extremely sensitive to changes in processing conditions (Guffey and Hunter 1989).

The elemental composition of selected heavy oil samples produced at 425°C (797°F) are listed in Table 35. Both the nitrogen concentration and the H/C atomic ratios show a trend of change to a point where the values become relatively constant. The constant values occur after four cycles of the heavy oil. The relatively constant nitrogen concentrations and H/C atomic ratios suggest that an equivalent of steady state has been achieved.

Model-Compound Analyses

Model compounds were used during this study to follow their fate during the processing required to achieve a condition equivalent to steady state in the PDU. Phenanthrene and anthracene were selected as the model compounds to represent aromatic compounds, and n-octadecane was selected to represent saturated hydrocarbons in the heavy oil. These three compounds occur naturally in the heavy oil produced in both the PDU and BSU. Therefore, monitoring these compounds is a probe into the molecular level of the process and can yield important information regarding an equivalent to steady state. The results from analyses of the saturate and aromatic fractions from the heavy oils produced at 400°C (752°F) are listed in Table 36. Only the results from the experiments at 400°C (752°F) are reported because the results from heavy oils produced at the other temperatures were not significant.

The area percentages of anthracene and phenanthrene show a steady decrease through 11 cycles of the heavy oil; then the area percentages become relatively constant. This suggests that the composition of the heavy oil changed through the eleventh cycle. After the eleventh cycle, the composition of heavy oil did not change, suggesting that an equivalent to steady state had been achieved. This is significant because the model compound study measures the molecular composition of the heavy oil, and a constant composition at the molecular level is important for establishing steady-state operation.

The model compound n-octadecane was used as an indicator compound in two ways. First, it was monitored as the percentage of total ionization. Second, it was monitored as a ratio with n-nonadecane. The percentage of the total ionization shows a decrease through the eleventh cycle of the heavy oil as was observed for the aromatic hydrocarbon model compounds. This suggests that an equivalent to steady state has been achieved.

The ratio of n-nonadecane to n-octadecane (C_{19}/C_{18}) shows an increase through the tenth cycle of the heavy oil followed by a relatively constant value for the remainder of the samples. This is important. Both compounds are produced in the larger scale units, but additional n-octadecane was added to these experiments. When this ratio increases to a constant value, it shows that the n-octadecane is consumed by the system and n-nonadecane is supplied by the reactions until a steady-state composition is reached. This reasoning can be extended to other components in the SAE 50 weight oil. They will be consumed and formed by the process at approximately the same rate as the model compounds until a steady-state composition is obtained.

Theoretical Approach to Steady-State

The experimental data suggests that an equivalent to steady state can be achieved in approximately 11 cycles of the laboratory simulation reactor. A series of calculations have been performed to provide a theoretical estimate of the number of cycles required for comparison with the experimental data. Several alternative cases were selected for these calculations. The cases include; (1) dilution of the initial heavy oil with bitumen without the production of distillate, coke, or gas, and (2) production of 5 wt % distillate assuming that 0, 25, 50, 75, and 100% of the distillate was derived from the bitumen. Replacement of 95% of the initial heavy oil with a bitumen-derived heavy oil was assumed to represent the steady-state equivalent. The results of these calculations are listed in Table 37.

The estimate for the case considering only dilution as the mechanism for removal of the initial heavy oil will require 24 cycles of laboratory simulation reactor. Dilution requires significantly more cycles to remove 95 wt % of the initial heavy oil than the experimental data shows is required to reach a steady-state equivalent. This comparison indicates that at 400°C (752°F) the steady-state equivalent is not the result of dilution.

The number of cycles varies drastically depending upon the percentage of distillate produced from bitumen. The number of cycles varies from 11 to 41. As more bitumen is used to produce the distillate the higher the anticipated number of cycles required to reach a steady-state equivalent. The experimental data has shown that an equivalent to steady state is reached in 11 cycles. This is the same number of cycles that are calculated to remove 95% of the initial heavy oil if all of the distillate is produced from the initial heavy oil. This agreement between the experimental data and the calculation is coincidental because the calculation is a simplified approach and does not consider the complexity of the process. The important information to be gained from the comparison is that the number of cycles required experimentally is in the same range as the calculation predicts for production of distillate from use of reasonable amounts of bitumen and heavy oil. This indicates that the steady-state equivalent observed in the laboratory simulation reactor is the result of the formation of distillate from both the bitumen and the heavy oil and not from dilution of the initial heavy oil by the bitumen.

The Steady-State Condition

The objective of these experiments was to determine if an equivalent to steady state in the PDU could be achieved. The analytical results discussed here were directed toward monitoring the produced distillate and the heavy oil to determine if constant composition was attained. Constant composition of these products, as a function of the number of times the heavy oil was cycled, is defined as the criterion for an equivalent to steady-state operation.

The experiments conducted at 375°C (707°F) were terminated after nine cycles of the heavy oil because the data showed that the reaction rate was extremely low and that extensive recycling of the heavy oil would be required. These results show that an equivalent to steady state was not reached at 375°C (707°F) after nine cycles of the heavy oil. We assume that it is possible to achieve steady-state operation at this temperature, but the time required is extensive.

The experiments conducted at 425°C (797°F) were terminated after eight cycles of the heavy oil. This series of experiments was terminated because the reactions at this temperature could not produce enough heavy oil to meet the recycle requirements of the process. The heavy oil-to-bitumen ratio was decreased to increase the organic mass charge to the reactor and attempt to increase the fraction of heavy oil produced. The production of heavy oil did not increase and supply the additional quantity of heavy oil required for recycle. These data show that an equivalent to steady state may have been achieved after approximately four cycles of the heavy oil.

The results at 425°C (797°F) are interesting. If the heavy oil inventory can not be maintained at a level to meet the recycle needs, the ROPE process can not operate whether or not it is at steady state. However, these results lead to another consideration. The higher distillate yield at 425°C (797°F) has significant economic impact for this process and a hybrid form. If co-processing is applied in place of a recycle concept this technology can capitalize on the higher distillate yield and not rely on the required heavy oil inventory for recycle. The results show that the ROPE process can also be operated in a co-processing mode with increased distillate yields.

The experiments conducted at 400°C (752°F) were terminated after 14 cycles of the heavy oil. The analyses of the heavy oils and distillates show that an equivalent to steady state was achieved. The number of cycles of the heavy oil required to reach an equivalent to steady state varies from seven cycles for the nitrogen concentration in the produced distillates to 11 cycles for several of the other parameters. Considering what each of the analytical parameters measures and how each of these relates to the definition of steady state, we suggest that the asphaltene concentration, the H/C atomic ratios, and the concentration of the model compounds best reflect the chemical composition of the heavy oil and produced distillate.

If we use the parameters that best reflect the chemical composition of the products, the number of cycles of the heavy oil required to reach an equivalent of steady state is 10 to 11. It is interesting that two of these parameters (H/C atomic ratios of the distillate and the C_{12}/C_{18} ratio in the heavy oil) show that an equivalent to steady state was reached in 10 cycles. Two other parameters (area percentages of the total ionization of the aromatic and saturated model compounds) show that the required number of cycles is 11. This is good agreement among the principal parameters and adds a level of confidence to our conclusion that a steady-state equivalent was reached in 10 to 11 cycles of the heavy oil.

These results can be applied directly to steady-state operation in the PDU unit. Ten to 11 cycles of the heavy oil correlates to a approximately 8.5 hours of operation in the PDU. Previous research using the PDU-generated data shows that steady-state operation was achieved after 8 hours (Cha et al. 1986, 1988). The results from the laboratory simulation study confirm this earlier prediction of the length of time required to reach steady state and add additional significance to the results collected using the PDU.

Potential Catalytic Effects of the Sand Matrix

Asphalt Ridge tar sand is composed of extractable bitumen representing approximately 13 wt % of the tar sand. The sand matrix is carried through the process and requires additional process heat to raise this mass to the temperature of each zone. This represents a large heat sink, and the economics of the process can be improved if all of the sand does not have to be transported through the process. The justification for transporting the sand matrix through the reactor has been based on the assumption that the sand matrix has potential catalytic activity in the pyrolysis reactions, and that it is required to improve the distillate yield. However, this assumption has not previously been investigated. This assumption was an area of research addressed as part of this task. The objective of this research was to determine if the sand matrix has catalytic activity that will increase the yield of liquid product.

Four experiments were performed to investigate the potential catalytic activity of the sand matrix. The experiments were conducted at 400°C (752°F) because the results from the previous experiments show that this is the optimum operating temperature for the ROPE process with Asphalt Ridge tar sand. The material balance data for these experiments are listed in Table 38. The first two experiments listed in the table were performed using raw tar sand as the reactant feed. The third and fourth experiments were performed using a mass of extracted bitumen equal to the bitumen that would be present on the tar sand if equal weights of tar sand and heavy oil were used. These data show that the material balance closures range between 98.8 and 100.2 wt %. These closures are within the accepted error of the laboratory simulation reactor and are considered acceptable.

The yields of organic products are the parameters monitored during these experiments because they are the key parameters that will

demonstrate catalytic effects of the sand. Table 39 lists the distribution of the organic products collected from these experiments. The results are listed as the weight percentage of each product based on the total mass of organic material charged to the reactor for that experiment.

Examination of the results shows that the distillate production has the same cyclic yield trend as was observed in the previous experiments, and the overall yield for each series of experiments appears to be equivalent. The coke production from the two experiments performed with raw tar sand are the sums of the coke adhering to the walls of the reactor plus the coke associated with the spent sand. These masses of coke are comparable with the coke production observed in other experiments using raw tar sand as the resource. The experiments using only bitumen did not produce measurable coke on the walls of the reactor, and this suggests that the coke is suspended in the heavy oil. The gas composition among the four experiments is relatively constant and ranges from 1.1 to 1.8% with an average of 1.4%.

The results listed in Table 39 can be presented in a format that is better for evaluation of the organic product yields. The yields of each organic product from each pair of experiments were summed, and the weight percentage of each product was determined based on the sum of the organic charge to each pair of experiments. This nearly approximates the expected yield from a continuous process and normalizes the cyclic nature of the distillate production. Table 40 lists the results of this analysis.

The distillate yield, which is the most important yield of the process, is comparable in both sets of data. The yield from the experiments conducted with only bitumen is slightly higher than the yield using raw tar sand. This difference is outside the experimental error of the laboratory simulation reactor and is significant; however, this small difference in the two yields may not be significant for a continuous process.

The gas production between the two sets of data is comparable and does not show that the sand may have a catalytic effect. This is similar to the results for coke production. The recovery of heavy oil is interesting. The recovery of heavy oil using only the bitumen is slightly higher than the recovery when raw tar sand was used as the resource. The difference in the heavy oil yield is equivalent to the coke production when raw tar sand was used as the resource. We investigated this further.

The heavy oil collected after experiment number four was filtered, and the residue was extracted with pyridine. The remaining solid was a carbon residue (coke). The weight of this material was 1.9 g and represents the coke production from both experiments. The weight percentage (based on the total organic charge) of this mass of coke is 1.4 wt %. This value compares favorably with the amount of coke produced when raw tar sand is processed. If this percentage of coke is subtracted from the percentage of heavy oil, the actual percentage of heavy oil is 80.6 wt %. This compares favorably with the amount of heavy oil for the series of experiments using raw tar sand.

The adjusted summary of the organic product distribution using the weight of coke determined in the heavy oil is listed in Table 40. Examination of these results show that there is no significant catalytic effect of the sand matrix. The sand matrix appears to be an inert material that is carried through the process. If the sand matrix is not effective as a catalyst in the ROPE process, it represents a large, inert heat sink that requires additional energy to heat the process charge to the operating temperature of each zone.

Process energy requirements and operability can be improved by process modifications using these and other data. The current configuration of the ROPE process is designed to disengage the liquid from the solid material in the drying portion of the reactor. Results show that the tar sand bitumen will go into solution in recycled distillate at 200°C (392°F) within five minutes (Guffey and Hunter 1989). These results, coupled with the lack of catalytic activity of the sand matrix, suggest that the solid and liquid can be disengaged between the preheating and the pyrolysis zones of the process.

This modification may provide several potential process improvements. First, it will remove the inert sand matrix from the processing stream before the higher temperatures are reached, thus, reducing the energy requirements. Second, the major operational problem associated with the ROPE process is plugging in the area between the pyrolysis and drying screws. This plugging occurs because coking is the predominate reaction at the higher temperatures used to disengage the solids from the liquids. The coke builds up in the reactor and causes agglomeration of the sand particles resulting in plugging of the screw mechanism. Performing the disengaging at a temperature less than the pyrolysis temperature will minimize coke buildup and prevent plugging (Guffey and Hunter 1989). This will improve the operability of the process.

Third, once the sand is removed at a lower temperature, the screw mechanics will not be required in the downstream portion of the reactor, and a simpler design can be sought. A possibility that can be considered is a type of delayed coking process in which the residual heavy oil is recycled to regain its heat. A process such as this may have lower capital costs because there are fewer moving parts. The current process design (screw movement of solids) can be replaced with pumps because only a liquid is transferred.

A process of this design will face one problem that has to be addressed. This problem is the formation of coke that will be suspended in the heavy recycle oil. At high enough concentrations, this coke will form a nearly solid mass that can not be pumped through the process. There are two possible approaches to address the problem of dissolved coke. The first approach is to consider a settling tank to allow the coke to be removed by gravity. A second approach is to allow a small amount of sand to pass into the higher temperature regions of the reactor to act as a nucleus for coke deposition.

Pyrolysis of Model Polymers

The chemistry of pyrolysis of hydrocarbons in the presence of a recycle heavy oil has not previously been studied. This part of our research investigated a model pyrolysis system composed of model hydrocarbons in the presence of SAE 50 weight oil. The study used homogeneous resin polymers as the model hydrocarbon systems and was conducted with the objective of obtaining insight into the pyrolysis of different hydrocarbon structural types in the presence of a heavy oil. Three resin polymers were used individually for these experiments. Polystyrene was used to investigate the pyrolysis of alkyl substituents on an aromatic ring, polyethylene was used to investigate the pyrolysis of straight chain hydrocarbons, and polypropylene was used to investigate pyrolysis of branched hydrocarbons.

Pyrolysis as a Function of Temperature

Pyrolysis of each of the resin polymers was studied as a function of pyrolysis temperature to gain an understanding of the temperature dependence of each resin during pyrolysis and to identify temperatures to use for additional experiments. The temperature range chosen for these investigations was 375 to 425°C (707 to 797°F). This temperature range was sufficient for the studies of polypropylene and polystyrene, but this temperature was not high enough for adequate pyrolysis of the polyethylene resin. An additional experiment was conducted at 450°C (842°F) to provide sufficient data for the investigation of polyethylene.

The material balance data for these experiments are listed in Tables 41 through 43. The tables are organized so that all the data for a given resin polymer are in the same table. Examination of the material balance closures shows, that for the majority of the experiments, the closures are between 98.5 and 100.5%. This range of closures is considered to be well within the experimental error of the laboratory simulation reactor. The only experiment outside of this range is the experiment conducted at 400°C (752°F) using polyethylene. The material balance closure for this experiment is 97.2%. Examination of these data (Table 41) shows that the probable source of error is in the mass of distillate reported. A mass of 0.402 g of distillate is low compared to the masses of distillate produced at the two adjacent temperatures. This is further confirmed when the masses of heavy oil and gas produced at 400°C are compared with those produced at the two adjacent temperatures.

Several observations are evident from the data provided in Tables 41 through 43. First, none of the resin polymers yield significant quantities of distillate at 375°C (707°F). This result indicates this temperature is not the temperature of choice for additional experiments because there is not sufficient distillate produced to be significant based on the goals of this research. The mass of distillate produced from pyrolysis of each resin polymer increases as a function of temperature. This trend is expected because the rate of pyrolysis should increase as a function of temperature, thus increasing distillate yield.

Examination of the distillate production for the experiments investigating the pyrolysis of polyethylene (Table 41) and polystyrene (Table 43) show the distillate production at the maximum temperature is greater than the mass of resin polymer used as reactant. This result demonstrates that, at higher temperatures, the potential exists for all of the resin polymer to have been consumed during the reaction. Experiments conducted at the higher temperatures could result in a situation where only pyrolysis of the heavy oil is studied because all of the polymer is consumed in the reaction. Distillate production greater than the initial mass of resin polymer used was not observed in the experiment conducted at 425°C (797°F) for polypropylene (Table 42). This indicated that a higher temperature would have to be used to identify this point.

The temperatures used for the remaining experiments were selected based on the data listed in Tables 41 through 43. The experiments conducted using polyethylene and polypropylene were conducted at 425°C (797°F) and those investigating polystyrene were conducted at 400°C (752°F). These temperatures were selected because the data indicated that, for the duration of the experiment, there will be resin polymer in the reaction media. At the higher temperatures, it is possible to react all of the resin polymer and have only pyrolysis of the oil occurring. This situation would complicate the results and possibly mask important findings.

GC/MS Evaluation of Distillate Products

The distillate produced from each of the resin polymers, at the temperatures selected for additional study, were analyzed by GC/MS. The results of these analyses are listed in Tables 44 through 46. Examination of the list of compounds identified, their relative concentrations, the structures of the resin polymers, and a understanding of basic organic chemistry can lead to development of the fundamental reaction pathways followed during pyrolysis.

The results of the GC/MS analysis of the distillate produced from polyethylene at 425°C (797°F) are listed in Table 44. Examination of these results shows the majority of the compounds identified are branched alkanes and alkenes, and alkyl-substituted cyclic structures. This composition is not expected from pyrolysis of a linear alkane structure such as is expected from polyethylene. The high concentration of branched and cyclic compounds can be explained by the fact that the resin polymer is cross linked.

Cross linkages are formed by carbon-carbon bonds between polymer strands and results in the formation of a three dimensional network containing quaternary and tertiary carbon atoms. The carbon atoms not involved in the cross linking are primary and secondary carbon atoms. Pyrolysis of this network will cleave bonds that involve quaternary and tertiary carbon atoms in preference to bonds involving primary and secondary carbon atoms because the radical resulting from bond cleavage will be more stable if the cleavage occurs at these carbon atoms. Bond cleavage at these carbon atoms results in the formation of low molecular weight branched alkanes and alkenes.

The high concentration of cyclic structures results from rearrangement reactions to stabilize initially formed radicals. When a long carbon chain containing a radical site is present, it can fold back on itself and react at another carbon site to stabilize a fundamentally unstable n-alkyl radical. Cyclic structures are formed from this reaction. This can occur in competition with reaction pathways to form branched structures because hydrogen addition is not necessary for cyclization reactions. The number of carbon atoms in the ring structure is dictated by the structure of the chain and whether it contains carbon branches. Branched carbon atoms will increase the stability of intermediates in the reaction that control the hydrogen rearrangement step of the reaction. The result of these cyclization reactions will be five and six membered ring structures.

The results of the GC/MS analysis of the distillate produced from polypropylene at 425°C (797°F) are listed in Table 45. Examination of these results show this distillate is composed of branched and cyclic alkanes and alkenes. The composition of this distillate is similar to that produced from pyrolysis of polyethylene. This similarity is expected because the polymeric structure of polypropylene contains tertiary carbons and the resin network is cross linked.

The results of the GC/MS analysis of the distillate produced from polystyrene at 400°C (752°F) are listed in Table 46. Examination of these results shows the major components in this distillate are toluene, ethyl-benzene, styrene, and 1-methyl-styrene. These compounds are logical products from the pyrolysis of polystyrene. Figure 8 presents the structure of polystyrene and the major pyrolysis products. Examination of these structures allows identification of the different pyrolysis pathways.

The styrene monomer is the most abundant component in this distillate. Its formation during pyrolysis can begin by breaking of either of the bonds beta to the aromatic ring. The bond beta to the ring will be the preferred bond to break because it will have a lower bond energy than other bonds in the structure caused by the electron affinity of the aromatic ring structure. Rupture of a second bond beta to an adjacent aromatic ring will form an intermediate that only needs to undergo electron rearrangement to form a double bond resulting in the formation of styrene. Hydrogen does not have to be transferred to the reaction center which also makes this reaction preferred in a hydrogen deficient environment.

Ethyl-benzene is the second most abundant species formed from pyrolysis of polystyrene. The reaction pathway to form ethyl-benzene is similar to that to form styrene, except hydrogen must be transferred to the reaction center to form the saturated bond. The significant difference in concentration between styrene and ethyl-benzene indicates hydrogen transfer is a limiting step in this reaction.

Formation of 1-methyl-styrene also occurs from the cleavage of bonds beta to the aromatic ring. Selection of the bonds differs from the bonds that cleave during formation of styrene such that an additional

Figure 8. Structure of Polystyrene and Major Pyrolysis Products Identified by GC/MS

carbon atom is in the structure. The reaction pathway to form 1-methylethyenyl-benzene does not require hydrogen transfer from another species, but it does require internal hydrogen rearrangement to form the double bond.

Toluene is formed from the cleavage of two beta bonds on the same carbon atom. This reaction pathway requires the transfer of two hydrogen atoms to the reaction center to form the toluene and probably is the reason for the relatively low concentration of toluene in the distillate.

The above discussion of the potential reaction pathways of pyrolysis of the resin polymers leads one to understand that the preferred reactions will follow routes that utilize stable intermediates and cleavage will predominately occur at the weaker bonds. Reaction pathways that require the addition of hydrogen are not the preferred routes, but those that can form a stable product through internal rearrangements appear to be preferred.

Pyrolysis as a Function of Time

The pyrolysis of each of the resin polymers was studied as a function of time at the selected temperatures. The results from these experiments were used to define the time dependence of pyrolysis and establish the reaction order for each of the resin polymers. Additional kinetic relationships were not obtained from these experiments because the reaction system used for these studies was not designed for kinetic studies and use of this system for additional kinetic studies was felt to produce data with sufficient error that it would not provide valid kinetic results.

The material balance data for this series of experiments are listed in Tables 47 through 49. The material balance closures range between 98.5 to 100.5% and are considered to be within the experimental error of this reaction system. Examination of the distillate production shows the expected increase as a function of time. The mass of distillate produced was less than the mass of resin polymer used as reactant. This demonstrates that resin polymer was present at the end of each experiment and data from the experiments can be used to investigate the combined pyrolysis of the resin polymer and heavy oil.

The global reaction order for the production of distillate was determined for the pyrolysis of each polymer in heavy oil. A detailed discussion of chemical reaction kinetic theory is not within the scope of this report and will not be discussed in depth. Any additional information required for understanding basic kinetic theory can be obtained from a physical chemistry text book. The data from this series of experiments was evaluated using a first order rate equation, which is defined by the following integrated form:

$$\ln(a/(a-x)) = kt$$

Where a = the initial mass of resin polymer plus oil
 x = the mass of distillate produced at time t
 k = the rate constant at that temperature
 t = the reaction time

A plot of the concentration term $\{\ln(a/(a-x))\}$ as a function of time will be a straight line passing through the origin if the reaction follows first order kinetics. The slope of the line is the rate constant (k) at the experimental temperature.

The graphic presentation of the data for the pyrolysis of polyethylene, polypropylene, and polystyrene in heavy oil is presented in Figures 9, 10, and 11, respectively. Examination of these plots shows that the data for pyrolysis of each of the resin polymers follows first order reaction kinetics. The observation that the data follows first order reaction kinetics is not unexpected. Most pyrolysis processes can be modeled, at the global level, with first order reaction kinetics (Miknis et al. 1985). These results confirm that these reactions follow first order kinetics.

Figure 9. First-order Plot of Distillate Production from the Pyrolysis of Polyethylene and SAE 50 Weight Oil at 425°C

Figure 10. First-order Plot of Distillate Production from the Pyrolysis of Polypropylene and SAE 50 Weight Oil at 425°C

Figure 11. First-order Plot of Distillate Production from the Pyrolysis of Polystyrene and SAE 50 Weight Oil at 400°C

The composition of the distillate from the pyrolysis of polystyrene was discussed in an earlier section. In that discussion, four compounds were identified (toluene, ethyl-benzene, styrene, and 1-methyl-styrene) that result from the pyrolysis of polystyrene. Examination of the results from the GC/MS analysis also show that there are no other compounds identified in the distillate that can arise directly from pyrolysis of polystyrene. These observations make the investigation of polystyrene unique as compared to the other resin polymers and naturally occurring bitumens and kerogens. The capability to identify the specific products from pyrolysis of the polymer allows its decomposition to be studied at a level other than the global kinetics discussed above.

The reaction kinetics for the decomposition of polystyrene, in the presence of heavy oil, to the four products identified by GC/MS were evaluated in a manner similar to that used for the global kinetics discussed above. Figure 12 shows the graphic representation of these data. Examination of these data show the data does not fit a straight line. This indicates the reaction is not first order with respect to the mass of polystyrene. This is unusual since most pyrolysis processes are first order reactions.

The observations in these data may be explained by several reaction pathways, but based on the knowledge of pyrolysis and the shape of the curve, a pathway involving a reverse reaction is the most reasonable. The reaction pathway postulated in Figure 13 is an explanation of the observed data. Polystyrene undergoes pyrolysis to yield a radical

Figure 12. Plot of Distillate Production from the Pyrolysis of Polystyrene and SAE 50 Weight Oil at 400°C at an Oil to Polystyrene Mass Ratio of 3:1

Figure 13. Postulated Reaction Pathway for Pyrolysis of Polystyrene

intermediate that can undergo rearrangement or hydrogen abstraction to yield a stable molecule that is produced as distillate. In addition, the radical intermediate can follow the reverse reaction and combine with the polymer to yield a structure similar to the starting material.

When the experiment is first started, the reverse reaction represents a major pathway for the overall reaction, and the observed rate for the production of distillate is slow. As the reaction proceeds, the concentration of the polymer decreases, forcing a decrease in the predominance of the reverse reaction. This causes an increase in the observed reaction rate for the production of distillate. As more of the polymer is used in the reaction, the reverse reaction becomes less predominant, the observed rate of distillate production continues to increase, and the overall reaction approaches first order.

This reaction pathway explains the trends observed in the data presented in Figure 13. It is an arduous task to demonstrate this series of reaction steps directly since it is difficult to isolate the specific products and impossible to isolate the radical intermediates. The most straight forward approach to demonstrating this series of reaction pathways is through dilution of the starting polymer with the initial heavy oil. The results of the experiments investigating dilution of the polymer with heavy oil will be discussed in the next section.

Function of Recycle Heavy Oil

The experiments discussed in the previous sections were conducted using an oil to polystyrene mass ratio of 3:1. The discussion of these results has shown the pyrolysis reaction does not follow first order kinetics and the reason may be the result of a reverse reaction of a radical intermediate with the polymer. A possible approach to demonstrating this reaction pathway is to perform experiments at higher dilutions of the polystyrene in an attempt to limit the reverse reaction. This will limit the reverse reaction because the radical intermediate will be isolated from other polystyrene molecules which will allow it to follow other reaction pathways to produce a distillate product.

Two additional experiments were conducted at oil to polystyrene mass ratios of 10:1 and 13:1 to evaluate the dilution of the polystyrene. The two experiments were conducted in a manner such that the position of the cow collecting the distillate was changed at set time intervals. This experimental approach allowed collection of time sequence data in fewer experiments. Use of this approach collected all of the required data in two experiments rather than eight, if individual experiments had been performed.

The mass balance data for these two experiments is listed in Table 50. Examination of these results shows the closures for the two experiments are 99.8 and 99.0%. These closures fall within the window of 98.8 and 100.5% closure considered acceptable for experiments conducted in the laboratory simulation reactor. The mass of distillate collected for each of these experiments is less than the initial mass of

polystyrene indicating polystyrene is still present in the reactor at the end of the experiment. This shows the reaction being studied is the pyrolysis of polystyrene in the oil and not the pyrolysis of the oil.

The plot of the $\ln(a/(a-x))$ as a function of time for the experiment conducted at an oil to polystyrene mass ratio of 10:1 is presented in Figure 14. Examination of these data shows the function is not linear but is a closer approximation of a linear relationship than the data collected at a mass ratio of 3:1. These results indicate that the concentration of the polystyrene in the heavy oil does direct the reaction pathway.

The similar plot of the data collected at a mass ratio of 13:1 is shown in Figure 15. This plot is a linear function of the data and represents a first order reaction. These results confirm that the concentration of polystyrene in the heavy oil controls the reaction pathway and that the reverse reaction discussed above is probably the factor that governs distillate production at the higher polystyrene concentrations. These results can be extrapolated to the ROPE process as it applies to tar sands.

Figure 14. Plot of Distillate Production from the Pyrolysis of Polystyrene and SAE 50 Weight Oil at 400°C at an Oil to Polystyrene Mass Ratio of 10:1

Figure 15. Plot of Distillate Production from the Pyrolysis of Polystyrene and SAE 50 Weight Oil at 400°C at an Oil to Polystyrene Mass Ratio of 13:1

Previous research efforts at the PDU and BSU level have claimed the ROPE process can produce distillate yields greater than those observed from Fischer assay of the raw tar sand (Cha et al. 1986, 1988). The results from these studies have also shown that increased production of oil and gas results in decreases in distillate yield. These claims have frequently been questioned because most commercial processes can not control operating conditions well enough to limit coke production and give distillate yields comparable to Fischer assay.

The experiments conducted with polystyrene show the pyrolysis reaction pathway is controlled by the concentration of polystyrene in the heavy oil. At lower concentrations, the reaction proceeds to produce distillate. At the higher concentrations, a reverse reaction limits distillate production and tends to yield a polymeric structure. These same reaction pathways can be applied to tar sand conversion in the ROPE process.

Figure 16 presents the reaction pathway for the pyrolytic conversion of tar sand bitumen in a heavy oil. Pyrolysis of the bitumen will lead to the formation of a radical intermediate. Through rearrangement or hydrogen abstraction the radical will form a stable product to be produced as distillate. In addition, the pyrolytic reaction of the bitumen can follow a pathway to produce the carbon residue, coke.

Figure 16. Postulated Reaction Pathway for the Pyrolysis of Bitumen

The heavy oil present in the process functions, at least in part, as a diluent to isolate the bitumen and radical intermediates. This allows the radical intermediate to proceed to form the stable distillate. In the absence of the heavy oil diluent or at high concentrations of bitumen in heavy oil, the reverse reaction to combine the radical intermediate with the bitumen will be the major pathway. This will tend to keep a relatively high concentration of bitumen in the reactor and allow the reaction to proceed to produce coke. The conversion of the bitumen to coke will decrease the relative distillate yield. In the ROPE process, the heavy oil acts to isolate the reactants to improve distillate yield as compared to other processes that do not utilize a recycle oil. This is the reason distillate yield from the ROPE process is comparable to that obtained by Fischer assay.

CONCLUSIONS

The chemical and physical processes that control the ROPE process have been addressed in a series of experiments in the laboratory simulation reactor. The following conclusions can be drawn from this research.

1. Distillate products are not produced from the tar sand bitumen at temperatures below 350°C (662°F) in this process. Any distillate product collected below this temperature is from distillation of the lower boiling components in the recycle oil.

2. The hydrogen-to-carbon atomic ratios of the distillate products produced in the recycle oil pyrolysis and recycle oil drying zones is constant at all pyrolysis temperatures and experiment durations. These results show a stable product composition and suggest that this parameter is not suited for use as a process indicator.

3. The hydrogen-to-carbon atomic ratios of the heavy oils from the recycle oil pyrolysis zone show a decrease with increasing experiment temperature and length of time into each experiment. The decrease in the ratios show that hydrogen is released from the heavy oil to the distillate products or to the product gas stream. The hydrogen-to-carbon atomic ratio of the heavy oils produced in the recycle oil pyrolysis zone may be used for process diagnostics of the processing concept.

4. The majority of the coke production occurs in the recycle oil drying zone. This is probably caused because the process may not be able to transfer hydrogen to reaction centers in this zone of the reactor. The processing implication is that a minimum of organic material should be sent to this zone because the coke produced represents carbon lost to the processing concept.

5. The model-compound studies demonstrate that hydrogen transfer is a viable mechanism in this concept. Hydrogen is transferred from hydroaromatic species to the pyrolysis reaction center through a cyclohexadienyl carrier radical. Hydrogen transfer in the recovery of distillate products from tar sand bitumen will be limited by the concentration of hydroaromatic species in the tar sand bitumen. If the hydrogen source is hydroaromatic species in the tar sand bitumen, then recycling the heavy oil to the system will not limit distillate production by hydrogen transfer. The hydrogen source will be continuously renewed by the addition of raw tar sand.

6. An equivalent to steady state in the PDU can not be achieved in our reactor system at 375°C (707°F) in a reasonable length of time with Asphalt Ridge tar sand because the reaction rate is too slow to make the necessary modifications to the heavy oil and bitumen to achieve steady-state conditions.

7. The ROPE process can not operate for extended periods of time at 425°C (797°F) with Asphalt Ridge tar sand because the quantity of heavy oil recovered from the process is not sufficient to meet the heavy oil inventory requirements for recycle.

8. Using Asphalt Ridge tar sand, an equivalent to steady state in the PDU can be achieved in the laboratory simulation reactor after 10 or 11 cycles of the heavy oil. This is equivalent to about 8.5 hours of operation in the PDU. This estimate is in agreement with the estimate determined from previous experiments conducted in the PDU.

9. The ROPE process can not operate at 425°C (797°F) because the heavy oil inventory can not be maintained. However, the results from this study show that the process can be used for heavy oil co-processing, removing the need for a recycle stream, and can generate high yields of distillate.

10. The sand matrix associated with Asphalt Ridge tar sand does not have significant catalytic activity for the production of a distillable liquid product. This means that if the solids can be disengaged from the liquid at a lower temperature, the process can attain lower energy requirements, lower capital costs, and better operability.

11. Pyrolysis of the model polymers; polyethylene, polypropylene, and polystyrene (in the presence of SAE 50 weight oil) follow first order reaction kinetics for the total production of distillate.

12. The reaction order for the pyrolysis of polystyrene in the presence of SAE 50 weight oil to yield its decomposition products is concentration dependent. At higher dilutions of the polystyrene, the reaction is first order. The postulated reaction pathway to explain these observations involves a reverse reaction of a radical intermediate that forms a polymeric structure similar to polystyrene.

13. The heavy recycle oil functions as a diluent in the ROPE process and limits a reversible reaction similar to that observed for polystyrene. Controlling the reversible reaction improves distillate yield in the ROPE process because pyrolysis products can not follow the reverse reaction pathway and form coke.

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DISCLAIMER

Mention of specific brand names or models is for information only and does not imply endorsement.

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Table 1. Properties of Asphalt Ridge Tar Sand from Duplicate Analyses

Property	Composition	
	First Extraction	Second Extraction
Bitumen Content, wt %	13.3	13.3
Toluene Extract, wt %	13.1	13.2
Elemental Composition, wt %		
C	85.1	85.3
H	10.8	10.8
N	0.9	0.9
S	0.6	0.7
O (by difference)	2.6	2.3
H/C atomic ratio	1.52	1.52
Pyridine Extract, wt %	0.2	0.1

Table 2. Material Balances for the Experiments Investigating the Tar Sand Preheat Zone

	Experimental Temperature, °C			
	200	230	260	200
Reactants				
Recycle Oil, g	99.6	100.9	100.2	100.0
Tar Sand, g	68.0	79.6	76.6	73.8
Total, g	167.6	180.5	176.8	173.8
Products				
Sand-Oil, g	151.4	162.4	146.2	158.3
Samples, g	15.3	15.5	20.1	14.4
Distillate, g	0.2	3.5	10.3	0.2
Sample Tube, g	0.5	0.4	0.3	0.2
Total, g	167.4	181.8	176.9	173.1
Closure, %	99.9	100.7	100.1	99.6

Table 3. Material Balances for the Experiments Investigating the Recycle Oil Pyrolysis Zone

	Experimental Temperature, °C				
	350	375	400	425	375
Reactants					
Recycle Oil, g	100.3	100.3	100.1	100.1	100.1
Tar Sand, g	77.1	74.5	76.5	75.9	74.8
Total, g	177.4	174.8	176.6	176.0	174.9
Products					
Sand-Oil, g	120.3	98.6	82.1	77.4	87.7
Samples, g	22.3	21.7	17.1	14.5	25.4
Distillate, g	33.4	53.8	76.1	83.5	59.6
Sample Tube, g	0.3	0.4	0.3	0.3	0.2
Total, g	176.3	174.5	175.6	175.7	172.9
Closure, %	99.4	99.8	99.4	99.8	98.9

Table 4. Material Balances for the Experiments Investigating the Recycle Oil Drying Zone

	Experimental Temperature, °C			
	400	425	450	400
Reactants				
Recycle Oil, g	42.1	41.9	41.9	42.3
Spent Sand, g	50.6	50.3	50.0	50.0
Heavy Oil, g	15.1	15.0	15.0	15.0
Total, g	107.8	107.2	106.9	107.3
Products				
Sand-Oil, g	53.3	51.2	53.3	72.3
Samples, g	19.9	17.0	13.3	18.2
Distillate, g	24.6	37.9	39.0	16.6
Sample Tube, g	0.3	0.2	0.3	0.2
Total, g	98.1	106.3	105.9	107.3
Closure, %	91.0	99.2	99.1	100.0

Table 5. Elemental Balance Closures for the Experiments Investigating the Tar Sand Preheat Zone

Experiment Temperature, °C	Elemental Balance Closure, wt %			
	Carbon	Hydrogen	Nitrogen	Sulfur
200	100.4	100.5	88.8	128.1
230	100.0	99.4	74.4	139.7
260	101.3	100.8	71.6	78.4

Table 6. Elemental Balance Closures for the Experiments Investigating the Recycle Oil Pyrolysis Zone

Experiment Temperature, °C	Elemental Balance Closure, wt %			
	Carbon	Hydrogen	Nitrogen	Sulfur
350	98.3	98.7	60.5	112.1
375	99.3	99.0	61.7	147.4
400	98.9	96.2	67.9	125.9
425	99.0	96.8	85.2	132.8

Table 7. Elemental Balance Closures for the Experiments Investigating the Recycle Oil Drying Zone

Experiment Temperature, °C	Elemental Balance Closure, wt %			
	Carbon	Hydrogen	Nitrogen	Sulfur
400	103.9	101.1	48.8	100.0
425	98.3	101.6	50.0	97.7
450	99.9	105.3	45.0	88.6

Table 8. Hydrogen-to-Carbon Atomic Ratios of the Distillate Products from the Recycle Oil Pyrolysis Zone

Time into Experiment	Experimental Temperature, °C			
	350	375	400	425
After Adding Tar Sand	1.89	1.83	1.77	1.71
End of Experiment	1.87	1.83	1.75	1.78

Table 9. Hydrogen-to-Carbon Atomic Ratios of the Distillate Products from the Recycle Oil Drying Zone

Time into Experiment	Experimental Temperature, °C		
	400	425	425
After Adding Tar Sand	2.10	1.87	1.98
End of Experiment	2.05	1.93	1.95

Table 10. Two-Way Analysis of Variance of the H/C Atomic Ratios of the Distillate Products from the Recycle Oil Pyrolysis Zone

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Rows	3	0.0237	0.0079	8.68	9.28
Columns	1	0.0001	0.0011	0.12	10.13
Error	<u>3</u>	<u>0.0027</u>	0.0009		
Total	7	0.0266			

Table 11. Two-Way Analysis of Variance of the H/C Atomic Ratios of the Distillate Products from the Recycle Oil Drying Zone

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Rows	2	0.0313	0.0157	9.10	19.0
Columns	1	0.0001	0.0001	0.04	18.51
Error	2	<u>0.0034</u>	0.0017		
Total	5	0.0348			

Table 12. Hydrogen-to-Carbon Atomic Ratios of the Heavy Oils from the Recycle Oil Pyrolysis Zone

Time into Experiment	Experimental Temperature, °C			
	350	375	400	425
Initial Sample	1.80	1.80	1.80	1.80
Before Adding Tar Sand	1.79	1.76	1.72	1.73
After Adding Tar Sand	1.76	1.77	1.73	1.70
End of Experiment	1.76	1.74	1.71	1.67

Table 13. Hydrogen-to-Carbon Atomic Ratios of the Heavy Oils from the Recycle Oil Drying Zone

Time into Experiment	Experimental Temperature, °C		
	400	425	425
Initial Sample	1.80	1.80	1.80
Before Adding Tar Sand	1.87	1.87	1.87
After Adding Tar Sand	1.86	1.83	1.91
End of Experiment	1.89	1.81	1.91

Table 14. Two-Way Analysis of Variance of the H/C Atomic Ratios of the Heavy Oils from the Recycle Oil Pyrolysis Zone

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Rows	3	0.0071	0.0024	5.96	3.86
Columns	3	0.0139	0.0046	11.56	3.86
Error	<u>9</u>	<u>0.0036</u>	0.0004		
Total	15	0.0246			

Table 15. Two-Way Analysis of Variance of the H/C Atomic Ratios of the Heavy Oils from the Recycle Oil Drying Zone

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Rows	2	0.0041	0.0021	2.60	4.14
Columns	3	0.0107	0.0036	4.50	4.76
Error	<u>6</u>	<u>0.0048</u>	0.0008		
Total	11	0.0196			

Table 16. Selected Model-Compound Recoveries from the ROPE Simulation Experiments

Experiment Temperature, °C	Model Compound Recovery, wt %	
	9,10-Dihydroanthracene	9,10-Dihydroanthracene Plus Anthracene
200	100.3	100.3
230	100.1	100.1
260	112.0	112.0
350	40.6	105.1
375	38.0	92.3
400	50.1	118.2
425	64.2	129.5

Table 17. One-Way Analysis of Variance of Selected Model-Compound Recoveries from the ROPE Simulation Experiments

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Columns	1	4543	4543	7.98	4.75
Error	<u>12</u>	<u>6831</u>	569		
Total	13	11374			

Table 18. Selected Model-Compound Recoveries from the ROPE Distillation Experiments

Experiment Temperature, °C	Model Compound Recovery, wt %	
	9,10-Dihydroanthracene	9,10-Dihydroanthracene Plus Anthracene
230	128.0	138.3
260	123.3	140.9
350	54.9	95.1
375	43.5	88.3
400	38.6	57.8

Table 19. One-Way Analysis of Variance of Selected Model-Compound Recoveries from the ROPE Distillation Experiments

Source	Degrees Freedom	Sum of Squares	Mean Square	F _{ratio}	F _{0.05}
Columns	1	1745	1745	1.09	5.32
Error	<u>8</u>	<u>12826</u>	1603		
Total	9	14571			

Table 20. Mass Balances for the Heavy Oil Recycle Experiments Conducted at 375°C

Experiment Number:	1	2	3	4	5	6	7	8	9
Reactants, g									
Tar Sand	98.9	99.7	103.6	100.2	100.8	100.1	100.1	100.9	90.0
Heavy Oil	100.0	100.2	100.2	100.1	100.2	100.1	100.0	100.0	90.0
Total	198.9	199.9	203.8	200.3	201.0	200.2	200.1	200.9	180.0
Products, g									
Distillate	0.0	0.4	0.7	1.1	3.6	2.6	0.7	3.2	0.1
Heavy Oil	113.3	113.5	110.3	108.3	109.1	107.7	112.6	94.7	94.5
Gas	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Coke	0.7	0.5	0.7	0.6	1.0	0.4	0.3	0.8	0.5
Sand	84.4	87.7	90.5	86.9	86.8	86.5	86.8	87.6	77.6
Total	198.3	202.1	202.2	197.0	200.5	197.2	200.4	186.3	172.7
Closure, %	99.7	101.1	99.2	98.4	99.8	98.5	100.1	92.7	95.9

Table 21. Mass Balances for the Heavy Oil Recycle Experiments Conducted at 400°C

Experiment Number:	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Reactants, g														
Tar Sand	100.6	100.4	110.7	100.0	99.9	100.0	95.0	95.1	79.7	76.4	75.1	70.2	52.9	50.7
Heavy Oil	100.0	100.0	100.0	100.0	100.0	100.0	95.0	95.0	79.6	76.4	75.1	70.1	52.7	50.4
Total	200.6	200.4	210.7	200.0	199.9	200.0	190.0	190.1	159.3	152.8	150.2	140.3	105.6	101.1
Products, g														
Distillate	1.1	4.7	6.9	8.8	0.6	10.8	6.0	4.5	8.4	3.3	4.6	15.2	0.4	9.5
Heavy Oil	111.0	106.0	105.7	102.1	112.6	101.2	100.1	88.8	80.4	82.0	78.2	61.7	56.5	43.6
Gas	0.9	0.6	0.6	0.7	0.3	0.7	0.6	0.8	1.0	0.5	0.5	0.9	0.4	0.8
Coke	0.5	0.5	0.6	0.5	0.6	0.5	0.3	0.5	0.4	0.4	0.5	0.4	0.3	2.3
Sand	87.1	88.6	96.7	87.2	85.7	87.1	83.3	82.6	70.2	66.6	66.2	62.1	46.5	44.9
Total	200.6	200.4	210.5	199.3	199.8	200.3	190.3	177.2	160.4	152.8	150.0	140.3	104.1	101.1
Closure, %	100.0	100.0	99.9	99.7	99.9	100.2	100.2	93.2	100.7	100.0	99.9	100.0	98.6	100.0

Table 22. Mass Balances for the Heavy Oil Recycle Experiments Conducted at 425°C

Experiment Number:	1	2	3	4	5	6	7	8
Reactants, g								
Tar Sand	99.9	82.4	97.4	84.0	67.7	55.2	50.4	39.2
Heavy Oil	100.1	81.3	65.3	55.2	45.0	37.5	33.0	22.8
Total	200.0	163.7	162.7	139.2	112.7	92.7	83.4	62.0
Products, g								
Distillate	21.7	21.0	15.5	8.7	8.9	2.5	7.9	0.8
Heavy Oil	86.3	70.2	59.5	55.3	42.6	39.8	29.4	25.9
Gas	1.5	1.2	1.1	0.9	0.5	0.5	0.7	0.3
Coke	0.6	0.6	0.5	0.5	0.4	0.3	0.4	0.2
Sand	87.6	70.0	85.0	73.6	60.1	49.9	45.5	34.7
Total	197.7	163.0	161.6	139.0	112.5	93.0	83.9	61.9
Closure, %	98.9	99.6	99.3	99.9	99.8	100.3	100.6	99.8

Table 23. Weight Percentage of Heavy Oil Recovered from Each Experiment

Number of Heavy Oil Cycles	Heavy Oil Recovered, wt %		
	375°C	400°C	425°C
1	113.3	111.0	86.2
2	113.3	106.0	86.3
3	130.0	105.7	91.0
4	108.1	102.1	100.2
5	108.8	112.6	94.7
6	107.6	101.2	106.1
7	112.7	105.4	89.1
8	94.7	93.5	113.6
9	105.0	101.0	
10		107.3	
11		104.1	
12		88.6	
13		109.2	
14		89.1	

Table 24. Organic Product Distribution for the Heavy Oil Recycle Experiments at 375°C, wt %

Number of Heavy Oil Cycles	Distillate	Heavy Oil	Coke	Gas
1	0.0	99.9	0.6	0.0
2	0.3	99.9	0.4	0.0
3	0.6	90.5	0.5	0.0
4	1.0	95.3	0.5	0.0
5	3.1	95.9	0.7	0.0
6	2.3	94.8	0.3	0.0
7	0.6	99.2	0.3	0.0
8	2.9	87.6	0.5	0.0
9	0.1	92.5	0.5	0.0

Table 25. Organic Product Distribution for the Heavy Oil Recycle Experiments at 400°C, wt %

Number of Heavy Oil Cycles	Distillate	Heavy Oil	Coke	Gas
1	1.0	97.6	0.4	0.8
2	4.1	93.3	0.4	0.6
3	5.6	85.1	0.5	0.5
4	7.8	90.0	0.4	0.6
5	0.5	99.2	0.5	0.3
6	9.5	89.1	0.4	0.6
7	5.6	92.8	0.3	0.5
8	4.2	82.3	0.4	0.7
9	9.3	89.0	0.5	1.2
10	3.8	94.6	0.5	0.6
11	5.4	91.8	0.5	0.5
12	3.3 ^a	94.2 ^a	0.5	1.2
13	0.7	94.5	0.6	0.7
14	0.4 ^a	93.1 ^a	2.9	1.4

^a Experiment bumped and heavy oil was carried over with the distillate. Values corrected for heavy oil carry over are reported.

Table 26. Organic Product Distribution for the Heavy Oil Recycle Experiments at 425°C, wt %

Number of Heavy Oil Cycles	Distillate	Heavy Oil	Coke	Gas
1	19.4	76.0	0.5	0.8
2	22.7	76.0	0.6	0.7
3	19.8	75.8	0.7	0.7
4	13.0	83.1	0.8	0.6
5	16.4	78.7	0.7	0.4
6	5.6	88.5	0.7	0.5
7	19.7	73.7	1.1	0.9
8	2.9	92.0	0.6	0.4

Table 27. Asphaltene Concentration^a of the Recovered Heavy Oils from the Heavy Oil Recycle Experiments, wt %

Number of Heavy Oil Cycles	375°C	400°C	425°C
1	0.0	0.9	0.1
2	0.0	0.5	0.3
3	0.1	1.1	1.2
4	0.1	4.7	6.4
5	0.1	4.1	6.9
6	0.1	4.7	15.6
7	0.2	8.1	12.0
8	0.2	10.9	16.6
9	0.3	11.4	
10		12.0	
11		12.4	
12		14.0 ^b	
13		18.1	
14		13.5 ^b	

^a Concentration based on total organic material charged to reactor.

^b Corrected for heavy oil carryover into distillate fraction.

Table 28. Compound Class Distribution for the Heavy Oils at 375°C, wt %

Number of Heavy Oil Cycles	Saturates	Aromatics	Resins
1	59.0	25.6	15.4
2	61.1	24.7	15.1
3	58.5	25.8	12.6
4	61.7	26.1	12.2
5	53.7	25.1	18.3
6	49.0	19.2	15.4
7	52.7	26.6	17.0
8	51.0	21.5	15.0
9	56.4	30.7	15.4

Table 29. Compound Class Distribution for the Heavy Oils at 400°C, wt %

Number of Heavy Oil Cycles	Saturates	Aromatics	Resins
1	67.4	27.1	3.9
2	49.6	38.4	10.1
3	47.0	19.1	26.7
4	42.6	28.7	14.5
5	51.0	26.3	20.0
6	50.6	19.5	27.0
7	59.8	25.2	16.1
8	50.2	26.5	22.2
9	57.0	21.7	21.3
10	53.5	24.6	22.0
11	48.9	48.9	2.6
12	35.1	20.3	44.7
13	45.6	30.2	24.6
14	44.0	31.1	24.5

Table 30. Compound Class Distribution for the Heavy Oils at 425°C, wt %

Number of Heavy Oil Cycles	Saturates	Aromatics	Resins
1	48.3	15.5	34.7
2	51.0	28.5	20.6
3	42.6	47.2	10.2
4	58.3	32.7	9.4
5	48.1	30.1	21.9
6	43.0	27.9	27.9
7	42.3	27.7	30.0
8	52.2	31.0	18.6

Table 31. Elemental Analyses of Selected Distillate Samples from the Heavy Oil Recycle Experiments at 400°C, wt %

Number of Heavy Oil Cycles	C	H	N	S	H/C Atomic Ratio
1	82.8	13.5	0.0	0.8	1.96
3	86.6	12.8	0.0	0.5	1.77
5	85.7	13.5	0.0	0.5	1.89
7	85.9	13.0	0.0	0.5	1.82
9	85.8	13.2	0.1	0.0	1.85
11	87.8	11.8	0.2	0.0	1.61
13	82.7	12.2	0.3	0.0	1.77
14	86.9	12.9	0.2	0.0	1.78

Table 32. Elemental Analyses of Selected Distillate Samples from the Heavy Oil Recycle Experiments at 425°C, wt %

Number of Heavy Oil Cycles	C	H	N	S	H/C Atomic Ratio
2	85.6	13.4	0.0	0.0	1.88
4	86.2	13.4	0.1	0.0	1.87
6	86.2	13.5	0.1	0.0	1.88
8	85.6	13.3	0.1	0.0	1.86

Table 33. Elemental Analyses of Selected Heavy Oil Samples from the Heavy Oil Recycle Experiments at 375°C, wt %

Number of Heavy Oil Cycles	C	H	N	S	H/C Atomic Ratio
1	86.5	13.2	0.2	0.5	1.83
3	86.0	12.7	0.4	0.5	1.77
7	86.1	12.1	0.6	0.5	1.69
9	86.4	11.7	0.8	0.5	1.63

Table 34. Elemental Analyses of Selected Heavy Oil Samples from the Heavy Oil Recycle Experiments at 400°C, wt %

Number of Heavy Oil Cycles	C	H	N	S	H/C Atomic Ratio
1	85.0	12.9	0.2	0.5	1.82
3	86.1	12.5	0.4	0.5	1.74
5	86.8	12.3	0.5	0.5	1.70
7	86.8	11.9	0.7	0.5	1.65
9	86.5	11.5	0.9	0.5	1.60
11	87.3	11.4	1.0	0.5	1.57
13	87.5	10.8	1.3	0.5	1.48
14	86.8	10.4	1.2	0.5	1.44

Table 35. Elemental Analyses of Selected Heavy Oil Samples from the Heavy Oil Recycle Experiments at 425°C, wt %

Number of Heavy Oil Cycles	C	H	N	S	H/C Atomic Ratio
2	86.7	12.8	0.3	0.6	1.77
4	87.0	11.8	0.7	0.5	1.63
6	86.1	10.9	0.9	0.6	1.52
8	87.2	11.9	0.7	0.6	1.64

Table 36. Results of GC/MS Analysis of SARA Fractions from the Heavy Oils Produced at 400°C, area %

Number of Heavy Oil Cycles	Aromatic Fraction Model Compound ^a	Saturate Fraction	
		Model Compound ^b	C ₁₉ /C ₁₈
1	36.9	3.6	0.0
2	22.0	2.3	0.1
3	21.0	1.5	0.3
4	15.3	1.2	0.4
5	9.3	1.7	0.4
6	8.8	0.9	0.5
7	8.7	0.9	0.8
8	3.4	0.4	1.1
9	2.7	0.2	1.7
10	1.5	0.2	2.0
11	1.0	0.1	1.7
12	0.7	0.1	2.3
13	0.8	0.1	2.4
14	0.9	0.1	2.4

^a Area of the response of anthracene plus phenanthrene divided by the total ionization multiplied by 100%.

^b Area of the response of normal octadecane divided by the total ionization multiplied by 100%.

Table 37. Calculated Number of Cycles to Reach Steady State

Dilution	Percentage Bitumen Derived Distillate					Experimental
	0%	25%	50%	75%	100%	
24	11	13	16	22	41	11

Table 38. Mass Balances for the Experiments Investigating the Potential Catalytic Effects of the Sand Matrix

Experiment Number:	Tar Sand		Bitumen Only	
	1	2	3	4
Reactants, g				
Tar Sand	64.9	49.2	0.0	0.0
Bitumen	0.0	0.0	8.0	7.2
Heavy Oil	64.6	49.1	64.1	57.5
Total	129.5	98.3	72.1	64.7
Products, g				
Distillate	13.6	4.8	7.9	13.7
Heavy Oil	56.3	47.1	62.9	49.3
Gas	1.3	0.6	1.0	0.9
Coke	0.9	0.7	0.0	0.0
Sand	57.7	44.5	0.0	0.0
Total	129.8	97.7	71.8	63.9
Closure, %	100.2	99.4	99.6	98.8

Table 39. Organic Product Distribution for the Experiments Investigating the Potential Catalytic Effects of the Sand Matrix, wt %

Experiment Number:	Tar Sand		Bitumen Only	
	1	2	3	4
Distillate	18.6	8.6	11.0	21.2
Heavy Oil	76.9	84.6	87.2	76.2
Gas	1.8	1.1	1.4	1.4
Coke	1.2	1.3	0.0	0.0

Table 40. Summary of Organic Products from Experiments using Raw Tar Sand or Extracted Bitumen, wt %

Resource Charge	Tar Sand	Bitumen Only	
		Uncorrected Result	Corrected for Suspended Coke
Distillate	14.3	15.8	15.8
Heavy Oil	80.2	82.0	80.6
Gas	1.5	1.4	1.4
Coke	1.2	0.0	1.4

Table 41. Material Balances for the Experiments Investigating the Pyrolysis of Polyethylene as a Function of Temperature

	Experimental Temperature, °C			
	375	400	425	450
Reactants				
Recycle Oil, g	74.98	75.00	75.01	75.00
Polyethylene, g	25.00	25.01	25.00	25.00
Total, g	99.98	100.01	100.01	100.00
Products				
Heavy Oil, g	98.73	96.65	89.02	68.46
Distillate, g	0.38	0.40	8.89	28.65
Coke, g	0.00	0.00	0.00	0.00
Gas, g	0.00	0.16	1.54	2.50
Total, g	99.10	97.21	99.44	99.61
Closure, %	99.1	97.2	99.4	99.6

Table 42. Material Balances for the Experiments Investigating the Pyrolysis of Polypropylene as a Function of Temperature

	Experimental Temperature, °C		
	375	400	425
Reactants			
Recycle Oil, g	75.02	75.08	75.00
Polypropylene, g	25.00	25.02	25.00
Total, g	100.02	100.10	100.00
Products			
Heavy Oil, g	98.15	88.35	83.66
Distillate, g	0.53	9.49	14.89
Coke, g	0.00	0.00	0.00
Gas, g	0.81	1.01	1.50
Total, g	99.50	98.86	100.05
Closure, %	99.5	98.8	100.1

Table 43. Material Balances for the Experiments Investigating the Pyrolysis of Polystyrene as a Function of Temperature

	Experimental Temperature, °C			
	375	390	400	425
Reactants				
Recycle Oil, g	75.02	75.00	75.00	75.00
Polystyrene, g	25.01	25.00	25.00	25.00
Total, g	100.02	100.00	100.00	100.00
Products				
Heavy Oil, g	99.04	92.18	86.34	65.11
Distillate, g	0.16	6.95	12.48	33.72
Coke, g	0.00	0.00	0.00	0.00
Gas, g	0.00	0.64	0.29	1.50
Total, g	99.06	99.77	99.10	100.32
Closure, %	99.0	99.8	99.1	100.3

Table 44. Compounds Identified by GC/MS in the Distillate Produced from Pyrolysis of Polyethylene at 425°C

Retention Time, min	Compound Identified	Area Percentage
0.5	2-butene	0.89
1.0	2,2-dimethyl-propane	0.57
1.2	2-methyl-3-hexene	0.08
1.3	1,1-dimethyl-cyclopropane	0.17
1.4	1,2-dimethyl-cyclopropane	0.75
1.5	1,3-pentadiene	0.20
1.9	ethenyl-cyclohexane	0.08
2.0	2-methyl-1-pentene	0.38
2.2	3-methyl-1-hexene	0.62
2.3	2,3-dimethyl-2-butene	0.14
2.5	2,2,3,4-tetramethyl-pentane	0.27
2.6	1-hexene	0.99
2.7	methyl-cyclopentane	1.43
2.9	2-hexene	0.47
3.0	hexane	0.48
3.2	3-methyl-2-pentene	0.68
3.5	ethyl-cyclobutane	0.08
3.8	2,4-dimethyl-pentane	0.41
3.9	3,4-dimethyl-hexane	0.32
4.4	3-methyl-cyclopentene	0.32
4.8	4,4-dimethyl-cyclohexane	0.22
5.0	3,4-dimethyl-2-pentene	1.25
5.2	4-methyl-1-hexene	0.30
5.3	1,4-hexadiene	0.10
5.4	2,3,3-trimethyl-hexane	0.18
6.1	3,5-dimethyl-heptane	0.44
6.4	1-heptene	0.17
6.5	butyl-cyclopentane	0.34
6.8	1,5-dimethyl-cyclopentene	0.19
6.9	heptane	0.63
7.2	2-methyl-heptene	1.80
8.3	2,4,4-trimethyl-2-pentene	0.74
9.4	3-ethyl-1,4-hexadiene	0.41
10.2	2,2,4,4-tetramethyl-pentane	0.38
10.3	3-methyl-octane	1.02
10.6	4-methyl-heptane	0.86
11.0	3-methyl-heptane	0.30
11.5	3,4-dimethyl-2,4-hexadiene	0.16
11.7	2-methyl-1-heptene	0.33
12.0	1-octene	0.39
12.5	2,2,3-trimethyl-butane	0.37
12.6	octane	0.78
13.4	2-methyl-3-heptane	0.28
13.6	1,3,5-trimethyl-cyclohexane	0.87
15.0	Mixture of C ₄ substituted cyclopentanes	15.21
15.3	2-(1-methyl-ethyl)-thiophene	1.21

Table 44. Compounds Identified by GC/MS in the Distillate Produced from Pyrolysis of Polyethylene at 425°C (continued)

Retention Time, min	Compound Identified	Area Percentage
15.5	5-methyl-1-hexene	0.40
16.3	2,3,4-trimethyl-hexane	0.31
16.4	2,5-dimethyl-2,4-hexadiene	0.40
16.6	3-ethyl-2-heptene	0.09
16.7	2,3-dimethyl-octane	0.17
17.4	1,1,2-trimethyl-cyclohexane	0.23
18.5	2,2,3,3-tetramethyl-hexane	1.05
19.0	4-ethyl-2-octene	0.49
19.1	3,5,5-trimethyl-1-hexene	0.78
21.8	2,5-dimethyl-octane	0.39
22.4	1-(methylethyl)benzene	0.11
23.1	4-ethyl-3-octene	0.86
23.7	3-ethyl-2-methyl-heptane	0.22
24.2	5-ethyl-2-methyl-heptane	2.27
24.7	4-methyl-undecane	1.89
26.8	2,2,3,3,5,6,6-heptamethyl-heptane	0.58
27.0	2,5-dimethyl-undecane	1.17
28.4	1-butyl-2-(2-methylpropyl)-cyclopropane	1.09
29.0	undecane	1.17
30.1	7-methyl-tridecane	0.41
31.1	1,4-dimethyl-2-(2-methylpropyl)-cyclohexane	0.30
31.7	4-methyl-undecane	0.16
32.0	2,2,-trimethyl-heptane	0.17
32.8	1,1-dimethylethyl-cyclohexane	0.30
33.7	dodecane	0.91
34.4	2,5-dimethyl-undecane	0.40
42.4	hexadecane	0.31

Table 45. Compounds Identified by GC/MS in the Distillate Produced from Pyrolysis of Polypropylene at 425°C

Retention Time, min	Compound Identified	Area Percentage
1.0	2-butene	0.58
1.5	1,2-dimethyl-cyclopropane	0.20
1.6	1,1-dimethyl-cyclopropane	0.25
2.0	2-methyl-1-propene	0.25
2.1	2-methyl-pentane	0.61
2.2	2,3-dimethyl-2-butene	0.38
2.5	2,4-dimethyl-1-pentene	1.62
2.7	3-methylene-pentane	0.10
2.8	hexane	0.26
3.1	3-methyl-2-pentene	0.49
3.4	4-methyl-1-pentene	0.10
3.8	3,4-dimethyl-hexane	0.12
4.1	3-hexen-1-yne	0.12
4.4	1,2-dimethyl-cyclopentene	0.62
5.0	2,4-dimethyl-2-pentene	0.34
5.1	4,4-dimethyl-2-pentene	0.33
6.0	3-methyl-hexane	0.21
6.9	1,2-dimethyl-cyclopentane	0.24
7.0	1-heptene	0.25
7.7	heptane	0.57
7.8	2-hexen-4-yne	0.29
9.3	2,4,4-trimethyl-2-pentene	0.42
11.3	cyclohexanemethanethiol	0.27
12.2	4-methyl-heptane	2.41
12.5	3-methyl-heptane	0.14
13.3	2-methyl-1-heptane	0.41
13.5	1-octene	0.36
13.9	1,1,3,4-tetramethyl-cyclopentane	0.80
14.3	octane	0.77
16.9	1,4-pentadiene	5.88
17.1	2-ethyl-1-dodecene	1.11
17.2	1,3,5-trimethyl-cyclohexane	0.40
17.8	C ₁ substituted cyclohexane	0.40
18.2	1-nonene	0.19
18.7	3-methyloctane	0.13
19.4	2-methylpropyl-cyclopentane	0.25
19.8	1-tridecene	0.63
20.4	nonane	0.76
20.8	4-decene	0.67
22.2	2,4-dimethyl-octane	0.30
23.2	3,5,5-trimethyl-1-hexene	0.38
23.9	3-ethyl-heptane	0.38
25.0	2-methyl-4-nonene	0.21
25.8	1-butyl-1-methyl-2-propyl-cyclopropane	0.37
26.0	decalin	0.43
26.6	3-hexene	2.39
28.1	1-pentyl-2-propyl-cyclopropane	0.40

Table 45. Compounds Identified by GC/MS in the Distillate Produced from Pyrolysis of Polypropylene at 425°C (continued)

Retention Time, min	Compound Identified	Area Percentage
29.0	2,2,3,3-tetamethyl-hexane	0.62
30.0	2,2,5,5-tetamethyl-3-hexene	2.67
31.1	undecane	0.63
35.4	dodecene	0.58
35.9	dodecane	0.83
39.7	C ₇ -substituted cyclohexane	0.71
39.9	6-methyl-undecane	0.70
40.8	C ₈ -substituted octane	5.29
44.7	tetradecane	0.72

Table 46. Compounds Identified by GC/MS in the Distillate Produced from Pyrolysis of Polystyrene at 400°C.

Retention Time, min	Compound Identified	Area Percentage
0.9	2-butene	0.24
1.0	1,1-dimethyl-cyclopropane	0.17
1.1	methyl-cyclopropane	0.18
1.2	hexane	0.30
1.3	3-methyl-pentane	0.34
1.4	3,4-dimethyl-pentane	0.39
1.5	2,4-dimethyl-hexane	0.16
1.6	2,2,4-trimethyl-pentane	0.55
1.7	heptane	0.41
1.8	2,4,4-trimethyl-1-pentene	0.43
2.0	2,4,4-trimethyl-2-pentene	0.32
2.5	toluene	3.35
2.6	3,5-dimethyl-heptane	1.07
3.0	2-methyl-1-heptene	0.30
3.1	1-ethyl-2-methyl-cyclopentane	0.18
3.3	octane	0.54
4.5	ethyl-benzene	7.49
5.3	3,4-dimethyl-2,4-hexadiene	0.16
5.5	styrene	33.19
6.2	3-methyl-1-hexene	0.40
6.9	6-methyl-1-heptene	0.96
7.1	4-ethyl-3-octene	0.41
7.3	octene	0.35
7.0	2,6-dimethyl-octane	1.40
8.3	3-methyl-1-pentene	0.32
8.4	3,5,5-trimethyl-1-hexene	0.25
9.0	2,3-dimethyl-1-pentene	0.31
9.3	1-methyl-styrene	5.90
9.8	1-ethyl-3-methyl-benzene	0.39
10.1	5-methyl-1-pentene	0.39
10.4	decene	1.00
11.0	decane	1.41
11.4	2,4,4-trimethyl-3-pentene	0.18
12.0	1-ethyl-2-methyl-cyclohexane	0.23
13.5	3-methyl-octane	0.50
13.7	3,3,5-trimethyl-heptane	0.24
13.9	2,6-dimethyl-octane	0.25
14.2	1-butyl-2-(2-methylpropyl)-cyclopropane	0.68
15.1	undecene	1.63
15.6	undecane	1.69
16.8	C ₄ -substituted benzene	0.34
18.5	2,5-dimethyl-dodecane	0.26
19.7	dodecene	0.93
20.3	dodecane	1.07
24.2	tridecene	0.33
24.7	tridecane	0.72

Table 47. Material Balances for the Experiments Investigating the Pyrolysis of Polyethylene as a Function of Time at 425°C

	Experimental Time, min			
	15	30	45	60
Reactants				
Recycle Oil, g	75.00	75.00	75.01	75.00
Polystyrene, g	25.01	25.01	25.00	25.00
Total, g	100.01	100.01	100.01	100.00
Products				
Heavy Oil, g	97.72	92.66	89.02	86.69
Distillate, g	1.22	5.95	8.89	11.33
Coke, g	0.00	0.00	0.00	0.00
Gas, g	1.04	1.39	1.54	1.82
Total, g	99.98	99.99	99.44	99.84
Closure, %	100.0	100.0	99.4	99.8

Table 48. Material Balances for the Experiments Investigating the Pyrolysis of Polypropylene as a Function of Time at 425°C

	Experimental Time, min			
	15	30	45	60
Reactants				
Recycle Oil, g	75.01	75.00	75.00	75.00
Polystyrene, g	25.00	25.01	25.00	25.00
Total, g	100.01	100.01	100.00	100.00
Products				
Heavy Oil, g	95.60	91.57	83.66	79.25
Distillate, g	3.11	5.88	14.89	18.59
Coke, g	0.00	0.00	0.00	0.00
Gas, g	1.25	1.55	1.50	2.00
Total, g	99.95	99.00	100.05	99.85
Closure, %	99.9	99.0	100.1	99.8

Table 49. Material Balances for the Experiments Investigating the Pyrolysis of Polystyrene as a Function of Time at 400°C

	Experimental Time, min			
	15	30	45	60
Reactants				
Recycle Oil, g	75.01	75.00	75.00	75.03
Polystyrene, g	25.00	25.00	25.00	25.00
Total, g	100.01	100.00	100.01	100.03
Products				
Heavy Oil, g	95.47	90.53	86.34	80.56
Distillate, g	3.73	7.38	12.48	18.91
Coke, g	0.00	0.00	0.00	0.00
Gas, g	0.50	0.68	0.29	0.38
Total, g	99.70	98.58	99.10	99.84
Closure, %	99.7	98.6	99.1	99.8

Table 50. Material Balances for the Experiments Investigating the Effects of Heavy Oil to Polystyrene Mass Ratio at 400°C

	Oil to Polystyrene Mass Ratio	
	10:1	13:1
Reactants		
Recycle Oil, g	100.00	130.00
Polypropylene, g	10.00	10.00
Total, g	110.01	140.00
Products		
Heavy Oil, g	104.85	133.63
Distillate, g	3.90	3.72
Coke, g	0.00	0.00
Gas, g	1.08	1.31
Total, g	109.83	138.66
Closure, %	99.8	99.0

**DATE
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