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TAR SAND

IN SITU COMBUSTION SIMULATION TESTING OF TAR SAND

Lyle A. Johnson, Jr.

Background

Previous laboratory studies conducted by WRI have evaluated the potential of steamflood, hot-gas pyrolysis, reverse combustion, and dry- and wet-forward combustion for the in situ production of bitumen from Utah tar sands (Romanowski and Thomas 1985a-d; Johnson and Thomas 1988; Johnson et al. 1980, 1982). These studies have shown that all of the processes are effective to varying degrees for producing oil from Asphalt Ridge and Tar Sand Triangle tar sands. Based on the results of these studies, forward combustion using steam-oxygen injection was selected as the process for further study, for the following reasons: (1) the product oil quality is improved relative to steamflood produced oils, (2) the coke formed from pyrolysis of the oil exceeds fuel requirements for the process, (3) frontal velocities with steam-oxygen injection are faster than those with air injection, and (4) the plugging problems experienced with air-only combustion simulations are reduced when steam-oxygen injection is used. More detailed studies (Romanowski and Thomas 1986a, b) of the process parameters which affect the application of forward combustion to Utah tar sands showed that:

- Ignition temperature for tar sand was 343-399°C (650-750°F).

- Coke produced from the pyrolysis of tar sand was sufficient (even for the leaner Tar Sand Triangle material) to provide thermal energy for the process.

- Using steam-oxygen injection gave higher oil yields than using straight-air injection.

- Reduced fuel consumption and oxygen requirements were found in the steam-oxygen tests versus the air-combustion tests.

- The combustion-front velocity was increased in the steam-oxygen tests because of improved process efficiency.

- The product oil quality was improved with respect to the bitumen for in situ combustion. The air-combustion process produced better quality oil than the steam-oxygen process because the steam-produced oil in the steam-oxygen process diluted the pyrolysis-produced oil.

- The steam-oxygen tests in the richer tar sands did not experience the severe plugging problems that were characteristic of the air-combustion process.

Objectives

Based on the review of the results of the initial one-dimensional tests of Sunnyside tar sand, it was decided that the plugging problem needed to be further studied so that it might be prevented in future testing. Objectives of this study were thus to run simulations to evaluate steam-oxygen combustion as a production process for selected deposits and to identify the mechanisms that caused reactor plugging in simulations using Sunnyside tar sand. A three-dimensional simulation was also conducted to further evaluate the process for the Asphalt Ridge deposit.

Procedures

Two Utah and one California tar sands were used. The Asphalt Ridge tar sand deposit, located in the Uinta Basin of Utah, is a low-sulfur (<0.5%), 10° API bitumen with a viscosity in excess of 1,000,000 centipoise (cP). The second Utah tar sand is from the Sunnyside tar sand deposit located in east-central Utah. The Sunnyside bitumen has an API gravity of 8°, a sulfur content of 0.7 wt % and a viscosity of 1,000,000 cP at reservoir temperature. The third tar sand was from the Arroyo Grande deposit in

California. The bitumen has a 2.6° API gravity with 3.5 wt % sulfur and a viscosity in excess of 1,000,000 cP at reservoir temperature. Simulations using Arroyo Grande tar sand contribute to the development of evaluation criteria for in situ combustion of tar sand by providing data on a geologically diverse deposit that has characteristics similar to Utah deposits.

Three reactor systems were used to perform the tests. The physical simulations to investigate the steam-oxygen combustion process performance were conducted in WRI's tube and block reactors. The investigation of the plugging problem in the Sunnyside tar sand simulations was conducted in both a slim tube system called a laboratory reference reactor (LRR) and the tube reactor system.

The LRR is a 3/4-inch i.d. by 12-inch long retort constructed of stainless steel into which 130 g samples were placed. The injected gases (N_2, N_2/O_2, or N_2/O_2/steam) were monitored with rotameters. Steam was produced with a metering pump and heat exchanger. Product gas was passed through a series of condensers and knockouts to remove liquid products and then analyzed by an on-line gas chromatograph. All liquid samples were collected and weighed for material balance calculations.

The tube reactor is capable of simulating the thermal recovery process of forward combustion, in addition to the processes of steam displacement, hot-gas pyrolysis, and reverse combustion. The reactor tube (3 5/16-inch i.d x 32-inch long) is uniformly packed with approximately 18 lb of tar sand and is vertically oriented within a series of insulated shield heaters. Auxiliary equipment includes inlet gas injection and product gas metering devices, a steam generator, a gas heater, product separation equipment, a continuous oxygen analyzer, and a gas chromatograph. The entire system is instrumented and interfaced to a data acquisition computer which records temperatures, pressures, and flow rates every 5 minutes.

The block reactor, a three-dimensional experimental apparatus, is a unique and versatile, microprocessor-controlled, high-pressure reactor. The main component of the system is a large pressure vessel into which an encapsulated sample as large as 2 x 2 x 7 ft is placed. The 1000 psig pressure vessel is a thick-walled, horizontal, cylindrical unit 9-ft long and 6 ft in diameter. The vessel is sealed using 6-ft and 2-ft diameter screw-on domed ends.

The fluid handling system consists of an injection system, a product collection and sampling system, and a product gas flaring system. Injection capabilities include independent or co-injection of gases (air, N_2, CO_2, and steam) at rates up to 35 scfm (85 lb/hr steam) at 1000 psig and 482°C (900°F). Fluid production during the test can exit from up to seven production ports, depending on the injection-production scheme desired. At any one time, gas and liquid products from up to four of the production ports can be simultaneously monitored by passing the individual product streams through one of four parallel knockout pots where liquids are collected and measured. The gas then enters a gas cleanup system where the cleaned gas is measured for volume and analyzed by an on-line gas chromatograph.

For this simulation, a 2 x 2 x 1-ft block was reconstructed from crushed tar sand material. To produce the block, a bulk density equal to that of the one-dimensional simulations was maintained during packing. The block was completed with a production and injection well and 18 temperature monitoring wells.

Results

One-Dimensional Asphalt Ridge Simulations

Three one-dimensional simulations were conducted using Asphalt Ridge tar sand at steam-to-oxygen ratios of 3.1:1, 4.3:1, and 6.0:1, and oxygen fluxes of 10.8, 8.6, and 8.0 scfh/ft^2. Ignition was established between 343 and 399°C (650 and 750°F) in all simulations, and the combustion front was successfully propagated through the tar sand bed. The peak combustion temperatures for the tests ranged from 649 to 871°C (1200 to 1600°F). The shape of the temperature profiles as the combustion front moved down the tubes is similar to those given by several other investigators. Similar combustion temperatures have been reported by other investigators burning similar reservoir materials at the same oxygen flux.

As the combustion fronts advanced, the injection pressure rapidly increased to the maximum pressure, ranging from 630 psig for the lowest steam-to-oxygen ratio to 400 psig for the highest steam-to-oxygen ratio. The injection pressures remained high for a period of time, then decreased sharply before starting a slow pressure increase throughout the remainder of the tests. During the high pressure period for all three tests, 25 and 40% of the total product oil was produced.

The fuel deposition during the simulations ranged from 10.9 wt % of the initial bitumen to 9.2 wt % based on the nonpyrolysis-produced carbon monoxide, carbon dioxide, and hydrogen in the produced gas, the excess product water, and the residual coke on the spent sand. Fuel laydown decreased as the steam-to-oxygen ratio, and therefore the steam concentration, increased. The higher steam concentration (1) improved the displacement efficiency of the process by removing a larger portion of the bitumen from the reaction tube before it pyrolyzed to produce coke and (2) increased suppression of coking by the steam.

The overall material balances for the one-dimensional tests averaged 98.4%, while the carbon balance had a slightly lower average of 97.7%. Oxygen and hydrogen balances averaged 93.6 and 97.8%, respectively. The high average closure of all balances gave confidence in the simulation results.

Oil yield for the simulations was consistently high, ranging from 80.1 to 80.3 wt % of initial bitumen. The anticipated trend of increasing oil yield with increasing steam-to-oxygen ratio was observed. The volumetric oil yields were slightly higher (82.2 to 93.0% original oil in place) than the weight percentage of oil recovery because of the upgrade condition of the product oil. The product oils from the three one-dimensional simulations were all upgraded compared with the initial bitumen with lower molecular weights, percentage residual compounds (compounds with >538°C [1000°F] boiling point), and viscosities. The initial bitumen API gravity for the product oils ranged from 14.1 to 15.0°, compared with 10.2° for the original bitumen.

Three-Dimensional Asphalt Ridge Simulation

The three-dimensional simulation test was preheated for 6 hours by electrical wellbore preheat with a low sweep of nitrogen gas. Ignition was accomplished by switching from nitrogen to air with the wellbore heater activated. When ignition was determined, oxygen was added to the air stream. During the ignition cycle, the injection pressure increased from 30 psig to approximately 400 psig, at which point air injection was terminated and steam injection initiated. The injection pressure steadily increased to a maximum of 670 psig as the total injection was increased to maintain an approximate flux of 40 scfh/ft^2 at the 482°C (900°F) isotherm. The steam-to-oxygen ratio during this period averaged 3.0:1.

The peak combustion temperatures for the thermocouple locations nearest the injection well were approximately 538°C (1000°F) and were used as the indicators for successful ignition. The vertical combustion front then moved rapidly between the injection and production wells to produce a heated channel between the process wells. Peak temperatures during the enriched air period, with its rapidly advancing combustion front, ranged from 538 to 927°C (1000 to 1700°F).

Following the start of steam injection, the combustion front stagnated between the process wells. It is postulated that the steam began to move bitumen from the edges of and into the heated channel. This movement of steam-displaced oil into the combusted region was indicated by observed secondary and tertiary combustion peaks.

The volumetric sweep of the combustion simulation was 26.1% for the combusted zone, with an additional 6.0% for the pyrolysis zone. This 32.1% total sweep is well below the theoretical 50% sweep of an unconfined five-spot pattern. The lower sweep was caused by the rapid growth of a channel between the injection well and the production well, which limited the areal extent of the sweep zone.

Fuel deposition, as determined from the nonpyrolysis-produced gas composition and residual coke, was 56.9 wt % of the initial bitumen within the sweep area. This value is five times higher than the 10.9 wt % fuel deposition of the one-dimensional test operated at nearly identical pressure and steam-to-oxygen ratio. This result tends to support the hypothesis that additional bitumen and/or product oils were swept into the existing heated channel and were directly combusted, pyrolyzed, or cracked to produce additional fuel that had to be consumed before the front could advance.

The oil yield for the three-dimensional simulation was 41.3 wt % of the original bitumen from the sweep zone, compared with an average of 83.5% for the one-dimensional simulations. The overall material balance was 96.2%, slightly less than the 98.4% average for the one-dimensional simulations. However, the carbon balance was 100.3%, higher than the average for the one-dimensional tests. The oxygen and hydrogen balances were 96.2 and 84.7%, respectively.

Product oil from this test was significantly upgraded compared with the original bitumen and even the one-dimensional product oils. Production of an upgraded oil indicates that a large portion of the heavier components of the product oil was either pyrolyzed or cracked to produce lighter fractions.

One-Dimensional Simulations with Sunnyside Tar Sand

Five simulations of the in situ forward-combustion process and one one-dimensional simulation of hot-gas injection (HGI) were conducted on a Sunnyside tar sand containing 11.6 wt % bitumen. The combustion simulations used steam-oxygen, air-oxygen, or air as the injectant. The HGI simulation used nitrogen, carbon dioxide, and steam. Vigorous combustion was established in all combustion simulations as indicated by the complete utilization of the injected oxygen and the production of carbon monoxide and carbon dioxide. Ignition temperatures were in the range of 343 to 371°C (650 to 700°F) for all tests.

The three simulations with steam-oxygen experienced severe plugging of the reactor tube within hours of establishing oxygen injection. Attempts to resolve the plugging problem, including venting the production system to relieve the high pressure and increasing the guard heater temperature in the plugged region, were unsuccessful.

To evaluate the plugging problem three additional one-dimensional simulations were conducted. The three simulations were an enriched-air dry-combustion, an air-only dry combustion, and a HGI simulation. Enriched air was selected to minimize the effect that steam or its condensation may have on the plugging problem. Within 5 hours of establishing oxidant injection, the same plugging problem experienced in steam-oxygen tests was again occurring. Neither pressure venting of the injection end of the reactor tube nor increasing the temperature of the entire tube overcame the plugging problem.

A sample of the residual oil in the zone ahead of the pyrolysis zone was extracted from the spent sand. The oil saturation had increased from the original 11.6 wt % to 14.6 wt %. The viscosity of this residual oil at 91°C (195°F) was 207,000 cP, a 150-fold increase over the original bitumen viscosity of 1,300 cP at the same temperature.

The dry forward-combustion test with air as the only injectant also plugged within 4 hours of ignition. The injection pressure began to mirror that of the previous two simulations, however, increasing the temperature with the guard heaters in the zone immediately ahead of the combustion and pyrolysis zones reduced the plugging problem to a point where the test could be conducted at a constant injection rate and pressure. This test produced 46% of the bitumen as a highly upgraded oil by establishing and maintaining a sharp combustion front throughout the tube. However, even though the yield and the product oil quality are good, extrapolating this type of process to a field test is not practical.

The HGI test was conducted with a nonoxidative atmosphere consisting of carbon dioxide and steam which approximated the gas typical to the pyrolysis zone in the steam-oxygen tests. The tube was preheated in an identical manner as the combustion tubes so that initial bitumen mobilization and displacement would be the same. The temperature of the guard heaters was increased from the top of the tube to the bottom in such a manner as to simulate the advance of the combustion front. Within 5 hours the injection pressure had increased to greater than 950 psig. This pressure profile was very similar to those for the previous combustion tests. One pressure venting and repressurization cycle was conducted in an attempt to displace the plug, but it was not successful. The test was terminated at this point and the sample material was removed for analysis.

During the test, 8.8 wt % of the initial bitumen was produced. This product oil was very similar in quantity and appearance to the oil produced in the combustion simulations. Analysis of the HGI tube material extracted from the plug region showed a viscosity three to four times greater than the original material, indicating that the oil bank was being formed by the heavier components of the bitumen. Functional group analysis of the material indicated the viscosity increase was caused by devolatilization in the top of the plug, with condensation in the bottom of the tube.

The performance of the HGI simulation compared to that of the Sunnyside combustion tests indicates that the oxygen flux in the injected gas is not the controlling factor in the plugging experienced in the Sunnyside simulations. What appears to be the cause of the plugging in the combustion simulations is the formation of a highly viscous, highly saturated region produced by conventional fluid flow, with the alteration of the flowing material by a combination of devolatilization and oxygen incorporation.

To further evaluate the Sunnyside plugging problem, twenty LRR experiments were conducted. Nitrogen, oxygen, and steam were injected into the tar sand at 149°C (300°F) or 204°C (400°F). Organic material was extracted from the top half, bottom half, or the entire tube based on the amount of material remaining after each test. For those runs when steam was used, it was found that not enough bitumen could be extracted from only half of the bed material, so the entire bed of spent tar sand was extracted for analysis. Infrared functional group analyses, compound type analysis, viscosities (at three temperatures), and specific gravities (at two temperatures) were conducted.

The LRR experiments indicated that two mechanisms contribute to an increase in bitumen viscosity and, therefore, the plugging of the reactor during simulations. These two mechanisms are devolatilization in the upper portions of the tube and the apparent production of more viscous, polar materials in the oxidative environment. The ketone, a polar material, concentration in the reacted bitumens generally increases with the material's viscosity. The material from the top of the tubes is generally more viscous than the material from the bottom of the tube. This indicates devolatilization of the top material and dilution of the bottom material with condensed material from the top. The effect of the reactor temperature on the resultant viscosity is that, as the initial reactor temperature was increased, the viscosity of mobile (extractable) material decreased. This may be due to coking of some of the heavier material and production of lighter products that concentrate in the lower section of the tube.

Arroyo Grande One-Dimensional Simulations

The two Arroyo Grande, one-dimensional simulations were conducted at steam-to-oxygen ratios of 4.3:1 and 6.4:1, both with an oxygen flux of 8.0 scfh/ft^2. Ignition of both tests occurred in the range of 343-399°C (650-750°F) and the combustion front propagated through the tube without any problems. The peak combustion temperatures were 737 and 684°C (1359 and 1264°F). These temperatures are comparable to those of previous steam-oxygen tests using Asphalt Ridge tar sand. The maximum injection pressure for both simulations was 17.5 psig. This low injection pressure is in drastic contrast to the high pressures (400-630 psig) observed in simulations using Asphalt Ridge tar sand and the total plugging of the tubes in the Sunnyside simulations. The one operational condition that may have caused this reduction in injection pressure was the slightly higher preheat temperature used in these simulations than in the majority of the other simulations.

The fuel (coke) deposition during the simulations was 15.8 and 15.2 wt % of the initial bitumen. Fuel deposition is calculated from the nonpyrolysis-produced carbon dioxide, carbon monoxide, and hydrogen in the product gas, the excess product water, and the residual coke on the spent sand. This fuel deposition is higher than the 9 to 13 wt % for the comparable Asphalt Ridge tests, but is not unexpected based on the heavy original nature of the Arroyo Grande bitumen compared to the Asphalt Ridge bitumen.

The overall material balances for the simulations averaged 98.7%. Carbon, oxygen, and hydrogen balances averaged 92.7, 103.3, and 98.7%, respectively. The high average closure of all balances, typical of similar simulations, gave confidence in the simulation results.

Oil yield for the simulations were 55.7 and 69.3 wt % of initial bitumen, with an increasing oil yield trend with increasing steam-to-oxygen ratio. The observed oil yields were lower than the yields obtained for simulations with similar saturations using the lighter Asphalt Ridge tar sand. The product oils from the two Arroyo Grande simulations were highly upgraded compared with the initial bitumen.

Conclusions

The three one-dimensional and one three-dimensional simulations of steam-oxygen forward combustion using Asphalt Ridge tar sand showed that as the steam-to-oxygen ratio increases, the fuel deposition decreases, yielding a higher recovery rate and combustion front velocity. The three-dimensional tests showed that channeling of the combustion front increases fuel consumption and oxygen demand while reducing oil yield. All tests showed significant increases in produced oil quality.

One-dimensional simulations using Sunnyside tar sand did not perform as expected. The tar sand can be ignited at a temperature of 343 to 371°C (650 to 700°F). However combustion could not be maintained because of plugging of the reactor. The plugging is undoubtedly caused by an increase in the viscosity of the oil bank material. Two mechanisms have been identified which contribute to this increase in viscosity: (1) devolatilization of the bitumen by the flow of hot gas ahead of the combustion zone, leaving behind a more viscous material and (2) oxygenation of the bitumen-yielding materials that are more polar, and hence, more viscous. Plugging during forward combustion will be a problem in Sunnyside tar sand. However, development of an ignition and operational procedure that produces a sharp combustion front may eliminate the plugging problem.

Arroyo Grande simulations showed that an extremely heavy tar sand can be successfully produced by steam-oxygen combustion without the plugging problem experienced with the similar Sunnyside resource. The simulations also validated the trends of decreasing fuel deposition and oxygen demand with increasing steam-to-oxygen ratio, and the increase of product oil yield and frontal velocity with increasing steam-to-oxygen ratio that were noted in previous simulations using Asphalt Ridge tar sand. The product oil quality was also significantly improved compared to the original bitumen.

The difference between the results of the Asphalt Ridge and Arroyo Grande simulations show that extrapolations from one tar sand resource to another is not accurate enough to base predictions upon. Laboratory simulations must be conducted prior to the field application of any process to a given resource.

Related Publications

Johnson, L.A., Jr., and J.J. Duvall, 1988, Physical Simulations of In Situ Forward Combustion Using Sunnyside and Arroyo Grande Tar Sand. Laramie, WY, DOE/MC/11076-2652.

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VALIDATION OF STEADY-STATE OPERATING CONDITIONS FOR THE RECYCLE OIL PYROLYSIS AND EXTRACTION (ROPE^{TM}) PROCESS

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R. William Grimes

Background

Major obstacles to the commercialization of tar sand are the high costs associated with mining, processing, and upgrading of the raw tar sand oil and refining the upgraded tar sand oil to produce salable products. To promote tar sand commercialization at a reduced financial risk, new processing technologies are required. WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPE^{TM}) process. The process consists of four major steps: (1) preheating and extracting the hydrocarbonaceous material with recycled product oil, (2) pyrolyzing the extracted material at a low temperature (≤399°C [750°F]) in the presence of recycled product oil, (3) completing the pyrolysis of the residue at a higher temperature (>399°C [750°F]) in the absence of product oil, and (4) combusting the solid residue and pyrolysis gas to produce process heat. To simulate the process, WRI has developed 2-inch and 6-inch diameter screw pyrolysis reactor (SPR) systems. Numerous tests on three different tar sand resources had encouraging results (Cha et al. 1986, 1987, 1988, 1990; King 1989; Thomas et al. 1989; and Guffey and Holper 1990).

Objective

The objective of this task was to conduct long-term tests to prove process efficiency and to provide steady-state process evaluation criteria on the ROPE process.

Procedures

The 6-inch diameter SPR used for this study was significantly modified compared to SPR systems used in previous tests. These modifications, the operation of the modified reactor system, and the feed materials are discussed by Johnson and Grimes (1992). In summary, the system consisted of the following subsystems:

- Slurry preparation
- Slurry pumping to provide a constant reactor feed rate
- Preheat-screw reactor for water removal and bitumen solubilization
- Pyrolysis screw for the production of selected products
- A drying reactor composed of two intermeshing screws to prevent coke buildup in the segment
- Heavy product oil recycle with a calibrated metering tank
- Heat exchangers and knockouts on individual reactor segments for product oil segregation
- Sweep gas injection to remove the vaporized products from the reactor segments
- Product gas cleanup
- Spent solids collection tank

Two experiments were conducted in the modified 6-inch SPR using Asphalt Ridge tar sand. For the first test, BSPR-8, SAE-50 weight oil was used to fill the transition sections and the heavy oil metering tank and to produce the initial tar sand slurry. After the initial charge of SAE-50 weight oil, no further additions of the SAE-50 weight oil were required since sufficient quantities of heavy and product oil were being produced. The second test, BSPR-9, was initiated with heavy oil and product oil produced during BSPR-8. After the initial oil charge, no further BSPR-8 oils were required. All operating conditions were maintained as steady as possible for the tests. The average operating conditions are given in Table 1.

Table 1. Average Operating Conditions

	BSPR-8	BSPR-9
Tar sand composition, wt %		
Bitumen	9.6	10.0
Water	6.0	2.4
Sand	83.9	86.9
Insolubles	0.5	0.7
Operating time, hr	194	197
Tar sand, lb/hr	70.0	81.6
Recycle oil, lb/hr	70	80
Average reactor temperatures, °F		
Preheat screw	395	447
Pyrolysis screw	728	746
Drying screw	939	957
Average residence time, min[a]		
Preheat screw	15	15
Pyrolysis screw	40	35
Drying screw	50	50

[a] Residence time for the individual screws is based on pretest calibrations using varying rpm settings.

The products consisted of oils obtained from the three knockouts and from the heavy oil recycle tank, spent sand, and produced gas. As appropriate, these products were analyzed for the following: viscosity, specific gravity, hydrocarbon-group types, and elemental composition (oil); residual carbon (spent sand); and CO_2, CO, H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C4's, and C4+ hydrocarbons (produced gas).

Results

Operational times for the two extended tests, BSPR-8 and BSPR-9, were 194 and 197 hours, respectively. The feed rate and temperatures for the three reactor sections were stabilized after 36 hours for BSPR-8 and 4 hours for BSPR-9. The 36-hour time to stabilize BSPR-8 was caused by problems with the slurry feed pump. The pump problem resulted in a 20-hour shutdown period to modify the slurry system. Following this modification, stability was quickly re-established.

Overall material balances were essentially the same, with 99.91% closure for BSPR-8 and 99.95% closure for BSPR-9. The total closure for the two tests was 99.93%. The approximate 100% closure for the overall and total organic balances show a high degree of accuracy for the testing protocol. These closures are acceptable for determining the steady-state operation of the ROPE process.

The normalized oil yields for BSPR-8 and BSPR-9 were 76.0 and 80.4 wt % of the bitumen, respectively. Normalized oil yield was determined by (1) reducing the quantity of heavy oil produced in each test by the quantity of recycle oil used to initiate each test, (2) determining the percent of initial bitumen each product represented, and (3) normalizing the total percentage of products to 100%. The total overall oil yield for the two tests, 78.7 wt %, was approximately the same as the total oil yield from Fischer Assay of the same material, 78.0 wt %. The amounts of normalized coke produced for the two tests were 18.6 and 15.6 wt % of the bitumen for BSPR-8 and BSPR-9, respectively. The distributions of the products for the individual and combined tests are given in Table 2.

From the specific gravity and viscosity data for product oils from the BSPR-8 and BSPR-9 tests it was estimated that the effect of the SAE-50 weight oil used to initiate BSPR-8 on the properties of the heavy recycle oil had essentially been eliminated after 120 hours. The SAE-50 weight oil has a specific gravity of 0.90 and a viscosity of approximately 300 cP at 38°C (100°F). Therefore, steady-state conditions were projected to exist for the final 74 hours of BSPR-8. The change in the feed rate and the preheat and pyrolysis temperatures between BSPR-8 and BSPR-9 caused a minor change in the properties of the produced fluids. However, the upset of the system lasted less than 48 hours, as indicated by the properties of the produced oils. Therefore, steady-state operation was reestablished and maintained for over 149 hours at the conditions used in BSPR-9. The determination of the amounts of carbon on the spent sand further confirms the time required for the system to return to steady-state operation.

The elemental analyses of the produced oils obtained from four sources show generally constant values after the establishment of steady-state conditions, as did the specific gravity and viscosity data. A decrease in the hydrogen content in the heavy recycle oil, from 11.8 wt % down to less than 11 wt %, supports the hypothesis that the effect of the initial SAE-50 weight oil is eliminated after 120 hours of BSPR-8 operation. The original bitumen had a hydrogen content of 10.9 wt %.

Table 2. Oil Yield for Steady-State Tests, Normalized to 100 wt % of Bitumen

	Fischer Assay	BSPR-6[a]	BSPR-8	BSPR-9	Combined Tests
Pyrolysis temperature, °F	932	750	728	746	--
Oil					
Light	--	--	37.8	33.2	35.0
Heavy	--	--	38.2	47.2	43.7
Total	78.0	83.3	76.0	80.4	78.7
Gas	4.0	6.7	5.4	4.0	4.5
Coke	18.0	10.0	18.6	15.6	16.8

[a] Cha et al. 1988

Conclusions

The following conclusions can be made from the two extended-time (approximately 200 hours) Asphalt Ridge tests of the ROPE process:

- Tar sand can be processed using the ROPE process without major operational problems.

- Oil yields slightly greater than Fischer Assay were obtained when the Asphalt Ridge tar sand was pyrolyzed in the presence of recycled product oil composed of heavy oil produced from the bitumen.

- If a recycle oil other than a product of the material being processed is used to initiate the process, the effect of the oil can be eliminated within approximately 120 hours and steady-state conditions can be expected. If a heavy product oil derived from the material being processed is used as the starting recycle oil, then steady-state operations can be established and maintained within 1 to 2 days.

- The oils produced by the ROPE process are highly upgraded compared to the bitumen and can be used as a refinery feedstock for the production of diesel fuel.

Related Publications

Cha, C.Y., F.D. Guffey, and L.J. Romanowski, 1987, Tar Sand Pyrolysis with Product Oil Recycling-Progress Report. Laramie, WY, DOE/MC/11076-2642.

Cha, C.Y., L.A. Johnson Jr., and F.D. Guffey, 1990, Investigation of the ROPE^{TM} Process Performance on Sunnyside Tar Sand. Laramie, WY, DOE/MC/11076-2912.

Guffey, F.D., and P.A. Holper, 1990, Laboratory Simulation Studies of Steady State and Potential Catalytic Effect in the ROPE^{TM} Process. Laramie, WY, DOE/MC/11076-3032.

Johnson, L.A. Jr., and R.W. Grimes, 1992, Recycle Oil Pyrolysis and Extraction (ROPE^{TM}) Process, Validation of Steady-State Operation Conditions, Laramie, WY, WRI-92-R059.

King, S.B., 1989, Processing of Arroyo Grande Tar Sand Using the Recycle Oil Pyrolysis and Extraction (ROPE^{TM}) Process. Laramie, WY, DOE/MC/11076-2991.

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1989, Evaluation of the Potential End Use of Oils Produced by the ROPE^{TM} Process from California Tar Sand. Laramie, WY, DOE/MC/11076-2950.

DEVELOPMENT OF AN INCLINED LIQUID FLUID-BED REACTOR SYSTEM FOR PROCESSING TAR SAND

Lyle A. Johnson, Jr.

Background

A new processing technique and reactor system for the surface processing of tar sand has been investigated by WRI. The process is referred to as ROPE^{TM} (recycle oil pyrolysis and extraction) and consists of two pyrolysis steps for recovering products that require minimal upgrading. The initial step is low-temperature (<427°C [800°F]) retorting of the tar sand in the presence of recycled product oil. Then the retorted sand is further pyrolyzed at a higher temperature (>482°C [900°F]) in the absence of recycled product oil. One reactor system being developed, based on the ROPE process, is an inclined liquid fluid-bed reactor (ILFBR).

The advantages of an inclined fluid-bed reactor are high heat transfer rates, high solids throughput, and the flexibility of the system to operate with a wide range of residence times. This latter item can be addressed by changing the bed angle and/or the fluidizing velocities of the system. Also, a nearly horizontal, inclined bed provides plug flow for solids at more uniform residence times and permits a wider range of particle sizes to be used. Uniform residence time is attained by the vertical flow of gas through the nearly horizontally flowing solid and liquid bed. An added advantage of the fluid bed is the absence of internal moving parts.

An ILFBR system was designed and constructed based on data obtained during WRI development of the screw pyrolysis reactor (SPR) systems (Cha et al. 1987, 1988) and on cold-flow model studies (Johnson and Cha 1987). The shakedown tests using this reactor system showed that most of the bitumen could be recovered from Asphalt Ridge tar sand.

Objective

The objective of this investigation was to evaluate an ILFBR system when modified to improve operability.

Procedures

The original ILFBR system is described in the report by Merriam and Cha (1987). Modifications to an existing ILFBR system consisted of changes in the product collection, the product oil recycle, and the tar sand feed components of the reactor system. Knockout pots on the product collection system were enlarged to permit additional settling time for entrained liquids, and a vertical baffle was added so the gas must traverse a larger portion of the vessel before exiting. Also, a cyclone separator was added to the composite gas line to remove any entrained liquids and solids that may pass the condensers and knockouts. The slurry feed system was changed so that the feed did not drop vertically onto the disparger plate, but entered the unit horizontally with an increased amount of recycle oil.

A test was conducted with the modified ILFBR to determine the operability of the system. The test used Asphalt Ridge tar sand and product oil from a previous Asphalt Ridge 6-inch SPR ROPE test as the initial recycle oil. The test used the operational parameters identified in 2-inch-diameter SPR tests as producing the best oil yield-oil quality combination. The slurry feed for this test was approximately 20 lb/hr (9.0 kg/hr) of a 1:1 tar sand/product oil mixture. The three fluidization sections had operating temperatures of 316, 371, and 399°C (600, 700, and 750°F). The recycle oil reflux zone and the residual bitumen pyrolysis (high-temperature) zone were operated at 399 and 524°C (750 and 975°F), respectively.

The test was conducted for 11 hours, with occasional interruptions for equipment adjustments and repairs. At the end of 11 hours, the test was terminated because there was still excessive liquid carryover into the gas cleanup system and there was no indication of solids return from the high-temperature region of the pyrolysis screw.

Results

The liquid collected from the gas cleanup system during the test amounted to more than 45 wt % of the total recycle oil and bitumen fed to the fluidized bed. From simulated distillation tests, about 27 wt % of the total recycle oil and bitumen is distillable up to 399°C (750°F). Therefore, at least 40% of the collected liquid was from entrainment of liquid droplets in the fluidizing gas stream or from extensive pyrolysis of the material in the plugged region because of the extended time it remained in the 399°C (750°F) zone. The amount of entrained or pyrolysis-produced liquid may have been higher than 40% of the collected liquid because a considerable amount of liquid carryover past the cyclone was evident during cleanup of the system. The amount of entrained and pyrolysis-produced liquid may be approximated by simulated distillation analysis.

Following the test, the fluidized bed was opened for inspection. A blockage had developed beginning in the second fluidizing zone and continuing through most of the third. The material removed from this blockage was fairly cohesive and closely resembled raw tar sand. Only a small amount of sand was removed from the pyrolysis screw. It was also noted that the seals on the three disparger sections, especially in the second and third zones, had failed during the test from heatup and cooldown cycles. This had gone unnoticed because of their location within the insulating blanket.

The failure of the test to operate satisfactorily may be attributed to (1) excessive entrainment of liquid in the fluidizing gas and/or (2) failure to maintain sufficient fluidizing gas velocities in the three zones because of external leakage of the gas.

In the first case, liquid entrainment would increase the density of the slurry phase as it progressed down the fluid bed. As the density increased, so must the minimum fluidizing velocity. But since the fluidizing gas rate and, therefore, the fluidization velocity were constant in the test, at some point the required minimum fluidization velocity for the increasingly dense slurry would be greater than the fluidizing velocity in the zone. The bed, especially solids, would cease to move, causing a buildup within that area.

In the second case, the fluidizing velocity within a zone would decrease proportionally to the amount of gas escaping from the disparger outside of the bed. When the fluidizing gas velocity became less than the required minimum fluidization velocity, the slurry would not continue to move as a single uniform mass. It would separate into solid and liquid dominant phases, and the solid dominant phase would settle out. If entrainment was occurring at the same time, then plugging would occur more rapidly than with either cause alone.

Two approaches are proposed to overcome the problems identified in this test. To prevent leakage of the fluidizing fluid before it passes through the disparger, the seal between the disparger and the fluidizing fluid supply system should be changed to a positive (i.e., welded) seal. As for the liquid entrainment problem, many possible solutions exist. Areas to be considered for solving this problem are: (1) maintaining fluidization velocities closer to the minimum fluidization velocity for the slurry, (2) adding a spray system within the disengaging space of the fluid bed to increase coalescence of the entrained liquid and to replenish the liquid content within the fluid bed, and (3) modifying the system to a liquid-solid system rather than the present gas-liquid-solid system.

Conclusions

Although several problems occurred during the development of the ILFBR system, the development of such a system will be valuable for the processing of variable feed resources that require different operating parameters. To progress with development, two different approaches should be investigated. These are (1) adding a spray system to induce coalescence and to replenish the liquid content within the fluid bed and (2) changing the system so the feed slurry is fluidized by liquid, thereby eliminating the injected gas phase. In either case, simulated distillation analysis should be conducted on the produced oils to determine what percentage of the excess produced oil is from entrainment or pyrolysis.

Related Publication

Johnson, L.A., Jr., 1987, Development of an Inclined Liquid Fluid-Bed Reactor System for Processing Tar Sand. Laramie, WY, DOE/MC/11076-2951.

AN EVALUATION OF OIL PRODUCED FROM ASPHALT RIDGE (UTAH) TAR SAND AS A FEEDSTOCK FOR THE PRODUCTION OF ASPHALT AND TURBINE FUELS

Kenneth P. Thomas
P. Michael Harnsberger
Frank D. Guffey

Background

The potential end use of the bitumen from the Asphalt Ridge (Northwest) tar sand deposit in Utah was previously evaluated by Thomas et al. (1986). In that investigation, it was determined that the bitumen and a vacuum distillation residue met ASTM specifications as viscosity-graded asphalts, AC-5 and AC-30, respectively. In addition, the materials possessed unusual properties regarding performance. Wenger et al. (1952) and Bunger (1979) also investigated the potential of producing asphalt from several tar sand bitumens and concluded that the products compared well with petroleum-derived asphalts and ASTM specifications.

The potential of producing transportation fuels, in particular aviation turbine fuels, from tar sand bitumens has also been investigated. Under contract to the U.S. Air Force, the Ashland Petroleum Company (Moore et al. 1987) and the Sun Refining and Marketing Company (Talbot et al. 1986) have produced small quantities of specification-grade JP-4 and JP-8 fuels from Big Clifty (Kentucky) and Sunnyside (Utah) tar sands. Thomas et al. (1986) have also evaluated the potential of producing aviation turbine fuels from vacuum distillates of Asphalt Ridge (Northwest) tar sand bitumen. Based on molecular composition data, they concluded that the distillates have the potential to be hydrogenation feedstocks for the production of aviation turbine fuels.

Objective

The objective of this study was to evaluate the potential end uses of Asphalt Ridge tar sand by studying the properties of oil produced by the wet, forward combustion of a block of that material.

Procedures

The oil evaluated in this study was produced from a block of Asphalt Ridge tar sand using a wet, forward combustion process (Johnson and Romanowski 1987). A composite of the oil was subjected to vacuum distillation to produce a residue and a distillate.

Asphalt ASTM specification tests were performed on the residue in accordance with the procedures set forth in Method D 3381 (ASTM 1991) for viscosity-graded asphalts. However, viscosities were determined on a Brookfield viscometer instead of by Methods D 2170 and D 2171. Method D 3381 contains two tables that define the minimum and maximum specification values for paving asphalts. The second table contains the more restrictive set of values. The other test procedures applied to the residue included the thin-film accelerated-aging test (TFAAT) and an evaluation of briquettes to water susceptibility.

The chemical and physical properties of the distillate sample (elemental composition, molecular weight, density, viscosity, and distillation data) were obtained using standard WRI or ASTM procedures. The hydrocarbon-group-type distribution of the neutral fraction was determined using a gas chromatographic/mass spectrometric (GC/MS) method.

Results

Asphalt Potential

Vacuum distillation of the thermally-produced oil resulted in 46.6 wt % residue boiling above 412°C (775°F). The viscosity of the +412°C (+775°F) residue measured at 60°C (140°F) was 1174 P, which is within the specification limits for an AC-10 viscosity-graded asphalt.

Examination of the data from the residue analysis (Table 1) indicates that the material would pass the ASTM Method D 3381 Table 1 requirements for an AC-10 viscosity-graded asphalt. The residue also meets all of the D 3381 Table 2 requirements for an AC-10 asphalt except the requirement for the 135°C (275°F) viscosity (250 cP required). The lower viscosity (202 cP) indicates that the residue has a higher temperature susceptibility than allowed for D 3381 Table 2 asphalts. The penetration value for the residue (102) is also somewhat high compared with the specification values, although there is not a maximum value for penetration. These findings are consistent with other data previously obtained on tar sand products derived from Asphalt Ridge (Northwest) tar sand bitumen which were evaluated with respect to asphalt specifications (Thomas et al. 1986).

Rheological analysis of the sample before and after TFAAT aging indicates that the residue had an extremely low aging index (Table 2). In most cases, a low aging index is good from the standpoint of long-term pavement embrittlement; however, the extremely low aging index may indicate that the asphalt will not harden properly, resulting in low pavement stability. It may also indicate resistance to rapid age hardening. It may be possible to offset this problem by blending the residue with a higher viscosity-graded asphalt or conducting the vacuum distillation to a higher final boiling point, thus producing a more viscous residue.

Table 1. Results of ASTM D 3381 Specification Tests on +412°C Residue

Test	Specifications for AC-10	+412°C Residue
Viscosity, 60°C, P	1000 ±200[a]	1174
Viscosity, 135°C, cP, min	150[b], 250[c]	202
Penetration, 25°C, 100 g, 5 sec, dmm, min	70[b], 80[c]	102
Flash Point, Cleveland open cup, °C, min	219[a]	263
Solubility in trichloroethylene, %, min	99.0[a]	99.9
Tests on residue from thin-film oven test		
Viscosity, 60°C, P, max	5000[a]	3124
Ductility, 25°C, 5 cm/min, cm, min	50[b], 75[c]	105+

[a] Value common to ASTM D 3381 Tables 1 and 2
[b] ASTM D 3381, Table 1
[c] ASTM D 3381, Table 2

Table 2. Rheological Characteristics of Unaged and TFAAT-Aged Petroleum Asphalts and +412°C Residue

Sample	Dynamic Viscosity, Poise, 60°C		Tan Delta		Aging Index
	Unaged	Aged	Unaged	Aged	
+412°C Residue	1.23×10^3	4.89×10^4	24.8	6.4	39.8
Boscan asphalt	8.11×10^2	1.79×10^5	9.1	3.0	220.7
California Coastal asphalt	1.27×10^3	1.72×10^5	9.9	4.0	135.4

Tan delta = viscous flow modulus/elastic modulus
Tan delta determined at $G^* = 2.2 \times 10^4$
Aging Index = aged viscosity/unaged viscosity

Rheological measurements were made in the dynamic mode, which facilitates obtaining the elastic and viscous flow components of viscosity. The elastic modulus and viscous flow modulus are related to viscosity by: $\eta^* = [(G')^2 + (G'')^2]^{1/2}/\omega$, where η^* = dynamic viscosity, G' = elastic modulus, G" = viscous flow modulus, and ω = shear frequency. The elastic modulus has been related to the ability of a system to recover from deformation caused by a load. The viscous flow modulus has been related to plastic or permanent deformation of a system caused by a load. The tan delta (viscous flow modulus/elastic modulus) is a ratio used to measure the relative contribution of each component to the viscosity (Ferry 1961). A high tan delta at low temperatures has been related to the ability of a system to relieve low temperature thermal stress by a creep flow mechanism. However, at higher temperatures, such as 60°C (140°F), a high tan delta may indicate a tender asphalt (an asphalt that flows too easily under stress and, thus may be prone to rutting).

Although there are no direct correlations between tan delta values and pavement performance properties, tan delta values may indicate tendencies for certain pavement problems to occur. The tan delta values for both the unaged and aged residues are quite high compared with those for petroleum asphalts. The tan delta values (both unaged and aged) are compared at the same G*, or complex dynamic modulus. The G* value can be called the stiffness value; therefore, the tan deltas are all compared at the same asphalt stiffness. Relative to petroleum asphalts, the tan delta values of both unaged and aged samples are significantly higher, indicating that the viscous flow component of viscosity has more influence on the properties of the asphalt than does the elastic component. As a result, the asphalts may be tender.

The water susceptibility test is an indirect measure of the resistance of an asphalt-aggregate mixture to moisture-induced damage. The +412°C (+775°F) residue performed quite well when compared with petroleum asphalts. The two aggregates (Hol limestone and Texas silica) used in the test are very susceptible to water stripping. The Hol limestone aggregate is essentially calcium carbonate with very few crystal imperfections. Most petroleum asphalts survive only about 5 cycles with this aggregate, the exception being the California Coastal asphalt, which survived 23 cycles. This large number of cycles is due primarily to the fact that the California Coastal asphalt contains a high concentration of carboxylic acids that interact strongly with this carbonate aggregate. The Texas silica aggregate is a highly moisture-sensitive aggregate.

Although the residue briquette only survived 2 cycles, this result represented some improvement because the commonly used Boscan asphalt only survived 1 cycle.

Aviation Turbine Fuel Feedstock Potential

In general, the chemical and physical properties of the -412°C (-775°F) distillate are improved with respect to the original bitumen and the thermally-produced oil. For example, the molecular weight is decreased from 690 amu for the bitumen (320 amu for the thermally-produced oil) to 220 amu for the distillate, and the viscosity of the distillate is only 15 cP at 16°C (60°F) (Table 3). The chromatographic separation of the distillate fraction provides quantitation of the neutral and polar fractions. The neutral fraction represents 64.7 wt % of the distillate fraction. The polar fraction represents 35.3 wt % by difference. These results indicate that a majority of the distillate fraction is composed primarily of hydrocarbon compounds, while the polar fraction contains the undesired heteroatomic compounds.

The neutral fraction was further analyzed by combined GC/MS to determine the hydrocarbon-group types present in the distillate fraction. These results indicate that the neutral fraction is composed primarily of aromatic species that include alkylbenzenes, indanes/tetralins, naphthalenes, fluorenes, and anthracenes/phenanthrenes. These aromatic hydrocarbon types comprise 87.1 wt % of the neutral fraction. Saturated hydrocarbons account for the remaining 12.9 wt % of the neutral fraction. The tricyclic alkanes are the most predominant saturated hydrocarbon class present in this subfraction. Only a trace (1.9 wt %) of alkanes was found in the fraction.

The high aromatic content of the neutral fraction indicates that the distillate has potential use as an advanced aviation turbine fuel feedstock. Hydrogenation of the distillate fraction would be necessary to saturate the aromatic ring systems and remove the heteroatom-containing species. Depending on the degree of hydrogenation, the intermediate may satisfy feedstock requirements for the production of either a high-density fuel or an endothermic fuel (Smith et al. 1986). The degree of hydrogenation required to produce a high-density fuel (JP-8X) is severe, but current prototypic specifications for JP-8X allow for up to 30 vol % aromatic hydrocarbons to be present in the finished fuel.

Table 3. Chemical and Physical Properties of the Bitumen and Its Products

Property	Bitumen	Thermally-Produced Oil	IBP-412°C Distillate
Carbon, wt %	85.8	86.4	87.0
Hydrogen	11.5	11.6	11.8
Nitrogen	1.1	1.1	0.6
Sulfur	0.4	1.3	0.7
Oxygen (by difference)	1.2	-	-
H/C Ratio	1.61	1.60	1.62
Gravity, °API	10.1	16.0	22.8
Molecular weight	690	320	220
Viscosity, cP			
16°C	-	-	15
38°C	-	134	-
60°C	59,000	41	-

Production of a prototypic endothermic-type fuel would require more complete hydrogenation than that required for the production of a high-density fuel. The greater severity of hydrogenation is required because endothermic-type fuels are envisioned to be composed of entirely saturated ring systems that would undergo dehydrogenation reactions during hypersonic flight by adsorbing heat from aircraft surfaces.

The relatively low concentration of alkanes in the distillate fraction (1.2 wt %) is advantageous for production of both high-density and endothermic-type fuels. A low concentration of alkanes in the finished fuels should not adversely affect either the freeze point or density requirement specified for high-density fuels. In addition, a low concentration of alkanes will not have a significant impact on the relative concentration of cyclic saturated hydrocarbons required in endothermic-type fuels.

Conclusions

The +412°C (+775°F) distillation residue met all of the specification tests for Table 1 requirements of an AC-10 asphalt. In addition, the residue met all of the more stringent Table 2 requirements but one, the viscosity requirement at 135°C (275°F). This indicates the residue has a higher temperature susceptibility than allowed by Table 2 requirements. The residue also had an unusually low aging index, indicating that it may not set properly or it is resistant to rapid age hardening. Results from successive freeze-thaw cycling indicate that the residue, when coated on appropriate aggregates, is comparable to or better than some petroleum asphalts coated on the same aggregates. This indicates the residue is resistant to moisture-induced loss of strength.

The -412°C (-775°F) distillate of the thermally-produced oil was improved in quality with respect to the bitumen and the produced oil. Significant reductions were noted in molecular weight and viscosity. Combined GC/MS analysis of the neutral fraction of the distillate indicated it is composed of primarily 3-ring saturate-type compounds and 2- and 3-ring aromatic-type compounds. It is believed that these aromatic compounds, upon hydrogenation, could serve as the basis for the production of high-density or endothermic aviation turbine fuels.

Related Publications

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1994, An Evaluation of Oil Produced from Asphalt Ridge (Utah) Tar Sand as a Feedstock for the Production of Asphalt and Turbine Fuels, accepted for publication in Fuel Sci. and Tech. Int.

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1987, Potential End Uses of Oil Produced by Wet Forward Combustion of Asphalt Ridge Tar Sand. Laramie, WY, DOE/MC/11076-2451.

EVALUATION OF THE POTENTIAL END USE OF OILS PRODUCED BY THE ROPE^{TM} PROCESS FROM CALIFORNIA TAR SAND

Kenneth P. Thomas
P. Michael Harnsberger

Background

The evaluation or production of transportation fuels and asphalts from tar sand has been the subject of numerous publications. Thomas et al. (1986, 1987) evaluated oil recovered by wet, forward combustion and bitumen recovered by steamflood from the Asphalt Ridge tar sand deposit in Utah. Bunger (1979) and Wenger et al. (1952) also investigated the potential of producing asphalt from several tar sand bitumens and concluded that the products compared well with petroleum-derived asphalts and met ASTM specifications.

Under contract to the U.S. Air Force, the potential for producing aviation turbine fuels from tar sand bitumens was studied. Ashland Petroleum Company and the Sun Refining and Marketing Company each produced specification-grade JP-4 and JP-8 turbine fuels from both Big Clifty (Kentucky) and Sunnyside (Utah) tar sands. Ashland concluded that high-quality aviation turbine fuels can be produced from tar sand bitumens, but that in today's market the cost is not competitive. Their processing scheme included asphalt residual treatment (ART^{SM}), reduced crude conversion (RCC^{SM}), and hydrotreatment (Moore et al. 1987). Sun also produced specification-grade turbine fuels using a process that consisted of hydrovisbreaking and catalytic hydrotreating or hydrocracking (Talbot et al. 1986).

Objective

The objective of this study was to evaluate the potential end uses of two oil streams produced from California tar sand by the ROPE^{TM} process. A distillate and its hydrogenated process intermediates were evaluated as transportation fuels. A residue prepared from the heavy product oil stream was evaluated as an AC-10 asphalt.

Procedures

The distillate and heavy product oil were obtained during process development unit (PDU) run SPR-111 (King 1989). Tar sand from the Arroyo Grande deposit near Edna, California, was processed in the reactor. The distillate was obtained from the second knockout, and the heavy product oil was obtained from the heavy oil outlet of the screw reactor.

Hydrogenation of the distillate was conducted in a bench-scale, fixed-bed system, operated in the downflow, once-through mode. Six process intermediates were collected during steady-state operation of the reactor. The chemical and physical properties (elemental composition, specific gravity, and distillation range) of the distillate and the process intermediates were obtained using ASTM (ASTM 1991) or standard procedures developed by WRI. The hydrocarbon-group-type distribution of the distillate and a process intermediate were determined using a gas chromatographic/mass spectrometric (GC/MS) procedure.

After the removal of very fine solid material from the heavy product oil, it was subjected to vacuum distillation to produce a residue suitable for evaluation as an asphalt. The asphalt ASTM specification tests were performed on the residue in accordance with the procedures set forth in Method D 3381 for viscosity-graded asphalts.

However, viscosities were determined on a Brookfield viscometer instead of by Methods D 2170 and D 2171. Method D 3381 contains two tables that define the minimum and maximum specification values for paving asphalts. The second table contains the more restrictive set of values. Other test procedures applied to the residue were the thin-film accelerated-aging test (TFAAT) and an evaluation of briquettes to water susceptibility.

Results

Transportation Fuel Potential

The chemical and physical properties of the distillate and three of the process intermediates are listed in Table 1. The sample number of the process intermediate corresponds to the test number listed by Thomas and Harnsberger (1989). In general, the trace amounts of nitrogen and sulfur decreased with increasing severity of the reactor operating conditions and were less than that contained in the original distillate. In addition, the percentage of oil distilling above 371°C (700°F) decreased from 19.1 to 13.0 wt % with increasing severity and was less than that contained in the distillate. The distillate originally contained 26.7 wt % distilling above 371°C (700°F). The hydrogen-to-carbon atomic (H/C) ratio of Sample #6 increased from 1.70 for the distillate to 1.89, and the specific gravity decreased from 0.8972 to 0.8355.

Because Sample #6 contained part-per-million levels of heteroatoms and had the highest H/C ratio, it was analyzed by GC/MS for hydrocarbon-group types (Table 2). The data in Table 2 are divided into the approximate boiling ranges for the production of gasoline (IBP-177°C/IBP-350°F) and jet and diesel fuel (177-371°C/350-700°F). The distillate contained no material distilling in the gasoline feedstock range, whereas Sample #6 contained about 47 wt % distilling in this range. This hydrotreated product still contained some alkenes (14 wt %), which need to be hydrogenated before a stable fuel can be produced from this fraction.

Table 1. Chemical and Physical Properties of the Distillate and Selected Process Intermediates

Property	Distillate	Sample #1	Sample #2	Sample #3
Elemental composition, wt %, (ppm)				
Carbon	84.8	86.4	86.0	85.6
Hydrogen	12.1	13.2	13.4	13.6
Nitrogen	0.5	(400)	(<20)	(<20)
Sulfur	1.7	(910)	(66)	(140)
Oxygen	1.4	ND	ND	ND
Hydrogen-to-carbon atomic ratio	1.70	1.82	1.86	1.89
Specific gravity, 16°C	0.8972	ND	ND	0.8355
Distillation data, vol %, ASTM D 2887				
IBP-177°C	6.8	11.5	11.2	13.6
177-371°C	66.5	69.4	71.3	73.4
+371°C	26.7	19.1	17.5	13.0

ND = not determined

Table 2. Results of Hydrocarbon-Group-Type Analysis of the Distillate and Sample #6 Determined by GC/MS, wt %

Hydrocarbon Type	Distillate 177-371°C[a]	Sample #6 IBP-177°C	Sample #6 177-371°C
Alkanes	32.0	7.7	27.7
Alkenes	26.6	14.2	15.4
Monocyclic alkanes	0	19.0	2.2
Dicyclic alkanes	0	0	1.2
Total saturate hydrocarbons	58.6	40.9	46.5
Alkylbenzenes	0.4	5.9	2.1
Indanes/tetralins	4.7	0	3.8
Naphthalenes	1.6	0	0
Fluorenes	1.1	0	0
Anthracenes/phenanthrenes	0.3	0	0
Total aromatic hydrocarbons	8.1	5.9	5.9
Total hydrocarbons	66.7	46.8	52.4

[a] 30.9 wt % of the sample was not analyzed because it was in the polar fraction

Unfortunately, this fraction, after hydrotreating to convert the alkenes to alkanes, will have too high of a concentration of alkanes to be suitable for the production of gasoline or gasoline-blending stock. Too high of a concentration of these alkanes will have a detrimental effect on the octane rating of the finished fuel. The distillate contained about 67 wt % distilling in the jet and diesel fuel feedstock range, whereas Sample #6 contained about 52 wt % distilling in this range. Again the hydrotreated product still contained some alkenes (15 wt %), which will have to be hydrogenated before a stable fuel can be produced. Upon hydrogenation, the alkenes are converted to alkanes. Consequently, the 177-371°C (350-700°F) distillate from the process intermediate is not suitable for the production of conventional or high-density aviation turbine fuels because the alkane content is too high. The limit for this class of compounds in a high-density turbine fuel is 10 vol %. High concentrations of alkanes in aviation turbine fuels can have an adverse effect on the freeze point of the fuel. However, because of the high alkane content of this distillate range, this fraction is valuable as a diesel fuel blending stock. In diesel fuels, alkanes are valuable because they have a positive effect on the cetane number.

Asphalt Potential

After vacuum distillation of the filtered heavy product oil to an equivalent temperature of 416°C (780°F), the viscosity of the residue was 1381 poise (P) at 60°C (140°F), slightly high for an AC-10 asphalt. Therefore, 6.06 g of the 385 to 416°C (725 to 780°F) distillate (0.9% of the total material, 11.5% of the 385 to 416°C/725 to 780°F distillate, or 4.4% of the total distillate) were added back to the residue. Using the data from simulated distillation analysis, 80.7 wt % residue is reached at 410°C (770°F). This resulted in a residue with a viscosity of 1060 P at 60°C (140°F).

Examination of the data listed in Table 3 for the residue shows that it did not pass one of the ASTM Method D 3381 requirements for an AC-10 viscosity-graded asphalt.

Table 3. Results of ASTM D 3381 Specification Tests on +410°C Residue

Test	Specifications for AC-10	+410°C Residue
Viscosity, 60°C, P	1000 ± 200[a]	1060
Viscosity, 135°C, cP, min	150[b], 250[c]	200
Penetration, 25°C, 100 g, 5 s, dmm, min	70[b], 80[c]	97
Flash point, Cleveland open cup, °C, min	219[a]	290
Solubility in trichloroethylene, %, min	99.0[a]	98.1
Tests on residue from thin-film oven test		
Viscosity, 60°C, P, max	5000[a]	3153
Ductility, 25°C, 5 cm/min, cm, min	50[b], 75[c]	80

[a] Value common to ASTM D 3381 Tables 1 and 2
[b] ASTM D 3381, Table 1
[c] ASTM D 3381, Table 2

The requirement not met was the trichloroethylene solubility test. This is an indication of the difficulty in removing solids to a level of 99+% solubility of the residue and the extreme fineness of the solids in the original heavy oil. All other values obtained in the testing show that the residue meets the requirements in D 3381 Table 1, but not the more stringent requirements in D 3381 Table 2. With the exception of the solubility value, these results are quite similar to findings previously reported on other tar sand asphalts (Thomas et al. 1986, 1987).

The data from rheological analysis of the sample before and after TFAAT aging are listed in Table 4. These data suggest that the residue had an extremely high aging index. An asphalt with such a high aging index will be very susceptible to cracking and embrittlement, even in the most favorable climates. The extremely high aging index may be the result of the fine solid material in the residue catalyzing an oxidation process, or perhaps the solid material promotes molecular structuring after aging resulting in the large observed viscosity increase.

Table 4. Rheological Characteristics of Unaged and TFAAT-Aged Petroleum Asphalts and +410°C Residue

Sample	Dynamic Viscosity, Poise, 60°C		Tan Delta		Aging Index
	Unaged	Aged	Unaged[a]	Aged[b]	
+410°C Residue	1.06×10^3	1.66×10^7	13.8	1.08	15,660
Wyoming Sour	1.50×10^3	3.04×10^5	17.8	1.52	202.6
Boscan asphalt	8.11×10^2	1.79×10^5	8.5	1.19	327.3
California Coastal asphalt	1.27×10^3	1.72×10^5	10.4	1.21	557.3

Tan delta = viscous flow modulus/elastic modulus
Aging Index = aged viscosity/unaged viscosity
[a] Tan delta determined at $G^* = 1.9 \times 10^4$
[b] Tan delta determined at $G^* = 2.1 \times 10^6$

Rheological measurements were made in the dynamic mode, which facilitates obtaining the elastic and viscous flow components of viscosity. Definitions of the rheological parameters are provided in the preceding article of this report.

The tan delta value for the unaged residue falls in the range typical of petroleum asphalts; however, the tan delta value for the aged residue is significantly lower than the aged petroleum asphalts. This is another indication that the residue will be subject to cracking and embrittlement. The tan delta values are compared at the same G^*, or complex dynamic modulus. The G^* value can be called the stiffness value; therefore, the tan deltas are all compared at the same asphalt stiffness. In effect, the extremely high viscosity of the aged residue is factored out in this comparison.

The water susceptibility test is an indirect measure of the resistance of an asphalt-aggregate mixture to moisture-induced damage. The residue performed adequately when compared with petroleum asphalts. The Teton aggregate used in the test is very susceptible to water stripping, whereas the Wyoming limestone shows moderate resistance to water stripping. Although the sample prepared with the Teton aggregate broke on the first cycle as did the petroleum asphalts, other binders that have been tested on this aggregate have virtually disintegrated on the first cycle. The sample prepared with the +410°C (+770°F) residue on the Wyoming limestone aggregate showed improvement over the petroleum asphalt. The petroleum asphalt briquette broke after 14 cycles, whereas the briquette prepared with the +410°C (+770°F) residue survived more than 30 cycles without breaking. Wyoming Sour petroleum asphalt is a common asphalt used in the region where both aggregates are obtained. The California Coastal petroleum asphalt is another common asphalt that was chosen for comparison. These two petroleum asphalts were chosen for comparison purposes only and do not necessarily represent the results of all petroleum asphalts coated on these two selected aggregates.

Conclusions

A series of hydrotreating experiments was conducted on the distillate obtained from PDU run SPR-111. In general, the amounts of heteroatoms decreased with increasing severity of the reactor operating conditions. A process intermediate (Sample #6) was selected and analyzed for hydrocarbon-group types, and the subsequent data were arranged according to gasoline and jet and diesel fuel production. The data show that the fraction of Sample #6 distilling in the gasoline feedstock range is inappropriate for the production of either gasoline or gasoline-blending stock because it is too high in alkanes. The fraction of material distilling in the jet and diesel fuel feedstock range is also inappropriate for the production of aviation turbine fuels because it is too high in alkanes. However, the presence of alkanes makes this fraction valuable for the production of diesel fuel.

After filtration and distillation of the heavy product oil, a +410°C (+770°F) residue met all of the ASTM specification tests for viscosity-graded asphalts except the solubility specification. This specification was not met because the residue still contained a small amount of fine solid material. The residue had a very high aging index, which suggests that it is quite susceptible to rapid age hardening or molecular structuring and that a pavement constructed with this material will be subject to excessive embrittlement. Results from successive freeze-thaw cycling show that the residue is comparable to petroleum asphalts when it is coated on the same, appropriate aggregates.

Related Publication

Thomas, K.P., and P.M. Harnsberger, 1989, Evaluation of the Potential End Use of Oils Produced by the ROPE™ Process from California Tar Sand. Laramie, WY, DOE/MC/11076-2950.

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COAL RESEARCH

GROUNDWATER REMEDIATION ACTIVITIES AT THE ROCKY MOUNTAIN 1 UNDERGROUND COAL GASIFICATION TEST SITE

Steven R. Lindblom

Background

The Rocky Mountain 1 (RM1) underground coal gasification (UCG) test was the most extensive UCG experiment to be conducted outside the former Soviet Union. The RM1 test was designed to simultaneously test two UCG process configurations: elongated linked well (ELW) and controlled retracting injection point (CRIP). The test was conducted from November 16, 1987 through February 26, 1988 near Hanna, Wyoming. Testing of the ELW process lasted approximately 57 days, ending on January 16, 1988. A total of 4,430 tons of coal was gasified using the ELW process and the average higher heating value (HHV) of the product gas was 261 Btu/scf on a dry gas basis. The CRIP experiment lasted 93 days, ending on February 26, 1988. A total of 11,280 tons of coal was gasified. The average dry gas HHV was 287 Btu/scf. Restoration of groundwater at the site was required by the Wyoming Department of Environmental Quality.

Objectives

The objectives of groundwater remediation at the RM1 site were to minimize postburn contaminant generation from pyrolysis products by accelerating the cooling of the ELW and CRIP cavities, to maximize the removal of potential organic and inorganic groundwater contaminants from the subsurface, and to prevent transport of contaminants away from the UCG cavities.

Procedures

Two restoration activities were carried out: venting, flushing, and cooling of the cavities shortly after completion of the test burns, and groundwater pumping and treatment operations.

Procedures for the first activity were based on the results of laboratory research and numerical modeling that indicated that postburn operation was critical to reducing the impact of UCG on groundwater quality. The key concept of the postburn operation was steam stripping, which allowed potential organic and inorganic groundwater contaminants to be mobilized in the UCG cavity. Steam for stripping the cavities was provided by injecting steam through the process wells immediately after gasification and by influxing groundwater that flashed to steam in the hot cavities. Sustained venting of the postburn UCG cavity was critical because the venting promoted groundwater influx into the postburn UCG cavities and because the venting provided the means to transport the mobilized contaminants to the surface. This transport prevented contaminant introduction into the underground strata surrounding the UCG cavities.

The second activity was designed to maintain the flow of UCG affected groundwater into the two cavities in the Hanna coal seam where it could be pumped to the surface and treated for removal of contaminants. The groundwater pumping and treatment restoration operations were carried out in the summers of 1988 and 1989. A pump was placed near the bottom of each UCG cavity. The volume of water pumped from the cavities was based on the calculated cavity void volume or on indications that water levels in the cavities were dropping below the level of the pump intakes. The treatment system used in the first restoration was designed to remove oils, dissolved nitrogen and sulfur species, dissolved metals, and organic compounds. The treatment system consisted of six steps:

- Gravitational separation and air flotation were used to separate oil and water.

- In a flocculation chamber, a chlorine solution was added to oxidize cyanide and ammonia. This was followed by the addition of a 50% sodium hydroxide solution to raise the pH and react with heavy metals to form and precipitate metal hydroxides.

- A tube settler allowed precipitates to settle out. The precipitated solids were removed and incinerated on-site.

- A two-stage pressure filter was used to remove suspended solids. The filter consisted of an anthracite coal stage to remove the coarser particles, followed by a silica sand stage for the finer solids.

- In a clearwell compartment, 93 to 98% sulfuric acid was added to reduce the high pH resulting from the addition of sodium hydroxide in the flocculation chamber.

- Two carbon adsorber units, each containing 100 ft^3 of activated charcoal, were used to remove organic compounds.

The treated water was stored in a holding tank and then applied to the land surface using an atomizing spray system.

The treatment system for the second restoration operation was modified based on the effectiveness of the first treatment system and consisted of two steps:

- A two-stage pressure filter consisting of anthracite coal and silica sand was used to remove suspended solids.

- Two carbon adsorber units were used to remove organic compounds. The same activated carbon used in the first treatment system was reused for the second system.

Treated water was applied to the land surface in the same manner as was done in the first treatment. Water samples were collected from various stages of each treatment operation.

Results

Steam was injected into and produced from each of the two cavities for several days immediately after gasification to cool the cavities and to remove residual contaminants. The cavities were continuously vented to remove effluents and to enhance groundwater influx.

The ELW cavity was flushed with steam for approximately 10 days and remained vented for approximately 65 additional days. During venting and flushing, the following materials were brought to the surface: 207 kg of phenols, 974 kg of total organic carbon (TOC), 171 kg of sulfides, 103 kg of sulfates, 969 kg of ammonia, 14 g of arsenic, and 356 g of boron.

The CRIP cavity was flushed with steam for 10 days and remained vented for an additional 145 days. During the venting and flushing, the following materials were brought to the surface: 328 kg of phenols, 666 kg of TOC, 368 kg of sulfides, 114 kg of sulfates, 1209 kg of ammonia, 60 g of arsenic, and 186 g of boron.

For the first pumping and treatment restoration operation, approximately 2,100,000 gallons of water were pumped from the two cavities and treated. The treatment system effectively removed dissolved organics and ammonia from the groundwater. Concentrations of selected analytes in the treated water from September 15-20, 1988 included 0.3 mg/L of ammonia, 0.638 mg/L of boron, and 15 mg/L of TOC, and less than 0.020 mg/L of total phenol. Concentrations of these analytes in the untreated cavity water on September 20, 1988 were 6.4 mg/L of ammonia, 0.387 mg/L of boron, 27 mg/L of TOC, and 0.021 mg/L of phenol. The treatment system was not effective in removing boron from groundwater because boron does not easily form hydroxide compounds when mixed with sodium hydroxide and therefore did not precipitate out of the groundwater during treatment. Total dissolved solids increases of 23 to 47% were observed between the untreated and treated water. These increases resulted from the addition of chlorides, sodium, and sulfates (i.e., chlorine, sodium hydroxide, and sulfuric acid) during the treatment.

During the second pumping and treatment restoration operation, approximately 1,570,000 gallons of groundwater were treated for the removal of dissolved organics. This treatment system did not use the addition of chemicals because in the first treatment system, these had only a small beneficial effect and resulted in a high TDS level in the treated water. The treatment system was not effective in removing dissolved organics from the cavity water because of contamination in the carbon adsorbers. Large quantities of chloroform (CF) and bromodichloromethane (BDCM) were detected in the treated water but not in the untreated cavity water. This was the same carbon used in the first treatment and it is probable that the chlorine added as part of the first treatment system partially chlorinated some organic compounds that adsorbed onto the activated carbon. Because the carbon adsorber units were sealed and stored onsite between treatments, it is possible that anaerobic bacterial reactions broke down the higher molecular weight organic compounds into lower molecular weight compounds such as CF and BDCM. These compounds could have loaded the activation sites on the activated carbon and greatly reduced the effectiveness of the carbon adsorption treatment. After treatment, the quality of cavity water was very similar to baseline conditions and generally improved during pumping. Boron was the only parameter significantly higher than baseline concentrations.

Flushing and pumping of the cavities during restoration operations resulted in water levels in the coal seam being at least 250 ft below baseline elevations in the area of the UCG cavities. These levels indicated a cone of depression in the coal seam potentiometric surface centered near the cavities. This resulted in groundwater flow from the site periphery toward the cavities. Water levels subsequently returned to baseline conditions.

Conclusions

The venting, flushing, and cooling of the RM1 UCG cavities followed by two pumping and treatment restoration operations were successful in containing and treating contaminants. Steam injection and the groundwater influx provided cooling of the cavities, reducing postburn pyrolysis, which was identified in the numerical modeling and laboratory research as a major source of groundwater contamination from UCG. Groundwater influx also stripped contaminants from the surrounding coal, char wall, and cavity, preventing transport of contaminants away from the cavities. Thus, a large quantity of the contaminants generated during gasification and most of the contaminants generated after gasification were transported to the surface.

Most UCG-induced analyte concentrations were significantly reduced after the first pumping and treatment restoration. This was particularly evident in the change in phenol concentrations in the cavity water during pumping. The first pumping and treatment operation was effective in lowering the concentrations of all analytes of concern except boron. However, the addition of chemicals increased TDS levels in the treated water. The second treatment system was not effective in removing targeted analytes because of contamination in the system itself. Even so, the results have shown that pumping and treating UCG cavity water can be an effective method for restoring groundwater quality.

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GROUNDWATER MONITORING AT THE ROCKY MOUNTAIN 1 UNDERGROUND COAL GASIFICATION TEST SITE

Steven R. Lindblom

Background

The Rocky Mountain 1 (RM1) underground coal gasification (UCG) test was conducted from November 16, 1987 through February 26, 1988, near Hanna, Wyoming, to test simultaneously two UCG process configurations and to address environmental concerns associated with UCG. The target for gasification was the Hanna No. 1 coal seam, a 30-ft seam of bituminous-rank coal lying at depths between 330 and 390 ft below the surface. The coal seam is the primary aquifer at the site and is essentially bounded by adjacent stratigraphic units of sandstone, claystone, and shale.

Contamination of groundwater may have occurred at previous UCG sites due to insufficient consideration of potential environmental impacts. However, laboratory research performed by Western Research Institute has shown that contamination may be controlled through careful site selection and the use of operational procedures developed to reduce generation, deposition, and transport of contaminants.

Objectives

A major objective of the RM1 test was to demonstrate that underground coal gasification can be successfully carried out in an environmentally safe manner. Groundwater monitoring was performed to verify the effectiveness of procedures used during the RM1 UCG test to control contaminant generation, deposition, and transport; to assess the long-term impacts of the UCG process on site hydrology; and to comply with Wyoming Department of Environmental Quality permitting and restoration requirements.

Procedures

Baseline groundwater sampling and analyses were done on a quarterly basis, beginning in August 1986. These activities continued during the UCG test and long-term groundwater monitoring began at the completion of gasification operations (February 26, 1988). The last sample collection was performed in December 1992. Twenty-two wells were designated for sampling during postburn groundwater monitoring. Of these, eight were outer ring wells completed into the Hanna No. 1 coal seam, eight were inner ring coal seam wells, four wells were completed into the overburden, and two were process wells completed into the UCG cavities.

Three different suites of samples were collected for analyses during postburn monitoring activities. The sample suites consisted of a full suite, a limited suite, and a compliance suite. An extensive quality assurance and control program was followed to ensure sample and analysis quality. Quality assurance and quality control samples included rinsates of the sampling system, duplicate samples from wells with historically higher levels of contamination, and standard samples of known concentration.

Water levels were measured in the wells across the site at the start of each sampling event. Each well was purged for a minimum of 80 minutes at approximately 1 gallon per minute. Field parameters of Eh, pH, conductivity, temperature, flow rate, and water level were measured every 20 minutes during the purging process and recorded in a laboratory notebook. Strict chain of custody procedures were followed after each sample collection.

Results

Water level measurements made since the end of groundwater restoration activities have shown that water levels in the second overburden unit and the understrata have essentially remained constant. Water levels in the adjacent overburden unit have gradually recovered to near baseline levels. Water levels in the Hanna No. 1 coal seam have essentially recovered from the effects of the UCG tests and groundwater restoration activities. Baseline water elevations in the Hanna No. 1 coal seam varied between 6880 and 6915 ft above sea level. The water level measurements of December 1992 indicated groundwater elevations of approximately 6900 ft.

With few exceptions, groundwater quality is at, or near, baseline quality. Some analytes (TOC, TDS, and ammonia) in groundwater samples from wells in the west and southwest areas of the site were consistently higher in concentration than in samples from wells in other areas of the site. This pattern was also observed during the baseline evaluation and test monitoring. These higher concentrations may have resulted from influx of water with naturally higher concentrations of these parameters from off the site. The higher transmissivity of the coal seam in this area would facilitate movement of groundwater onto the site in response to hydraulic gradients induced by UCG and restoration operations.

Low concentrations of benzene have persisted in a few wells at the site. Two coal seam wells have often yielded water containing benzene. Benzene concentrations in groundwater samples from one well have varied from less than 0.010 mg/L to 0.044 mg/L, while values in the other well have ranged from less than 0.010 mg/L to 0.019 mg/L. Concentrations have stabilized over the last 2 years at approximately 0.020 mg/L.

For some parameters, the groundwater quality in the UCG cavities is slightly worse than in the surrounding strata. Sulfate and TDS concentrations are above baseline in one of the UCG cavities. Boron concentrations remain an order of magnitude above baseline concentrations in both cavities. Other parameters have stabilized at concentrations at or below baseline.

Conclusions

The RM1 test had significant temporary impacts on the hydrology of the primary aquifer at the site. Lesser impacts were detected in the strata above the coal seam and no impacts were observed below the coal seam. Water levels, which had decreased over 200 ft near the center of the site during the UCG tests and postburn activities, have completely recovered. The groundwater flow patterns observed during the baseline site evaluation have been reestablished. No remaining effect on groundwater elevations is apparent.

The UCG tests did affect groundwater quality at the site. However, long-term monitoring has shown that the procedures used during the test and the postburn restoration measures were effective in containing and removing most contaminants from the subsurface environment. Boron in the two UCG cavities remained an order of magnitude above baseline concentrations. This is not the case over the remainder of the site, as boron in groundwater samples from all other wells has remained below baseline concentrations for the last 2 years. Low concentrations of benzene have frequently been detected in a few inner ring coal seam wells. The benzene is probably associated with coal tars in the vicinity of these wells. The majority of wells at the site have shown no evidence of benzene. Total organic carbon and total dissolved solids concentrations have often been detected above baseline levels in peripheral wells along the western edge of the site; however, it is doubtful that these higher concentrations resulted from byproducts of the UCG tests. Except for these instances, water quality parameters at the site at the end of 1992 were at or below baseline levels.

Related Publications

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Crader, S.E., 1989, Sampling and Analyses Report for Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming, March, 1989. Laramie, WY, WRI-89-R052.

Crader, S.E., 1989, Sampling and Analyses Report for Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming, June, 1989. Laramie, WY, WRI-89-R050.

Crader, S.E., 1989, Sampling and Analyses Report for Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming, September, 1989. Laramie, WY, WRI-89-R049.

Crader, S.E., 1989, Sampling and Analyses Report for Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming, December, 1989. Laramie, WY, WRI-90-R003.

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Crader, S.E., and S.R. Lindblom, 1990, Sampling and Analyses Report for June 1990 Quarterly Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming. Laramie, WY, WRI-90-R033.

Lindblom, S.R., 1990, Sampling and Analyses Report for September 1990 Quarterly Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming. Laramie, WY, WRI-90-R041.

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Lindblom, S.R., and V.E. Smith, 1993, Final Report, Rocky Mountain 1 Underground Coal Gasification Test, Hanna, Wyoming: Groundwater Evaluation. Laramie, WY, Laramie, WY, GRI-93/0269.

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Moody, C.M., 1990, Topical Report, Rocky Mountain 1 Underground Coal Gasification Test, Hanna, Wyoming: Changes in Groundwater Quality and Subsurface Hydrology. Laramie, WY, GRI-90/155.

Moody, C.M., J.D. Schreiber, and J.M. Mason, 1987, Volume II: Geohydrology and Process Well Evaluation of the Proposed Rocky Mountain 1 Underground Coal Gasification Site, Hanna, Wyoming. Laramie, WY, WRI-91-R052.

Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, March, 1988. Laramie, WY, WRI-88-R047.

Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, June, 1988. Laramie, WY, WRI-88-R045.

Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, September, 1988. Laramie, WY, WRI-88-R046.

INITIAL STUDY OF COAL PRETREATMENT AND COPROCESSING

T. Fred Turner

Background

Laboratory studies suggest that coke formation during hydropyrolysis can be prevented by a prior treatment that involves immersing the coal in an inert liquid at temperatures between approximately 350 and 400°C (662 and 752°F) (Berkowitz and Speight 1973). Such treatment removes moisture in the coal and raises its calorific value by as much as 10 to 12%. After the coal is coprocessed, it is more stable than the dried coal before the coprocessing step.

It is speculated that the presence of a suitable liquid within the pore system of the coal stops the collapse of the pores that occurs at the onset of coking. The presence of the liquid can also improve the access of hydrogen to the pores. The presence of the liquid, especially a hydrogen-donor liquid, can thus enhance hydrogen transfer within the pore system, thereby reducing potential coke-forming reactions.

Finally, the heavy oil that is coprocessed with the coal will be upgraded compared with the original material. Previous testing suggests that the primary mechanism for this upgrading step is distillation, which reduces the viscosity and the gravity of the product oil.

Objective

The objective of this study was to conduct an initial evaluation of the potential for enhancing liquid yields by integrating coal pretreatment and coprocessing technologies.

Procedures

Two eastern coals were studied. The first was a Herrin seam (Illinois No. 6) low moisture bituminous coal from the Peabody Coal Company River King Mine, pit 3, near New Athens, Illinois. The second coal was provided by Consolidation Coal Company and was a high moisture, Pittsburgh No. 8, filter cake coal. This material was a wet, pasty material that could not be processed as received and had to be air dried prior to pretreatment in an inclined fluidized-bed (IFB) reactor. The properties of these coals are shown in Table 1. The heavy oil used in the coprocessing tests was produced from mild-gasification experiments conducted on western, Powder River Basin coal in a fluidized-bed pyrolyzer (Merriam and Jha 1991). Properties of the oil are shown in Table 2.

The thermal-pretreatment stage of the experiments was performed in an IFB reactor (Boysen et al. 1990). The dried coal exiting the reactor was immediately immersed in a preheated, tared barrel of heavy oil. The dried coal-heavy oil slurry produced from the pretreatment step was fed into an inclined screw pyrolysis reactor (SPR) using a screw feeder. As the slurry mixture moved through the first two-thirds of the SPR, the coal and oil were heated, vapor products were swept from the system, and the upgraded oil was condensed in knockout pots. The remaining coal and heavy oil were exposed to higher temperatures in the last third of the screw conveyor. Here additional oil was recovered, and the coal stabilized. Depending on the temperature, residence time, and heavy oil injection rate, a dried or semidried product exited the SPR and was collected for the liquefaction tests to be conducted as a separate task. In a fully integrated operation, the IFB and the SPR reactor systems would be combined as one unit. However, to better understand the operation of the two systems each was operated independently in a semibatch mode.

Table 1. Properties of Raw Coals

	Herrin	Pittsburgh No. 8	
	as received	as received	air dried
Proximate, as received wt %			
Moisture	3.4	30.6	1.3
Volatile Matter	36.6	23.7	33.0
Ash	10.5	5.5	9.8
Fixed Carbon	49.5	40.2	56.0
Proximate, moisture free wt %			
Volatile Matter	37.9	34.1	33.4
Ash	10.9	7.9	9.9
Fixed Carbon	51.2	57.9	56.7
Ultimate, moisture free wt %			
Carbon	66.3	64.3	74.7
Hydrogen	4.7	5.4	4.9
Nitrogen	1.2	1.2	1.4
Sulfur	3.6	1.3	1.4
Oxygen (diff)	13.3	19.9	7.7
Heating Value, Btu/lb	11,771		13,343
Fischer Assay, wt %			
Oil	13.53		13.55
Water	10.69		4.72
Gas	6.99		5.53
Spent Coal	68.79		76.19

Results

The results of the analysis of the products resulting from the pretreatment tests indicate that, in general, higher temperatures and longer residence times result in higher fines production for both coals (11 to 27 wt %). However, the results of pretreatment had only a minor effect on the properties (proximate, ultimate, and Fischer assay) of the Herrin and Pittsburgh No. 8 coal products.

The significant result of the coprocessing tests is that the weight of the char formed during coprocessing is greater than the weight of the coal feed. This increase must result from conversion of heavy oil to char. For the Herrin pretreated coal the fraction of heavy oil forming char and the fraction of char formed from the heavy oil are reduced as the coprocessing temperature increases. The percent of heavy oil forming char goes from 82 to 63%. Similarly, the percent of the product char that is derived from the heavy oil drops from 66 to 57%. However, the tests with unpretreated Herrin coal, show dramatically different behavior, a factor of two different than tests with the pretreated coals. Only 35% of the product char is oil derived and only 39% of the heavy oil forms char. Clearly, the pretreated coal binds the heavy oil more strongly than the unpretreated coal.

The coprocessing series with the Pittsburgh No. 8 coal were performed with a higher starting oil-to-coal ratio (~3:1). However, less heavy oil formed char (36 to 39%), and less product char was derived from heavy oil (51 to 56%) than in similar experiments with pretreated Herrin coal. The percent of heavy oil forming char in the Pittsburgh No. 8 tests is as low as that of the unpretreated Herrin coal coprocessing series.

Table 2. Properties of Coal-Derived Heavy Oil

Proximate, as received wt %	
Moisture	12.99
Volatile Matter	86.96
Ash	.01
Fixed Carbon	.04
Proximate, moisture free wt %	
Volatile Matter	99.94
Ash	0.01
Fixed Carbon	0.05
Ultimate, moisture free wt %	
Carbon	80.7
Hydrogen	8.1
Nitrogen	0.9
Sulfur	0.6
Oxygen (diff)	9.7
Solubility Profile, wt %	
Pentane Solubles	61.8
Toluene Solubles	29.2
THF Solubles	8.4
Residuum	0.6
Specific Gravity	1.0427

Proximate, ultimate, and Fischer assay analyses of the solid products were conducted. However, it was not always possible to complete the Fischer assay analysis on the spent coal material. In many cases the solid material swelled so much that the system plugged. On disassembly, the analyst discovered a solid, "foamed" material filling the reactor and outlet tubing.

The average char heating value for the solid products resulting from all tests using pretreated Herrin coal was 14,300 Btu/lb. In general, the solid products from pretreated Pittsburgh No. 8 coal also had increased heating values with respect to the original coal. In addition, a plot of the heating value of the original coals and the chars increased as the volatile content as determined by proximate analysis of the materials increased. This is attributed to increasing amounts of heavy oil coated on the chars.

Conclusions

Drying, regardless of the conditions, reduces fixed carbon (or coke) in the Herrin and Pittsburgh No. 8 coals by only a minor amount, typically 1 to 7 wt %. However, the drying conditions do have an effect on the amount of fixed carbon formed during coprocessing. Coprocessing of a Herrin coal pretreated in a CO_2 atmosphere increases fixed carbon by as much as 18 wt % over the raw coal. Coprocessing the same coal pretreated in a CO_2/steam atmosphere results in an increase in fixed carbon content of as much as 51 wt %. This obviously has a negative effect on any subsequent hydroprocessing, with fixed carbon being more difficult to convert. Unpretreated coal showed a net reduction of fixed carbon during coprocessing.

The heating values of the solid products of coprocessing show an increase over raw coal. This is presumably because of the incorporation of heavy oil components into the coal structure. This may also be the reason for the "foaming" occurring during Fischer assay analysis. Excessive swelling such as this may limit processing options.

The reactivity of the coals is increased by pretreatment. This is seen both in the increased fixed carbon production and in the binding of heavy oil to the solid. A substantial amount, up to about 80%, of the original heavy oil ends up in the solid product. The resulting solid product is typically over 50 wt % heavy oil-derived for the pretreated Herrin coal tests. When the coal is not thermally pretreated, less oil ends up in the solid product.

Related Publication

Vaillancourt, M., T.F. Turner, and L.J. Fahy, 1991, Initial Study of Coal Pretreatment and Coprocessing. Laramie, WY, WRI-92-R002.

EVALUATION OF COAL PRETREATMENT PRIOR TO COPROCESSING

Frank D. Guffey

Background

Western Research Institute (WRI) has been conducting research to develop a mild-gasification process to produce a stabilized char product for use as a fuel (Merriam et al. 1990). The process also produces a heavy liquid with limited economic value. The composition of this liquid does not make it attractive as refinery feedstock because of its high molecular weight and heteroatom content. This liquid, because of its limited economic value, may be suited as a solvent for coal-oil coprocessing.

Coal-oil coprocessing began receiving attention in the early 1970s as a potential process for simultaneously upgrading heavy oils and coal to produce liquid products more suited for introduction into refineries. Reported results have demonstrated that the coprocessing concept can be applied to a variety of feedstocks and that yields can be increased over processing the two feedstocks independently (Speight and Moschopedis 1986; McMillen et al. 1991). Applying coprocessing technology to upgrading the liquid produced from mild gasification of coal offers several technological benefits.

Swelling of coal before it undergoes liquefaction reactions has been shown to increase the liquid product yield (Joseph 1991). Coal can be made to swell by two procedures: (1) interaction with polar solvents and (2) thermally, at moderate temperatures. In addition, it has been shown that a coal swollen in a solvent will allow the solvent to penetrate the coal structure and disperse a catalyst dissolved in it (Warzinski 1990). The mild-gasification liquid is polar because of the high heteroatom content and it has the potential of inducing coal swelling. If an oil-soluble catalyst precursor is used, it can be dissolved in the liquid and be readily dispersed as the coal swells. Uniform dispersion of the catalyst should improve liquid yield during coprocessing.

Objectives

The objectives of this study were (1) to evaluate the potential of using the coal-derived solid produced from a process development unit as a feedstock for additional coprocessing and (2) to evaluate coal pretreatment to induce coal swelling and promote dispersion of iron-based, disposable catalyst precursors, into the coal structure.

Procedures

The two coals used in this study were Herrin seam coal and a filter cake coal produced from Pittsburgh No. 8 seam coal. Properties of the coals are listed in Table 1 of the preceding summary report (page 83). Both of the coal samples were dried in an inclined fluidized-bed (IFB) dryer as discussed in the preceding summary report. The coal-derived liquid used as the coprocessing material was generated by mild gasification of coal during another project conducted by WRI (Merriam et al. 1990). Physical properties of the mild-gasification liquid are listed in Table 2 of the preceding summary report (page 84). Ferrocene and iron pentacarbonyl were the two catalyst precursors evaluated.

The coprocessing studies were conducted in 7.5-inch long by 0.75-inch o.d. stainless tubing bombs. Normally, 1.0 g of IFB dried coal and 3.0 g of the mild-gasification liquid were charged to each tubing bomb. The catalyst precursor was added at a weight to represent 1.0 wt % of the metal on the basis of the coal charge. Carbon disulfide was added as an excess to ensure sulfiding of the metal catalyst during coprocessing. After loading, each tubing bomb was frozen at -80°C (-112°F) and evacuated to remove air.

A pretreatment step under a helium atmosphere was performed as part of each coprocessing experiment to ensure good mixing of the reactants, to swell the coal, and to allow the liquid-catalyst precursor solution to enter the coal structure. The pretreatment tests were performed by pressurizing the bombs with 20 psig of helium (pressure at room temperature) and placing them in a sand bath at the pretreatment temperature for the desired time period. The pretreatment was not performed under hydrogen so the results of this study could be used to evaluate the effects of coal swelling without interference from effects of low-temperature hydroliquefaction (Derbyshire et al. 1990). Pretreatment at 90°C (194°F) for 30 minutes was selected as the base condition for this study because this condition provides sufficiently high temperature to decrease viscosity of the coprocessing liquid and allow good mixing of the reactants without thermally altering the coal structure. Pretreatment at 275°C (527°F) for 30 minutes was performed to swell the coal by both thermal and solvent interaction with the coal, and allow the liquid and dissolved catalyst access to the coal structure before coprocessing.

After venting the helium, the tubing bombs were then pressurized to 800 psig by addition of hydrogen (pressure at room temperature). The tubing bombs were heated in a sand bath set at 400°C (752°F) and shaken at a rate of 100 cycles per minute for 60 minutes. At the end of each experiment, the tubing bombs were rapidly cooled to quench the reactions.

The tubing bombs were vented into a chamber of known volume, the pressure measured, and a sample of gas taken for analysis. The tubing bombs were disassembled, the components placed in extraction thimbles, and extracted with tetrahydrofuran (THF) for 48 hours. The THF was removed from the soluble fraction with a rotary evaporator until a constant weight of the extract was achieved. The residual solid material from the extraction was dried in a vacuum oven at 80°C (176°F) for 24 hours and the weight determined. The dried solid was ashed at 427°C (800°F) for 16 hours. The weight of residual organic material (unconverted coal) was determined by difference. The concentrations of hydrogen and other product gases were determined by gas chromatography. Coal conversion and hydrogen consumption values were determined.

The experiments to investigate coprocessing of the IFB dried coal and coal pretreated in the 2-inch process development unit were performed in a stirred-batch autoclave. The batch autoclave was charged with the mild-gasification liquid and coal at a weight ratio of 2:1. The catalyst and sufficient carbon disulfide to ensure an excess of sulfur to convert the catalyst to the sulfide form were added last. The autoclave was sealed and charged with hydrogen at 1500 psig. The autoclave was then brought to a reaction temperature of 400°C (752°F) as fast as possible and held there for 1 hour. The reactor was cooled by opening the tube furnace and blowing air through the cooling coils attached to the reactor.

An oil fraction was generated from the THF-soluble product by solubility in cyclohexane. The elemental composition of the THF-soluble product and the cyclohexane soluble oil was determined using conventional methods.

Results

Examination of the material balance closures for the tubing bomb tests shows they range from about 102 to 108 wt %. These values are typical of the reaction system and are considered to be acceptable since material balances from other studies are frequently below 90 wt % (Ceylan and Stock 1991).

Coal conversions for each coal are significantly higher when iron pentacarbonyl is used as the catalyst precursor compared to ferrocene. This confirms work by other researchers (Kamiya et al. 1988; Watanabe et al. 1984). The results indicate iron pentacarbonyl is either more easily converted to the more active sulfided form than is ferrocene or it is better dispersed in the coal structure. In all of the experiments using iron pentacarbonyl as the catalyst precursor, higher conversion was observed for pretreatment at 275°C (527°F), as compared with pretreatment at 90°C (194°F).

Coal conversion data for the two experiments using Herrin coal performed without catalyst show the experiment conducted at 275°C (527°F) had higher conversion than the experiment conducted at 90°C (194°F). The increase in the coal conversion is caused by disruption of the weaker bonds (carboxylic acid functions and ethereal linkages) in the coal structure during the higher temperature pretreatment (Derbyshire et al. 1990).

For the conditions studied, changes in temperature and time in the presence of the catalyst precursor did not significantly affect coal conversion or hydrogen consumption. However, the differences between the experiments conducted with the catalyst as compared to those without are significant and the large differences in coal conversion and hydrogen consumption demonstrate catalyst activity is increasing coal conversion.

Comparison of the coal conversion and hydrogen consumption data for the two experiments conducted using the filter cake product from Pittsburgh No. 8 coal without the iron pentacarbonyl catalyst precursor shows the results are comparable, within experimental error. The absence of increased coal conversion with increased pretreatment temperature, which differs from the experiments using Herrin coal, is attributed to the lower reactivity of filter cake product.

Increasing the pretreatment time at 90°C (194°F) from 30 to 45 minutes increased the coal conversion from 22.2 to 50.0 wt %. This is a significant increase and shows the coal will undergo a significant degree of swelling caused by solvent interactions at the lower pretreatment temperature, if the residence time is sufficient. The coal conversion and hydrogen consumption observed for the experiment conducted with pretreatment at 90°C (194°F) and residence time of 45 minutes are comparable to the values observed at the shorter pretreatment residence time at 275°C (527°F).

For the two experiments conducted in the batch autoclave with Herrin coal and the mild-gasification liquid, one of the experiments was conducted in the absence of the iron pentacarbonyl catalyst precursor and the second with the added catalyst precursor. The results of these experiments are listed in Table 1. The material balance closures were 101.6 and 99.4 wt %.

The results show the coal conversion in both experiments are significantly higher than was observed in the tubing bomb experiments. This is attributed to the higher hydrogen pressure as compared to the tubing bomb experiments (1500 versus 800 psig), resulting in increased coal conversion to THF-soluble product and produced gas. The length of time (35 to 40 minutes) required to heat the autoclave from 350 to 400°C (662 to 752°F) is also sufficiently long to allow the coal to undergo low-temperature hydroliquefaction. Low-temperature hydroliquefaction has been demonstrated to drastically improve coal conversion by utilizing slower reaction rates of coal dissolution to compensate for diffusion limitations of hydrogen availability (Derbyshire et al. 1986). The hydrogen consumption is lower for the batch-autoclave experiments as compared to the tubing bomb experiments and is attributed to the lower liquid to coal mass ratio which decreases the amount of hydrogen added to the mild-gasification liquid.

Three thermally-pretreated Herrin coal samples (Vaillancourt et al. 1991) were coprocessed in the batch autoclave with the mild-gasification liquid to evaluate the pretreatment approach using the process development unit. Each sample was tested with and without the iron pentacarbonyl catalyst precursor. The material balance closures ranged from 98.6 to 102.7 wt %.

Table 1. Results from Stirred-Batch Autoclave Experiments Coprocessing IFB-Dried Herrin Coal with Iron Pentacarbonyl as the Catalyst Precursor at 400°C (752°F)

	Without Iron Catalyst	With Iron Catalyst
Reactants, g		
Coal	50.04	26.25
Coal Liquid	100.70	52.00
Catalyst	---	1.75
Hydrogen	8.17	8.82
Total	158.91	88.82
Products, g		
Unconverted Coal	2.42	0.57
Mineral Matter	6.75	3.85
THF Solubles	126.34	63.45
Produced Gas	8.12	7.15
Hydrogen	6.98	8.05
Water[a]	10.91	5.23
Total	161.52	88.30
Closure, %	101.6	99.4
Coal Conversion, wt %	94.4	97.5
Hydrogen Consumption, wt % of coal	2.7	3.4

[a] Water determined by oxygen balance

The presence of the iron pentacarbonyl catalyst precursor enhanced the conversion of the thermally-pretreated coals. Without the catalyst present only 85 to 87 wt % of the coal was converted to THF-soluble product. The addition of the catalyst increased the conversion to approximately 96 wt %. Similarly, the hydrogen consumption also increased with the addition of the catalyst. It is interesting to note that no differences between the three thermal-pretreatment regimes can be detected from the coprocessing results. All of the tests run without catalyst are quite comparable. The same can be said for the coal-oil coprocessing tests that included the catalyst precursor.

The thermal pretreatment of the coals adversely affected the coal-oil coprocessing under hydrogen pressure. Comparison of the results from the experiments conducted on the thermally-pretreated coals with those on the dried coal show that there was less coal conversion. Even without the catalyst added, the sample that was only dried exhibited coal conversion comparable to the pretreated samples with the catalyst present. The hydrogen consumption for the thermally-pretreated coals without the catalyst was considerably lower than the dried coal as well as all of the tests in which the catalyst was added.

Conclusions

From the results of this investigation, the following conclusions can be made:

- Iron pentacarbonyl is more effective as a catalyst precursor than is ferrocene for conversion of the Herrin coal and the filter cake coal product derived from Pittsburgh No. 8 coal.
- Induced coal swelling in the presence of the mild-gasification liquid is a viable means of dispersing the catalyst. However, the two coals studied exhibit different degrees of improved yield from the pretreatment.
- The filter cake product exhibited a higher degree of swelling and better catalyst dispersion, as defined by increased coal conversion, than did the Herrin coal. The filter cake product showed a broader range of coal conversion percentages because of the induced swelling.
- Even though the filter cake product showed a greater tendency to swell and disperse the catalyst, the Herrin coal showed higher coal conversion in the tubing bomb experiments due to its higher reactivity.
- Results from analysis of the product obtained from coprocessing the Herrin coal showed it was upgraded in terms of oxygen content and hydrogen-to-carbon (H/C) atomic ratio when compared to the mild-gasification liquid.
- The thermal pretreatment of the coals adversely affected the coal-oil coprocessing under hydrogen pressure. Thermally-pretreated coals coprocessed without catalyst present exhibited about 86 wt % conversion as compared to 96 wt % for coal that was only dried.
- The addition of the iron pentacarbonyl catalyst precursor to the thermally-pretreated coals did improve the conversion to nearly that of the dried coal.

Related Publications and Presentations

Publications

Guffey, F.D., F.A. Barbour, and R.F. Blake, 1992, Induced Coal Swelling and Co-Processing with a Mild-Gasification Produced Liquid. Fuel Sci. and Tech. Int., 10:(7) 1207-1232.

Guffey, F.D., F.A. Barbour, and R.F. Blake, 1991, Evaluation of Coal Pretreatment Prior to Co-Processing. Laramie, WY, WRI-92-R026.

Presentations

Barbour, F.A., F.D. Guffey, and R.F. Blake, 1992, Coal/Oil Co-Processing with a Mild Gasification Produced Liquid. Confab '92, Winter Park, CO.

Guffey, Frank, D., 1992, Coal Liquefaction and Catalysis. Meeting of the Denver Coal Club, Denver, CO.

INVESTIGATIONS INTO COAL COPROCESSING AND COAL LIQUEFACTION

Kenneth P. Thomas

Background

The conversion of coal to a liquid that is suitable as a feedstock to a petroleum refinery is a process that is dependent upon several different variables. These variables include temperature, pressure, coal rank, catalyst type, nature of the feed to the reactor, and type of process. Western Research Institute initiated research in the area of coal liquefaction to address the impact of some of these variables upon the yield and quality of the coal-derived liquid. The principal goal was to improve the efficiency of the coal liquefaction process. With respect to catalyst type, two different approaches have been investigated. These were (1) coprocessing a heavy liquid, such as crude oil, with coal, using a dispersed catalyst and (2) direct liquefaction of coal using a supported catalyst.

Another important consideration in coal liquefaction is hydrogen utilization. This is because the incorporation of externally-supplied hydrogen during conversion of this very aromatic fossil fuel to, for example, transportation fuels is very expensive. There are a number of ways in which hydrogen can participate in the direct liquefaction of coal (Finseth et al. 1985). These include hydrogenolysis, alkyl bond scission, and hydrogenation.

Objectives

The objectives of this study were: (1) to evaluate coal/oil pretreatment conditions that are expected to improve the liquid yield through more efficient dispersion of an oil-soluble, iron-based catalyst, (2) to characterize the coke deposits on novel, supported catalysts after coal liquefaction experiments and to correlate the carbon skeletal structure parameters of the coke deposit to catalyst performance as measured by coal liquefaction product yield, and (3) to determine the modes of hydrogen utilization during coal liquefaction and coprocessing. The study was divided into three subtasks: coal coprocessing, ^{13}C solid-state nuclear magnetic resonance (NMR) investigation of coke deposits on catalysts used in coal liquefaction, and hydrogen utilization.

Procedures

Two coals were used in the coal coprocessing study. The Illinois No. 6 (Herrin seam) coal sample was a bituminous coal obtained from the Peabody Coal Company River King Mine, pit 3, near New Athens, Illinois. The second coal sample was a Powder River Basin, subbituminous coal obtained from the Amax Coal Company, Eagle Butte Mine near Gillette, Wyoming. Both of the coal samples were dried in an inclined fluidized-bed dryer as part of another study to evaluate coal pretreatment (Merriam et al. 1990). Lloydminster crude oil was used for coprocessing. A 500-mL sample of this oil was distilled at 130°C (266°F) and 20 inches of mercury vacuum to remove low boiling components in the oil. The resultant heavy oil was used for this study. Iron pentacarbonyl was selected as the catalyst precursor because previous research had shown that it has good catalytic activity for coprocessing (Guffey et al. 1992; Watanabe et al. 1984) and because recent analysis has shown it has good economic value for coprocessing (Anderson et al. 1993).

For the coke deposits on catalysts part of the study, catalysts of the cobalt-molybdenum (CoMo) type were prepared on four different surface-modified alumina supports. The preparation of the catalyst, the modified supports, and the evaluation of the modified supports as coal liquefaction catalysts have been described in detail by Zhang (1993). The cobalt-molybdenum (CM) catalysts that were evaluated were TiO_2-coated alumina support via impregnation (CM/TA-I), ZrO_2-coated alumina support via impregnation (CM/ZA-I), TiO_2-coated alumina support via deposition (CM/TA-D), and carbon-coated alumina support via pyrolysis (CM/CA-P). The alumina blank support was Amocat 1A. Details of the coal liquefaction experiments in the catalytic coal liquefaction microreactor unit and the calculation of liquefaction yields have been described by Zhang (1993). Three materials were used as the coal paste feed to the unit. These were coal from Arco's Black Thunder Mine (Wyoming), deashed residue material derived from this same coal by the Wilsonville R&D Facility (S/N 99672), and Allied 24 CB raw creosote oil.

The ^{13}C solid-state NMR spectra of the coke deposits on the catalysts were obtained using a Chemagnetics CMX 100/200 NMR spectrometer operating at a frequency of 25 MHz. Cross-polarization with magic angle spinning (CP/MAS) and dipolar dephasing techniques were used to determine the carbon types present in the coke. Spectra were obtained at a spinning rate between 3.5 - 3.8 kHz. A total of 10,000 acquisitions were summed using a pulse width of 5.1 μsec, a pulse delay of 1 sec, a contact time of 1 msec, and a sweep width of 16 kHz. For the dipolar dephasing experiments, an additional delay of 40 μsec after the pulse was used before data acquisition. The ^{13}C spectra were externally referenced to liquid tetramethylsilane (TMS) based on the solid-state spectrum of hexamethylbenzene (HMB) as the secondary reference and assigning 17.21 ppm to the shift of the aliphatic carbons of HMB relative to liquid TMS (Hayashi and Hayamizu 1989).

The NMR structural parameters for the coke deposited on the catalyst were determined from ^{13}C cross polarization and dipolar dephasing spectral data. An important structural parameter is the aromatic cluster size. This parameter is calculated from the fraction of aromatic bridgehead carbons (Solum et al. 1989).

For the hydrogen utilization subtask, solid-state ^{13}C NMR measurements were made using a large-volume sample spinner (2.1 mL) and a spinning rate of ~3.8 kHz. Other instrument parameters were a pulse delay of 1 sec, a contact time of 1 msec, 6.3 μsec pulse width, sweep width of 16 kHz, 1,000 data acquisition points, and a line broadening factor of 50 kHz. These values are typical of those used in solid-state NMR measurements of coals.

Liquid-state ^{13}C NMR measurements were made using a JEOL GSX-270 NMR spectrometer. Typical conditions for recording a spectrum were ~10 μusec pulse width, 0.8 sec acquisition time, 10 sec pulse delay, 32,000 time domain data points, and gated decoupling with the decoupler on during data acquisition. Chromium(III) acetylacetonate was used as a relaxation agent.

A detailed description of the treatment of the NMR data has been given by Miknis et al. (1993). Samples for evaluation were obtained from the UOP Bench-Scale Coprocessing Unit and the Wilsonville Direct Liquefaction Facility. The material processed by UOP was an Illinois No. 6 coal and Lloydminster vacuum residue. The material processed at Wilsonville was a subbituminous coal obtained from the Black Thunder Mine. Details concerning the sources of the samples and the operation of the processes are contained in the reports by Guffey et al. (1993) and Piasecki et al. (1991).

Results

Results of the coal coprocessing subtask indicated that the Lloydminster crude oil will function as a solvent for coprocessing either Illinois No. 6 or Powder River Basin coal. However, it does not appear to be as effective as the coal liquid derived from mild gasification of a Wyodak coal used in an earlier study (Guffey et al. 1992). Coal conversions of 58.5 to 61.3 wt % were obtained in this study, compared to 76.2 and 71.2 wt % obtained in the earlier study. The lower coal conversions observed in this study are attributed to solvent effects.

These effects, as they relate to the solvent capabilities for coal-derived products, are expected to be more effective using mild-gasification liquids than crude oils.

The application of low-temperature hydrogenation as part of the pretreatment approach did provide an increase in the coal conversion for coprocessing experiments with Powder River Basin coal. There was not a comparable increase in coal conversion noted for Illinois No. 6 coal.

In the coke deposits on catalysts part of the study, the impact of using modified, supported catalysts on direct coal liquefaction yield was evaluated. An Amocat alumina support was modified with TiO_2, ZrO_2, and carbon by means of different techniques to coat the alumina surface and consequently change its surface properties. Four CoMo catalysts were then prepared using these modified supports. These catalysts possess essentially the same pore structure as Amocat 1A catalyst but with slightly smaller pore volumes and specific surface areas. The coal liquefaction experiments indicated that the catalysts' overall performance did not significantly depart from those of the Amocat 1A catalyst. However, differences in conversion yield did exist for the catalysts as a result of the different coating materials on the alumina surface.

CM/TA-I performed as well as the Amocat 1A catalyst in terms of cyclohexane solvent conversion. CM/ZA-I performed less efficiently than the CM/TA-I catalyst particularly in terms of cyclohexane and conversion yield. The difference is explained by the strong metal-support interaction (SMSI) effect of TiO_2 (but not ZrO_2) which enhances hydrocracking and hydrogenation activities and resists deactivation due to active metal sintering. CM/TA-D gave the poorest coal conversion yield. As a result of changes in the acidic properties of the surface by vapor deposition technique, coke had deposited on CM/TA-D which led to catalyst deactivation and, thus, poor conversion yield. CM/CA-P gave a coal conversion yield that was between the yields noted for catalysts CM/TA-I and CM/TA-D. Carbon coated on alumina overcomes the drawbacks associated with alumina and allows complete sulfiding of active metals.

The total aromatic carbons and, specifically, the amount of aromatic quaternary carbons of the coke deposited on the spent catalyst correlated with the coal conversion performance of the catalysts. Although a relationship is not necessarily a cause and effect correlation, the results indicate that the catalyst (CM/TA-D), which promotes the most coke deposition, also performs poorly in terms of coal liquefaction conversion. This relationship holds only for the catalysts that have TiO_2 and ZrO_2 deposited on the alumina support. The catalyst CM/CA-P with carbon deposited on the alumina support not only had a large amount of coke deposited on its surface after coal liquefaction service, but also performed quite well in terms of coal conversion yield.

The structural properties of the coke deposited on the spent catalysts depend on the initial pore volume of the fresh catalyst and on the percentage of surface coating of the alumina support by TiO_2, ZrO_2, and carbon. A linear relationship was found between the pore volume and the size of the aromatic cluster of the coke (the larger the pore volume, the greater the cluster size). Also, a linear relationship was observed between the amount of coating material and the number of aromatic carbons per aromatic cluster. When the amount of material coating the surface of the alumina support was high, the size of the aromatic cluster of the coke was small. This effect may be related to the pore volume in that a higher surface coating resulted in reduced pore volume.

For the hydrogen utilization subtask, the UOP bench-scale coprocessing of Illinois No. 6 coal with Lloydminster vacuum residue showed that only about 13% of the feed coal aromatic carbon was hydrogenated; whereas for Wilsonville two-stage catalytic/catalytic runs with a Black

Thunder subbituminous coal, almost two-thirds of the feed coal aromatic carbon was hydrogenated.

Gas production, both hydrocarbon and heteroatomic gases, accounted for most (90%) of the hydrogen consumed during UOP bench-scale coprocessing. During direct coal liquefaction at Wilsonville, most of the hydrogen consumed in the first stage for both run periods (G and J) involved heteroatom reactions. More than twice as many moles of hydrogen were consumed in the second stage during period J than during period G (46.3 versus 20.7) of Wilsonville Run 263. This was attributed to the addition of Criterion 324 support catalyst whose effect was to increase the slurry throughput during period J. For the Wilsonville overall two-stage liquefaction, Run 263, the major differences in the hydrogen consumption reactions between the two run periods involved the matrix cleavage and heteroatomic gas reactions. The greater number of moles of hydrogen consumed during period J could be accounted for mainly by the net hydrogen utilization for these reactions.

Conclusions

Conclusions from the study results are:

- The Lloydminster crude oil is a suitable solvent for coprocessing either of the coals studied. For the Illinois No. 6 coal, the coal conversion values obtained with Lloydminster crude oil were lower than those from experiments using a mild gasification-produced coal liquid.
- The application of low-temperature hydrogenation as part of the pretreatment approach provided significant increases in the liquid product yield for experiments coprocessing Powder River Basin coal.
- Higher yields of tetrahydrofuran-soluble material and oil fractions were observed from coprocessing the Powder River Basin coal as compared to coprocessing Illinois No. 6 coal.
- Amocat blank alumina support was modified with TiO_2, ZrO_2, and carbon by means of different techniques. Results of the coal liquefaction experiments indicated that the catalysts' overall performances did not significantly depart from those of the Amocat 1A catalyst. However, differences in conversion yield did exist for the catalysts as a result of different coating materials on the alumina surface.
- CM/TA-I performed as well as the Amocat 1A catalyst in terms of cyclohexane solvent conversion. CM/ZA-I performed less efficiently than the CM/TA-I catalyst particularly in terms of cyclohexane and conversion yield. The difference is explained by the SMSI effect of TiO_2 (but not ZrO_2) which enhances hydrocracking and hydrogenation activities and resists deactivation due to active metal sintering.
- CM/TA-D gave the poorest coal conversion yield. As a result of changes in the acidic properties of the surface by the vapor deposition technique, more carbonaceous residue (coke) had deposited on CM/TA-D leading to catalyst deactivation and, thus, poorer conversion yields.
- CM/CA-P gave a coal conversion yield that was between the yields noted for catalysts CM/TA-I and CM/TA-D. Carbon coated on alumina overcomes the drawbacks associated with alumina and allows complete sulfiding of active metals.
- The total aromatic carbons and aromatic quaternary carbons in the coke deposited on the spent catalysts correlated with coal conversion performance. This relationship holds only for catalysts that have TiO_2 and ZrO_2 deposited on the alumina support. CM/CA-P not only has a large amount of coke deposited on its surface after coal liquefaction service, but also performs quite well in terms of coal conversion yield.