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**Investigation of the ROPE[®] Process
Performance on Sunnyside Tar Sand**

Topical Report

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SUMMARY

Western Research Institute (WRI) is developing the Recycle Oil Pyrolysis and Extraction (ROPE[®]) process. Results to date indicate that this process could assist existing surface recovery process economics by producing higher yields of feedstocks from tar sand for the production of unleaded gasoline and advanced aviation turbine fuel. The ROPE[®] process also will assist in situ recovery process economics by producing a diluent to decrease the pour point and viscosity of produced bitumen for pipeline transportation and by producing a solvent for solvent extraction processes.

The main objectives of this research were to determine the optimum pyrolysis temperature for Sunnyside tar sand and to verify the operability and efficiency of the ROPE[®] process at steady-state conditions for production of feedstock materials. The experiments were conducted in the 2-inch screw pyrolysis reactor (SPR) developed by WRI.

Four 24-hour tests and one 105-hour test were performed in the 2-inch SPR using Sunnyside tar sand. The 24-hour tests were designed to predict the optimum pyrolysis temperature for oil yield. The 105-hour test was conducted to confirm the optimum pyrolysis temperature with sufficient operating time to reach steady-state conditions with respect to product compositions.

The following conclusions can be drawn from the Sunnyside tar sand 2-inch SPR tests:

- Sunnyside tar sand can be processed without any major operational difficulty by the ROPE[®] process.
- Oil yields greater than Fischer assay were obtained during the 2-inch SPR tests. Oil yield greater than 80 wt % of the bitumen was obtained from the 105-hour test. The variation in oil yield was small in the temperature range of 600 to 700°F (316 to 371°C), which provides a wide operating range. The pyrolysis temperature of the Sunnyside tar sand was approximately 100°F (38°C) lower than the optimum pyrolysis temperature for Asphalt Ridge tar sand.
- The ratio of heavy oil to light product oil is strongly dependent upon the pyrolysis temperature and increases with a decrease in the reaction temperature. The gas yield increases with the increase in pyrolysis temperature but the residual carbon in the spent sand decreases with the increase in pyrolysis temperature, reaches minimum at 675°F (357°C), and then increases with further increase in the pyrolysis temperature.
- ROPE[®] process product oils from Sunnyside tar sand have market application as blending stocks for the production of diesel fuels, but they are not suited for the production of unleaded gasoline or high-density aviation turbine

INTRODUCTION

Major obstacles to the commercialization of tar sand are the high costs associated with mining and processing, the upgrading of the raw tar sand oil, and refining the upgraded tar sand oil to produce salable products. In order to encourage tar sand commercialization with much reduced financial risks, new processing technologies need to be developed. The overall objective of the Western Research Institute has been to develop a new process that produces (1) oil yields greater than other existing pyrolysis processes, (2) transportation and aviation fuel feedstocks, (3) a diluent to decrease the pour point and viscosity of bitumen for pipelining, and (4) a solvent for extraction processes.

WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPE[®]) process. The process, in its entirety, consists of four major steps: (1) preheating and extracting the hydrocarbonaceous material with product oil, (2) retorting the extracted material at a low temperature ($\leq 750^{\circ}\text{F}/400^{\circ}\text{C}$) with recycle product oil, (3) completing the pyrolysis of residue at a higher temperature ($>750^{\circ}\text{F}/400^{\circ}\text{C}$) in the absence of product oil recycling, and (4) combusting the solid residue and pyrolysis gas to produce the required process heat.

WRI constructed and operated two reactor systems to test the ROPE[®] process. The smaller system (2-4 kg/hr solids-throughput capacity) is a 2-inch diameter screw pyrolysis reactor (SPR), which is used to conduct a large number of short-duration tests to determine optimum operating conditions (Figure 1). The larger system (20-40 kg/hr solids-throughput capacity) is a 6-inch diameter SPR, which is used to conduct longer duration tests to confirm the optimum conditions determined in the 2-inch SPR tests.

Previously, tests were conducted in the 2-inch SPR and 6-inch SPR using Asphalt Ridge, Utah, and Arroyo Grande, California, tar sand to determine the effects of pyrolysis temperature and residence time on the oil yield and product distribution. Also, these tests produced samples for the evaluation of product oil characteristics (Cha et al. 1987, 1988; Vaughn et al. 1990). The product oil samples were analyzed to determine the distribution of hydrocarbon types and to relate this distribution to that found in other fuel types.

Results from these tests suggest that the ROPE[®] process will assist existing surface and in situ recovery process economics in the following ways: (1) by producing a diluent to decrease the pour point and viscosity of produced bitumen for pipeline transportation, (2) by producing a solvent for solvent extraction processes, (3) and by producing feedstocks for the production of unleaded gasoline and advanced aviation turbine fuel.

Figure 1. Two-Inch Screw Pyrolysis Reactor System

OBJECTIVES

The objectives of this project were to determine the optimum pyrolysis temperature for the ROPE[®] process and to confirm that temperature at steady-state conditions by conducting tests in the 2-inch SPR. In addition, the characteristics of the product oil were determined.

EXPERIMENTAL APPARATUS AND PROCEDURE

Screw Pyrolysis Reactor Systems

The ROPE[®] process has been designed to facilitate both laboratory experimentation and commercial application. The design for the 2-inch system is shown in Figure 1. The design of the 6-inch SPR is similar to that for the 2-inch system. The systems consist of the following major subsystems:

- Feed system including a preheating screw reactor
- Pyrolysis screw reactor
- Drying (inclined pyrolysis) screw reactor
- Heavy product oil recycle system
- Reflux condensers and knockouts
- Sweep gas injection system
- Spent solids tank

The initial preheat screw conveyor controls the feed rate and temperature of tar sand into the reactor system. Batches of tar sand are weighed, sampled, and fed into the feed hopper. The feed rate is calculated by measuring the time required to empty the feed hopper, and the feed rate is controlled by adjusting the feed screw rotation speed. Heat, if required, is provided by electric heaters placed around the screw conveyor to preheat the feed. Product oil may also be added in this screw to initiate bitumen extraction from the tar sand. This screw reactor is sealed from the pyrolysis screw reactor by the inventory of product oil and tar sand that is in the system.

The slurry of sand, bitumen, and product oil then enters the pyrolysis screw reactor. Heavy oil is recycled cocurrently to the incoming slurry, and pyrolysis of the total mixture occurs. The residence time of the slurry mixture is controlled by the feed rate and the speed of the screw conveyor in the pyrolysis reactor. Electric heaters also surround the pyrolysis screw reactor, and the conversion of recycle heavy oil is controlled by adjusting the reactor temperature. The relative rates of recycle heavy oil conversion and hydrocarbon extraction are monitored by measuring the liquid levels in the product oil and heavy oil tanks.

Residual hydrocarbons on the sand, that escape extraction and evaporation in the pyrolysis screw reactor, are pyrolyzed at a higher temperature in the drying screw reactor. A level of heavy oil is maintained in the lowest section of the drying screw to provide a seal between the two pyrolysis systems. Electric heaters surrounding the

drying screw reactor heat the extracted sand to maximum temperatures of 800-975°F (427-524°C). This final pyrolysis temperature is controlled to produce a dry material containing only residual carbon and mineral matter. To minimize residual hydrocarbon pyrolysis at high temperatures in the drying screw reactor, the tar sand feed rate is adjusted to maximize extraction of hydrocarbons in the preheating and pyrolysis reactors.

Separate condensers and knockouts (KO1, KO2, KO3, and KO4) collect product oil from each of the three screw reactors. Condensed product oil from each knockout is measured separately to determine the effectiveness of the pyrolysis process. After these measurements are made, the product oils from the pyrolysis screw reactor (KO2 and KO3) are combined and retained. The product from KO4 is retained for use as product oil injection into the pyrolysis screw reactor. Condensed liquids from the preheating screw reactor (KO1) are also collected and retained separately.

Nitrogen is used to sweep distilled products from each of the pyrolysis and drying screw reactors. The nitrogen sweep rate and product gas concentration are measured to calculate the product gas production rate using a nitrogen balance. The outlet gas flow rate is also measured every hour using a bubble tube.

Spent sand is collected in a tank at the end of the drying screw reactor. The material is sampled periodically to determine if any changes are occurring in the spent sand properties. Each sample is weighed to determine the spent sand production rate.

Operational Procedures

Four 24-hour tests, test numbers 1 through 4, and one 105-hour test, number 5, were performed in the 2-inch SPR using Sunnyside tar sand. The 24-hour tests were started using SAE50 weight motor oil as the initial recycle oil (Table 1). The SAE50 weight was used to provide a commonality point between the initial tests and has been used in other test series to provide the same condition. The effect of using SAE50 weight and its lifetime in the reactor system are presently being studied. The 105-hour test was initiated with a mixture of KO2, KO3, and KO4 product oil produced during the 3rd and 4th 24-hour tests (Table 1). The KO2 product oil produced during the initial 33 hours of the 105-hour test was retained. The KO4 product oil and heavy oil produced for the initial 33 hours were recycled for the final 72 hour steady-state period of the 105-hour test. The 24-hour test conditions were used to determine the optimum pyrolysis temperature and to produce an initial recycle oil for the 105-hour test.

Based on the optimum pyrolysis temperature from the initial four tests, the 105-hour test was designed to produce oil at steady-state conditions. This long-term test was operated in two phases, an initial phase with a pyrolysis temperature of 600°F (316°C) to produce a larger amount of heavy recycle oil and a second phase at 650°F (343°C) to provide products in a steady-state environment. The heavy oil was not recycled in the initial phase, and the product oil produced from

previous tests was continuously injected. The initial 33-hour and final 72-hour phases were conducted without any break in operations. This test and all other tests were conducted with minimal operational problems.

For this reactor system operated at the set rpm value for each screw, the residence time for the preheat (feed), the pyrolysis, and the drying screws are 10, 20, and 30 min, respectively. These residence times were measured for each screw segment by using dry sand as feed and correlating screw rpm with the weight of the produced sand.

The bitumen content of the raw tar sand and the spent sand were determined by Soxhlet extraction using toluene and pyridine as the solvents. The extraction was performed by first extracting the tar sand with toluene for 16 hours. Then, the remaining bitumen was extracted with pyridine for an additional 16 hours. The solvent was removed from the extracts by rotary evaporation. The material extracted with both solvents was combined into a single sample prior to analysis. The residual carbon remaining on the sand after extraction and the residual carbon remaining on the spent sand were determined by weight loss from combustion at 400°C (750°F).

RESULTS AND DISCUSSION

Test Results

The tar sand used for these tests was prepared by crushing and screening large samples from a quarry at Sunnyside, Utah. A composite sample of the feed material for each test was prepared by taking approximately 10 g of the material during every charge to the feed hopper. The bitumen content for the composite material for each test was determined by solvent extraction with residual carbon determined by combustion of the extracted sand. The bitumen content ranged from 8.9 to 10.9 wt % with a total organic content of 9.5 to 11.6 wt % (Table 2). A mass balance Fisher assay of the Sunnyside tar sand was performed to provide a base line for comparison of the ROPE[®] process (Tables 3 and 4).

The bitumen in the Sunnyside tar sand is a heavy, viscous hydrocarbon with a specific gravity of 0.997 and an in-place viscosity exceeding 1.6×10^8 cP (Table 5). The bitumen is a near solid at ambient temperature with over 68% of the material having a boiling point greater than 1000°F (538°C). Sulfur content is only 0.46 wt % with a hydrogen-to-carbon ratio of 1.62.

For the four 24-hour tests, the overall material balances varied from 96.1 to 105.2 percent closure and are assumed acceptable for the determination of the optimum pyrolysis temperature (Table 6). Calculated product yields from the four 24-hour tests are summarized in Table 7. The determination of the optimum temperature was based on the residual carbon content in the spent sand (Figure 2) and the product yields. Based on the higher oil and the relatively low residual carbon content, the selected optimum pyrolysis temperature is 650°F (343°C).

Product gas yields and gas compositions for the four tests are presented in Tables 7 and 8, respectively. Generally, a significantly higher weight percent of total organics was produced as gas as the pyrolysis temperature was increased. The methane and higher hydrocarbon concentrations were higher for the 725°F (385°C) test, indicating that more cracking occurred. The higher rate of cracking is also evident by the higher residual carbon content.

The measured oil yield for the entire 105-hour test of 82.3 wt % (Table 9) is in excellent agreement with the 82.4 wt % oil yield for the 650°F (343°C) 24-hour test. The calculated oil yield of 81.2 wt % for this test (Table 10) also supports the measured oil yield and is 124% of the Fisher assay oil yield. The measured residual carbon content for the individual phases (the 600°F (316°C) and the uppermost 650°F (343°C) points on Figure 2) are also in agreement with the results of the 24-hour test and support the validity of the 105-hour test data. The product distribution for the individual test phases when compared with the distributions for the four initial tests gives an excellent correlation for the test series (Figure 3).

Overall material, total organic material, and elemental balances for the 105-hour test is contained in Tables 11, 12, and 13, respectively. Closure near 100 percent for the overall and total organic balances indicates a high degree of accuracy for the test data. Excellent carbon and hydrogen balance closures were obtained. The sulfur balance closure was high but is considered acceptable because of the small total amount of sulfur present in the entire materials system. Because of the problems in accurately measuring less than 1 wt % nitrogen content of the oils (Table 14) it was not possible to achieve the proper nitrogen balance. In addition, the ammonia in the product gas was not measured.

Product gas yields and compositions for the 105-hour test are presented in Tables 9 and 15, respectively. The weight percentage of total organics produced as gas for the entire 105-hour test, 13.2 %, is in close agreement with the percentage produced during the equivalent 24-hour test (12.1%). The methane and higher hydrocarbon concentrations were also similar indicating that the same degree of cracking had occurred. A comparison of the gas yields (Table 10) and composition of the gas (Table 15) for the separate phases of the 105-hour test show that more cracking occurred during the final 72 hours than in the first 33 hours. This comparison suggests that the optimum pyrolysis temperature may be closer to 600°F (316°C) than the predicted 650°F (343°C).

Figure 3 suggests that the change in the oil yield is very small in the pyrolysis temperature range of 600 to 700°F (316 to 371°C). Also, the pyrolysis temperature is approximately 100°F (38°C) lower than that determined for the Asphalt Ridge tar sand (Cha et al. 1987). Consequently, we expect that the process cost for Sunnyside tar sand will be lower than the cost for Asphalt Ridge tar sand.

Figure 2. Residual Carbon in Spent Sand for Sunnyside Tar Sand Tests

Figure 3. Product Distribution for Sunnyside Tar Sand Tests

End Use Evaluation of Product Oil

Hydrocarbon-type distributions were determined for three product oils from the two phases of the 105-hour test. Because this test was conducted with tar sand product oil only and for a long period of time, we felt that the hydrocarbon-type distributions would closely simulate commercial results.

Total saturates and aromatics for the three product oils were determined on composite samples for the individual phases. The KO2 and KO4 oils were evaluated to determine their potential market value as a fuel or fuel-blending stock (Tables 16 and 17). This evaluation divides the combined GC/MS data into distillate regions by correlating the boiling points of normal alkanes to their gas chromatographic retention times. Two distillate ranges were selected for this evaluation: IBP-350°F (IBP-177°C), which represents a motor gasoline or blending stock, and 350-700°F (177-371°C), which represents aviation turbine fuel, high-density aviation fuel feedstock, and diesel fuel.

Previous research on the ROPE[®] process demonstrated that the product composition is directly related to the chemical composition of the feed resource. Resources that are more aliphatic in nature form products that are aliphatic and are good sources of diesel fuel. Aromatic feeds produce aromatic products that are applicable for use as octane boosters for unleaded gasoline. The Sunnyside tar sand is an aliphatic tar sand and should form products that are aliphatic. This is confirmed by the low specific gravity values of the products from Sunnyside tar sand (Table 14).

Examination of the results in Table 16 shows that the hydrocarbon-type distribution of the IBP-350°F (IBP-177°C) distillate fractions does not compare well with that of unleaded gasoline. The major differences occur in the concentrations of the alkenes and alkylbenzenes. The products contain higher concentrations of alkenes and lower concentrations of alkylbenzenes than does unleaded gasoline. This difference in the distributions will adversely affect the octane rating of the fuel. These products will have to be hydrostabilized before they can be marketed, and this will hydrogenate the alkenes to produce additional alkanes. These will predominately be normal alkanes that do not have high octane values. Alkylbenzenes will have to be added to these products to produce an unleaded gasoline.

The results in Table 17 suggest that the 350-700°F (177-371°C) distillate range of the products may have market value as a blending stock for the production of diesel fuel. The products have high concentrations of alkanes and alkenes. The alkenes, upon hydrogenation, will form alkanes. The majority of the alkanes in the hydrotreated products will be normal alkanes and can be used as a blending stock to improve the cetane rating of diesel fuel. The products do not contain significant concentrations of dicyclic saturate or aromatic compounds and are not suited for the production of high-density aviation turbine fuels.

Table 1. Test Conditions for Sunnyside ROPE[®] Tests

Test Number	1	2	3	4	5
Pyrolysis Temperature, °F	700	725	675	650	650
Tar Sand Feed Rate, g/hr (nominal)	2,000	2,000	3,000	3,000	3,000
Starting Recycle Oil	SAE50	SAE50	SAE50C	SAE50	Product Oil
Test Duration, hr	24	24	24	25	105
Total Tar Sand Fed, g	40,000	36,000	70,5000	73,500	300,771

Table 2. Bitumen Content of Tar Sand Feeds

Test Number	1	2	3	4	5
Bitumen Content, wt % of tar sand	10.87	9.71	9.86	8.90	10.11
Residual Carbon After Extraction, wt % of tar sand	0.71	0.58	0.50	0.57	0.67
Total Organics, wt % of tar sand	11.58	10.29	10.36	9.47	10.78

Table 3. Product Distribution and Elemental Composition Determined by Fisher Assay Analysis of
Sunnyside Tar Sand

Sample	Mineral					Total
	Carbon	Carbon	Hydrogen	Nitrogen	Sulfur	
Oil, g	0	6.56	0.91	0.05	0.03	7.55
Water, g	0	0	0.04	0	0	0.04
Gas, g	0	0.34	0.10	0	0.01	0.45
Spent sand, g	0.46	2.01	0.05	0.04	0.49	89.29
Total, g	0.46	8.91	1.10	0.09	0.53	97.33 ^a
Feed, g	0.40	9.90	1.10	0.05	0.72	99.17 ^a
Recovery, %	115.00	90.00	100.00	180.00	73.61	99.13

^a The difference between the given values and 100% recovery is absence of a measured oxygen component.

**Table 4. Gas Composition Determination by Mass Balance Fisher Assay
Analysis of Sunnyside Tar Sand**

Gas	Mole % of Gas	Weight % of Gas
Hydrogen	33.11	3.47
Carbon monoxide	2.93	4.19
Carbon dioxide	10.09	23.00
Hydrogen sulfide	1.33	2.12
Carbonyl sulfide	0	0
Methane	30.57	24.83
Ethylene	2.49	3.54
Ethane	7.84	11.93
Propylene	3.59	7.64
Propane	4.26	9.49
Isobutane	0.74	1.08
n-Butylene	1.77	5.00
n-Butane	1.28	3.71
Total	100.00	100.00

Table 5. Properties of Sunnyside Bitumen

Carbon, wt %	86.3
Hydrogen, wt %	11.7
Nitrogen, wt %	0.87
Sulfur, wt %	0.46
Oxygen (by difference) wt %	0.67
H:C Ratio	1.62
Molecular Weight	680
Specific Gravity @60 °F, g/cm ³	0.997
Viscosity, cP	
@100 °F	1.6×10^8
@140 °F	1.4×10^7
@195 °F	1.6×10^5
Distillation Data, wt %	
IBP-400 °F	0
400-500 °F	0.5
500-600 °F	2.1
600-700 °F	4.2
700-800 °F	6.5
800-900 °F	9.7
900-1000 °F	8.2
>1000 °F	68.8

Table 6. Overall Material Balances for the 24-Hour Tests

Test Number:	1	2	3	4
IN				
Tar Sand, g	40,000	36,000	70,500	73,500
Starting Oil, g	<u>14,975</u>	<u>15,025</u>	<u>15,060</u>	<u>15,795</u>
Total In, g	54,975	51,025	85,560	89,295
OUT				
Spent Sand, g	32,420	31,363	61,412	72,401
Light Oil, g	6,582	7,375	9,321	8,027
Heavy Oil, g	13,182	9,452	10,664	12,743
Product Gas, g	<u>901</u>	<u>865</u>	<u>1,470</u>	<u>793</u>
Total Out, g	53,085	49,055	82,867	93,964
% Closure	96.6	96.1	96.9	105.2

* Total in for four tests = 280,855 g
 Total out for four tests = 278,971 g
 % closure = 99.3

Table 7. Calculated Product Yields for the 24-Hour Tests

Test Number:	1	2	3	4
Pyrolysis Temperature, °F	700	725	675	650
Gas Yield, wt % of bitumen	20.7	24.7	21.2	12.1
wt % of tar sand	2.25	2.40	2.09	1.08
C _{RS} , wt % of spent sand	0.91	1.63	0.78	1.11
C _{RE} , wt % of tar sand	0.71	0.58	0.50	0.57
Residual Carbon, C _{RB}				
wt % of tar sand	0.18	0.95	0.25	0.49
wt % of bitumen	1.9	9.2	2.5	4.4
Bitumen, g	4,348	3,496	6,951	6,542
wt % of tar sand	10.87	9.71	9.86	8.90
Oil, g	4,769	1,802	4,925	4,975
wt % of bitumen ^a	110.1	51.5	70.9	76.1
Calculated Oil Yield,				
wt % of bitumen	77.6	65.5	76.3	82.4

^a Measured oil yield

C_{RB} = Residual carbon produced from bitumen, wt % of tar sand

C_{RS} = Residual carbon in spent sand, wt % of spent sand

C_{RE} = Residual carbon remained in sand after solvent extraction,
wt % of tar sand

C_B = Bitumen content in tar sand, wt % of tar sand

Y_G = Product gas yield, wt % of tar sand

C_{RB} = (C_{RS} - C_{RE}) (1 - C_B/100), % of tar sand

Calculated oil yield = [(C_B - Y_G - C_{RB})/C_B] × 100, wt % of bitumen

Table 8. Composition of Product Gas for the 24-Hour Tests, volume percent on dry basis

Test Number:	4	3	1	2
Pyrolysis Temperature, °F	650	675	700	725
H ₂	28.00	19.65	21.20	14.86
CO	1.16	0.8	0.89	0.51
CO ₂	10.61	7.50	6.60	4.52
CH ₄	17.85	17.23	16.64	19.16
C ₂ H ₆	8.15	8.70	8.86	10.20
C ₂ H ₄	5.38	6.18	5.71	8.07
C ₃ H ₈	5.41	6.35	5.93	6.86
C ₃ H ₆	7.72	8.97	8.07	10.42
C ₄ s	9.37	15.64	14.50	13.84
C ₅ s	6.33	8.91	11.60	11.58
H ₂ S	0.02	0	0	0

Table 9. Measure Product Yields for the 105-Hour Test, weight percent of bitumen

Oil	82.3
Gas	13.2
Residual Carbon	5.6
Total	101.1

NOTE: If the extra organics is subtracted from oil, the oil yield would be 81.2% of bitumen.

Table 10. Calculated Oil Yield for the 105-Hour Test, weight percent of bitumen

	F.A.	Initial 33 hr	Final 72 hr	Overall
Pyrolysis Temp., °F	932	600	650	
Gas	4.7	10.6	14.4	13.2
Residual Carbon	29.8	6.3	5.2	5.6
Oil	65.5	83.1	80.4	81.2
Oil Yield, = 124% of F.A.				
F.A. = Fisher Assay				

Table 11. Overall Material Balance for the 105-Hour Test

IN	
Tar Sand, g	300,771
Product Oil, g	<u>23,789</u>
Total In, g	324,560
OUT	
Spent Sand, g	268,306
Light Oil (KO2), g	21,718
Light Oil (KO3), g	56
Light Oil (KO4), g	13,869
Heavy Oil, g	13,196
Product Gas, g	4,022
Product Water, g	<u>1,882</u>
Total Out, g	323,049
% Closure	99.5

Table 12. Total Organic Balance for the 105-Hour Test

IN	
Total Organics in Tar Sand, g	32,240
Starting Oil, g	<u>23,789</u>
Total, g	56,029
OUT	
Oil, g	48,839
Gas, g	4,022
Residual Carbon, g	<u>3,512</u>
Total, g	56,373
% Closure	99.7

Table 13. Elemental Balances for the 105-Hour Test

	Carbon	Hydrogen	Nitrogen	Sulfur
IN				
Tar Sand, g	28,072	3,559	265	140
Starting Oil, g	<u>20,554</u>	<u>3,093</u>	<u>24</u>	<u>95</u>
Total, g	48,626	6,652	289	235
OUT				
Spent Sand, g	3,511	-	-	-
Oil, g	42,152	5,903	154	186
Gas, g	<u>2,700</u>	<u>653</u>	<u>-</u>	<u>103</u>
Total, g	48,363	6,556	154	289
% Closure	99.5	98.6	53.3	123.0

Table 14. Oil Compositions and Properties for the 105-Hour Test

	Bitumen	Starting Product Oil	KO2 (1)	KO2 (2)	KO4	Heavy Oil
Carbon, wt %	86.3	86.4	86.5	86.3	86.5	86.1
Hydrogen, wt %	11.7	13.0	12.8	13.2	11.9	10.9
Nitrogen, wt %	0.87	0.1	0.1	0.1	0.4	0.5
Sulfur, wt %	0.46	0.4	0.3	0.3	0.4	0.5
Oxygen, wt %	0.67	0.1	0.3	0.1	0.8	2.0
H/C Ratio	1.62	1.81	1.78	1.84	1.65	1.52
Viscosity, cP @140°F	1.4 x 10 ⁷	6.35	3.95	2.15	8.45	893
Density, g/cm ³ @60°F	0.997		0.793	0.759	0.863	1.018

NOTE: KO2 (1) = Product oil from the initial 33-hour period

KO2 (2) = Product oil from the final 72-hour period

KO4 = Product oil from the final 72-hour period

Table 15. Composition of Product Gas for the 105-Hour Test, volume percent on dry basis

Component	Fisher Assay Gas	Initial 33 hr (Pyrolysis Temp. 600°F)	Final 72 hr (Pyrolysis Temp. 650°F)
H ₂	33.23	26.24	28.12
CO	2.94	1.68	1.61
CO ₂	10.13	15.43	9.41
CH ₄	30.68	20.78	22.04
C ₂ H ₆	7.87	7.44	7.50
C ₂ H ₄	2.50	3.99	4.01
C ₃ H ₈	4.28	2.83	5.24
C ₃ H ₆	3.60	5.71	5.34
C ₄ 's	3.80	9.44	11.39
C ₅ 's	-	4.15	3.29
H ₂ S	1.33	2.31	2.05

Table 16. Comparison of Hydrocarbon-Group Types Identified in the IBP-350°F Distillate Fraction from the 105-Hour Test Product Oils with Unleaded Gasoline

Hydrocarbon Type	Unleaded	Phase 1	Phase 2	
	Gasoline	KO2	KO2	KO4
<u>Saturate Hydrocarbons, wt %</u>				
Alkanes	24.1	21.8	25.1	24.8
Monocyclic alkanes	24.7	19.7	20.4	21.8
Alkenes	--	36.2	35.7	36.3
Dicyclic alkanes	<u>0.0</u>	<u>0.8</u>	<u>0.3</u>	<u>0.2</u>
Total	48.0	78.5	81.5	83.1
<u>Aromatic Hydrocarbons, wt %</u>				
Alkylbenzenes	41.9	20.8	18.3	16.7
Indanes/Tetralins	6.6	0.7	0.3	0.4
Napthalenes	2.7	0.0	0.0	0.0
Fluorenes	--	0.0	0.0	0.0
Anthracene/Phenanthrene	<u>--</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>
Total	51.2	21.5	18.6	17.1
Wt % of Sample	--	27.4	31.8	16.9

Note: All values are relative wt %

Table 17. Comparison of Hydrocarbon Group-Types Identified in the 350-700°F Distillate Fraction from the 105-Hour Test Product Oils with Prototype High-Density Fuel and Diesel Fuel

Hydrocarbon Type	Prototype		Diesel Fuel	Phase 1		Phase 2	
	High-Density Fuel			KO2	KO2	KO4	
<u>Saturate Hydrocarbons, wt %</u>							
Alkanes	4.6		52.7	30.0	36.3		34.5
Monocyclic alkanes	12.2		7.4	0.6	0.5		0.4
Alkenes	--		--	47.0	55.0		52.2
Dicyclic alkanes	54.6		0.0	1.3	0.2		0.1
Tricyclic alkanes	12.3		--	2.3	0.4		0.8
Total	83.7		60.1	81.2	92.4		88.0
<u>Aromatic Hydrocarbons, wt %</u>							
Alkylbenzenes	8.2		6.9	5.6	3.6		5.6
Indanes/Tetralins	6.8		10.5	9.3	3.0		4.2
Hexahydrofluorenes	1.1		--	--	--		--
Napthalenes	0.0		16.0	1.7	0.6		0.9
Hexahydrophenanthrenes	--		--	--	--		--
Dihydrofluorenes	0.1		--	--	--		--
Fluorenes	--		6.2	1.0	0.3		0.7
Anthracene/Phenanthrene	0.0		0.2	1.2	0.0		0.7
Dihdropyrenes	--		--	--	--		--
Total	16.2		39.8	18.8	7.5		12.1
Wt % of Sample	--		--	60.5	57.2		69.0

Note: All values are relative wt %

Note: All values are relative wt %

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the Sunnyside tar sand 2-inch SPR tests:

- Tar sand can be processed using the ROPE[®] process without any major operational difficulty.
- Oil yields greater than Fischer assay were obtained when the Sunnyside tar sand was pyrolyzed in the presence of recycled oil at 600 to 700°F (316 to 371°C). An oil yield greater than 80 wt % was obtained from the 105-hour test.
- The pyrolysis temperature of Sunnyside tar sand in the presence of recycled oil was approximately 100°F (38°C) lower than the pyrolysis temperature of Asphalt Ridge tar sand. Also, the oil yield did not change significantly in the pyrolysis temperature of range 600 to 700°F (316 to 371°C), which will provide a wide operating window.
- The gas yield was more than two times the gas yield for Asphalt Ridge tar sand, but the residual carbon remaining on the spent sand was less than one-half of that for the Asphalt Ridge tar sand.
- The gas yield increases with the increase in the pyrolysis temperature. However, the residual carbon on the spent sand decreases with temperature, reaches the minimum at about 675°F (357°C), and increases with further increase in the pyrolysis temperature.
- The ratio of heavy oil to light product oil is strongly dependent upon the pyrolysis temperature and increases as the reaction temperature decreases.
- ROPE[®] process product oils from Sunnyside tar sand have market application as blending stocks for the production of diesel fuels, but they are not suited for the production of unleaded gasoline or high-density aviation turbine fuels.

We recommend that additional SPR tests be conducted with tar sand from AMOCO's actual site area and product oil from AMOCO's processing of Sunnyside tar sand as initial recycle oil. One test should be a 24-hour 2-inch SPR tests at the pyrolysis temperature designated by AMOCO for varification of operational parameters. If the parameters agree with those from prior tests, then a 6-inch SPR test should be conducted for a minimum of 5 days to provide sufficient product oils for refining studies. These two tests will provide additional data for the economic evaluation and scale-up of the process.

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REFERENCES

- Cha, C.Y., F.D. Guffey, and L.J. Romanowski, 1987, Tar Sand Pyrolysis with Product Oil Recycling--Progress Report. Laramie, WY, DOE Report DOE/MC/11076-2642.
- Cha, C.Y., L.J. Fahy, and F.D. Guffey, 1988, Asphalt Ridge Tar Sand Recovery Using the ROPE[®] Process. Laramie, WY, DOE Report DOE/MC/11076-2659.
- Vaughn, P., C.Y. Cha, and F.D. Guffey, 1990, ROPE[®] Processing of a California Tar Sand in a Two-Inch Screw Reactor. Laramie, WY, DOE report in progress.

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