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PRESSURIZED FLUIDIZED-BED HYDRORETORTING OF RAW AND BENEFICIATED EASTERN OIL SHALES

by

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Abstract

The Institute of Gas Technology (IGT) with U.S. Department of Energy (DOE) support has developed a pressurized fluidized-bed hydroretorting (PFH) process for Eastern oil shales. Bench-scale tests have been conducted with raw and beneficiated shales in an advanced multipurpose research reactor (AMRR). Raw Alabama shale and raw and beneficiated Indiana shales were retorted at 515°C using hydrogen pressures of 4 and 7 MPa. Shale feed rates to the AMRR were 15 to 34 kg/h. High oil yields and carbon conversions were achieved in all tests. Oil yield from Alabama shale hydroretorted at 7 MPa was 200% of Fischer Assay. Raw and beneficiated Indiana shales hydroretorted at 7 MPa produced oil yields of 170% to 195% of Fischer Assay, respectively. Total carbon conversions were greater than 70% for all tests conducted at 7 MPa.

Introduction

A number of retorting approaches have been tested for hydrogen deficient Eastern oil shales over the past decade, however the results of these tests show that the highest oil yields are obtained by retorting these shales in the presence of hydrogen at elevated pressures.[1,2] A recent economic evaluation of shale retorting conducted by Foster Wheeler,[3] under contract to the U.S. Department of Energy (DOE), has shown that fluidized-bed retorting of Eastern shale produces a lower cost oil than does moving-bed or fluidized-bed retorting of Western oil shale.

Most of the oil shale research work conducted by IGT and funded [by the U.S. DOE, Phillips Petroleum Co., the Gas Research Institute (GRI), and the American Gas Association (A.G.A.)] through 1987 focused on the development of the process for moving-bed hydroretorting. The results of this work concluded that oil yield decreases and gas yield increases with increasing particle size. Hydroretorting of beneficiated shale significantly improves the overall economics of producing oil, and process economics could be significantly improved by hydroretorting small particles and developing advanced beneficiation technology for oil shale.

Efforts to improve the economics of hydroretorting have led to the development of a second-generation hydroretorting process, the PFH process, at IGT. A DOE-funded program for the development of an advanced hydroretorting process has enabled a database to be generated for the PFH processing of Eastern shales in laboratory-scale batch and continuous units.[4]

The exact components that make up the integrated PFH process, depend upon whether the feedstock is raw or beneficiated shale. A block flow diagram of major integrated PFH process components for beneficiated shale is shown in

Figure 1. This paper will describe results applicable to the retorting section of the PFH process.

The PFH process has several advantages over moving-bed hydroretorting. Moving-bed hydroretorting requires the feed shale to be sized from 0.3 to 2.5 cm. Mining and crushing operations reduce approximately 20% of the resource to fines that can not be processed in moving-bed retorts.[5] Since the PFH process uses shale sized below 0.3 cm, the entire shale resource can be utilized. In addition to full resource utilization, the PFH process produces higher oil yields than moving bed hydroretorting because oil yield decreases with increasing particle size above 0.3 cm.[6] This effect is shown in Figure 2.

The fluidized bed provides the opportunity for higher oil yields as well as higher selectivity to oil, lower hydrogen consumption, shorter shale residence time, and greater shale throughput. The smaller shale particles used in the PFH process improve the carbon selectivity to oil. Hydrogen consumption is reduced because it takes about half as much hydrogen to make oil ($CH_{1.4}$) as it does to make gas (CH_3). Compared with the moving-bed hydroretorting process, the PFH process should require much shorter shale residence time. The use of a fluidized bed and smaller shale particles will result in large increases in the mass and heat transfer rates. New Albany shale fluidization rate studies in nitrogen, argon, and steam environments have found short residence times to be effective.[7,8] Shorter residence times in a fluidized bed means PFH reactors can be smaller and less costly than moving-bed hydroretorting reactors.

Results of four bench-scale tests are presented in this paper. All tests were conducted at approximately 520°C with a shale residence time of 25 minutes. A shale size consist of -20+100 mesh was used for these bench-scale tests. Superficial gas velocities were at or above the shale complete fluidization velocities for all tests. Two tests, OSAMRR-4 and -5 were conducted with Alabama Chattanooga shale at pressures of 4.14 and 6.89 MPa, respectively. Two tests, OSAMRR-9 and OSAMRR-10, were conducted with raw and beneficiated Indiana New Albany shale at a hydrogen pressure of 6.89 MPa.

Detailed results of the four tests are presented below. Carbon conversions, oil yields and gravities, sulfur conversions, product compositions and properties are also presented and discussed.

Analyses of the feed shales used for all the bench-scale tests are presented in Table 1. Feed ultimate analyses, heating values, densities and sieve analyses are presented for the raw Alabama Chattanooga shale and the raw and beneficiated Indiana New Albany shales. The feeds used for both tests using Alabama shale were from the same riffled batch. A sample of the raw Indiana New Albany shale was crushed and beneficiated then briquetted and sized to a nominal -20+50 mesh before testing. The shale was ground to a nominal 10-micron size and then beneficiated by column flotation to concentrate the kerogen by removing the mineral matter. The shale carbon content was increased by beneficiation from 13.0% to 28.1% which also resulted in a Fischer Assay oil yield increase from 54 to 108 l/tonne. The sulfur contents of the two feed shales from Indiana were similar which corresponds to a 50% reduction in sulfur-to-carbon ratio after beneficiation.

A schematic diagram of the bench-scale unit including auxiliary equipment used for the PFH tests reported here is shown in Figure 3. The bench-scale unit is an experimental fluidization facility designed to operate at any combination of temperatures up to 1000°C and pressures up to 7 MPa. The major pieces of equipment include a feed hopper, reactor, residue receiver, filters, gas-fired preheater, coolers and condensers, and recycle compressors. A sketch of the reactor and pressure shell construction is shown in Figure 4. Details of the construction and operation of the bench-scale unit are available in a previous publication.[9]

Discussion of Results

A summary of the operating conditions and results of tests conducted with Alabama shale, OSAMRR-4 and -5, is presented in Table 2. Results of OSAMRR-9 and -10 conducted with raw Indiana New Albany shale and beneficiated Indiana shale at the same nominal operating conditions of 6.89 MPa, and a residence time of 30 minutes is also shown in Table 2. Beneficiated shale was briquetted (without binder) and sized to a nominal -20+50 mesh before testing. The experimental operating conditions listed include the temperature, pressure, shale residence time, shale and gas feed rates, gas superficial velocity, and steady-state run times. Results include the carbon and sulfur conversions, oil yield, and the oil specific gravity.

Carbon conversion to oil for OSAMRR-4 using Alabama shale was 42.1%. This corresponds

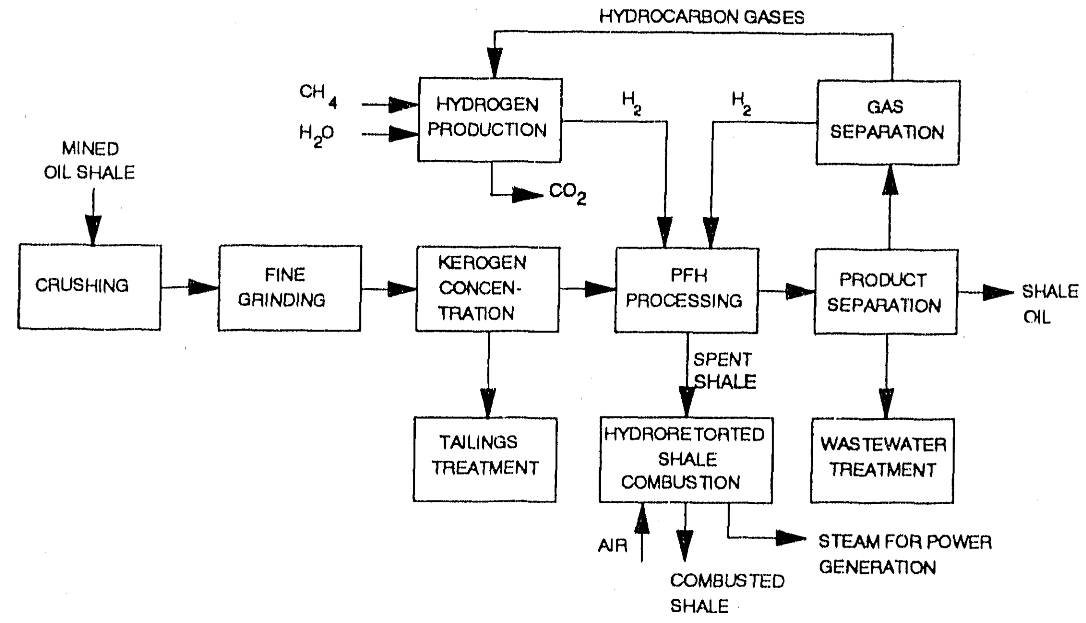

Figure 1. Major components of PFH process concept.

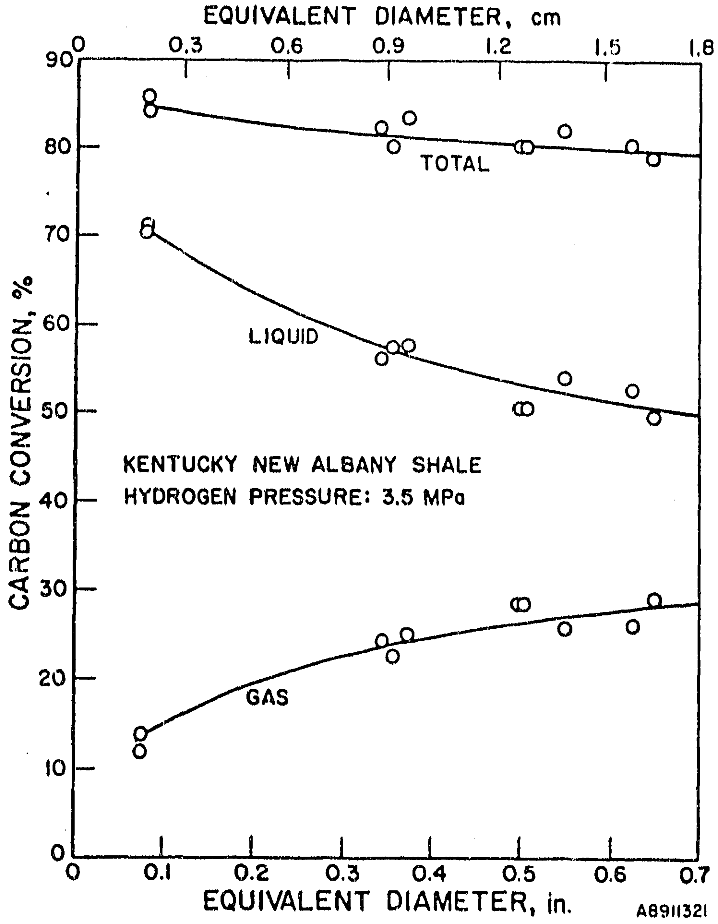

Figure 2. Variation of oil and gas yield with particle size.

Table 1. Feed Shale Analyses.

Test	OSAMRR-4,-5		OSAMRR-9		OSAMRR-10	
Sample	Feed Al Shale		Feed In Shale		Feed IN Ben. Shale	
Moisture, wt %	0.94		1.56		1.88	
Ultimate Analysis, wt % dry						
Ash	73.59		80.25		61.11	
Carbon	16.02		13.03		28.10	
Organic Carbon		15.94		12.95		28.05
CO_2		0.24		0.28		0.19
Hydrogen	1.57		1.48		2.81	
Sulfur	9.05		2.93		2.77	
Nitrogen	0.49		0.35		0.74	
High-Temperature Water	3.26		3.56		6.09	
Oxygen (from HTW)		2.90		3.16		5.41
Gross Heating Value, MJ/kg	7.60		5.81		12.5	
Density, g/cc						
Bulk	0.98		0.99		0.71	
Particle (Hg)	2.00		1.91		1.22	
True (He)	2.28		2.32		1.92	
Sieve Analysis (wt %), mesh						
-20	4.4		1.1		0.3	
-20+30	23.4		30.3		23.4	
-30+40	24.9		23.5		26.1	
-40+60	25.7		21.9		23.3	
-60+80	15.1		13.3		9.2	
-80+100	5.7		6.4		3.7	
-100+Pan	0.8		3.5		14.0	
Total	100.0		100.0		100.0	

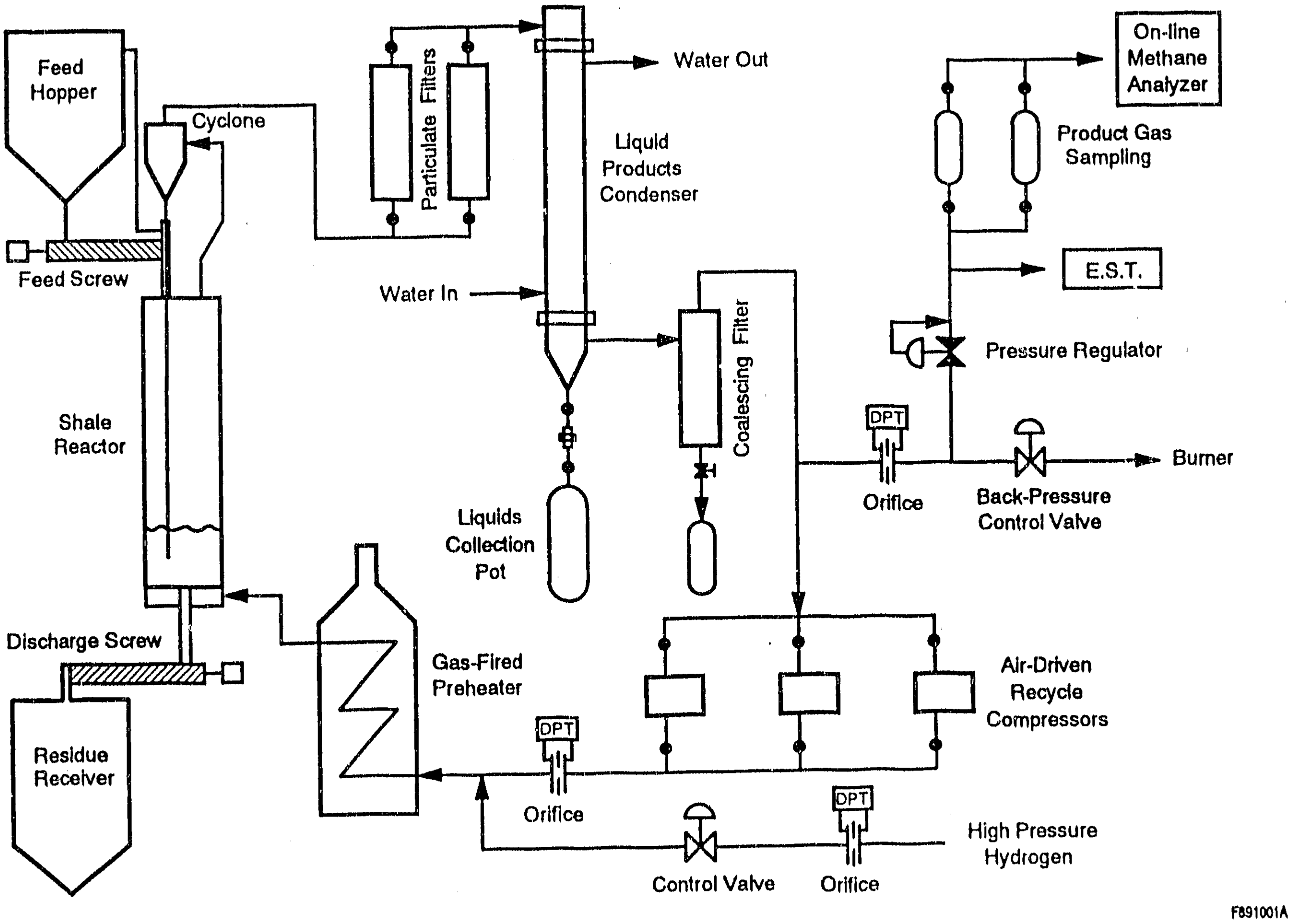

Figure 3. Schematic diagram of the bench-scale PFH test unit.

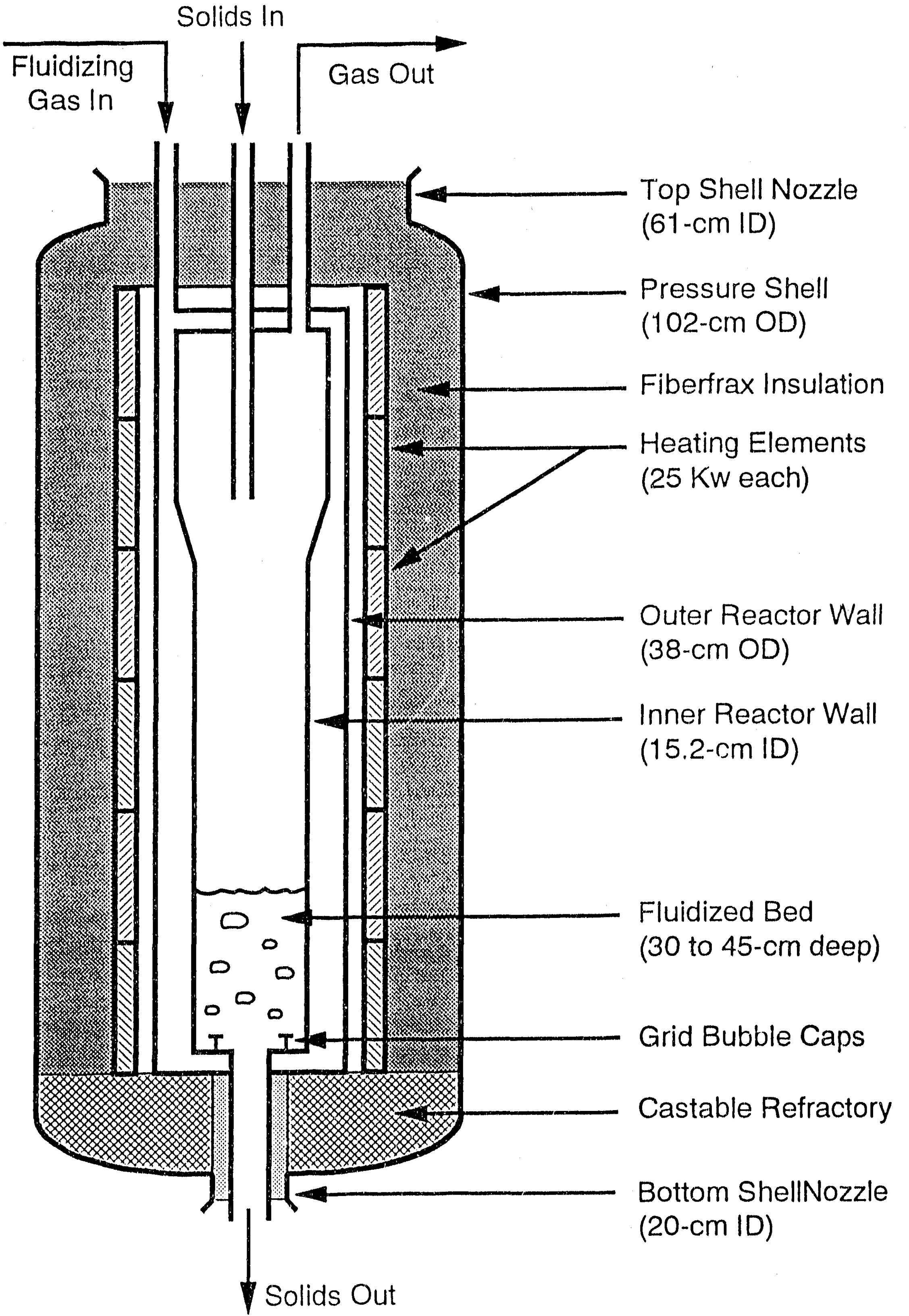

Figure 4. AMRR reactor and pressure shell construction.

Table 2. Operating Conditions and Results.

Test	OSAMRR-4	OSAMRR-5	OSAMRR-9	OSAMRR-10
Shale	Alabama	Alabama	Indiana	Indiana Beneficiated
Operating Conditions				
Average Temperature, °C				
Reactor	519	523	513	519
Reactor Residence Time, min	26	24	26	19
Pressure, MPa	4.14	6.89	6.89	6.89
Shale Particle Size, mesh	-20+100	-20+100	-20+100	-20+50
Shale Feed Rate, kg/h	15.0	14.9	34.3	25.1
Gas Rate, m^3/h	393	574	561	501
Gas Velocities, m/s				
Superficial	0.38	0.34	0.34	0.30
Complete Fluidization	0.36	0.32	0.32	0.26
Shale Feeding Time, h	3.2	3.6	3.1	3.3
Steady-State Period, h	2.0	2.0	1.8	1.5
Product Carbon, % feed carbon				
Residue Shale	37.4	27.1	25.3	19.2
Product Gas	20.1	14.6	15.6	19.0
Oil	42.1	58.1	58.9	61.8
Water (as soluble hydrocarbon)	0.4	0.2	0.2	0.0
Total	100.0	100.0	100.0	100.0
Oil Yield, l/tonne	78.7	106.3	91.4	211.3
Oil Yield, % of FA	149	201	170	195
Oil Density, °API	7.8	5.2	10.6	12.5
Oil Density, g/ml	1.016	1.035	0.996	0.983
Product Sulfur, % feed sulfur				
Residue Shale	46.4	45.0	51.9	69.4
Product Gas	50.3	51.3	44.8	16.8
Oil	2.3	2.7	2.8	6.9
Water	1.0	1.0	0.5	6.9
Total	100.0	100.0	100.0	100.0

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to an oil yield of 149% of Fischer Assay. When the pressure was raised to 6.89 MPa in OSAMRR-5, the carbon conversion to oil increased to 58.1% of the feed carbon or 201% of the Fischer Assay oil yield. Carbon conversions to gas in the AMRR tests -4 and -5 were 20.1% and 14.6%, respectively.

The reconciled carbon conversions to oil for tests utilizing the raw and beneficiated Indiana New Albany shale were 59% and 62% corresponding to 170% and 195% of the Fischer Assay oil yield. Shale carbon conversions to oil and gas with the beneficiated shale feed were equal to or greater than the carbon conversions for raw shale.

Feed and residue shale ultimate analyses, heating values, densities and sieve analyses are presented in Table 3. PFH processing was found to reduce the Alabama shale bulk density by 5% to 10%. This small reduction is typical for the hydroretorting of Eastern shales. The feed shale particle and true densities are similar indicating a low particle porosity. Hydroretorting significantly increases particle porosity as indicated by the large difference in residue shale particle and true densities.

Densities of the Indiana New Albany shale were lower after beneficiation reflecting the increase in organic matter. The higher porosity of the densified beneficiated shale indicates a higher porosity than for the raw shale. PFH processing reduced the raw shale bulk density of the Indiana shale by 10%. The reduction in bulk density of the beneficiated shale due to PFH processing was greater because more organic material is converted to products from the shale. Hydroretorting significantly increased the porosity of both shales as indicated by the large difference in residue shale particle and true densities.

Only low levels of particle attrition were seen in the tests using Alabama shale feed. Forty-seven percent of the feed shale was below 40 mesh including 1% below 100 mesh. The residue shales were 44% and 57% below 40 mesh including 5% and 10% below 100 mesh. Fines collected in the cyclone represented 10% and 20% of the feed shale for Tests OSAMRR-4 and -5, respectively.

Particle attrition was low for both the raw and beneficiated Indiana New Albany shales. Retorting raw shale increased the -40 mesh fraction from 45% to 48%. Fines collected in the cyclone accounted for 9% of the feed shale. The beneficiated shale had 50 weight percent below 40 mesh both before and after beneficiation. Approximately 21% of the feed beneficiated shale was recovered as cyclone fines. Fines generation from the beneficiated shale was not excessive, and the fines could easily be recycled to the reactor.

Representative samples of product gas analyses from the steady-state periods for the tests which utilized Alabama shale as well as Indiana New Albany raw and beneficiated shale are presented in Table 4. The gas analyses shown are typical of the analyses throughout the steady-state period of both tests. The high hydrogen concentrations and low concentrations of hydrocarbons and hydrogen sulfide are a result of the high hydrogen-to-shale ratio used in these tests.

Product oil analyses are presented in Table 5. This table also includes the oil specific gravities, heating values, concentrations of selected trace metals and distillation data. Distillation was by ASTM method D86.

Concentrations of the selected trace metals for hydroretorting Alabama shale at 4.14 and 6.89 MPa are similar. Concentrations of arsenic and vanadium in the oil show hydroretorting Indiana raw and beneficiated shale are an order of magnitude lower than for the shale oil produced from Alabama shale.

The sulfur and nitrogen as well as the trace metals in the oils can be removed by conventional technology and the shale oil can be upgraded by conventional hydrotreating procedures.

Product oil group type analyses are presented in Table 6. Analyses show that the majority of the oil from all tests is composed of aromatic and polar compounds. Most of the hydroretorted shale product oil (88% to 96%) was found to be soluble in hexane, and was also analyzed for group types. One- and two-ring aromatics made up almost half (40% to 50%) of the oils. Aliphatics accounted for 13% to 22% of the oil, and 4-ring and polar compounds make up 27% to 31% of the oil. The level of aliphatic compounds was higher and polar compounds were lower for the Indiana shale oil compared to the Alabama shale oil.

The Environmental Sampling Train (EST) was used for all tests. A fraction of the AMRR product gas was passed through acid and base

Table 3. Feed and Residue Shale Analyses.

Test		OSAMRR-4	OSAMRR-5		OSAMRR-9		OSAMRR-10
Sample	Feed AL Shale	Res. Shale	Res. Shale	Feed IN Shale	Res. Shale	Feed IN Ben. Shale	Res. Shale
Moisture, wt %	0.94	0.00	0.00	1.56	0.00	1.88	0.00
Ultimate Analysis, wt % dry							
Ash	73.59	88.28	90.61	80.25	93.48	61.11	88.42
Carbon	16.02	7.19	5.34	13.03	3.84	28.10	7.81
Organic Carbon	15.94	6.97	5.05	12.95	3.77	28.05	7.34
CO_2	0.24	0.79	1.06	0.28	0.24	0.19	1.74
Hydrogen	1.57	0.47	0.38	1.48	0.40	2.81	0.47
Sulfur	9.05	5.04	5.01	2.93	1.77	2.77	2.78
Nitrogen	0.49	0.34	0.24	0.35	0.10	0.74	0.15
High-Temperature Water	3.26	2.19	2.15	3.56	2.58	6.09	3.52
Oxygen (from HTW)	2.90	1.94	1.91	3.16	2.29	5.41	3.12
Gross Heating Value, MJ/kg	7.60	3.56	2.85	5.81	1.53	12.5	3.20
Density, g/cc							
Bulk	0.98	0.95	0.90	0.99	0.87	0.71	0.55
Particle (Hg)	2.00	1.67	1.67	1.91	1.64	1.22	0.88
True (He)	2.28	2.64	2.64	2.32	2.65	1.92	2.60
Sieve Analysis (wt %), mesh							
+20	4.4	1.9	0.3	1.1	1.5	0.3	0.4
-20+30	23.4	28.6	17.9	30.3	27.3	23.4	23.0
-30+40	24.9	25.1	24.7	23.5	23.6	26.1	27.1
-40+60	25.7	21.8	25.1	21.9	21.6	23.3	25.7
-60+80	15.1	11.6	14.3	13.3	13.0	9.2	11.4
-80+100	5.7	5.7	7.3	6.4	6.9	3.7	5.0
-100+Pan	0.8	5.3	10.4	3.5	6.1	14.0	7.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 4. Product Gas Compositions.

Test	OSAMRR-4	OSAMMR-5	OSAMRR-9	OSAMRR-10
Component,* mol %				
Hydrogen	98.75	99.07	99.09	98.57
Carbon Dioxide	0.00	0.00	0.03	0.04
Carbon Monoxide	0.00	0.00	0.01	0.00
Methane	0.76	0.34	0.40	0.69
Ethane	0.25	0.16	0.24	0.44
Propane	0.02	0.05	0.07	0.12
Propene	0.00	0.00	0.00	0.02
i-Butane	0.01	0.01	0.01	0.01
n-Butane	0.00	0.01	0.01	0.02
C_6+	0.01	0.01	0.01	0.02
Hydrogen Sulfide	0.20	0.35	0.13	0.07
Total	100.00	100.00	100.00	100.00

* Representative steady-state gas.

Table 5. Product Oil Elemental Analyses and Distillation Data.

Test	OSAMRR-4	OSAMRR-5	OSAMRR-9	OSAMRR-10
Ultimate Analysis, wt %				
Ash	0.02	0.00	0.00	0.00
Carbon	85.74	85.91	85.80	84.94
Hydrogen	9.44	9.05	9.61	9.75
Sulfur	2.55	2.24	0.91	0.94
Nitrogen	1.41	1.52	1.84	1.94
Arsenic	6.3	6.2	0.72	0.39
Iron	7.9	11	21	10
Nickel	36	28	16	9.2
Vanadium	23	12	2.3	1.5
Specific Gravity (15°/15°C)	1.016	1.035	0.996	0.983
Gross Calorific Value, MJ/kg	40.0	40.3	40.5	41.0
Distillation wt % (D86), °C				
IBP*	102	102	104	118
5	217	224	182	165
10	236	253	210	192
20	263	289	258	244
30	316	311	298	288
40	344	353	314	331
50	370	376	358	364
60	391	394	378	385
70	403	--	388	399
Oil Recovery by 404°C, wt %	75.0	69.0	78.0	73.0

* Initial Boiling Point.

Table 6. Product Oil Hydrocarbon Group Types.

Test	OSAMRR-4	OSAMRR-5	OSAMRR-9	OSAMRR-10
Hexane Soluble Groups, * wt %	94	88	94	96
Aliphatics	17	13	21	22
1-Ring	35	30	23	23
2-Ring	15	14	18	17
3-Ring	<0.5	<0.5	3	3
4-Ring + Polar Groups	27	31	29	31
Hexane Insoluble Groups, wt %	6	12	6	4
Total	100	100	100	100

* Oil; Hexane dilution of 1:100.

scrubbers during steady-state operation. A 3N HCl solution was used for the acid scrubber, and a 6N NaOH solution was used for the base scrubber.

Results from acid and base scrub analyses are similar for the tests. Only a small amount of oil was entrained in the product gas and passed through the coalescing filters to be collected in the acid scrub. Nitrogen was recovered as ammonia with only trace levels of nitrates and nitrites observed. Sulfur recovery was mostly in the form of sulfides with little sulfate collected. Very low levels of cyanides and thiocyanates were detected. The compounds detected in the EST were all observed in low concentrations representing less than 1% of the converted carbon, nitrogen, and sulfur.

Summary of Results

Testing of Eatern shales in a bench-scale unit has produced high oil yields, 195% to 201% of Fischer Assay. Product oil produced from bench-scale PFH processing will be used for future upgrading studies. Hydroretorted beneficiated shale was produced for future combustion evaluation.

Acknowledgment

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