

Combustion characteristics of hydrotorted Alabama oil shale

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Pressurized fluidized bed hydrotorting of beneficiated eastern USA oil shale leaves sufficient carbon (15–27 wt%) in the retorted shale to warrant utilization of that calorific value by combustion. A sample of hydrotorted shale from a bench scale unit test (oil yield was 233% of Fischer Assay) was used as a feedstock for combustion tests using air. The tests were conducted at 815–1080°C, 0.1–7 MPa and residence times from 1 to 30 min in a thermobalance unit and a continuous (0.5 kg h⁻¹) fluidized bed laboratory scale unit. Thermobalance tests indicate that combustion of the shale begins at 260–315°C depending on the oxygen partial pressure used. Carbon conversions up to 100%, with greater than 99.5% recovery, of the gross calorific value of the shale were achieved.

(Keywords: oil shale; hydrotorting; combustion characteristics)

Results of oil shale retorting approaches for eastern USA oil shale during the last decade have clearly demonstrated that the highest possible oil yields are achieved by retorting in the presence of hydrogen at elevated pressure^{1,2}.

Research work conducted by the Institute of Gas Technology (IGT) has indicated that hydrotorting of beneficiated shale significantly improves the overall economics of producing oil. Process economics can be significantly improved by hydrotorting small particles and developing advanced beneficiation technology for oil shale. Efforts to improve economics of hydrotorting have led to the development of a second-generation process, the pressurized fluidized bed hydrotorting (PFH) process at IGT.

Components of the first PFH design (PFH-I) are shown in *Figure 1*. In this process, hydrogen is produced by steam reforming of methane. A non-conventional hydrogen generation method is used in a new PFH-II design presently being developed. Information on PFH processing of raw and beneficiated shales is available in previous publications^{3,4}. Beneficiated shale residue from both processes contains carbon which can be utilized to improve the PFH energy efficiency. Combustion results relating to the PFH-I process are presented.

EXPERIMENTAL

The combustion characteristics of hydrotorted beneficiated Alabama shale were determined in a series of thermogravimetric analysis (TGA) tests. The tests were conducted in an existing high pressure, high temperature thermobalance unit. The unit, shown schematically in

Figure 2, senses and records the instantaneous weight of a sample undergoing reaction at temperatures and pressures up to 1093°C and 7.0 MPa.

The thermobalance reactor is constructed from type 316 stainless steel pipe positioned inside a pressure shell. Furnace elements are placed inside the pressure shell (and outside the reactor tube). The pressure shell is filled with nitrogen and maintained at the same pressure as the reactor using a differential pressure controller. The feed gas flow is controlled with a mass flow controller. The exit gas system contains a back pressure controller, a dry test meter for measuring total gas flow, a liquid knockout trap and a gas sampling loop.

In a typical thermobalance test, a weighed, representative 1–2 g sample of hydrotorted shale is held in a stainless steel screen basket suspended from a force transducer by a stainless steel wire. The basket is pretreated at test conditions to prevent weight changes of the basket during the test. Thus, the transducer senses only changes in the weight of the sample in the basket. Both isothermal and non-isothermal tests are conducted in the unit. The sample basket is lowered into and raised out of the heated zone as required.

Laboratory scale combustion tests were conducted in a 5.08 cm diameter fluidized bed reactor. A schematic diagram of the unit configuration is shown in *Figure 3*. All vessels and lines are 316 stainless steel, and glass bombs are used to collect gas samples. A two-zone electric furnace is used to heat the reactor. All exit gas is metered, passed through a sodium hydroxide scrubber and then vented.

Continuous operation is achieved by using a calibrated feed screw to transfer shale from the feed hopper to the reactor. Shale is fed to the bottom of the reactor and discharged from the reactor through an overflow tube. Unsteady state and steady state receivers are used to

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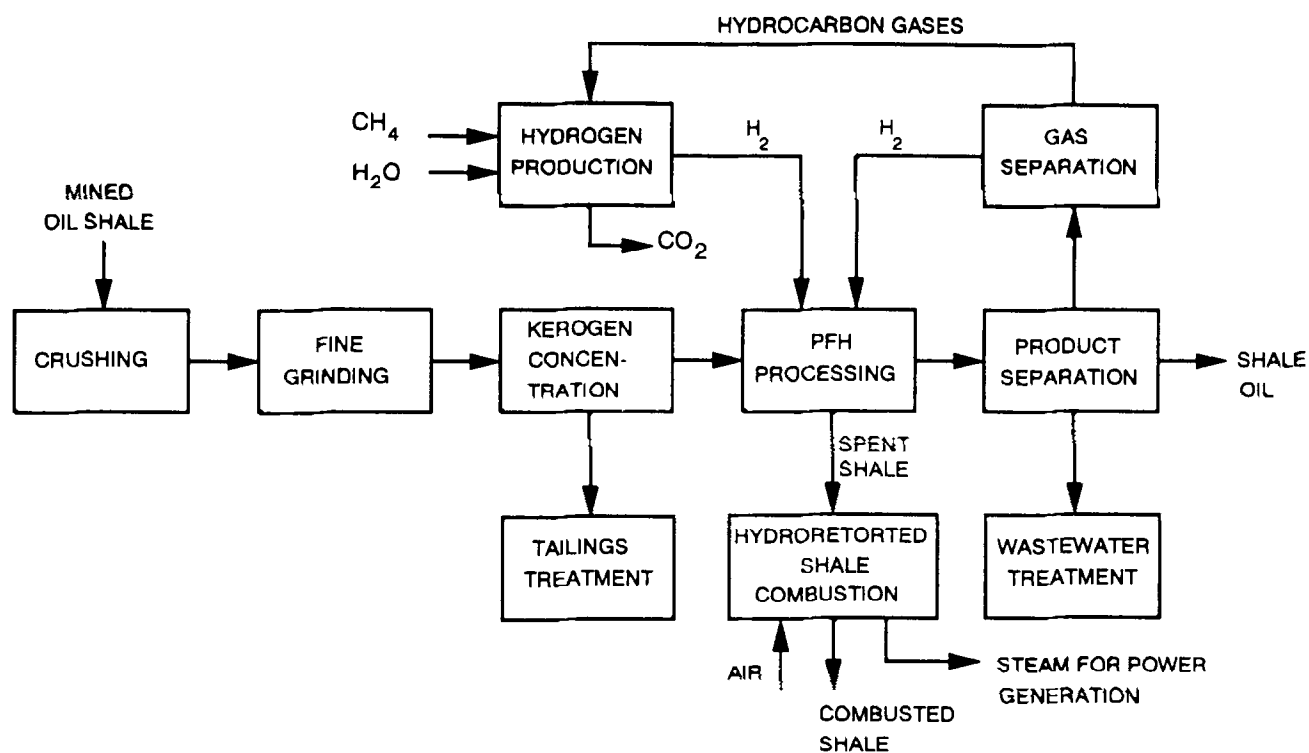


Figure 1 Major components of PFH-I process concept

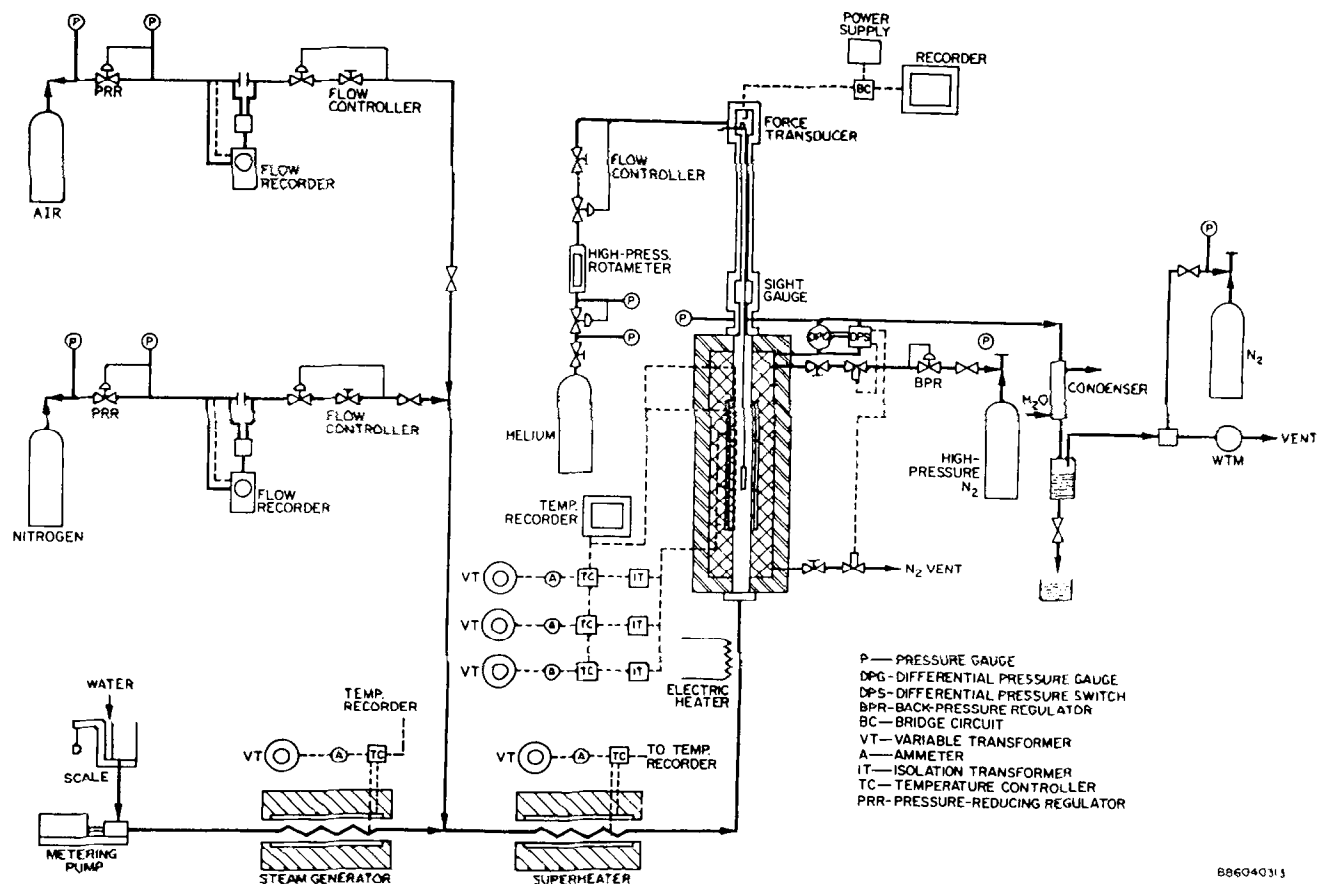


Figure 2 Schematic diagram of thermobalance unit

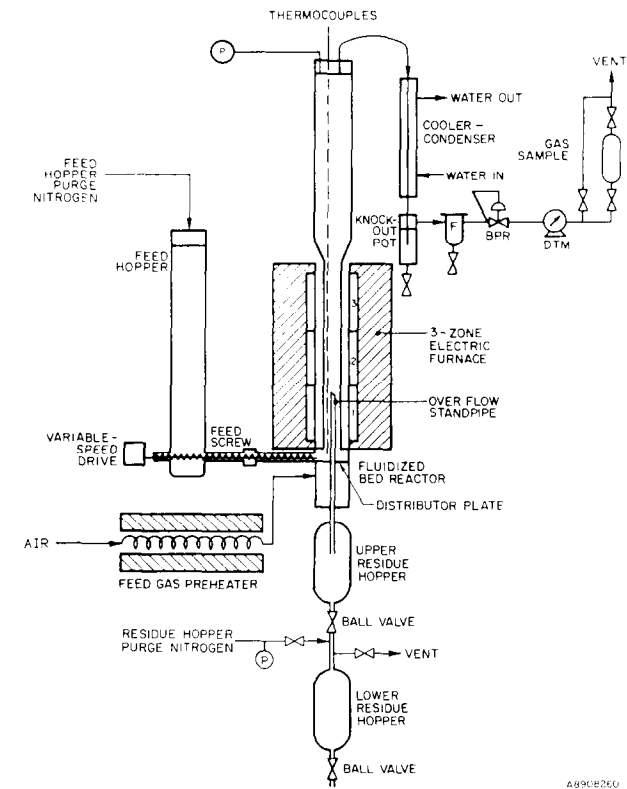


Figure 3 Schematic diagram of the laboratory scale thermobalance unit

collect the discharged residue shale. The feed gas is preheated with an electric furnace and fed through a sintered metal plate into the reactor. An internal sintered metal filter at the top of the reactor prevents the carry-over of shale fines into the exit gas line.

Steady state flow, temperature and pressure conditions are readily established. However, steady state operation is not initiated until after a time period equivalent to three bed turnovers to ensure solids have the proper time-temperature history.

DISCUSSION

A total of 17 thermobalance tests were conducted to determine combustion characteristics of hydroretorted, beneficiated Alabama shale. The first three tests were non-isothermal and involved heating a shale sample to 982°C in air at 0.2, 1.5 and 7.0 MPa. Eleven isothermal tests were conducted using a 20 min residence time; three other isothermal tests were conducted using 1, 2 and 5 min residence times. Isothermal test conditions ranged from 816 to 1093°C at pressures of 0.2–7.0 MPa.

The hydroretorted shale used in the thermobalance tests was generated in a laboratory scale continuous PFH test at 482°C and 4.2 MPa. The hydroretorted shale was screened to $-841+420\text{ }\mu\text{m}$ and riffled to produce the TGA feed shale. Analyses of the raw and hydroretorted Alabama shales are presented in Table 1. The sample weight totals more than 100% because metals in the shale mineral matter are oxidized during the analysis.

The carbon, sulfur and nitrogen conversions achieved during the PFH test used to generate the hydroretorted shale were 67, 44 and 55%, respectively. The hydroretorted shale sample contained a total of 24.2 wt%

carbon, hydrogen, sulfur and nitrogen. The shale gross calorific value was reduced from 14.8 to 7.1 MJ kg⁻¹ during PFH processing, which represents 32% of the original shale heat content.

A summary of the operating conditions and elemental conversions for the combustion characterization tests is presented in Table 2. Conversions are not presented for test 31-T-12 because at 1093°C, the shale sample sintered and could not be separated from the basket after the test.

Non-isothermal TGA tests were conducted in air at pressures of 0.2, 1.5 and 7.0 MPa. The corresponding oxygen partial pressures were 0.04, 0.32 and 1.5 MPa. Slow heating of the hydroretorted shale in air produces a large weight loss peak between 249 and 349°C. This is probably due to the onset of a self-sustained combustion reaction, which was not indicated by thermocouple readings. As the oxygen partial pressure increased, the combustion initiation temperature decreased. Results presented in Table 3 suggest that shale combustion can be initiated at temperatures as low as 250°C.

The 13 isothermal thermobalance tests in which the shale did not sinter were conducted at temperatures of 816–982°C and pressures of 0.2–7.0 MPa. Weight loss was high for all samples at this range of combustion conditions.

Carbon conversion increased from 57.3% at 1 min to 63.9% at 2 min and to nearly 100% for tests at 5 min. Detailed evaluations of carbon conversion rates at combustion temperatures above 816°C will require thermogravimetric testing at residence times of less than 5 min. Shale residence times in the continuous unit tests were too long to accurately measure the effects of temperature and pressure on carbon, but carbon conversions exceeded 99% over the temperature and pressure ranges studied.

Results of residence time tests at 927°C showed that the rate of sulfur conversion was slower than the rate of carbon conversion during shale combustion. Sulfur conversion increases with increasing temperature. The apparent decrease in sulfur conversion with increasing pressure for thermobalance tests may be caused by shale sintering in the thermobalance.

Weight loss versus time traces for thermobalance tests conducted at 816, 927 and 982°C and at a pressure of 1.5 MPa are presented in Figure 4. Weight loss rate increases with increasing temperature. The time required

Table 1 Analyses of raw and hydroretorted beneficiated Alabama shale^a

Sample	Beneficiated		Beneficiated and hydroretorted
Test unit		Thermobalance	Lab-scale continuous
Moisture (wt%)	1.5	0.0	0.0
Ultimate (wt% dry)			
Ash	53.7	79.1	81.1
Carbon	31.9	15.4	12.9
Hydrogen	3.2	0.8	0.8
Sulfur	9.2	7.5	7.3
Nitrogen	0.8	0.5	0.4
Gross calorific value (MJ kg ⁻¹)	14.8	7.1	6.3

^a Ultimate analyses of shale samples may exceed 100% due to oxidation of mineral matter

Table 2 Combustion characterization test conditions and results

Test No.	31-T-1	31-T-2	31-T-3	31-T-4	31-T-5	31-T-6	31-T-7	31-T-8
Operating conditions								
Temperature (°C)	982	982	982	927	927	927	816	982
Pressure (MPa)	0.2	1.5	7.0	0.2	1.5	7.0	1.5	1.5
Residence time ^a (min)	20	20	20	20	20	20	20	20
Heating mode		Non-isothermal		Iso ^b	Iso ^b	Iso ^b	Iso ^b	Iso ^b
Component conversion (%)								
Carbon	99.8	99.6	99.9	99.7	99.7	99.7	100.0	100.0
Hydrogen	92.3	94.3	95.2	97.1	97.1	97.1	98.1	98.0
Sulfur	97.7	98.4	96.1	98.5	94.8	82.9	93.0	95.8
Nitrogen	83.0	100.0	98.5	95.5	98.5	96.8	100.0	100.0
Total weight loss (%)	21.3	21.6	20.9	20.9	20.9	19.4	21.3	19.2

Test No.	31-T-9	31-T-10	31-T-11	31-T-16	31-T-16	31-T-15	31-T-14	31-T-17
Operating conditions								
Temperature (°C)	927	816	982	927	927	927	927	927
Pressure (MPa)	4.2	1.5	7.0	7.0	7.0	7.0	7.0	4.2
Residence time ^a (min)	20	20	20	1	2	5	20	20
Heating mode	Iso ^b	Iso ^b	Iso ^b	Iso ^b	Iso ^b	Iso ^b	Iso ^b	Iso ^b
Component conversion (%)								
Carbon	100.0	100.0	99.8	57.3	63.9	100.0	99.6	100.0
Hydrogen	98.1	98.0	97.0	91.5	89.2	97.1	95.2	99.0
Sulfur	86.6	94.2	79.5	38.3	34.9	86.8	93.5	94.8
Nitrogen	100.0	98.4	96.8	82.9	86.2	100.0	100.0	100.0
Total weight loss (%)	21.0	17.7	19.0	12.7	11.7	20.1	21.0	21.0

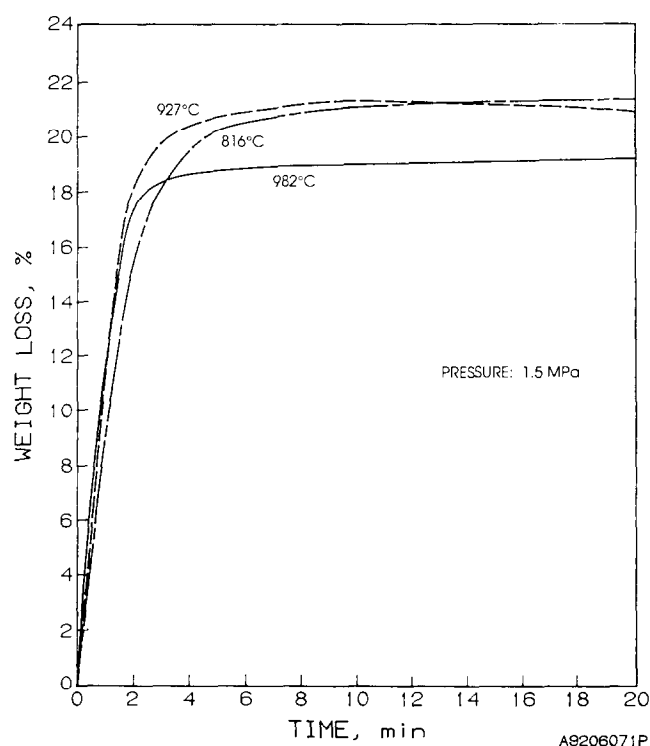
^a At maximum temperature^b Iso, isothermal**Table 3** Effect of oxygen partial pressure on combustion initiation temperatures (non-isothermal tests)

Test No.	O ₂ partial pressure (MPa)	Combustion initiation temperature (°C)
31-T-1	0.04	295–370
31-T-2	0.32	250–300
31-T-3	1.50	260–275

to complete 95% of the total weight loss decreases with increasing temperature from about 6 min at 816°C to 4 min at 927°C and 3 min at 982°C. The decrease in total weight loss as temperature is increased from 927 to 982°C appears to comprise an increase in organic matter conversion and a larger decrease in weight loss as a result of inorganic reactions.

The rate of weight loss also increases with increasing oxygen pressure, but the effect of pressure is smaller than the effect of temperature. At 927°C, the weight loss after 20 min was 21% at pressures from 0.2 to 7.0 MPa. However, 86% of the total weight loss is achieved in 2 min at 7.0 MPa, but only 81% of the weight loss occurs in 2 min at 0.2 MPa.

Total weight changes in the thermobalance combustion tests were not consistent with the elemental conversions. At a pressure of 1.5 MPa, conversions of the organic part of the shale (carbon, hydrogen and sulfur) increased with increasing temperature. However, the total weight loss decreased with increasing temperature from 21.3% at 816°C to 20.9% at 927°C and to 19.2% at 982°C. These results indicate the mineral matter in the shale gains

**Figure 4** Effect of temperature on shale weight loss

weight during combustion and that the mineral matter weight gain increases with increasing temperature.

Sintering was observed in the isothermal tests conducted at severe conditions. At 927°C, part of the

samples combusted at 4.2 and 7.0 MPa was sintered. At higher temperatures of 982 and 1093°C and a pressure of 1.5 MPa, more of the sample sintered. The residue from test 31-T-12 at 1093°C was entirely sintered and could not be separated from the basket after the test.

Ash fusion temperatures of combusted shale in reducing and oxidizing atmospheres are shown in Table 4. The initial deformation temperature (oxidizing atmosphere) of combusted shale was found to be 1288°C. Combustion temperatures used in the thermobalance tests were below this temperature.

Six fluidized bed combustion tests were conducted. The feed for the shale combustion tests was hydrotretorted shale product from a bench scale PFH test. For the first combustion test, the shale was sized to $-420 + 177\text{ }\mu\text{m}$; for the other five tests, the shale was sized to $-595 + 177\text{ }\mu\text{m}$. The wider size consist was used in the later tests so that a sufficient quantity of feed material would be available. The $-177\text{ }\mu\text{m}$ fraction of the shale was removed to minimize fines handling problems. Physical and chemical analyses of the feed and residue shale samples from the combustion tests are shown in Table 5.

Combustion tests were conducted at temperatures of 816–927°C and pressures of 0.4–1.5 MPa. Shale residence times ranged from 14 to 50 min, and the bed

height-to-diameter ratio was about two. The feed gas superficial velocity was $0.18\text{--}0.37\text{ m s}^{-1}$, which provided from 80 to 200% excess air to the reactor. Shale feed rates were $400\text{--}700\text{ g h}^{-1}$. Operating conditions and results of the combustion tests are summarized in Table 6.

The superficial velocities were greater than complete fluidization for the largest particles to prevent sintering of the shale during combustion. At lower velocities, the kinetic energy of the particles in the bed was insufficient to prevent sintering. In initial tests with gas velocities below 0.18 m s^{-1} , shale sintering occurred at combustion temperatures as low as 650°C. Sintering, however, is avoided when the bed is well fluidized. Combustion tests were conducted without sintering at 927°C.

The fluidization velocities needed to avoid sintering did not produce any significant attrition of the shale particles. In test 32-C-1, the feed shale contained 24.8% $-250\text{ }\mu\text{m}$ material; the combusted shale residue contained 22.4% $-250\text{ }\mu\text{m}$ material. The feed for the other five tests contained 9% $-250\text{ }\mu\text{m}$ material; the $-250\text{ }\mu\text{m}$ fraction of steady state residue solids from these tests ranged from 8.1 to 17.9 wt%. The increase in the $-250\text{ }\mu\text{m}$ fraction of the combusted shale observed in tests 32-C-7 and 32-C-8 may have been due, in part, to higher gas flow, which caused more mixing and solid–solid contact in the bed. It was also observed that the residue shale particles were smoother and more spherical in shape than the feed. The scrubbing action of the fluidized bed apparently eroded small surface irregularities from the particles, but did not cause significant particle breakage.

The colour of the solids was affected by combustion reactions. The hydrotretorted beneficiated shale was black, which reflected the high level of carbon still present. After combustion, the shale had a light, reddish-brown colour. The lighter the colour, the lower was the carbon content of the combusted shale. The colour of the combusted shale may reflect the presence of iron oxide.

Table 4 Combusted hydrotretorted beneficiated Alabama shale ash fusion temperatures

	Ash fusion temperature (°C)	
	Reducing	Oxidizing
Initial deformation	1107	1288
Softening	1174	1354
Hemispherical	1238	1399
Fluid	1302	1443

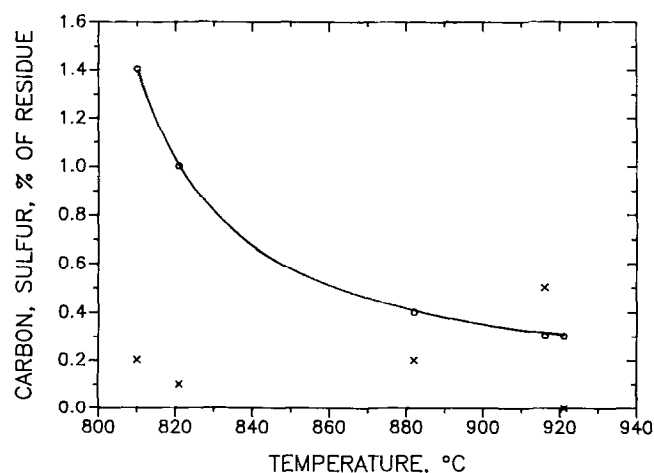
Table 5 Chemical and physical analyses of feed and residue solid samples from combustion tests^a

Test No.	32-C-1	32-C-1	32-C-3– 32-C-8	32-C-3	32-C-4	32-C-6	32-C-7	32-C-8
Sample	Feed	Residue	Feed	Residue	Residue	Residue	Residue	Residue
Ultimate (wt% dry)								
Ash	81.1	96.9	81.1	98.6	97.4	98.8	96.3	99.0
Carbon	12.9	1.1	12.9	0.5	0.1	0.2	0.2	0.0
Hydrogen	0.8	0.0	0.8	0.0	0.0	0.0	0.0	0.0
Sulfur	7.3	1.2	7.3	0.3	1.0	0.4	1.4	0.3
Nitrogen	0.4	0.1	0.4	0.0	0.0	0.0	0.0	0.0
Oxygen (HTW) ^b	2.4	0.4	2.4	0.7	0.4	0.5	0.6	0.3
Bulk density (g ml ⁻¹)	0.57	0.59	0.57	0.59	0.52	0.59	0.53	0.60
Sieve analysis (wt%), (μm)								
+ 595	0.8	1.8	9.4	4.2	12.2	1.4	4.2	3.9
– 595 + 420	5.2	1.3	49.8	61.5	56.8	49.5	50.9	35.4
– 420 + 250	69.2	74.5	31.7	26.2	21.9	38.6	28.5	42.8
– 250 + 210	13.6	10.6	5.1	5.1	6.3	5.0	9.3	8.3
– 210 + 177	7.0	6.9	2.6	0.9	0.7	2.1	2.0	4.7
– 177 + Pan	4.2	4.9	1.4	2.1	2.1	3.4	5.1	4.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gross calorific value (MJ kg ⁻¹)	6.3	n.a.	6.3	<0.02	<0.02	<0.02	<0.02	<0.02

^a Ultimate analyses of shale samples may exceed 100% due to oxidation of mineral matter
^b HTW, high temperature water

Table 6 Operating conditions and results from shale combustion tests

Test No.	32-C-1	32-C-3	32-C-4	32-C-6	32-C-7	32-C-8
Temperature (°C)	829	916	821	882	810	921
Pressure (MPa)	0.49	0.43	0.81	0.45	1.47	0.79
Shale residence time (min)	23	33	31	14	50	33
Bed height-diameter ratio	2.2	2.2	2.2	2.2	2.2	2.2
Steady state time (min)	60	60	60	55	38	55
Shale feed rate (g h ⁻¹)	569	404	391	718	382	476
Gas feed rate (SCM h ⁻¹) ^a	1.57	1.53	2.80	2.60	4.36	3.11
Gas superficial velocity (m s ⁻¹)	0.19	0.23	0.23	0.37	0.18	0.26
Excess air (%)	80	156	162	144	299	306
Component conversions (wt%)						
Carbon	93.0	97.1	99.5	98.5	99.0	100.0
Sulfur	85.9	96.3	88.3	96.1	83.6	96.8
Nitrogen	78.1	100.0	100.0	100.0	100.0	100.0
Oxygen (HTW)	84.6	77.0	84.7	82.8	78.2	88.3
Calorific value reduction (%)	n.a.	>99.5	>99.5	>99.5	>99.5	>99.5
Product gas composition (mol %)						
O ₂	9.9	10.1	4.6	9.7	6.9	11.7
N ₂	79.2	81.2	91.1	80.7	90.6	82.9
CO ₂	7.6	7.6	4.0	8.3	2.5	4.8
SO ₂	3.3	1.1	0.3	1.3	0.0	0.6
Total	100.0	100.0	100.0	100.0	100.0	100.0
Recovered carbon (% of feed)						
CO ₂	73.1	98.8	101.1	99.9	98.4	105.0
Liquids	n.a.	0.02	0.03	0.03	0.04	0.02
Sulfur recovered in product gas as SO ₂ (% of feed sulfur)	149	66	40	74	2	59

^aSCM, standard cubic metres**Figure 5** Effect of temperature on carbon (x) and sulfur (o) in residue

Elemental analyses of raw, beneficiated shale has shown iron concentrations in the range of 3–5 wt%.

High carbon and sulfur conversions were achieved in all combustion tests; measured gas phase products were carbon dioxide and sulfur dioxide (SO₂), exclusively. Carbon conversions ranged from 93 to 100%. Sulfur conversions ranged from 84 to 97%. The elemental conversions from these tests were consistent with those from thermobalance combustion characterization tests. Carbon conversion increased with increasing temperature, pressure and residence time. The differences,

however, were small. The carbon conversion achieved in test 32-C-1 (conducted at 816°C and 0.4 MPa) was 93%; all other tests had carbon conversions of 97–100%. At 871°C and 0.4 MPa, a 14 min residence time yielded a carbon conversion of 98.5%. Tests conducted in a thermobalance indicated that 5 min should provide adequate solids residence time for high carbon conversions.

Calorific value reduction was greater than 99% in all tests, as expected, at combustion conditions. Reductions in calorific value were higher than carbon and sulfur conversions in some tests. This reflects the conversion of residual carbon from a hydrocarbon form to a char carbon form during combustion and some uncertainty in elemental and calorific value analyses at very low concentrations and energy contents.

Sulfur conversions were lower than carbon conversions. Increases in sulfur conversion were achieved with increases in temperature and residence time, but increasing the pressure did not change the sulfur conversion.

Results of the continuous tests indicate high and fairly uniform conversion of carbon over the temperature range tested; also, this conversion shows no trend with pressure. The oxidation of sulfur, however, is clearly sensitive to temperature. These effects can be seen in Figure 5.

Essentially, all of the converted sulfur formed SO₂. Sulfur balances based on the SO₂ concentration were poor. Spot gas sample SO₂ concentrations varied by more than 50%. Non-uniform SO₂ production and/or

interaction of SO₂ with steel vessels and tubing may account, in part, for the poor sulfur recovery in most tests and for the apparent conversion of 149% of the feed sulfur in test 32-C-1 to SO₂.

The carbonyl sulfide (COS) content in the product gas from all tests was below the gas chromatography detection limit of 10 ppm. Therefore, less than 0.1% of the shale sulfur was converted to COS during combustion. The concentration of NO_x compounds was not measured in these combustion tests. However, based on shale nitrogen conversion during the tests, the maximum possible NO_x concentration in the fluidized bed product gas would have been less than 15 ppm. Product gas compositions were determined in the combustion tests by averaging the compositions of several spot gas samples.

CONCLUSIONS

At temperatures of 816–982°C and air pressures of 0.2–7.0 MPa, rapid and complete combustion of hydroretorted, beneficiated shale is achieved. Carbon conversions increase from greater than 50% in 1 min to almost 100% in 5 min. Sulfur oxidation, which is slower than carbon combustion, increases with increasing temperature. Shale mineral matter is not completely inert at combustion conditions. Oxidation of mineral matter produces a weight gain which increases with increasing temperature and pressure. Partial sintering occurs during fixed bed combustion of hydroretorted shale at 927°C, and sintering becomes more severe as the temperature and pressure are increased.

Fluidized bed combustion of hydroretorted, beneficiated shale is a practical method of improving the energy efficiency of the PFH process. Successful operation in a laboratory scale reactor has shown sintering can be

avoided by keeping the superficial velocity above the fluidization velocity of the largest particles in the bed. No significant particle attrition results from fluidized bed combustion of hydroretorted shale.

After hydroretorting at 510°C and 7.0 MPa in a bench scale PFH unit, the residue shale contained 12.9% carbon and 7.3% sulfur, and had a gross calorific value of 6.3 MJ kg⁻¹. Combustion reduced the calorific value of this hydroretorted shale by an average of more than 99.5% during the five laboratory scale continuous tests. The high calorific value recovery at all combustion conditions studied prevented determination of the effects of operating conditions on conversion.

Since carbon conversions were high over the temperature range tested and showed no trend with pressure, a near atmospheric combustion of spent shale at the lowest viable temperature using the shortest residence time would appear to be the most economical approach. This approach would also maximize the retention of sulfur in the ash.

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