

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
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FLASH PYROLYSIS OF OIL SHALE WITH VARIOUS GASES

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INTRODUCTION

The rapid heat-up rate (10^3 - 10^5 °C/sec) and short residence time pyrolysis (<10 sec) of carbonaceous materials such as coal (1, 2) and wood (3) particulates with high temperature (700° to 1000°C) gases has been shown to produce significantly higher yields of gaseous and liquid hydrocarbon products than conventional slow heat-up rate (1-10°C/sec) and longer residence time (mins to hrs) pyrolysis. In the flash pyrolysis of coal, it has been found that the yield of gaseous and liquid hydrocarbons for certain coals can be increased by as much as 36% beyond the Fischer Assay value (4). The principles of flash pyrolysis follow the sequence: (a) rapid heat-up, depolymerize and bond break the structure of the large polycyclic coal and wood cellulose and lignin polymer molecules to form smaller free radical units; (b) allow the lighter fraction molecules to react in the gas or liquid phases with each other or with a reactive pyrolysis gas such as hydrogen and (c) limit the residence time at pyrolysis temperature by rapidly cooling the reaction system to stabilize the reaction products and prevent repolymerization and charring of the hydrocarbon gases and liquids. These flash pyrolysis principles have been applied in several exploratory experiments performed with western oil shales and are described in this paper.

It is known that there are differences in the yield and type of liquid and gaseous hydrocarbon products that can be obtained depending on the thermal treatment and the origin of oil shale. It is well known that eastern (Devonian) U. S. Shales yield a lower Fischer Assay of organic material (~10 gal/ton) than western (Eocene) U. S. Shales (~30 gal/ton). The H/C molar ratio of organic matter in western shale runs around 1.5 while in eastern shale it runs approximately 1.0 (5). There is also evidence that the manner and the rate at which shale is heated up, as well as the residence time at temperature, can affect the yield and distribution of products. This information has been mainly obtained from thermogravimetric analysis (TGA) and in static (retort) experiments. There is also information available on hydrogenation (6) and superheated steam hydrolysis of oil shale (7). The work presented in this paper deals with the results of the flash pyrolysis of oil shale by heating with both reactive and non-reactive gases in an entrained tubular reactor.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The flash pyrolysis of oil shale was conducted in a highly instrumented 1" I. D. by 8 ft long entrained downflow tubular reactor system. The equipment has been previously described in detail (8). A schematic flowsheet of the system is shown in Figure 1. Ground oil shale in the particle-size range of 150 to 500 microns is fed by gravity into the top of the reactor from a feeder enclosed by a high pressure vessel connected to the reactor. The pyrolyzing gas is supplied from high pressure storage cylinders and is preheated in an electrically-heated stainless steel resistance tube prior to entering at the top of the reactor where it meets the shale particles. Gas temperatures up to 1000°C can be obtained. The reactor is constructed of Inconel, a high alloy metal, having an 0.5" wall thickness, capable of withstanding pressures ranging up to 3000 psi. The gas mixes, transfers heat, pyrolyzes and reacts with the shale particles as they concurrently flow down the 8 ft length of the reactor. Reactor temperatures can be controlled by four 2 ft long clam shell electrical heaters along the outside lengths of the 2" I. D. reactor. Below the heated length of the reactor, there is a 4 ft forced air finned cooling section in which the reaction system is rapidly cooled to temperatures between 250° and 300°C. This temperature range is sufficient to terminate the pyrolysis reaction and to prevent the liquid products from condensing and separating at this point. The gases enter a trap where the char and unvented shale is first separated and the effluent gas is then sent first through a water-cooled condenser (15°C) and then to a freon-cooled condenser (-40°C) where the liquid products are separated. The remaining gases are then reduced to atmospheric pressure, measured in a positive displacement meter and vented to the atmosphere. Flow rates of oil shale are in the order of 1 lb/hr and gases in the order of 1 or 2 SCFM. Steady state operation

in this flow system can usually be obtained in 10 to 15 mins.

Product analysis is obtained with an on-line programmable gas chromatograph which determines CH_4 , C_2H_4 , C_2H_6 , BTX (benzene, toluene, xylene) CO and CO_2 concentrations at 8 minute intervals. Gas sampling taps are provided every 2 ft along the length of the reactor. Products heavier than BTX (>C₉) are collected in the condenser traps and measured at the end of each experiment. The heavier hydrocarbons (naphthalene, anthracene, etc.) are collected, measured and analyzed. An analysis of the char is also made. From these data a complete mass balance can be made over the entire experimental run.

The shale residence times are calculated by summing the shale particle free fall velocity and the gas flow velocity. Heat-up rates are also estimated by calculations from the heat transfer of the gas to the particles.

The yields are based on the percent of organic carbon in the feed oil shale which is converted to product. A Western (Colorado Green River Formation) oil shale obtained from the Laramie Energy Technology Center was used in these experiments. An analysis of the oil shale is shown in Table I.

TABLE I
ANALYSIS^a OF COLORADO SHALE GREEN RIVER FORMATION

	<u>Wt %</u>
C	- 17.0
H	- 2.2
N	- 0.8
O	- 17.5
S	- 0.8
Ash	- 61.9
CO_2^b	- 16.5

a. Analysis made with organic C analyzer and TGA.

b. CO_2 based on % of elemental plus ash analysis.

RESULTS AND DISCUSSION

A series of runs were performed with three types of pyrolysis gases, methane, helium and hydrogen at a pressure of 500 psi. The flash pyrolyses with CH_4 and He were conducted at a reactor temperature of 800°C and the flash hydrolyses with H_2 gas are conducted at temperatures from 800° to 950°C. The reactor conditions, flow rates and residence times together with product yields including HC (hydrocarbon) gases, HC liquids and C oxides are summarized in Table II.

The data indicate that the inert gas He gave the lowest total HC gas and liquid yield (42.7%) followed by H_2 (61.7%) followed by CH_4 gas and which resulted in the highest yield (80.5%). There was no formation of ethylene with He or with H_2 , however, with CH_4 there was a significantly large yield amounting to 32.4% of the organic C in the shale converted to ethylene. In the case of H_2 , for the series of runs ranging from 800° to 950°C, the methane yield at 800°C (29.5%) is higher than with He (24.1%) and increases markedly as the temperature rises to 950°C at which point most of the organic C is converted to CH_4 (88.5%). Due to the high partial pressure of CH_4 in the CH_4 pyrolysis experiments, a CH_4 balance is difficult to make. However, within experimental error of the flow rate in and out of the reactor there does not appear to be any net production or destruction of methane. Blank and control experiments with oil shale feed before and after the experiments indicated no formation of ethylene or other products due to possible cracking of the methane on the walls of the reactor.

The liquid BTX (benzene, toluene, xylene) yield is highest with the methane pyrolysis (21.1%) which is about 2.5 times higher than with He (8.6%) or H_2 (8.9%). The improved yield with methane pyrolysis compared to the yield with the inert helium may be due to a free radical reaction such as CH_2 formed from the pyrolysis of the kerogen reacting with the CH_4 giving rise to ethylene. Another possibility may be attributed to preventing secondary reactions of ethylene and benzene by maintaining a high partial pressure of methane during methane pyrolysis.

The HC gaseous and liquid yields for the flash hydrolysis of Colorado Shale is plotted in Figure 2 as a function of reactor temperature. The trends show the high rate of increase of CH_4 yield with reactor temperature. The ethane yield decreases rapidly from 800°C (23.3%) to 900°C at which temperature ethane is no longer formed. The BTX (mainly benzene) goes through a maximum of 12.1% at 850°C.

TABLE II

 MAXIMUM YIELDS BY FLASH PYROLYSIS OF GREEN RIVER COLORADO OIL SHALE
 WITH VARIOUS PYROLYSIS GASES

 Constant Reactor Pressure of 500 psi
 Shale Particle Size 150-300 Micron

Pyrolysis Gas	CH ₄	He	H ₂	H ₂	H ₂	H ₂
Reactor Conditions						
Reactor temp. - °C	800	800	800	850	900	950
Gas flow rate - SCFM	1.13	1.13	1.52	1.52	1.52	1.52
- lbs/hr	2.85	0.71	0.48	0.48	0.48	0.48
Shale flow rate - lbs/hr	0.55	0.84	0.64	0.64	0.64	0.64
Residence time - sec	1.7	1.7	3.2	3.2	3.1	3.1
Product Yields (% Organic C Conversion)						
HC Gas						
CH ₄ , methane	-	24.1	29.5	49.9	72.7	88.5
C ₂ H ₄ , ethylene	32.4	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆ , ethane	22.1	10.0	23.3	12.8	0.0	0.0
C ₃ H ₈ , propane	4.9	-	-	-	-	-
Total HC Gas	59.4	34.1	52.8	62.7	72.7	88.5
HC Liquids						
BTX	21.1	8.6	8.9	12.1	10.1	8.5
Total HC, Liq. and Gas	80.5	42.7	61.7	74.8	82.8	97.0
C Oxides						
CO	8.5	6.1	14.7	19.6	22.7	29.5
CO ₂	7.7	7.4	0.0	0.0	0.0	0.0
Total CO _x	16.2	13.5	14.7	19.6	22.7	29.5
Total HC and C Oxides	96.7	56.2	76.4	94.4	105.5	126.5

It should be noted that the oxides of carbon (CO and CO₂) only indicate relative yields since CO₂ is evolved from the inorganic carbonates present in the shale. The increased yields of CO (14.7% to 29.5%) with no CO₂ formation obtained in the H₂ pyrolysis experiments at increasing temperatures are probably due to the shift reaction between H₂ with CO₂, forming CO and H₂O.

A second set of flash pyrolysis experiments was performed with mixtures of the Colorado oil shale and a New Mexico sub-bituminous coal. The elemental composition of the coal was C-60%, H-4.2%, O-16.8%, N-1.2%, S-0.8% and Ash-17.0%. The purpose of these experiments was to determine whether there is an interaction effect of the kerogen in the shale with the coal. The H/C molar ratio in kerogen is >1 equivalent to the stoichiometric formula, CH_{1.5}O_{0.7}. Coal has an H/C ratio of <1 equal to the formula, CH_{0.8}O_{0.2}. The thought was that the hydrogen deficiency in coal might be made up with the excess in kerogen for producing HC gases and liquids. The results with hydrogen as a pyrolysis gas at 1000 psi reactor pressure and with CH₄ as pyrolysis gas at a reactor pressure of 500 psi for an 80% coal-20% shale mixture are summarized in Table III. The yields given are based on the conversion to product from the sum total of carbon fed to the reactor contained both in the coal and the shale.

In the hydrogen experiment, the most prominent product yield is methane. As the temperature increases from 750° to 800°C, the methane increases rapidly from 45.4% to 76.8% while the ethane decreases from 14.6% to 1.8%. Comparing these results to those previously with shale alone at a hydrolysis pressure of 500 psi and 800°C, there appears to be a significant improvement in the conversion to methane. The CH₄ yield from shale alone is 29.5%. From coal, it is 15.8% (9). A calculation based on these yields by partial summing for the 80/20 shale/coal mixture would

indicate a methane yield of 23.1%, whereas 76.8% was actually obtained. For the benzene, a slightly higher yield is predicted (8.9%) than was obtained (7.1%). Thus, there appears to be an interaction effect of shale and coal under flash hydrolysis conditions.

In the series of experiments with methane pyrolysis at 500 psi, the ethane yield goes through a maximum of 14.1% at 900°C; the ethylene decreases rapidly from 12.8% at 850°C to 4.3% at 950°C, while the BTX increases significantly from 13.5% at 800°C to 24.6% at 950°C. The trends can be seen graphically in Figure 3. The total carbon conversion, which also includes the CO and CO₂ formation, appears to level off at about 60%, however, this would also include the CO₂ from mineral matter in the shale.

Based on the yields of ethylene and benzene for the methane pyrolysis of coal alone (10) and the yield from oil shale alone shown in Table II, it is predicted by fractional summing calculation that an 80/20 mixture of shale and coal would give a much higher yield for ethylene (19.2%) than was obtained (11.7%) but a slightly lower benzene yield (12.9%) than was actually obtained (13.5%). An interactive effect between the coal and the oil shale under methane pyrolysis conditions, thus, also appears to exist.

The combination of the conversion of the natural resources of coal, shale and natural gas to synthetic fuels and chemical feedstocks in one process step is an incentive for further exploration of flash pyrolysis reactions.

TABLE III

FLASH PYROLYSIS OF A MIXTURE OF 20% COLORADO SHALE (17% C) AND 80% NEW MEXICO SUB-BITUMINOUS COAL (60% C) WITH HYDROGEN AND METHANE AS PYROLYSIS GAS

Solids Particle Size 150-300 Microns

Pyrolysis Gas	H ₂	H ₂	CH ₄	CH ₄	CH ₄	CH ₄
Reactor Conditions						
Pressure, psig	1000	1000	500	500	500	500
Temperature, °C						
Gas flow rate - SCFM	1.71	1.71	1.53	1.53	1.53	1.53
- lbs/hr	0.54	0.54	3.86	3.86	3.86	3.86
Shale flow rate - lbs/hr	0.94	0.94	1.04	1.04	1.04	1.04
Residence time - sec	3.5	3.5	3.2	3.2	3.1	3.1
Product Yields (% Org. Carbon Conversion, Shale and Coal)						
HC Gas						
CH ₄ , methane	45.4	76.8	ND	ND	ND	ND
C ₂ H ₆ , ethane	14.6	1.8	8.6	11.5	14.1	10.8
C ₃ H ₈ , propane	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄ , ethylene	<u>0.0</u>	<u>0.0</u>	<u>11.7</u>	<u>12.8</u>	<u>8.9</u>	<u>4.3</u>
Total HC Gas	60.0	78.6	20.3	24.3	23.0	15.1
HC Liquids						
BTX	<u>7.3</u>	<u>7.1</u>	<u>13.5</u>	<u>17.7</u>	<u>21.0</u>	<u>24.6</u>
Total HC, Liq. and Gas	67.3	85.7	33.8	42.0	44.0	39.7
C Oxides						
CO	3.4	5.7	4.3	5.0	10.4	11.9
CO ₂	<u>0.0</u>	<u>0.0</u>	<u>3.8</u>	<u>4.2</u>	<u>4.9</u>	<u>5.0</u>
Total CO _x	3.4	5.7	8.1	9.2	15.3	16.9
Total HC and C Oxides	<u>70.7</u>	<u>91.4</u>	<u>41.9</u>	<u>51.2</u>	<u>59.3</u>	<u>56.6</u>

ND - Not determined.

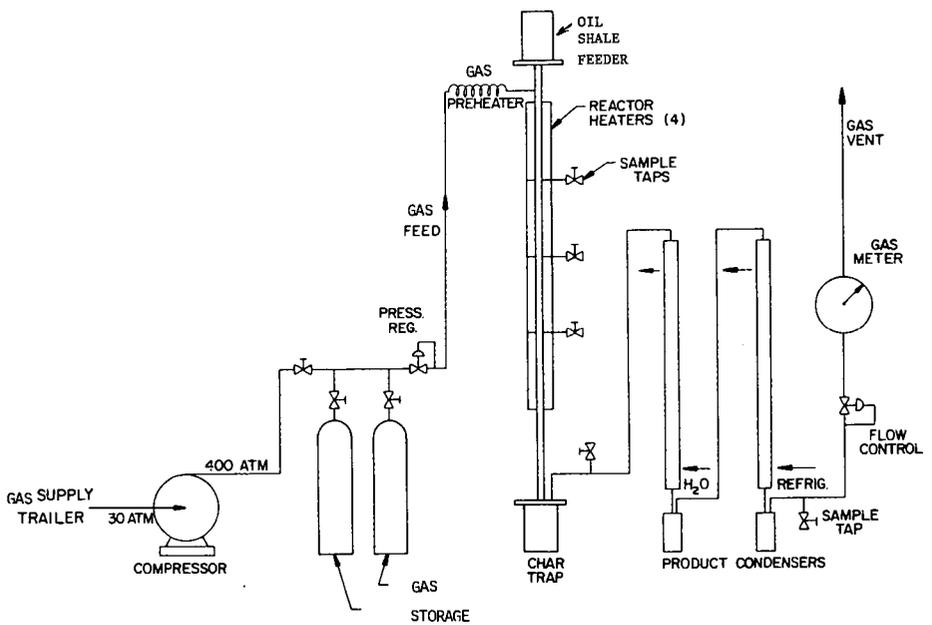


FIGURE 1. SCHEMATIC FLOWSHEET OF ENTRAINED TUBULAR REACTOR

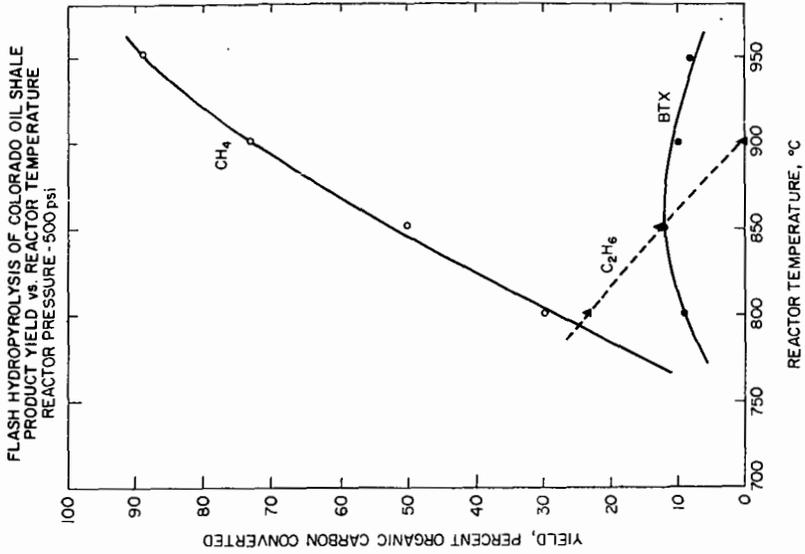


FIGURE 2

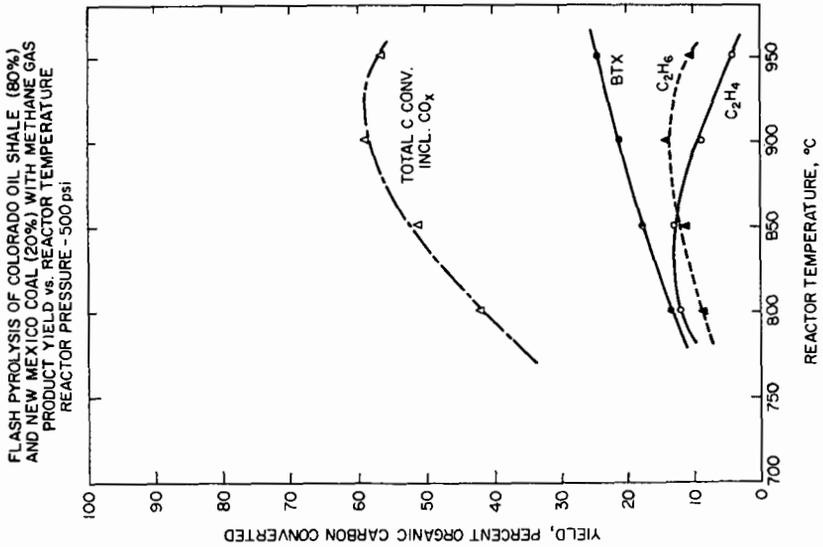


FIGURE 3

CONCLUSIONS

The flash pyrolysis of Colorado Oil Shale with methane at a temperature of 800°C and pressure of 500 psi appears to give the highest yield of hydrocarbon gas and liquid followed by yields with hydrogen and lowest with helium.

In the methane pyrolysis over 54.5% of the carbon in the kerogen is converted to ethylene and benzene. The flash pyrolysis with hydrogen (flash hydropyrolysis) of the oil shale at increasing temperatures showed a rapidly increasing amount of methane formed and a decrease in ethane formation, while the BTX (benzene mainly) yield remained at approximately 10%. At 950°C and 500 psi, almost all (97.0%) of the carbon in the kerogen is converted to liquid and gaseous hydrocarbons.

Experiments with a mixture of a New Mexico sub-bituminous coal and oil shale under flash hydropyrolysis and methane pyrolysis conditions indicated higher yields of methane and ethylene and slightly lower yields of benzene than predicted by partial additive calculations.

These exploratory experiments appear to be of sufficient interest to warrant a fuller investigation of the interaction of the natural resources, oil shale, coal and natural gas under flash pyrolysis conditions.

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