

THE FLASH HYDROPYROLYSIS OF LIGNITE AND SUB-BITUMINOUS COALS TO BOTH LIQUID AND GASEOUS HYDROCARBON PRODUCTS

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Introduction

Flash Hydropyrolysis (FHP) is a short residence time (1 to 10 sec) gas phase non-catalytic coal hydrogenation process in which coal is converted directly to liquid and gaseous hydrocarbon products. Pulverized coal is contacted with hydrogen at elevated pressure and heated at average rates of 20,000 to 30,000°C/sec causing thermally-induced fractures in the polycyclic structure of the coal molecule. The free radicals formed readily add on hydrogen thus increasing the hydrogen to carbon ratio of 0.8 in the feed coal to approximately 1 to 4 depending upon whether liquid or gaseous hydrocarbons are formed. The products are then rapidly quenched to terminate the reaction and to prevent any decomposition or recombination. The purpose of this work is to provide data on the process chemistry of the reaction by studying the liquid and gaseous products formed as they vary with such operating parameters as temperature, pressure, and residence time. These results are also applied to a kinetic model and an economic evaluation of a large scale integrated coal conversion processing plant. Experiments using catalysts and much lower heating rates were conducted by Hitsche et al (1) in the late 1950's. Small-scale non-catalytic, direct hydrogenation experiments were conducted by Graff et al (2) as further background information for the work reported here.

Experimental Equipment and Procedure

A schematic of the experimental equipment is shown in Figure 1 and a detailed description is reported elsewhere.(3,4) The system utilizes a 1-in. I.D. entrained down-flow tubular reactor with coal fed by gravity from above. Preheated hydrogen enters just above the 8 ft heated reaction zone and a 3 ft cooling section and char trap are below. The products formed in the reactor are kept in the gas phase at approximately 250°C and reactor pressure until reaching the two liquid product condensers, one water cooled and the other cooled by a refrigerant. The gaseous products and excess hydrogen are then reduced to atmospheric pressure and passed through a positive displacement integrating gas meter before being vented. The maximum operating conditions of the system (4000 psi and 800°C or 2500 psi and 900°C) are limited by the 10,000 hr rupture life of the Inconel 617 reactor. Problems unrelated to the mechanics of the system, mainly reactor plugging at high hydrogen pressures, even when using non-caking coal, has limited most experiments to a maximum of 2500 psi.

At the beginning of each experiment, the coal feeder is charged with approximately three pounds of coal ground to minus 100 mesh (< 150 μ). The experiments are generally of about two hour duration and coal and hydrogen are fed at approximately 1 lb/hr each. Product samples are taken every 8 minutes from one of four sample taps located every 2 ft along the length of the reactor. An on-line programmable gas chromatograph is used for determination of CO, CO₂, CH₄, C₂H₆, BTX (benzene, toluene, xylene) and H₂O. The heavier liquid hydrocarbon products (ΣC_9) are collected and measured at the end of the experiment. The use of the reactor sample taps provide information on both the yields and distribution of products as a function of gas and coal particle residence time. There is also another sample tap located down stream of the product condenser which provides information as to their efficiency.

Experimental Results

Product Yields and Distribution

The process chemistry of two coals are presently being studied, a North Dakota lignite and a New Mexico sub-bituminous. The ultimate analyses of these coals are given in Table 1. Since the detailed study of the sub-bituminous coal is not yet completed, more experimental data is available using the lignite. Figure 2 shows a summary of the BTX yields from the lignite at hydrogen pressures of 500 to 2000 psi and reactor temperatures of 700° to 800°C. The experimental points were not included because of their great number (≈ 50). The yield is expressed as fraction of carbon in feed coal converted to the hydrocarbon product. Maximum yields were generally observed between 775° and 800°C except at the highest pressure (2500 psi) studied in detail where the yield was approximately constant at 9% at temperatures between 725° and 775°C. A significant increase in yield is seen as the pressure is increased from 500 to 1000 psi. The yield increases from 4.5 to 7%. Further increases in pressure above 1000 psi show less significant increases in yield, the increase maximum yield going from 7 to 9% as the pressure is increased to 2000 psi. As the pressure is further increased to 2500 psi, no appreciable increase in yield above 9% is observed; only a reduction in temperature at which the maximum occurs. Although at 2500 psi the maximum yield was essentially constant over a broad range of temperatures, the coal residence time at which this maximum was observed decreased from a maximum of approximately 9 sec at 725°C to a minimum of 2 sec at 850°C as shown in Figure 3. At residence times greater than required to produce the maximum yield, significant decomposition of the BTX was observed. For example, in Figure 4, the results of an experiment conducted at 2500 psi and 825°C, the BTX is seen to decrease from the maximum observed of 8% at 2.5 sec to approximately 0 at 9.5 sec.

Since presently the minimum residence that can be measured is approximately 2 sec, it is possible that slightly higher BTX may exist at shorter residence time. This looks to be the case when considering the initial steep gradient of the BTX curve in Figure 4. The liquid hydrocarbon products of molecular weight greater than xylene cannot be measured with the on-line gas chromatograph because they tend to condense in the sample lines. For this reason, they are not included in the correlations given in Figure 4 which exhibit the effect of residence time on the product distribution. These liquids are collected in the condenser traps and measured and analyzed via gas chromatography at the end of each experiment. Generally, these heavier liquids have been found to be exclusively polynuclear aromatic hydrocarbons (PNA), approximately 40% of which is naphthalene. A typical composition of this liquid is given in Table 2. Only on very rare occasions has any phenols been found and then only in trace amounts. The maximum yield of these heavier liquids is generally of the same order as that of the BTX though obtained at a lower temperature. For example, in Figure 5 which shows the total yield of liquid hydrocarbon products from lignite at a hydrogen pressure of 2,000 psi, the liquids of $> C_9$ are seen to maximize at approximately 9% yield at a temperature of 750°C while the BTX maximum of approximately 10% occurs at 800°C. These heavier liquids are also seen to decompose very rapidly as the temperature is increased above 750°C to the extent that at 850°C only approximately 0.5% yield remains. Since the yield of BTX with temperature is shown to be much more uniform than the heavier liquids within the temperature range shown, the total yield of liquids is seen to peak at 18% and occurs at the same temperature at which the heavier liquids peak (750°C).

Although the yields obtained from sub-bituminous coal is still being investigated, a significant amount of information has been accumulated. In Figure 6, the maximum yield of BTX is shown to be as high as approximately 15% at 2000 to 2500 psi and decreases only to approximately 12% as the pressure is reduced to 1000 psi. Also, the temperatures at which the maximum yields are obtained decrease with increased pressure, going from 825°C at 1000 psi to 775°C at 2500 psi. When these yields plus the gaseous hydrocarbons formed ($CH_4 + C_2H_6$) are compared to the same products from lignite as shown in Figure 7,

a constant incremental yield of approximately 5% for both the BTX and gaseous hydrocarbons is observed for the sub-bituminous coal. This results in an overall 10% increase in yield of hydrocarbon products for the sub-bituminous coal compared to the lignite. The yield of heavier liquid products ($\geq C_9$) from the sub-bituminous, although not completely investigated, appears to be much lower than that obtained from lignite, ranging from 4.5 to 1.5% or less. When this is added to the maximum yields of BTX, however, the total liquid yield is on the average equal to or greater than that from lignite.

At temperatures of 850°C and greater, the liquid hydrocarbons are seen to decompose almost entirely to produce gaseous hydrocarbons, principally methane and ethane. This plus the additional gaseous products formed directly from the coal result in maximum gaseous yields ($CH_4 + C_2H_6$) shown in Figure 8. The formation of these products appear to be a direct function of the hydrogen pressure, increasing at the rate of 18% conversion for each 500 psi increase in pressure. These yields were all produced at a hydrogen to coal feed ratio of approximately 1 lb/lb and at coal residence times between 2.4 and 7 seconds. It was found that at shorter residence times the reaction has not reached completion and at longer residence times, decomposition of the methane reduced total yields. Also, since higher temperatures accelerate the decomposition, the competing reactions of formation and decomposition at 2000 to 2500 psi result in the maximum yield occurring at temperatures lower than the maximum studied (900°C). A total conversion of 88% to CH_4 and C_2H_6 was obtained at 875°C and 2500 psi pressure.

When the hydrogen to coal feed ratio is reduced by approximately 4 to a ratio of 0.25, some reduction in gaseous products is observed (Figure 9). Some or all of this reduction could be attributed to a reduction in hydrogen partial pressure caused by higher concentrations of product in the process stream.

The study of the New Mexico sub-bituminous coal is still in progress. The information to date indicates it behaves similarly to lignite in gasification except that greater yields are obtained at lower pressure, as shown in Figure 10. At 1000 psi the lignite yields approximately 35% gaseous products and the sub-bituminous 55%, an almost 60% increase over the lignite. The temperatures and residence times necessary to produce maximum gaseous products were approximately the same.

Sulfur and Nitrogen

To date, most of the detailed determinations of sulfur distributions in the products and effluents have been made on experiments using lignite. The distribution of the sulfur among the various forms in lignite is given in Table 3 and a summary of the disposition of this sulfur after hydrolysis is given in Table 4. In comparing these tables, it should be noted that in most experiments greater than 50% of the sulfur in the feed lignite is retained in the spent char. Approximately 64% of the sulfur in the lignite is in the organic form while 90% of the sulfur in the char was found to be in the organic form. Also, the liquid hydrocarbon products contained much less than the 0.3% sulfur considered to be the maximum allowable for further hydrotreating. The sulfur dissolved in the water produced is probably limited by the solubility of H_2S which is approximately 0.66 wt% at the temperatures ($\sim 0^\circ C$) at which the water is collected.

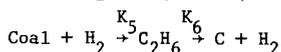
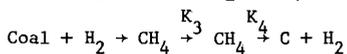
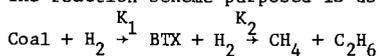
The nitrogen balance shown in Table 5 follows very closely the same distribution as the sulfur, again the largest single portion remaining in the char. In this case, the nitrogen dissolved in the water produced is not solubility limited since it is assumed to be in the form of ammonia which can be as high as 47 wt% at $0^\circ C$.

Reaction Scheme and Kinetic Model

In order to develop a reaction scheme and a kinetic model, the following assumptions were made:

- 1) Isothermal conditions exist along the length of the reactor.
- 2) Chemical reactions are the rate determining steps.
- 3) Only hydrocarbons and not oxides of carbon considered.
- 4) Methane and ethane from decomposition of BTX are small compared to that produced from coal.
- 5) Free carbon formed from decomposition of products has negligible reactivity.
- 6) Liquids heavier than BTX are intermediate species.

The reaction scheme purposed is as follows:



Realizing this scheme to be a first approximation of the true reaction mechanism, a kinetic model was developed and the appropriate rate constants calculated. Only those results from experiments using lignite and in which sufficient residence time data was available were used. The results are shown in Table 6. As can be seen from the calculated activation energies, all reactions are chemical reaction rate limiting rather than diffusion limiting except possibly for the decomposition of methane (K_4).

Economic Evaluation

A summary of the results from the more recent economic evaluation for utilization of FHP in an integrated coal conversion process (5) is given in Table 7. The feed coal was assumed to be lignite since at the initiation of the study little experimental data was available using sub-bituminous coal. Three product slates were assumed, liquids only (motor gasoline and liquified petroleum gas-LPG), pipeline gas only, and co-products of liquids and pipeline gas. The plant capacity is assumed to be 25,000 to 30,000 tons per day of lignite, producing 47,700 bbl/day of motor gasoline in the liquid process or 395 MM SCFD of pipeline gas for the gas process. The net thermal efficiencies which include internal plant energy needs were calculated to vary from 61% for the all gas slate to 72% for the combined product slate to a low of 50% for the all liquids slate. The reason for the low efficiency of the all liquids slate is that the methane produced must be performed with steam to produce hydrogen. The capital costs, based on 1978 dollars, ranged from a low of \$839 million for the all liquids plant to a high of \$936 million for the all gases plant. In all cases, the two most costly items in the plants were the product separation from the recycle gas and the production of hydrogen. Combined, these represented approximately 50% of the capital investment. The flash hydroxypropolyzer only amounted to approximately 5% of the investment. The last entry in Table 8 shows the fuel oil equivalent cost of production for the three product slates. The most expensive at \$32.34/bbl is the all liquids, mostly due to the low net thermal efficiency and the most attractive or cheapest at \$23/bbl is for the mixed products.

Conclusions

The following conclusions can be drawn from this work so far.

- The maximum yield of BTX observed from the FHP of sub-bituminous coal is at least 50% greater than that from lignite (10% for lignite and 15% for sub-bituminous).
- The total liquids yields (BTX + \geq C₉) are approximately the same for both coals (~18-20%).
- Both coals can be hydrogasified to methane and ethane up to approximately 85% of the total carbon in the fuel at 2500 psi and 875° to 900°C.
- The sub-bituminous coal yields 60% more gaseous hydrocarbons at 1000 psi and 875° to 900°C than the lignite.
- The gaseous yields from both coals is directly proportional to the hydrogen pressure in the range of 500 to 2500 psi.

-Negligible quantities of the sulfur or nitrogen in the coal are found in the liquid hydrocarbon products.

-The FHP reactions are basically chemical rate and not diffusion rate controlled.

-In the commercial application of FHP, a mixed product slate of liquids and gases is the most economical.

References

1. Hiteschue, R. W., Anderson, R. B., and Schlesinger, M. D., Hydrogenation of Coal at 800°C, Ind. Engrg. Chem., 49, 2008 (1957).
2. Graff, R. A., Dobner, S., and Squires, A. M., Flash Hydrogenation of Coal. 1. Experimental Methods and Preliminary Results, Fuel, 55, 109 (1976).
3. Steinberg, M., Fallon, P. T., Doering, R., Farber, G., Smith, J., and Woodson, G., Safety Analysis Report on the Brookhaven Coal Flash Hydropyrolysis Experiment, BNL 21919 (October 1976).
4. Fallon, P. and Steinberg, M., Flash Hydropyrolysis of Coal, The Design, Construction, Operation, and Initial Results of a Flash Hydropyrolysis Experimental Unit, BNL 22519 (January 1977), presented at 173rd National American Chemical Society Meeting, New Orleans, La. (March 20-25, 1977).
5. Steinberg, M., Fallon, P., Dang, V., Bhatt, B., Ziegler, E., and Lee, Q., Reaction, Process, and Cost Engineering for the Flash Hydropyrolysis (FHP) of Coal, BNL 25232 (November 1978), presented at 71st Annual Meeting of the American Institute of Chemical Engineers, Miami Beach, Florida (November 12-16, 1978).

Table 1

ULTIMATE ANALYSIS (WT PCT DRY) OF LIGNITE AND SUB-BITUMINOUS COALS

	North Dakota Lignite	New Mexico Sub-Bituminous
Carbon	59.0	59.3
Hydrogen	4.0	4.2
Oxygen*	25.5	16.8
Nitrogen	0.9	1.2
Sulfur	0.6	0.8
Ash	10.0	17.7

*By difference.

Table 2

TYPICAL COMPOSITION OF OILS AND HEAVIER LIQUID HYDROCARBON PRODUCT ($\geq C_9$) FROM THE FLASH HYDROPYROLYSIS OF LIGNITE

	Wt %
Naphthalene	38.1
Other 2 ring aromatics (methyl naphthalene fluorene, etc.)	19.5
Three ring aromatics (phenanthrene, etc.)	11.1
Four ring aromatics (pyrene, etc.)	5.1
Five ring aromatics (chrysene, etc.)	3.1
High boiling fraction (asphaltenes)	23.1

Table 3

SULFUR DISTRIBUTION IN NORTH DAKOTA LIGNITE

Sulfur Form	% in Lignite	% of Total
SO ₄ (soluble)	0.089	14.8
FeS ₂ (pyritic)	0.129	21.6
Organic	0.382	63.6

Table 4

FLASH HYDROLYSIS OF LIGNITE
Sulfur Balance
 Sulfur Conc. in Lignite Feed - 0.6%

	% Distribution in product	Concentration in Product Stream (wt%)
Contained in liquid HC product	1	0.09
Contained in char	48-77	0.85-1.7
Dissolved in water produced	12-22	0.54-0.73
Vented to atmosphere	15-25*	0.1-0.15

*By difference.

Table 5

FLASH HYDROLYSIS OF LIGNITE
Nitrogen Balance
 Nitrogen Conc. in Lignite Feed - 0.9% N

	% Distribution in Product	Concentration in Product Stream (wt%)
Contained in liquid HC product	4	0.16
Contained in char	30-55	0.6-1.1
Dissolved in water produced	15-40	2.7-5.0
Vented to atmosphere	21-26*	0.19-0.23

*By difference.

Table 6

CALCULATED RATE CONSTANTS
 Pressure (P_{H_2}) 1500-2500 psi
 Temperature (T) 973-1173°K

$$k_1 = 3.16 \times 10^{12} P_{H_2}^{0.137} e^{-68700/RT}$$

$$k_2 = 1.33 \times 10^{14} P_{H_2}^{.004} e^{-71700/RT}$$

$$k_3 = 3.93 \times 10^4 P_{H_2}^{0.07} e^{-29700/RT}$$

$$k_4 = 97.5 P_{H_2}^{-0.043} e^{-15100/RT}$$

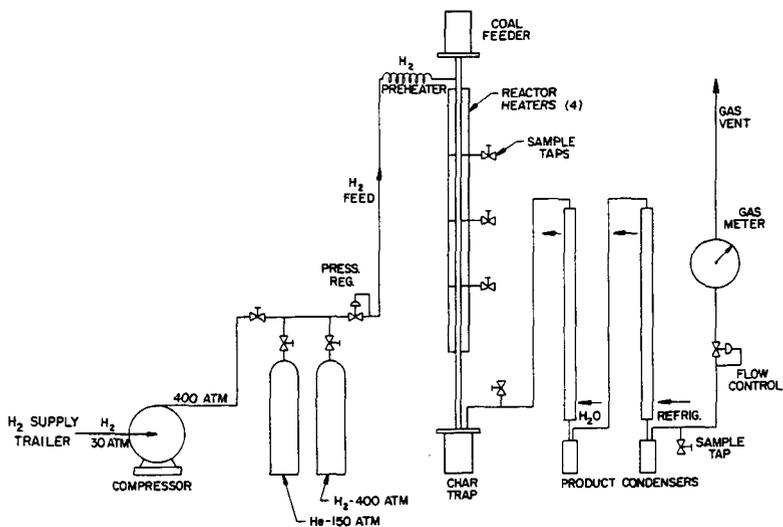
$$k_5 = 1.03 \times 10^8 P_{H_2}^{-0.12} e^{-44000/RT}$$

$$k_6 = 3.30 \times 10^{14} P_{H_2}^{1.17} e^{-85700/RT}$$

Table 7

FLASH HYDROLYSIS OF COAL
Manufacturing Cost of Product Fuel

<u>Main Fuel Product Made</u>	<u>Liquids</u>	<u>Liquids and Gases</u>	<u>Gases</u>
<u>Reactor Operating Conditions</u>			
Pressure, psi	2000 (136 ATM)	2000 (136 ATM)	2500 (170 ATM)
Temperature, °C	750°C (1382°F)	750°C (1382°F)	825°C (1517°F)
<u>Product Values</u>			
Pipeline gas	-0-	159 MM SCFD	395 MM SCFD
Motor gasoline	47,700 BB/D	47,700 BB/D	-0-
LPG	134 tons/D	134 tons/D	134 tons/D
<u>Operating Cost</u>			
	<u>\$ MM/yr</u>	<u>\$ MM/yr</u>	<u>\$ MM/yr</u>
Lignite @ \$20/ton	204.4	212.7	212.5
Catalyst and chemicals	5.5	5.5	5.0
Power @15 mills/kwh	1.1	6.8	8.3
Ash disposal	2.6	2.8	2.7
Ins. Maint. GA (8% of capital)	57.2	71.4	74.9
Operating labor	8.0	8.0	8.0
Total operating cost	278.8	307.2	311.4
Mortgage 10%	93.4	104.8	109.9
Depreciation @5% (20 yrs)	41.9	44.6	44.8
10% ROI and income tax	167.8	178.4	187.1
Total	\$581.9	\$635.0	\$653.2
Selling Price (Total FOE)	\$5.13/MM BTU	\$3.83/MM BTU	\$4.53/MM BTU
Pipeline gas, \$/MSCF)	\$5.13/MM BTU	\$3.83/MM BTU	\$4.53/MM BTU
Motor gasoline, (90 RON)	\$0.77/gal	\$0.54/gal	-0-
Fuel oil equivalent (FOE)	\$32.34/bbl	\$23.00/bbl	\$30.17/bbl



SCHMATIC FLOWSHEET OF ENTRAINED TUBULAR REACTOR EXPERIMENT

Figure 1

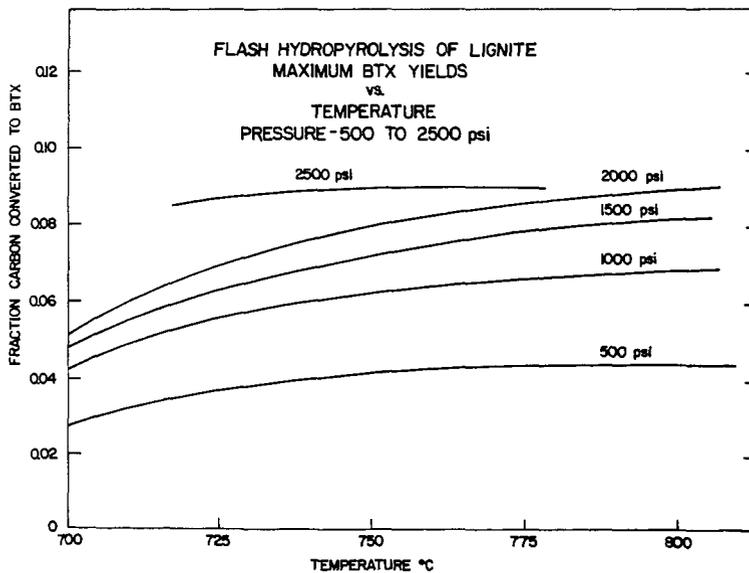


Figure 2

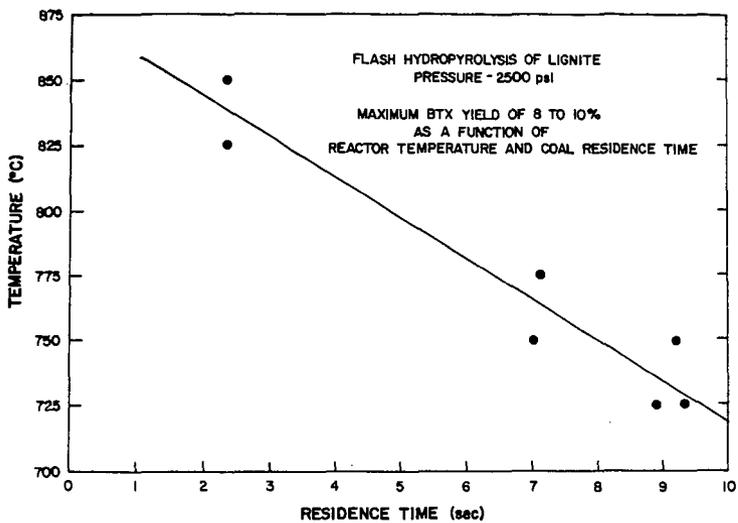


Figure 3

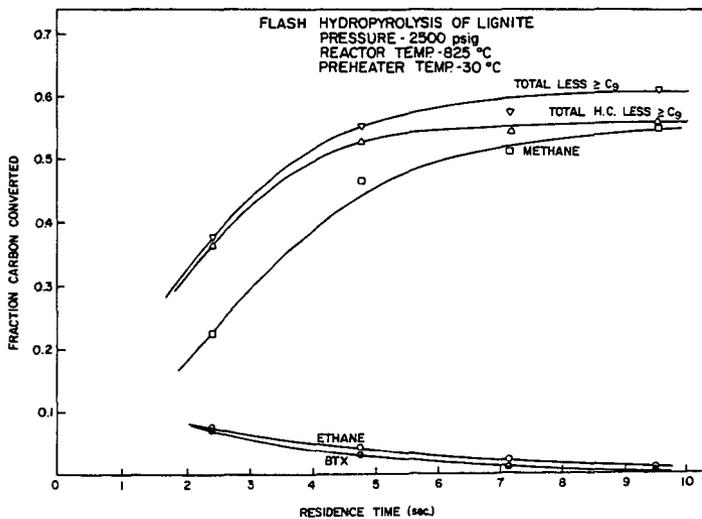


Figure 4

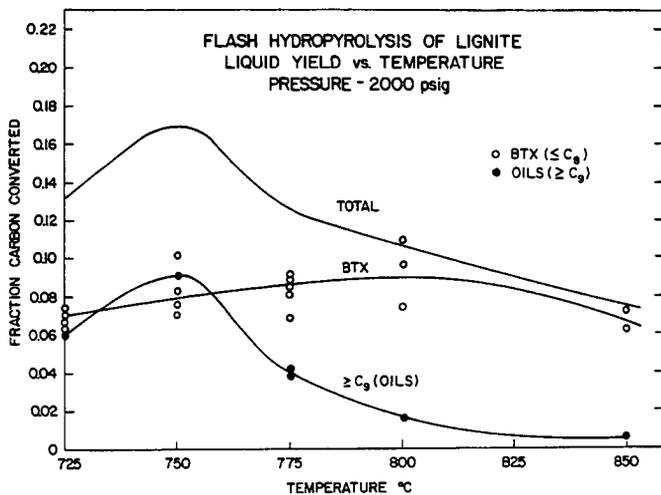


Figure 5

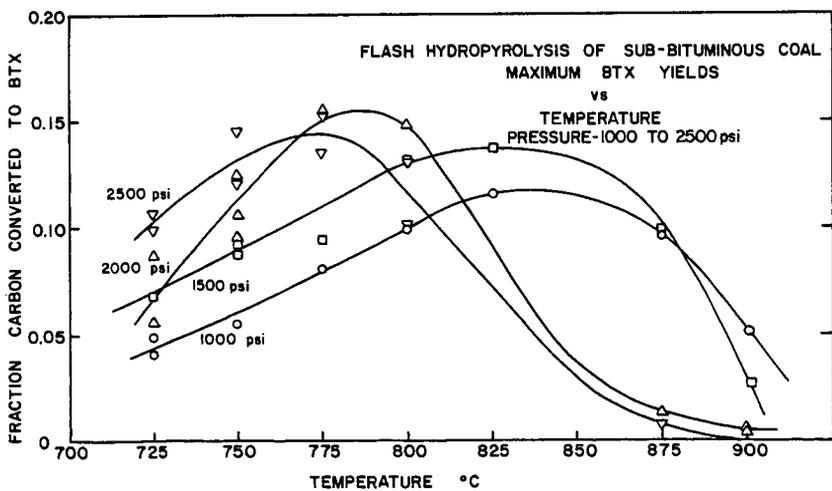


Figure 6

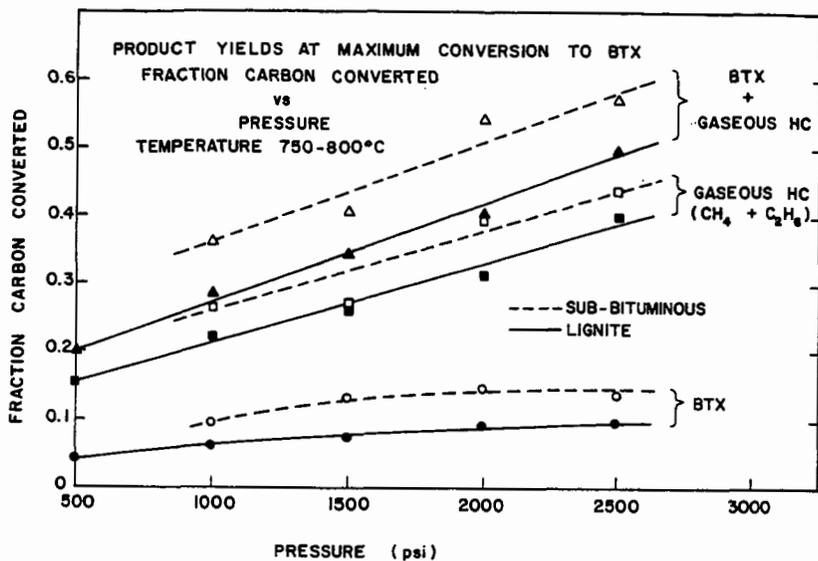


Figure 7

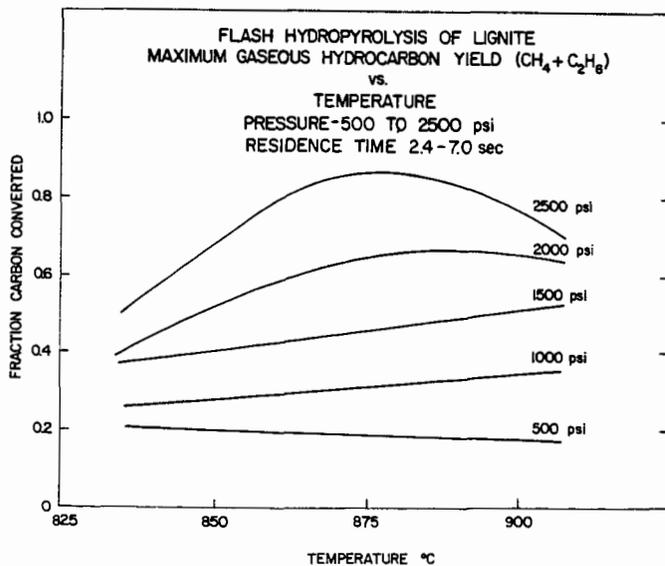


Figure 8

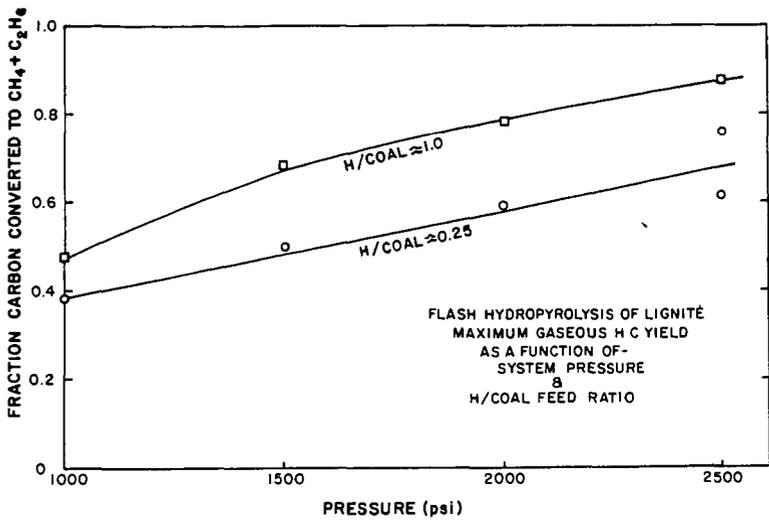


Figure 9

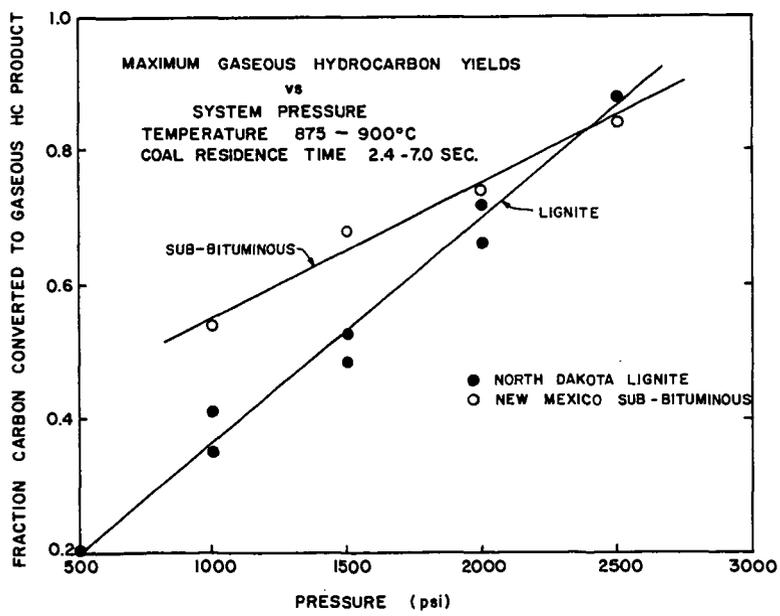


Figure 10