

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 ($< 150\mu$). 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.

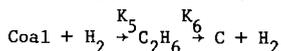
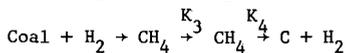
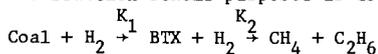
The nitrogen balance shown in Table 5 follows very closely the same distribution as the sulfur, again the largest single portion remaining in the char. In this case, the nitrogen dissolved in the water produced is not solubility limited since it is assumed to be in the form of ammonia which can be as 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 hydropropyrolzyer 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

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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).
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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

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

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

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

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

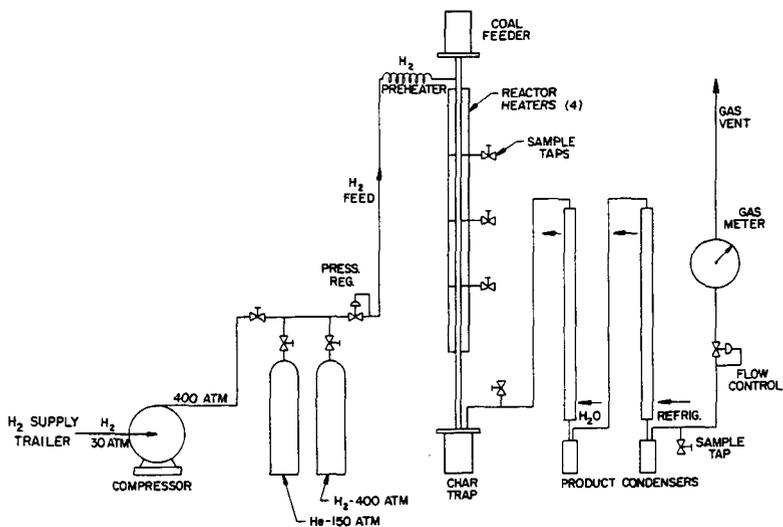
$$k_5 = 1.03 \times 10^8 P_{H_2}^{-0.12} e^{-44000/RT}$$

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

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

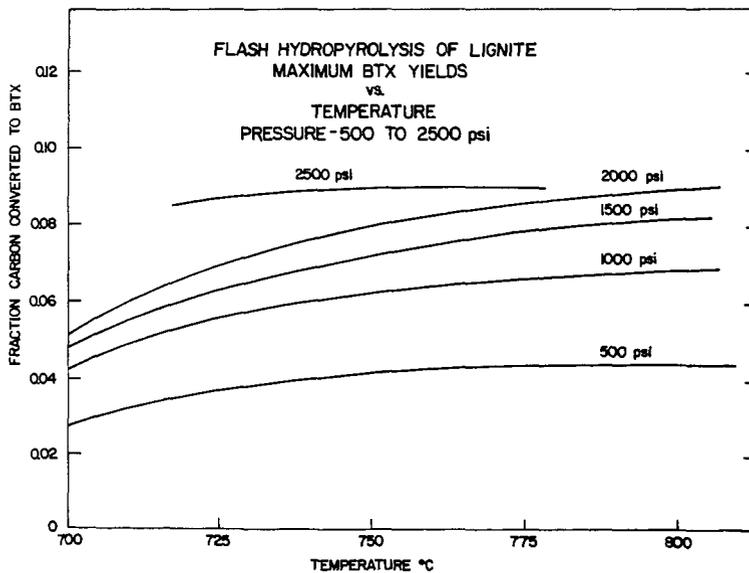


Figure 2

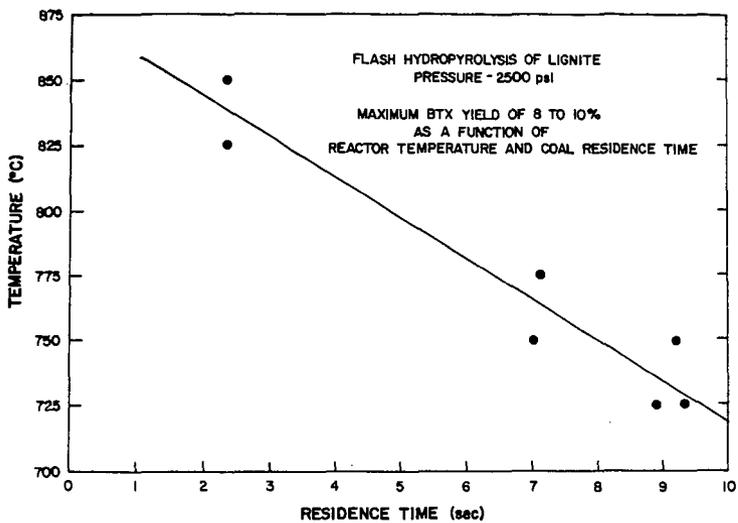


Figure 3

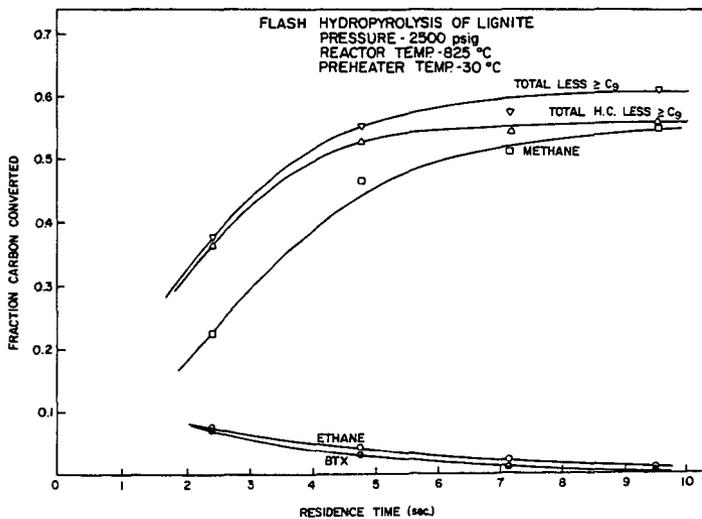


Figure 4

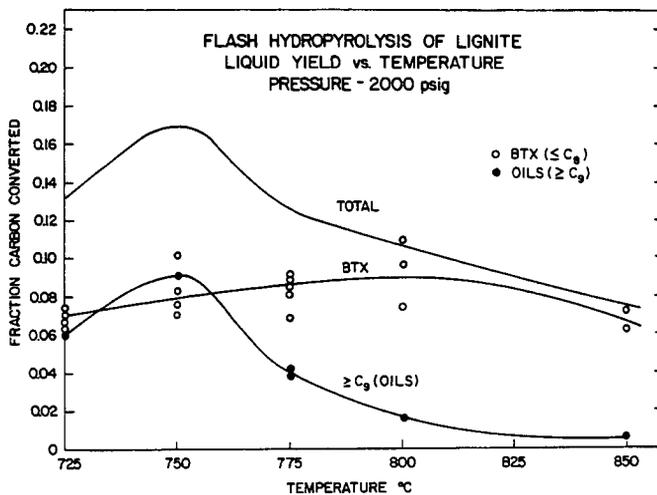


Figure 5

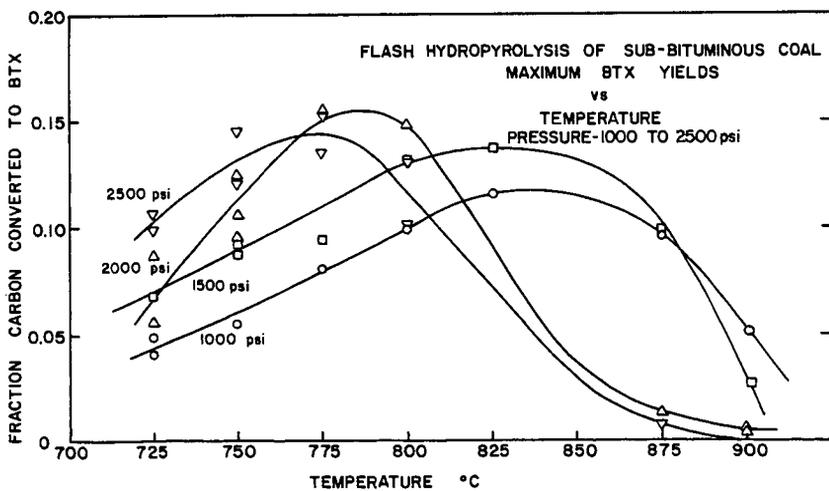


Figure 6

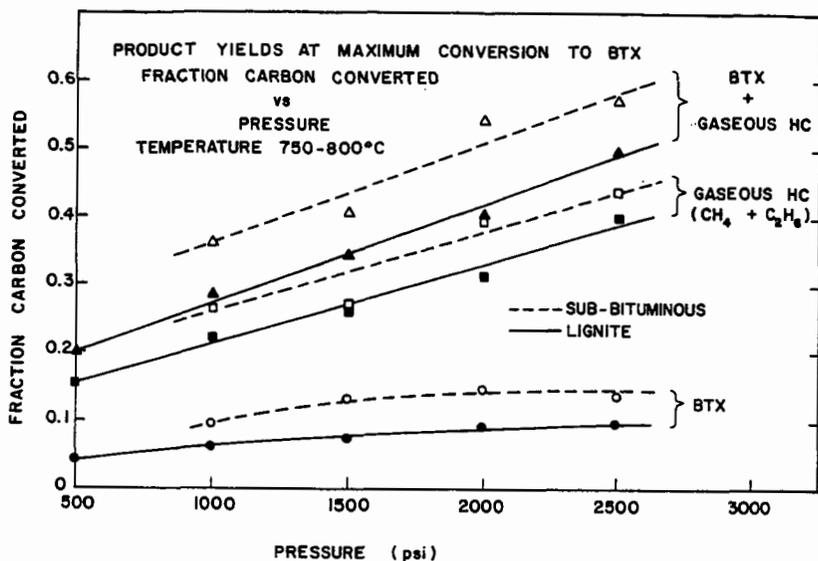


Figure 7

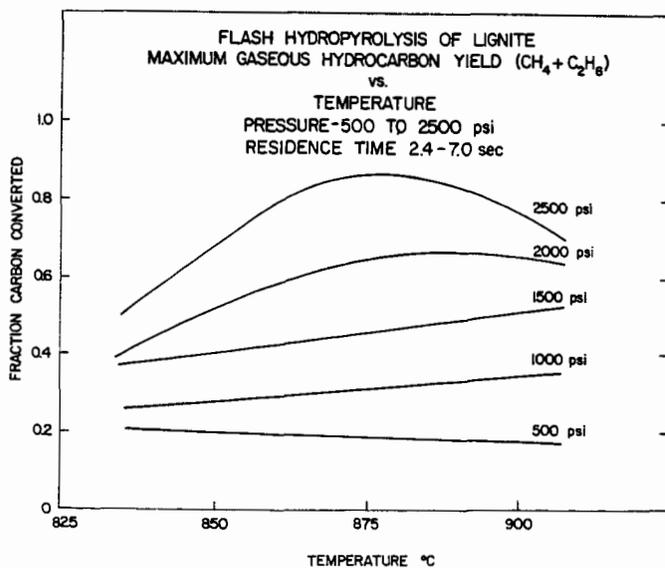


Figure 8

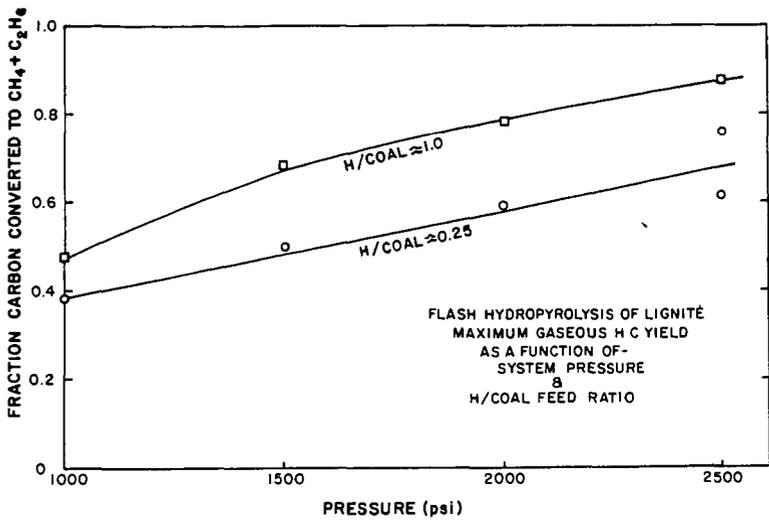


Figure 9

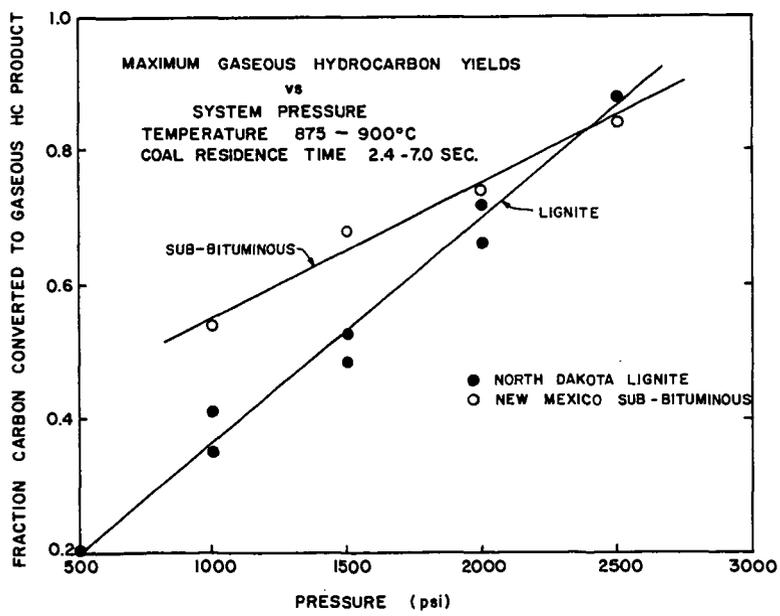


Figure 10

EXPERIMENTAL INVESTIGATION OF PEAT HYDROGASIFICATION

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INTRODUCTION

The availability and accessibility of peat as a domestic fossil resource have been well publicized by Minnesota Gas (Minnegasco) and the Institute of Gas Technology (IGT) (References 1 and 2). It has been established that peat, with an estimated 1440 quads (10^{15} Btu) of available energy, is second only to coal as the most abundant fossil energy resource in the United States. Also, hydrogasification tests at IGT (Reference 1) have shown that, due to peat's unique properties of high volatility and hydrogen-to-carbon ratio, peat is highly reactive yielding good conversion to methane.

Based on these studies and the concurrent DOE-sponsored* development of a short residence time coal hydrogasifier at Rockwell International, with the Cities Service Research and Development Company as a subcontractor, an additional task to the existing DOE contract was established to furnish a preliminary performance profile for peat in the Rockwell hydrogasifier. Rockwell and Cities Service have entered into an agreement to develop jointly short-residence-time, flash hydro-pyrolysis process technology. Acknowledgement is given to both Louis Jablansky and Melvyn-Kopstein of DOE for their administration of this add-on effort.

The background technology and details of development for the Rockwell hydrogasifier reactor have been previously reported over the last few years (References 3, 4, and 5). However, a brief review is necessary to establish the conditions under which the peat hydrogasification tests were made.

The Rockwell reactor is based on the application of rocket engine techniques to achieve rapid mixing-reaction at optimum temperature and residence time. Adjustment of reactor conditions, principally temperature and residence time, allows a range of product distribution from predominantly liquids to complete gasification to substitute natural gas (SNG). Intermediate conditions permit maximized yields of byproduct BTX (benzene, toluene, and xylene).

Successful operation has been demonstrated at engineering scales from 1/4- to 1-ton/h (tph) feedrates. This success was achieved by feeding dry, pulverized carbonaceous solids (coal or peat) into the reactor with a minimum of carrier gas (dense-phase flow) and there, achieving almost instantaneous mixing and concurrent heating with a preheated gaseous hydrogen stream. Reactor conditions were controlled to produce the desired products (liquids or gas). The current reactor development program (DOE Contract ET-78-C-01-3125) will optimize the injector-reactor configuration at 4 tph and be a full-scale element for straightforward, multi-element scaling to commercial-size reactors.

REACTOR SYSTEM

A description of the dense-phase, dry-solids feed system has been presented in previous papers and reports (References 3 and 4). Without modification, this

*Hydrogasifier Development for the Hydrane Process, Contract EX-77-C-01-2518, Louis Jablansky, Department of Energy (DOE) Program Manager.

system was used to feed dry, ground reed sedge Minnesota peat (<10% moisture and 78% through 200 mesh) with no problems at the 1/4-tph test level. Sieve analyses for a typical sample of peat and the resulting char are shown in Figure 1.

The reactor system (see Figure 2), as also described in References 3 and 4, uses a stream of hot hydrogen as the working fluid for the reaction. Hydrogen is preheated to 1100°F in an electrical heater, then to 2000 to 2100°F by combusting a small amount of hydrogen with oxygen in a preburner assembly. After rapid, injector-induced mixing (and heating) of the dry solids (coal or peat) with the hot hydrogen, the resulting reaction products are cooled at the appropriate residence time to achieve the desired product distribution. Cooling is accomplished with a water spray, which reduces the product gas temperature to 600 to 1000°F. The vapor phase products are separated from the char, and subsequently directed through a high-pressure, water-cooled condenser to remove water and any oils which may have been produced. The vapors are then sampled and regulated down to the appropriate venting pressure (<100 psig). Before venting, an activated-carbon, packed-bed adsorber is used to recover the vapor-phase BTX from the product stream.

Char is collected in a spherical receiver (located just under the water spray quench as shown in Figure 2) until completion of the test. Vapor-phase condensate is decanted (if necessary) to separate oil product for analysis. The char, gas, oil, condensed aqueous phase, and the activated carbon are analyzed to permit material balance calculations. It is important to mention that no modifications of the reactor system (as used for coal hydrogasification) are necessary to conduct the peat test.

PEAT TEST RESULTS

Ultimate and proximate analyses for the dried and ground peat, as received, are presented in Table 1. Eleven hydrogasification tests were conducted as shown in Table 2 at the 1/4-tph test level. Due to limited feed tank volume, test durations were ~6 to 10 min. The data are quite consistent, with high overall carbon conversions up to 84.2%, with the principal products being methane (CH₄) and carbon monoxide (CO). Small amounts (1 to 2%) of carbon dioxide were obtained. Except for the very low temperature Run 54, all of the liquids produced were essentially pure benzene.

TABLE 1
CHARACTERISTICS OF PEAT TESTED

	Minnesota Peat	
	As Received	Dry
Proximate Analysis (%)		
Moisture	9.40	—
Ash	16.87	18.62
Volatiles	53.76	59.34
Fixed Carbon	19.97	22.04
Ultimate Analysis (%)		
Moisture	9.40	—
Carbon	42.44	46.84
Hydrogen	4.50	4.97
Nitrogen	1.60	1.77
Chlorine	0.03	0.03
Sulfur	0.18	0.20
Ash	16.87	18.62
Oxygen (by diff.)	24.98	27.57
Heating Value (Btu/lb)	7,596	8,328

Figure 3 shows the effect of reactor residence time on overall carbon conversion and specific conversion to liquids (the difference is the conversion to gas). Liquid byproduct can be eliminated by high temperature (>1800°F) and longer residence time (>2.8 s). Data points are segregated into two reactor exhaust temperature groups. This graph shows that conversion is a function of residence time and temperature predominantly and essentially independent of pressure within the range of 500 to 1500 psig. The mild effect of reactor temperature is shown in Figure 4. The total carbon conversion increases slightly as reactor temperature is increased from 1550 to 1850°F. The apparent effect of pressure in Figure 4 is caused by the concurrent increase in residence time as pressure is increased in a given reactor configuration. Two different size reactor tubes were used to isolate the effect of pressure

from residence time. The low overall conversion and low conversion to gases of Run 54, which had a reactor temperature of only $\sim 1000^{\circ}\text{F}$, are dramatically shown in Figure 4.

Conversion to benzene as a function of reactor temperature is magnified in Figure 5. Conversion ranged from 0.0 to 11.7 wt % benzene as an inverse function of temperature and residence time. This graph (Figure 5) is useful for defining reactor conditions required for elimination of liquid product. One hundred percent selectivity to gases with an overall carbon conversion of 84% is attainable in a 3-s residence reactor at reactor temperatures above $\sim 1850^{\circ}\text{F}$. As shown in Table 2, analyses of the product gas composition for peat indicate that, in general, the carbon is converted primarily to CH_4 and CO at a mole ratio of $\sim 2:1$ (CH_4 to CO). Almost all of the carbon monoxide results from the relatively high oxygen content of the peat.

DISCUSSION

Using a computerized analytical model of the fluid dynamics and specific hydrogenation reactions, previously developed for coal conversion (Reference 6), peat results show consistent agreement with coal data (see Figure 6). The model assumes steady-state, one-dimensional (plug) flow, which is typical of the uniform flow patterns of rocket-type injectors at short distances from the injector face.

In order to compare these peat results for the Rockwell hydrogasifier with other peat hydrogenation investigations, the test data were plotted on a published IGT graph of hydrocarbon gas yield vs reactor temperature (Reference 1) for similar peat hydrogasification tests. Figure 7 shows this comparison. The Rockwell data are seen to be consistent with extrapolation of the IGT data to high reactor temperatures, and therefore to higher conversion levels. Together with the relative ease of processing peat in the unmodified Rockwell coal hydrogasifier, these high conversion levels provide encouraging support to the concept of peat hydrogasification to produce SNG. A commercial peat SNG plant might differ from one based on coal mainly in the more stringent requirements for drying the peat and for methanating the greater quantity of carbon monoxide.

CONCLUSIONS

The results of this experimental investigation clearly demonstrate that the Rockwell Flash Hydrogasifier is one of the most effective reactors for converting peat to SNG. Overall carbon conversions up to 84% with benzene byproduct yield ranging from 0 to nearly 12% were achieved. Both overall carbon conversion and conversion to benzene were found to be functions of reactor temperature and residence time, but not to depend upon reactor operating pressure. Rapid hydrogasification should be considered as a prime candidate for converting our abundant peat reserves to SNG.

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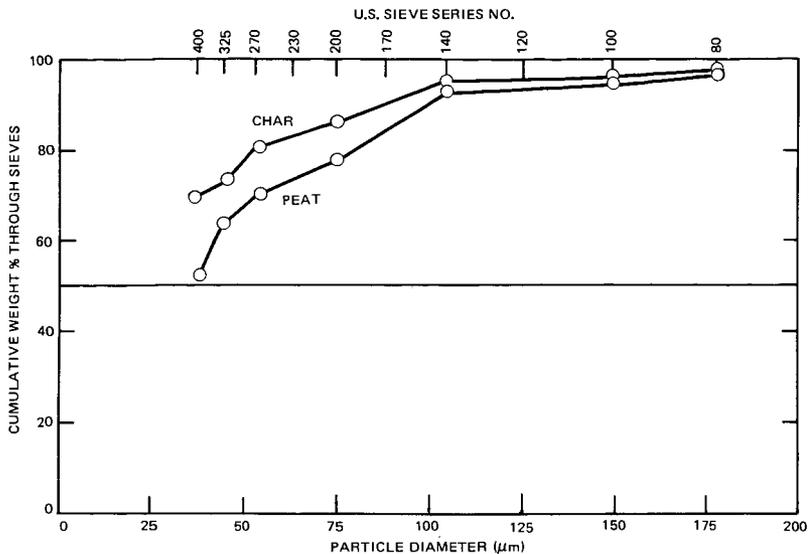
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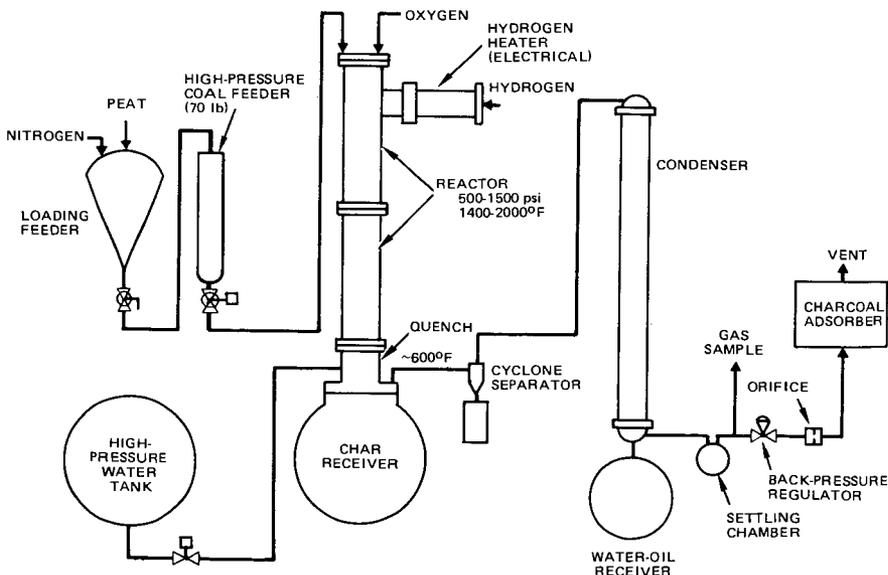
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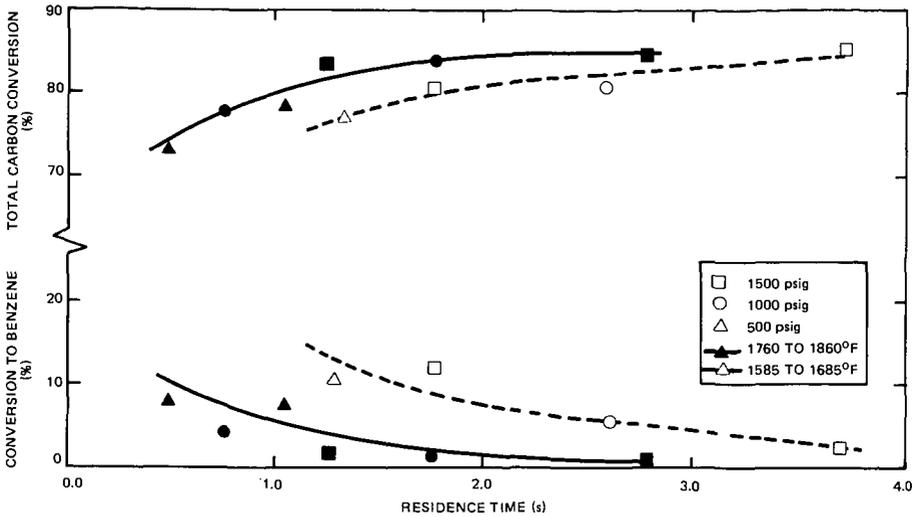
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Figure 1. Peat and Char Sieve Analyses



9317-101

Figure 2. Simplified Flow Diagram of Rockwell 1/4-TPH Hydrogasifier System



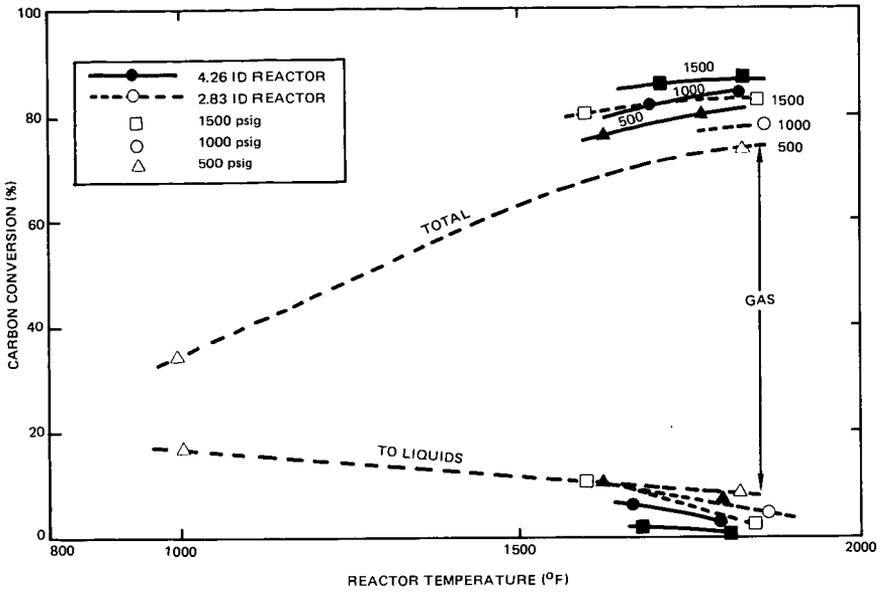
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Figure 3. Carbon Conversion as a Function of Reactor Residence Time

TABLE 2
TEST RESULTS

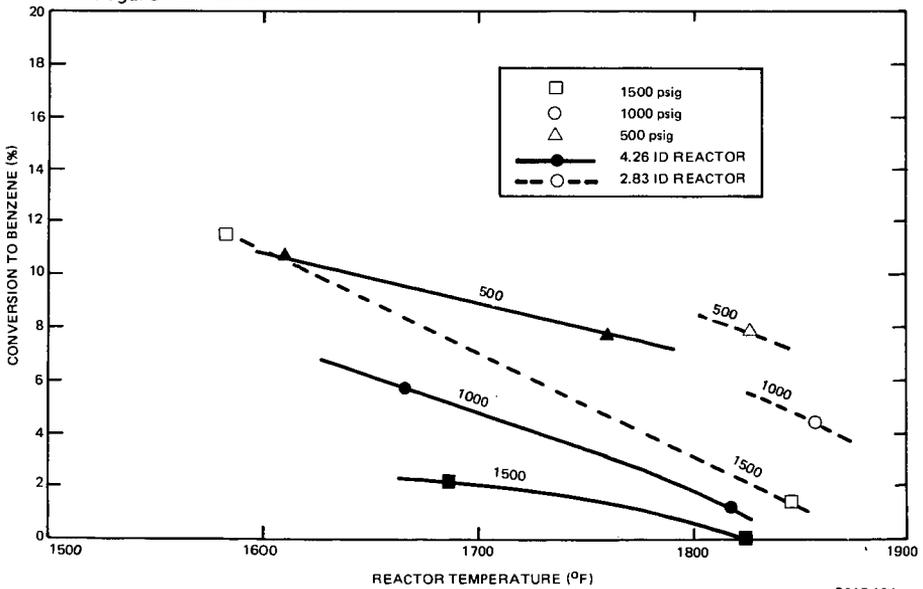
Run No.	Reactor Conditions					Carbon Conversion (%)				Heating Value (H ₂ -Free Basis) (Btu/scf)
	Diameter (in.)	P (psig)	T (°F)	τ _R (s)	H ₂ /Peat	Total	CH ₄	CO	Benzene*	
44	4.26	1500	1685	3.7	0.66	84.9	58.7	23.3	2.1	808
45	4.26	1000	1667	2.6	0.61	80.8	49.9	24.0	5.8	778
46	4.26	1000	1815	1.8	0.93	83.3	52.7	28.3	1.2	761
47	4.26	500	1610	1.3	0.53	76.6	39.8	24.8	10.5	731
48	4.26	500	1760	1.1	0.84	79.0	42.7	27.1	7.9	732
49	4.26	1500	1825	2.8	0.90	84.2	59.3	24.0	0.0	788
50	2.83	1500	1847	1.2	0.85	83.8	56.4	25.0	1.5	792
51	2.83	1500	1584	1.7	0.60	80.1	43.0	24.4	11.7	752
52	2.83	535	1825	0.5	0.57	73.4	38.9	25.3	7.9	726
53	2.83	1000	1857	0.8	0.91	77.4	46.7	25.3	4.4	760
54	2.83	500	998	0.8	0.59	34.2	1.6	7.2	16.2	330

*Liquids are vapor phase benzene for all tests except No. 54



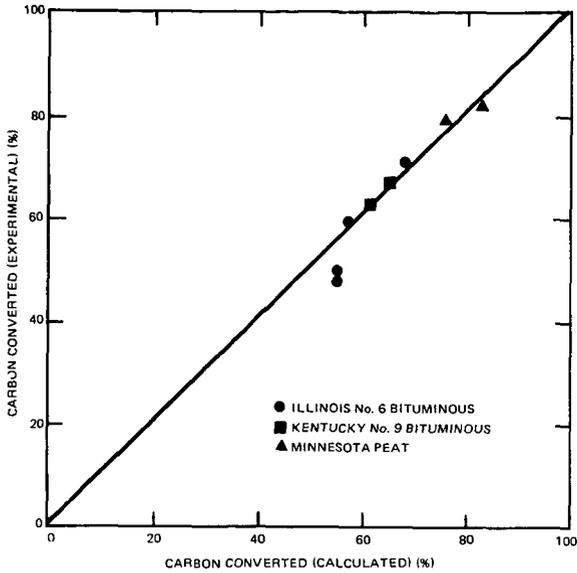
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Figure 4. Carbon Conversion as a Function of Reactor Temperature



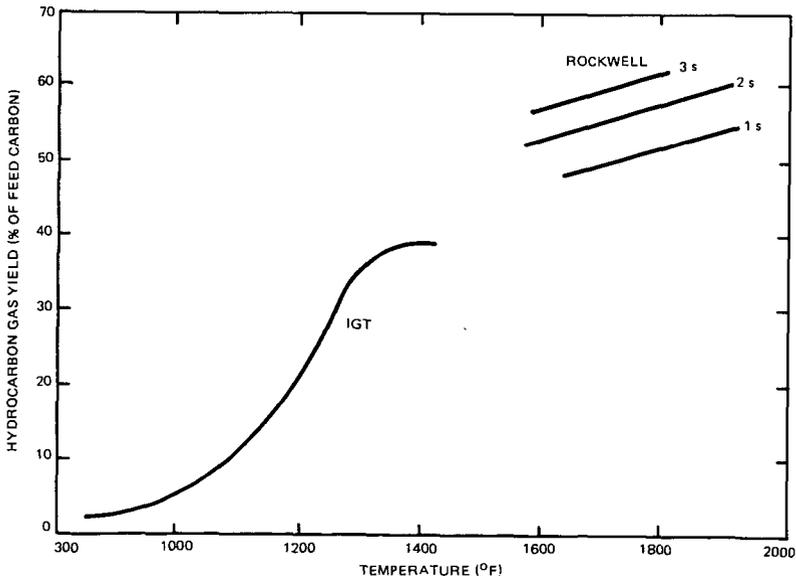
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Figure 5. Carbon Conversion to Benzene as a Function of Reactor Temperature



9317-105

Figure 6. Comparison of Reactor Model With Experimental Data



9317-106

Figure 7. Comparison of Hydrocarbon Gas Yields for Peat

FLASH HYDROGENATION OF LIGNITE AND BITUMINOUS COAL
IN AN ENTRAINED FLOW REACTOR

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Introduction

This paper is a report of some recent developments in an on-going investigation of short residence time hydrogenolysis of lignite and coal to produce fuel gases, ethane, gasoline blending stock constituents, fuel oil and spent char. The program has been underway for three years, and in addition to the bench-scale unit described here will include the construction and operation of a process development unit. In results obtained to date, both lignite and bituminous coal have been successfully processed in the bench-scale unit. In a typical run, approximately 50% of the feed carbon is converted to liquid and gaseous products; as much as 15% of the feed carbon has been found to report to the hydrocarbon liquid products, and 35% to carbon oxides, methane, ethane and minor amounts of propane and propylene. Heavy tars are not produced, allowing the spent char to be collected as a dry, free-flowing material. Approximately 50% of the feed carbon remaining in the spent char would be utilized in hydrogen production, and would be sufficient for a "balanced plant" operation.

Hiteshue, *et al.* (1) observed that when coal is heated rapidly in the presence of hydrogen at high pressure, high yields of gaseous and liquid products are obtained. Over the past several years, several development programs (2,3,4,5,6) have been implemented to explore the various aspects of rapid or "flash" hydrolysis in the light of eventual commercialization. The work described here is intended, in general, to complement the work of other investigators, and also elucidate the behavior of reactants and products during the course of the pyrolysis. The exploration of processing conditions appropriate for the recovery of maximum possible yields of liquids suitable for use as motor fuels is an important additional aspect of the IGT program. Johnson (4) postulated that the hydrocarbon liquids are released early in the pyrolysis, and are hydrogenated to methane and ethane in subsequent reaction steps.

In the work described here, our data show that in addition to relatively slow hydrogasification to methane and ethane, there is considerable vapor phase dehydroxylation of oxygenated monoaromatics (phenols + cresols) and dealkylation of substituted benzenes which results in significant changes in the distribution of BTX and oxygenated aromatics in the gasoline boiling range fraction of the hydrocarbon liquid products. The dehydroxylation and dealkylation reactions appear to be dependent upon both hydrogen partial pressure and temperature in a manner analogous to the vapor phase dealkylation of toluene in the presence of hydrogen described by Silsby and Sawyer (7).

Equipment

A flow diagram showing the major equipment in the bench-scale unit used in the work described here is shown in Figure 1. In operation, solids charged to the feed hopper are metered into a carrier stream of hydrogen; the hydrogen and entrained solids are then heated concurrently in a 1/8-in I.D. helical tube reactor which is 70 feet in length. A predetermined "temperature profile" is imposed over the length of the reactor by means of 12 independently controlled radiant heaters. The effluent from

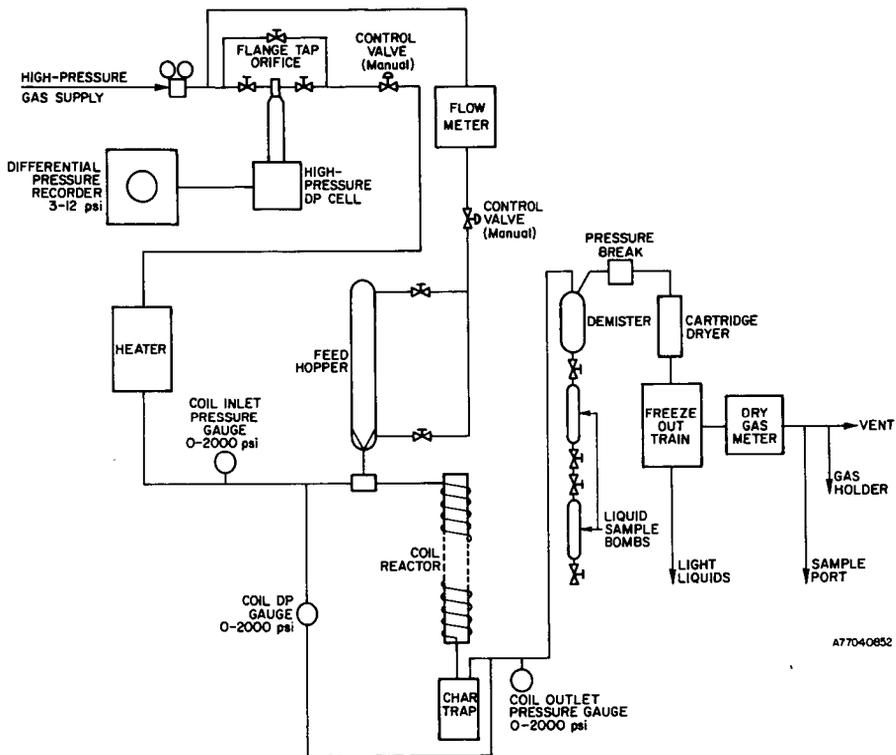


Figure 1. BENCH-SCALE UNIT

the reactor passes into the char trap where the spent char is disentrained and collected; the char-free gases are further cooled to ambient temperature to condense liquid products which are collected in sample bombs. The cooled gases are then reduced to essentially ambient pressure, and passed through a dryer and methanol/dry ice freeze-out train to strip benzene and other condensable materials from the make gas. The stripped gases are then metered, sampled, and vented.

A power plant grind (75% minus 200 mesh) of North Dakota lignite was used as solids feed in the work described here. Although feed gases can be preheated prior to mixing with feed solids, both the feed hydrogen and feed lignite were introduced into the reactor at ambient temperature. Runs using preheated hydrogen have been made, but analysis of data has not been completed at this writing; the results of these runs will be reported at a future time.

Experimental

In the experimental program described here, the objective was to explore the effect of heating rate on the distribution of feed carbon among products. Two kinds of temperature profile (Figure 2) were used in operating the equipment. In the first type, a linear heating rate was imposed on the lower end of the coil reactor. Due to a "chimney" effect, the upper end of the coil was heated by convection from the lower section, and idled at approximately 700°F. Using this first type of temperature profile, the feed was heated to a maximum temperature of 1500°F and quenched, with no appreciable residence time at 1500°F. In the second type of temperature profile, the lower section of the reactor was operated isothermally at 1500°F, and a linear heating rate imposed on the upper section of the coiled tube reactor, so that the reactants were held at 1500°F for times which were dependent upon the gas velocity chosen for a particular run.

Experimental Results

The operating conditions and results of the heating rate study are summarized in Table 1 which shows the distribution of carbon among products, the weight percent gasoline boiling range liquids obtained from the recovered liquids, and the weight percent of phenols + cresols and naphthalenes present in the gasoline boiling range liquids. Comparing Runs HR-1 and HR-3, it is apparent that with appreciable residence time at the maximum temperature (1500°F), feed carbon conversion actually decreased with increase in heating rate; a similar result was described by Johnson (4). At the higher heating rate, the liquid products were also more highly oxygenated, as measured by the amounts of phenols + cresols present in the gasoline boiling range liquids.

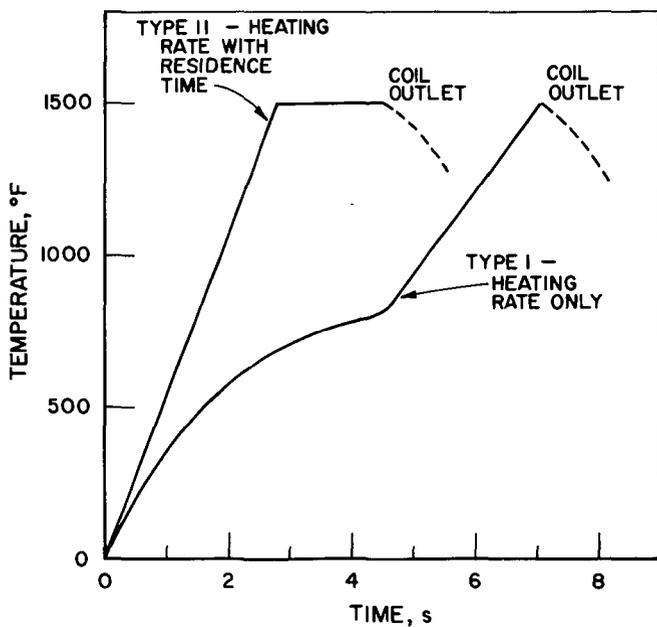
When a residence time at 1500°F was allowed, as in Runs HR-4 through HR-7, the methane yields improved considerably, and the degree of oxygenation of the liquid products as measured by the phenols + cresols in the gasoline boiling range liquids decreased. By inspection, however, there does not appear to be any effect that can be attributed to heating rate alone.

The intensity or severity of a time-temperature history can be measured by the magnitude of a severity function defined as -

$$\text{Severity Function} = \int_0^t k t \quad 1)$$

where k is a reaction rate constant and t is time. Using published data for the hydrogasification of anthracene (8), the rate constant can be calculated from -

$$k = k_0 e^{-E/RT} \quad 2)$$



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Figure 2. TEMPERATURE PROFILES USED IN HEATING RATE STUDIES

where k is 9.0×10^5 and E is 30,700 Kcals per gram mole. For the non-isothermal time-temperature histories used here, the value of the severity function was obtained by dividing the length of the coil into increments and calculating an incremental severity at the average temperature of the section. The value of the severity function was then obtained from -

$$\text{Severity Function} = \sum_{i=1}^n k \Delta t_n \quad 3)$$

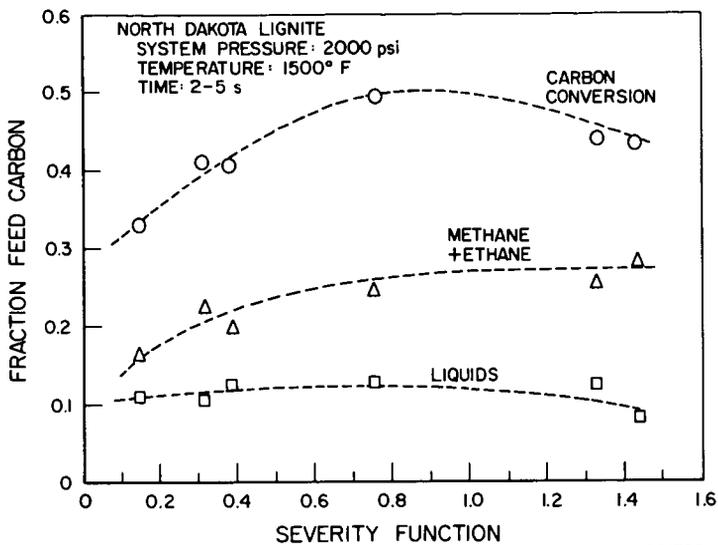
This severity function, based on anthracene hydrogasification kinetics is thus an arbitrary measure that can be used to characterize the thermal treatment under a given set of operating conditions. The data from the heating rate runs are plotted against severity function in Figure 3. From the figure, methane + ethane yield can be seen to increase with increase in severity function; while total carbon conversion passes through a maximum, suggesting that in a prolonged treatment, products are lost through thermal degradation. A similar result has been described by Steinberg, et al. (6). The total liquids yield also appears to decrease at high severity.

Table 1. OPERATING CONDITIONS AND SUMMARY OF RESULTS OBTAINED IN HEATING RATE STUDIES WITH NORTH DAKOTA LIGNITE

Run No.	HR-2	HR-1	HR-3	HR-4	HR-5	HR-7	HR-6
Coil Outlet Pressure	2000	2000	2000	2000	2000	2000	2000
Coil Outlet Temperature	1500	1500	1500	1500	1500	1500	1500
Severity Function	0.383	0.315	9.148	0.767	1.346	1.434	1.954
Heating Rate, °F/s	125	152	348	412	155	1275	780
H ₂ /MAF Feed Weight Ratio	0.44	0.26	0.48	0.43	0.30	0.55	0.45
Carbon Distribution, %							
Liquids	12.25	11.03	11.71	13.19	12.44	8.59	7.30
Carbon Oxides	9.47	9.05	8.18	11.27	9.72	10.35	8.47
Methane	12.40	10.90	10.59	16.34	17.35	19.47	19.69
Ethane + Light Gas	7.37	11.36	6.26	8.43	8.33	8.63	8.61
Char	52.20	51.23	58.87	52.51	52.52	54.55	52.69
Gasoline Boiling Range Liquid, wt % total liquids	51.8	55.2	49.5	54.1	54.5	67.5	58.5
Phenols + Cresols in C ₅ -400°F Liquid	22.7	18.0	31.2	7.1	1.6	0.2	Tr
Naphthalene in C ₅ -400°F Liquid	12.6	15.2	10.8	6.7	5.3	15.2	7.8
	No Residence Time at 1500°F			Variable Residence Time at 1500°F			

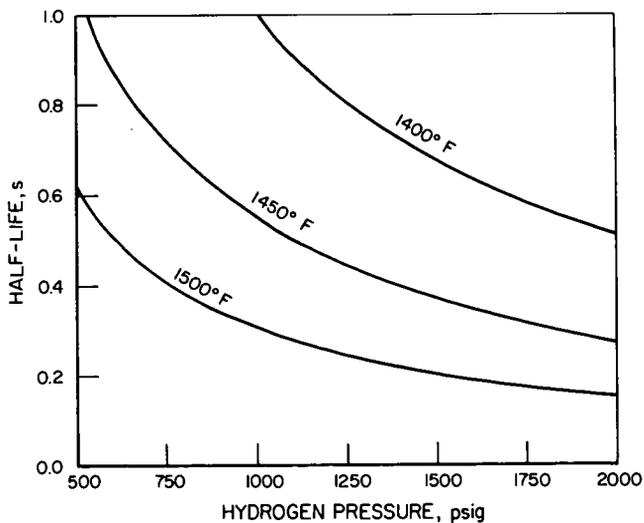
Discussion

Using kinetics published by Silsby and Sawyer (7), the change in the half-life of toluene with temperature and pressure was evaluated, and the results of these calculations are summarized in Figure 4. From the figure it can be seen that the dealkylation of toluene is accelerated by both an increase in temperature and hydrogen partial pressure. The observed changes in the composition of the gasoline boiling range liquids obtained from North Dakota lignite also appear to follow an analogous rule in which the dehydroxylation is accelerated by increase in hydrogen partial pressure (Figure 5). In a prior portion of the investigation, runs were made in the bench-scale unit at system pressures of 500, 1000, 1500, and 2000 psig, holding other parameters essentially constant. The fraction of phenols + cresols in the gasoline boiling range liquids was observed to decrease with increase in operating (essentially hydrogen) pressure while the fraction of BTX + ethylbenzene was observed to increase.



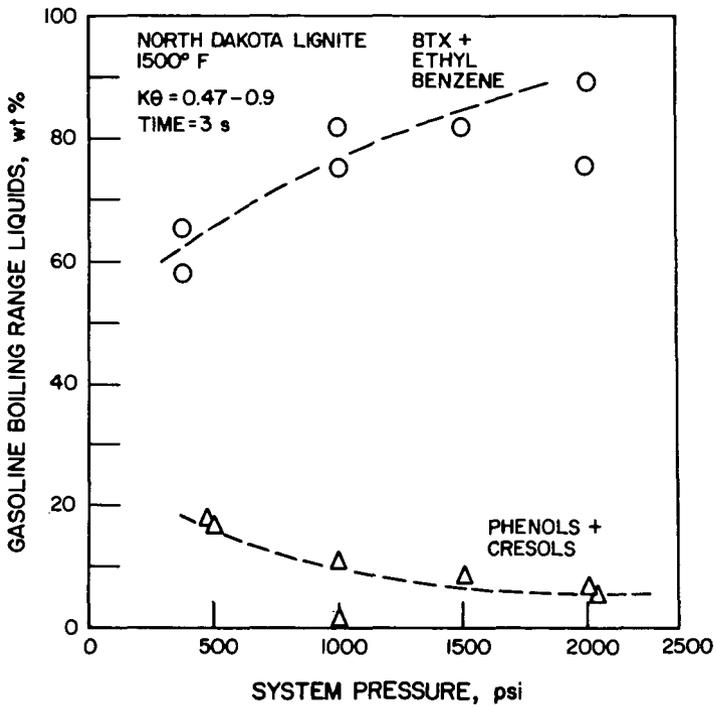
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Figure 3. CARBON CONVERSION, METHANE + ETHANE, AND LIQUIDS YIELDS IN HEATING RATE STUDIES



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Figure 4. CHANGE IN THE HALF-LIFE OF TOLUENE WITH TEMPERATURE AND HYDROGEN PARTIAL PRESSURE (6)



A79061325

Figure 5. CHANGE IN GASOLINE BOILING RANGE LIQUIDS COMPOSITION WITH PRESSURE

In the heating rate runs, the phenols + cresols fraction of the gasoline boiling range liquids was found to decrease with increase in severity function, as shown in Figure 6 with an attendant increase in BTX. The distribution of benzene, toluene, and xylene was observed to change as shown in Figure 7 which shows maxima for both toluene and xylene early in the pyrolysis with subsequent dealkylation to benzene. Finally, liquids, as they are devolved from the lignite at 1200° to 1300°F, are highly oxygenated, as shown in Table 2 which summarizes data from some runs with North Dakota lignite.

Table 2. OPERATING CONDITIONS AND SUMMARY OF RESULTS OBTAINED AT 1200° AND 1300°F WITH NORTH DAKOTA LIGNITE

Run Number	PS-3	PS-5
Coil Outlet Pressure, psig	1500	1500
Coil Outlet Temperature, °F	1300	1200
Severity Function	0.334	0.217
H ₂ /MAF Feed Weight Ratio	0.31	0.53
Carbon Distribution, %		
Liquids	14.61	11.58
Carbon Oxides	9.46	9.23
Methane	9.62	5.88
Ethane + Light Gas	6.23	5.07
Char	64.51	68.33
Analysis of Gasoline Boiling Range Liquids		
BTX + Ethylbenzene	22.9	8.3
C ₉ Aromatics	5.4	4.0
Indenes + Indans	5.1	4.0
Phenols + Cresols	52.3	76.1
Naphthalenes	5.4	3.3
Not Identified	8.9	4.3
Total	100.0	100.0

Conclusions

From the foregoing it appears that the hydrocarbon liquids obtained from North Dakota lignite are highly oxygenated as they are devolved from the lignite, and are converted to BTX in the vapor phase by reaction with hydrogen. The conversion of oxygenated compounds to BTX exhibits a pressure and temperature dependency very similar to the dealkylation of toluene in the presence of hydrogen described by Silsby and Sawyer (7). The distribution of feed carbon among products and the composition of the gasoline boiling range liquids is a function of severity of thermal treatment, and appears to be independent of heating rate when heating rates of 150°F/s or higher are used.

The pressure dependency of the dehydroxylation reactions would affect reactor operations, particularly at low hydrogen-to-coal feed ratios where the hydrogen partial pressure would be substantially reduced with the release of methane, steam, and other reaction products. At this writing, the experimental work is being extended to the study of the effects of using preheated hydrogen. Analysis of data has not been completed, however, and the results of these runs will be reported at a future time.

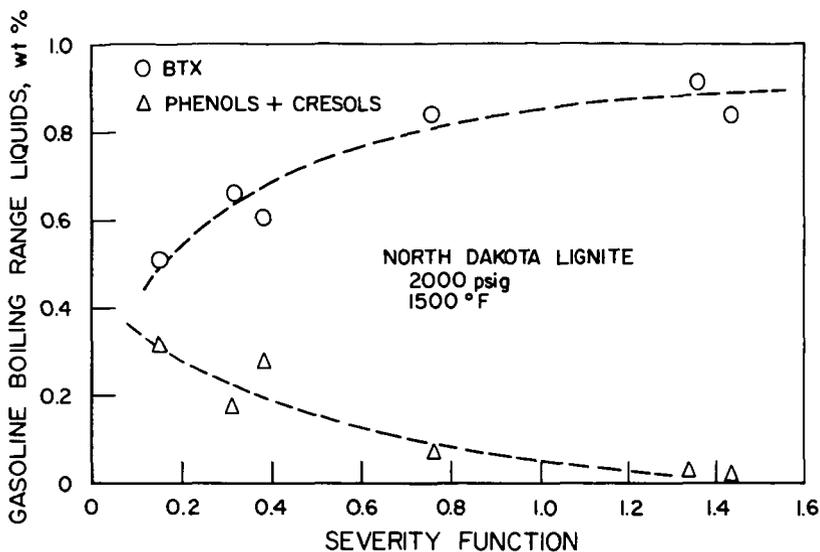


Figure 6. DISTRIBUTION OF BTX AND PHENOLS + CRESOLS WITH INCREASE IN SEVERITY A79061327

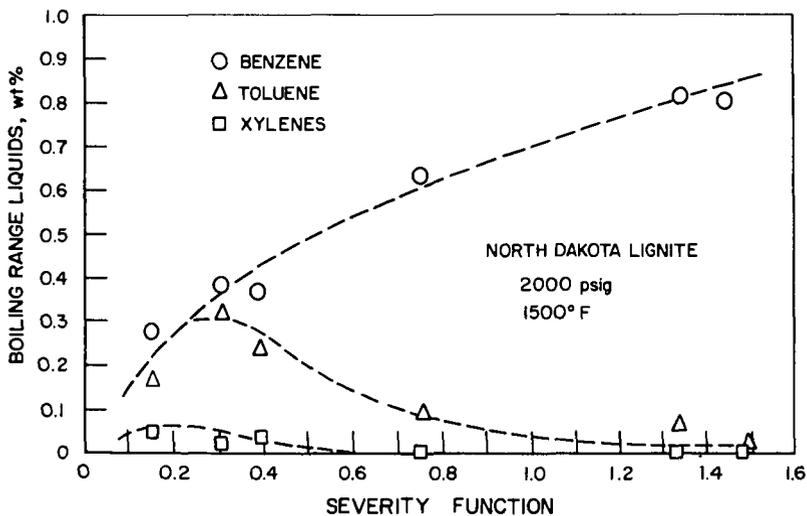


Figure 7. DISTRIBUTION OF BENZENE, TOLUENE, AND XYLENES IN THE BTX FRACTION OF GASOLINE BOILING RANGE LIQUIDS A79061324

Acknowledgements

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MECHANISM OF SHORT RESIDENCE TIME HYDROLYSIS
REACTION FOR MONTANA ROSEBUD SUBBITUMINOUS COAL

by

U. M. Oko, J. A. Hamshar, G. Cuneo and S. Kim

A. Introduction

Research into short residence time hydrolysis of coal has been in progress at Cities Service Research and Development Company since 1974. More than 150 individual coal runs were performed in this time period using a bench-scale reactor recently described (1). Cost estimates for SWG and benzene production were also published (2)(3).

Some 50 runs were performed on Montana Rosebud Subbituminous coal at various reactor conditions. The results of these runs were reported elsewhere (1)(4)(5). In this report, a kinetic model originally proposed by Feldmann (6) is used to calculate reaction rate constants for carbon conversion for these 50 runs, at four distinct temperature zones. Also, the effect of reactor conditions are statistically correlated with gas and liquid hydrocarbons and the results of this analysis is reported.

B. Kinetics of Carbon Conversion

High heat up rates of finely divided coal particles and short residence time of less than 2 seconds at 500-1500°C under hydrogen atmosphere (7) were shown to promote carbon conversion into gas and liquids. Several reaction models were proposed to explain the kinetics of this phenomenon. Recently, Russel et al (8) illustrated that the role of mass transfer by bulk flow and diffusion including kinetics of devolatilization in single particles of coal can be explained by assuming a first order devolatilization reaction with instantaneous heatup to isothermal state and relatively long reaction time. Their model consists of three sets of reactions: primary devolatilization, secondary deposition and hydrogenation. This model was shown to fit data generated by Anthony and Howard (9) from hydrolysis of single discrete coal particles in a batch reactor.

For continuously operating reactors a simpler model has been used by several investigators including Wen, Feldmann, et al (6)(10). In this model the rate of gasification is proportional to the hydrogen partial pressure and to the rapid-rate carbon material remaining in the coal. For coal gasification into methane this simple model can be used by assigning the carbon in the coal into three categories (6). Type 1 carbon is a highly reactive specie which is almost instantaneously flashed off during the rapid heatup step. Type 2 is the solid carbon which readily hydrogasifies and type 3 is the low reactivity char carbon which will react upon long duration exposure (in order of minutes) to the hot hydrogen atmosphere. Type 1 and 2 carbon are classified "rapid rate carbon" and in this report are considered as a single specie.

For hydrogasification reaction the "rapid rate carbon" and hydrogen interaction follows the rate reaction (6):

$$\frac{dX}{dt} = k P_{H_2} (\alpha - X) \quad (1)$$

where X is the fractional carbon conversion, P_{H_2} the hydrogen partial pressure, α the fraction of carbon available for reaction in the regime of consideration and k the reaction rate constant. Best fit for conversion data were found by Feldmann (6)(12) when $\alpha = 1$. Hence, at any given constant temperature:

$$\int_0^X \frac{dX}{1-X} = \int_0^t k P_{H_2} dt \quad (2)$$

$$\ln(1-X) = -k P_{H_2} t \quad (3)$$

where t is the coal/hydrogen contact time in the reactor. From equation 3, the reaction rate constant k , can be calculated.

C. Particle Residence Time in the Reactors

The Cities Service R & D Co. short residence time bench-scale reactor system shown in Figure 1 was previously described (4). It can accept interchangeable reactors to investigate the effect of wide spans of residence time on the extent of carbon conversion into gas hydrocarbons and liquid hydrocarbon products. When short residence times are desired, straight vertical reactors of different diameters are fitted inside the electric furnace cavity. For longer residence times, helical reactors can be fitted.

The problem of estimating particle residence time in vertical entrained straight reactors can be solved by estimating the terminal velocity of a single char particle, and then correcting this value for entrained flow. This method was used by Gray et al (11) who used the equation:

$$U_T = \left[\frac{3.1g (\rho_s - \rho_g) \bar{d}_p}{\rho_g} \right]^{1/2} \quad (4)$$

to estimate the terminal settling velocity (14). Correction factors which were applied following Wen and Huebler (10) increased the final particle velocity by a factor of about 3. For helical reactors, the problem of estimating particle residence time is further aggravated by the almost total lack of experimental or theoretical data. In our work, we met these shortcomings with glass cold-flow models of straight and helical reactors and measured average particle velocities in these models. The same flow regimes that were experienced in the bench-scale apparatus were used in the model studies. The average average particle velocities were found by feeding coal-char at controlled rate from feed hoppers located above the glass model. Coal char was used because in most of these tests particle residence time exceeded 0.5 seconds. Coal is converted into char-like material within 0.200 seconds at the temperature regimes of 825-1000°C.

Holdup of particles in the model, at constant flow conditions, was measured by simultaneously closing plug valves at the inlet and exit. The velocities were calculated from the weight of the solids trapped in the section and the feed rate to the model. This work was done by Ming-Tsai Shu and C. B. Weinberger of Drexel University (15).

With the glass model for the vertical straight reactor of length L , (4) we found that the average average particle velocity is very close to that of the superficial gas velocity. This greatly simplified the task of calculating particle residence times t :

$$t = L/\bar{V}_p(dp) \quad (5)$$

where $\bar{V}_p(dp)$ is the average average particle velocity in m/sec. For helical reactors, at gas velocity in the excess of 6.3 m/sec. the following semi empirical equation was derived by Shu (15) to estimate the average average particle velocity:

$$\frac{\bar{v}_g - \bar{v}_p(dp)}{v_g} = k_o \text{Re}^a R^b \left(\frac{D_H}{D_T}\right)^c \cdot \left(\frac{dp}{dp}\right)^d \quad (6)$$

where for char of Montana Rosebud subbituminous coal:

$$\begin{aligned} k_o &= 0.323 \\ a &= 0.139 \\ b &= 0.185 \\ c &= -.102 \end{aligned}$$

When calculating the average average flow velocity of char:

$$dp/\bar{dp} = 1 \quad (7)$$

and t , residence time, is calculated from equation 5. A plot of the average variable size particle velocity for a constant gas velocity of 6.3 m/sec is shown in Figure 2. The plot indicates that selective classification occurs in the helical reactor. This was also observed visually. The large particles tend to settle at the glass model wall and because of wall friction move slower than the fine particles. Also, when the feeding rate of particles into the model is increased, the average average particle velocity in it decreases. This is because the particles are not uniformly dispersed and tend to concentrate at the outer periphery of the helix.

When the superficial gas velocity is below 6.3 m/sec, equation 6 becomes increasingly unreliable and velocity of the particles must be interpolated from specific flow measurements generated by Shu (15). However, even at somewhat lower velocity the equation may be used to predict average average particle residence times. For example, workers at the University of Utah (17) using iron filings as tracer in coal which was treated in a helical reactor in hydrogen at 122 atm. and 482°C reported residence time of 9 seconds. The reactor was a tube of 0.48 cm internal diameter, 14.5 meters long which was coiled into a 12.7 cm diameter helix. The gas velocity in their tests was only 5.6 m/sec. Yet even with this low velocity, equation 6 predicts residence time of 10 sec.

D. Hydrogasification Kinetics of Montana Rosebud Subbituminous Coal

Fifty subbituminous coal runs were performed (4) over a range of conditions summarized in Table 1. The data was further divided into four temperature ranges from 827°C to 1000°C. Plot of $-\ln(1-x)$ versus $P_{H_2} t$ in sec. atm is displayed in Figure 3. Table 2 summarizes the equations of each of the lines indicating the quality of fit of each as obtained by regression analysis.

A plot of $\ln k$ vs. $1/T$ on Figure 4 for Montana Rosebud Subbituminous coal is compared with results for Pittsburgh Seam bituminous coal (11). The Arrhenius activation energies for both coals are relatively high: about 15 kcal/mole for the Pittsburgh seam coal and 27 kcal/mole for Montana Rosebud Subbituminous coal. This indicates that both reactions are chemically controlled.

E. Statistical Correlation of Factors Affecting The Formation of Products

Statistical treatment of the data from the fifty runs is used to determine which of the reactor variables: temperature, pressure, vapor residence time, coal to hydrogen ratio, solids residence time or particle diameter are most likely to affect the degree of carbon conversion. The treatment can be extended to the effects of conditions on the yield of the various product

FIGURE 1

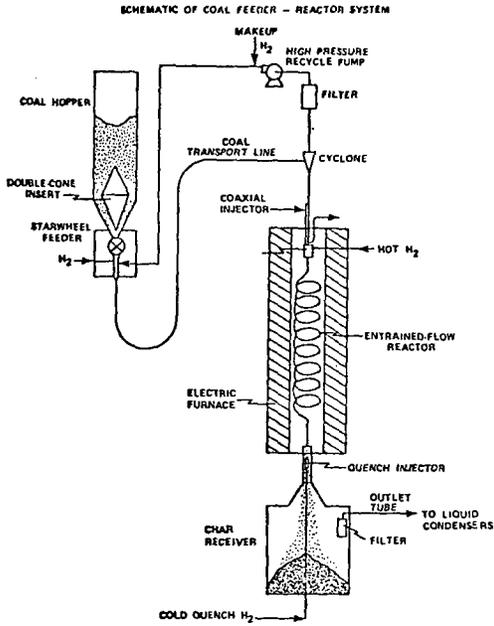


FIGURE 2

CHAR PARTICLES VELOCITY IN THE HELICAL REACTOR AS PREDICTED BY EQUATION

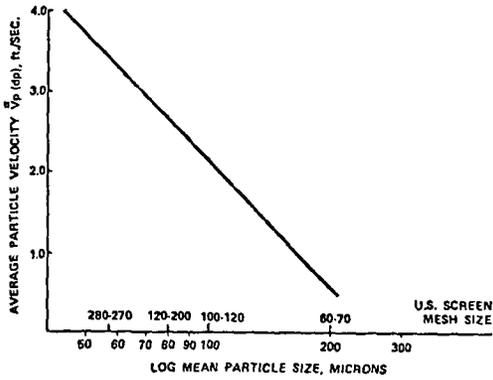


TABLE 1

RANGE OF OPERATING CONDITIONS FOR HYDROGASIFICATION
OF MONTANA ROSEBUD SUBBITUMINOUS COAL

	<u>Range</u>
Temperature - °C	825-1000
Pressure - atmospheres	34-160
Particle Residence Time - sec.	0.4-14.0
Superficial Gas Residence Time - sec.	0.3-4.0
Superficial Gas Velocity m/sec.	5.0-8.0
Hydrogen to Coal Weight Ratio	0.7-1.2

TABLE 2

DATA SUMMARY FOR EACH TEMPERATURE RANGE

<u>Temperature</u> °C	<u>No. of</u> <u>Data</u> <u>Points</u>	<u>Equation of line of best fit</u>	<u>r</u>	<u>$\frac{k}{\text{atm}^{-1} \text{hr}^{-1}}$</u>	<u>Equation</u> <u>No.</u>
827 ± 10°	15	$\ln(1-x) = 1.483 \times 10^{-4} P_{\text{H}_2} t + .3974$.861	.53	(8)
877 ± 10°	19	$\ln(1-x) = 2.36 \times 10^{-4} P_{\text{H}_2} t + .4036$.915	.85	(9)
902 ± 10°	8	$\ln(1-x) = 4.108 \times 10^{-4} P_{\text{H}_2} t + .3668$.892	1.48	(10)
927 ± 10°	8	$\ln(1-x) = 3.88 \times 10^{-4} P_{\text{H}_2} t + .3859$.972	1.40	(11)

FIGURE 3

PLOT OF $-\ln(1-X)$ vs. $P_{H_2} t$ - The slope of each of the lines is the reaction rate constant for Montana Rosebud Subbituminous Coal at the designated temperature

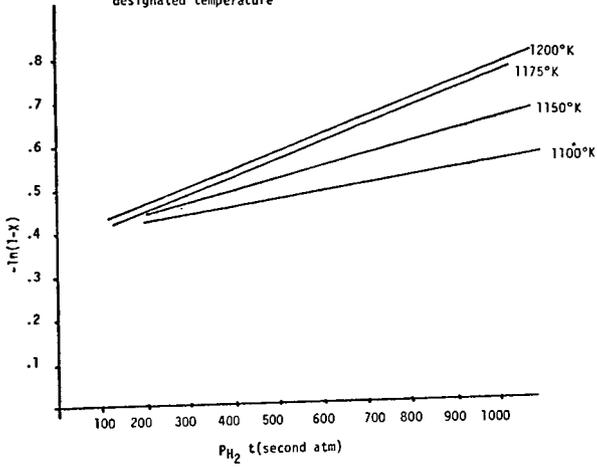
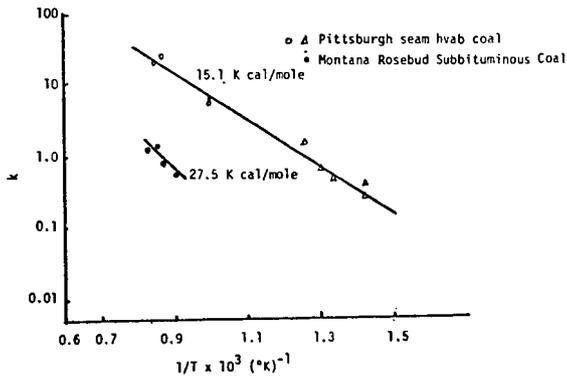


FIGURE 4

TEMPERATURE DEPENDENCE OF THE HYDROGASIFICATION REACTION RATE CONSTANTS FOR PITTSBURGH SEAM COAL (6) AND MONTANA ROSEBUD SUBBITUMINOUS COAL



fractions: gas, liquids, BTX and methane plus ethane. The computer program used for the analysis is available from IBM (16). It is capable of performing a stepwise linear regression followed by a polynomial fitting with orthogonal polynomials. With it, it is possible to analyze the effect of up to 40 variables. The results of the regression is expressed in a form of a linear equation:

$$y = b_0 + b_1x_1 + b_2x_2 + \dots b_nx_n \quad (12)$$

where x_1, x_2, \dots, x_n can be entered as independent transformation functions. The program selects the most effective functions to be fitted into the polynomial equation (12). In addition, it presents each dependent variable in order of importance and re-calculates the curve fitting correlation coefficient with each variable introduced. The forty functions shown in Table 3 were selected for each of the six independent variables:

T - temperature in degrees Kelvin
 P_{H_2} - hydrogen partial pressure - atmospheres
 t - residence time of solids in the reactor - gaseous
 X_g - gas residence time in the reactor - msec.
 $X_{H/C}$ - hydrogen to coal ratio - gm/gm
 dp - mean particle size - microns

and regressed against each of the dependent variables:

x - total fraction of carbon converted
 y_g - fraction of carbon converted to methane plus ethane
 y_e - fraction of carbon converted to liquid hydrocarbons
 y_b - fraction of carbon converted to BTX.

The following equations and correlation coefficients were obtained:

For total fraction of carbon converted:

$$X = \exp \left[\frac{-3276}{T} + .1282 \ln t + 1.761 \right] \quad r = 0.91 \quad (13)$$

For fraction of the carbon conversion into methane plus ethane:

$$y_g = \exp \left[\frac{-9428}{T} + .4457 \ln P_{H_2} + \ln t + 4.63 \right] \quad r = 0.93 \quad (14)$$

For fraction of the conversion into liquid hydrocarbons:

$$y_e = \exp \left[0.273 \ln P_{H_2} + 0.96 \ln t - 4.373 \right] \quad r = 0.67 \quad (15)$$

For fraction of carbon conversion to BTX:

$$y_b = \exp \left[\frac{-6814}{T} + .265 \ln t + 2.899 \right] \quad r = 0.87 \quad (16)$$

These results indicate that within limits of experimental conditions, and for the transformation functions selected gas residence time, hydrogen-to-coal ratio and mean particle diameter have no apparent effect on the degree of carbon conversion into any of the four products x , y_g , y_e , and y_b . The two most important variables seem to be temperature and solids residence time followed by the effects of pressure. Future work with other transformation functions and better modelling may however show that gas residence time may have effect on y_e .

Figure 5 illustrates the effects of temperatures and solids residence times on the total fraction of carbon converted. As expected, the effects of solids residence time are marginal compared to that of temperature. For example, in order to achieve $x = 0.3$, solids residence time of 15 seconds is required at 827°C but only 0.5 seconds if the temperature were to increase by 150°C.

Figure 6 illustrates the effect of temperature and pressure on conversion of carbon to methane and ethane. At constant pressure, the conversion rises steeply with the temperature but the effects of solids residence time are somewhat less pronounced than in Figure 5. At 880°C, $x = 0.3$ and only 60°C rise in temperature is required to drop the required solids residence time from 15 seconds to 0.5 seconds. The effect of pressure on conversion may even be smaller than that of solids residence time. When the pressure is reduced by about 34 atmospheres, the average reduction in conversion is less than 10% even at the high range of temperature. This is within the overall accuracy of gas analysis that can be claimed for this data.

Figure 7 illustrates the dependence of liquid yields on the partial pressure of hydrogen and on residence time. Because of poor correlation ($X = .67$), which indicates scatter in data and poor modelling, it is hard to draw more definitive conclusions. But when viewed with Figure 6 which has steeper slopes of carbon conversion to gas, it seems that optimum yield of liquid may be obtained at moderate temperatures, say 900°C and at hydrogen partial pressures which are as high as practicable.

Figure 8 suggests that conversion of carbon to BTX depends on the fraction of liquid hydrocarbons cracked to methane and ethane. Given long solids residence time with increasing temperature, most of the carbon will eventually be converted to gas probably undergoing intermediate liquefaction. BTX could be a product of liquid hydrocarbons which crack to produce methane and ethane. This may explain the positive slope of the yield curves and the relatively large effect of solids residence time on conversion.

TABLE 3

TRANSFORMATION EQUATIONS FOR REGRESSION ANALYSIS

X(1)	- Dependent Variable
X(2)	- Temperature
X(3)	- Total Reactor Pressure
X(4)	- Hydrogen Partial Pressure
X(5)	- Particle Residence Time
X(6)	- Gas Residence Time
X(7)	- Hydrogen/Coal Ratio
X(8)	- Mean Coal Feed Particle Size
X(11)	= $\text{ALOG}(X(1))$
X(12)	= $-1/X(2)$
X(13)	= $-\text{ALOG}(X(3))$
X(14)	= $\text{ALOG}(X(4))$
X(15)	= $\text{ALOG}(X(5))$
X(16)	= $-\text{ALOG}(X(6))$
X(17)	= $\text{ALOG}(X(7))$
X(18)	= $\text{ALOG}(X(8))$
X(19)	= $X(2)/X(3)$
X(20)	= $X(2)/X(4)$
X(21)	= $X(2)/X(5)$
X(22)	= $X(2)/X(6)$
X(23)	= $X(2)/X(7)$
X(24)	= $X(2)/X(8)$
X(25)	= $X(3)/X(4)$
X(26)	= $X(3)/X(5)$
X(27)	= $X(3)/X(6)$
X(28)	= $X(3)/X(7)$
X(29)	= $X(3)/X(8)$
X(30)	= $X(4)/X(5)$
X(31)	= $X(4)/X(6)$
X(32)	= $X(4)/X(7)$
X(33)	= $X(4)/X(8)$
X(34)	= $X(5)/X(6)$
X(35)	= $X(5)/X(7)$
X(36)	= $X(5)/X(8)$
X(37)	= $X(6)/X(7)$
X(38)	= $X(6)/X(8)$
X(39)	= $X(7)/X(8)$
X(40)	= $X(2) \times X(2)$
X(41)	= $\text{ALOG}(X(1))$
X(42)	= $\text{ALOG}(X(1))$
X(43)	= $\text{ALOG}(X(1))$
X(44)	= $\text{ALOG}(X(1))$
X(45)	= $1/X(2)$
X(46)	= $1/X(6)$
X(47)	= $1/X(7)$

FIGURE 5

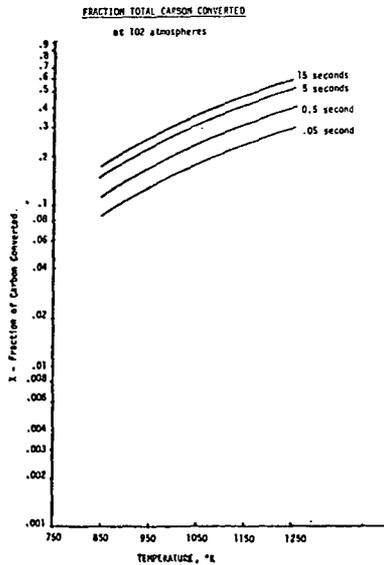


FIGURE 6

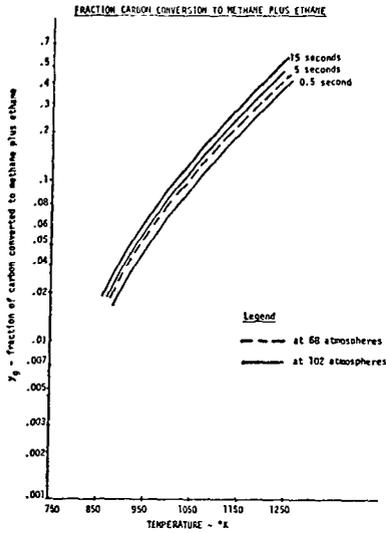


FIGURE 7

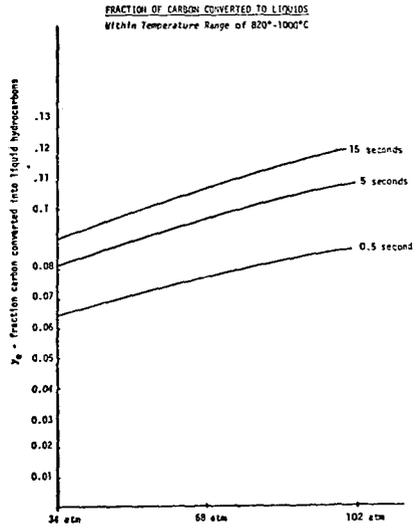
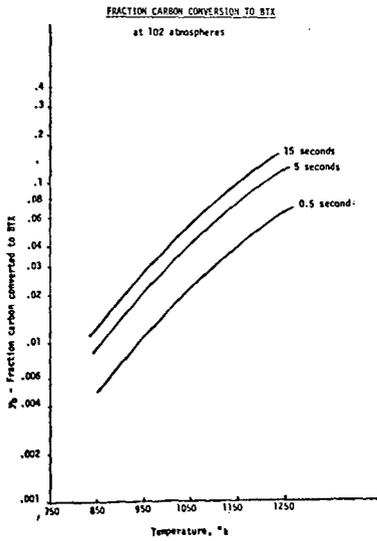


FIGURE 8



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G. Nomenclature

- BTX - benzene, toluene and xylene
- \bar{d}_p - average particle diameter - m^3
- D_H - helix diameter - microns
- D_T - helix tube internal diameter - m
- g - gravity constant - m/sec^2
- k - reaction rate constant - $atm^{-1} hr^{-1}$
- L - reactor length - m
- LHC - liquid hydrocarbons produced, including the BTX fraction as analyzed in the gas
- P_{H_2} - partial pressure of hydrogen
- r - correlation coefficient of regression of the line of best fit by the root mean square through the experimental data points
- Re - Reynold's number
- R - char to gas weight ratio
- t - time - sec.
- U_T - terminal settling velocity - m/sec.
- \bar{V}_g - average gas velocity - m/sec.
- $\bar{V}_p(dp)$ - average average particle velocity - m/sec.
- X - fraction of carbon converted
- X_g - gas residence time - msec.
- $X_{H/C}$ - hydrogen to coal ratio gm/gm
- y_p - fraction carbon converted to methane plus ethane
- y_e - fraction carbon converted to LHC
- y_b - fraction carbon converted to BTX
- ρ_s - particle density - kg/m^3
- ρ_g - gas density - kg/m^3
- α - fraction of carbon available for reaction

CORRELATION OF FLASH HYDROGENATION YIELDS WITH PETROGRAPHIC PROPERTIES

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INTRODUCTION

Recent studies (1,2) indicated that the rank (as measured by the carbon content) alone is not sufficient to predict the yield of volatiles from a coal during flash hydrogenation. The reason is that the rank provides only a gross means of chemical characterization. It is an average of different heterogeneous properties of coal, and does not adequately characterize the chemical structure.

As a consequence, two coals of the same rank may exhibit markedly different chemical properties, give different yields of volatiles and present different product distribution when subjected to flash hydrogenation (2).

On the other hand, a given maceral type occurring in different coals, has been reported to exhibit similar reactivity (3,4) in different processes.

Early work by the Bureau of Mines (5) established the clear dependence of the liquefaction behavior of a coal on its petrographic composition. Also, experimental results showed that vitrinites and exinites are the most readily liquefied (6), while fusinite is almost completely resistant to liquefaction (7).

After the new method of classification of maceral types by the reflected light was introduced (8), considerable information has been reported on the effect of petrographic composition on liquefaction (9-13).

The objective of the present paper is to show that it is possible to correlate flash hydrogenation yields with petrographic composition of the coal. The same type of correlation will be used to predict product distribution at fixed reaction conditions. Correlations based on the petrographic analysis of coal, can be used consequently, to build kinetic models of coal flash hydrogenation that would be applied to a large variety of coals.

EXPERIMENTAL

The experimental arrangements used in this study were similar to those described in previous papers (14). The analysis of products was performed by on-line mass spectrometry or by gas chromatography. Experiments were carried on at 100 atm. of hydrogen, a heating rate of 650°C/s., 10 s. of solids contact time, 0.6 s. of vapor residence time and temperatures from 600 to 1000°C.

A suite of eight U.S. coals from the Pennsylvania State University collection, from lignite to HVA, was used for this study. Their chemical properties and rank are tabulated in figure 1.

CORRELATION PROCEDURE

The fundamental assumption used for correlation purposes is that the total volatiles yield obtained during flash hydrogenation depends linearly on the maceral composition:

$$y = \sum_{i=1}^n r_i x_i \quad (1)$$

In a similar form, and since each one of the macerals can give a different product distribution, the yield of each one of the products can be assumed to depend linearly on the maceral composition:

$$Y_j = \sum_{i=1}^n r_{ij} x_i \quad (2)$$

From equations (1) and (2) and in order to have a consistent set of definitions; we can deduce the following properties:

$$0 < \sum_{i=1}^n r_i \leq 1 ; 0 < r_i \leq 1 ; r_i = \sum_j r_{ij} \quad (3)$$

Also, the following correlation was used to transform the units of carbon conversion (% of original carbon) and weight loss (% of original dmmf. coal) (15):

$$y = 1.14w - 13.7 \quad (4)$$

A computer program on multiple linear regression was used to find the values of r_i in equation (1). After several tests with combinations of different macerals, it was found that the total yield was a function of the percentage of vitrinite and pseudo-vitrinite only. Consequently, the concentration of these two macerals were used as variables in all the correlations.

RESULTS

For comparison purposes, the data on total yields was correlated with the rank of the coal (carbon percent d.m.m.f.). The correlation was very poor, presenting a correlation coefficient $\rho = 0.579$.

When vitrinite and pseudo-vitrinite content are used as variables, the correlation improves considerably. The correlation coefficient of

the regression now is $\rho = 0.99$. Note that the number of free parameters in the new correlation is the same as in the rank case.

The correlation defined by equation (2) was applied to the yield of individual components during flash hydrogenation of different coals at fixed conditions. Figure 2 shows the results of the correlations.

DISCUSSION AND CONCLUSIONS

In view of the success of the attempts of correlating yields and products distribution with the petrographic composition of different coals, it is possible to conclude that the maceral content of a coal provides more information with respect to its reactivity (at least with respect to flash hydrogenation) than its rank. This conclusion, however, is based on a small group of different coals (8 coals only) and should be verified further with a larger sample of coals.

The fact that the yield of individual components can be correlated with the maceral composition, offers excellent possibilities for the use of maceral content-based correlations in the analysis of kinetic data from flash hydrogenation, and possibly for similar processes. It should be kept in mind that different macerals can present different selectivities towards individual components. Also, secondary reactions of the individual components (e.g., in the gas phase) could introduce deviations in the correlations.

As a final conclusion, correlations based on the petrographic composition of coals are a promising tool that could allow prediction of reactivities, total volatile yields and product distribution for any coal in flash hydrogenation given only its maceral content.

NOMENCLATURE

- r_i : reactivity of the i^{th} maceral (dimensionless)
- r_{ij} : reactivity of the i^{th} maceral to give the j^{th} product (dimensionless)
- x_i : the maceral content of the coal (5) (weight % on dmmf coal)
- y : total volatile yield (% of the initial carbon converted)
- y_i : yield of i^{th} component (% of initial carbon converted)
- σ : standard deviation of the regression defined from

$$\sigma^2 = \sum_{-i=1}^n \frac{(y_i, \text{experim.} - y_i, \text{calc})^2}{(n-2)}$$

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Sample No.	Rank	Province	Age	State	Moist	M.M. direct	C dmmf	O dmmf	S Dry	DAF
PSOC 326	HVA	Eastern	Carb.	PA	2.21	21.18	84.49	5.56	4.36	5.28
PSOC 270	HVA	Eastern	Carb.	AL	1.27	17.72	85.15	4.85	2.34	2.77
PSOC 284	HVA	Interior	Carb.	IL	3.11	25.08	83.71	7.12	5.23	6.70
PSOC 314	HVA	RockyM.	Cret.	UT	4.08	11.55	81.47	10.13	0.76	0.84
PSOC 280	HVC	Interior	Carb.	IN	11.32	18.31	81.58	9.51	3.78	4.50
PSOC 248	S.8it. A	RockyM.	Cret.	WY	19.17	3.34	75.44	17.04	0.64	0.66
PSOC 240	S.8it. B	Pacific	Tert.	WA	19.73	16.47	73.96	18.98	0.50	0.60
PSOC 246	Lignite	NorthGr. Plains	Tert.	ND	34.12	10.99	71.85	21.22	0.65	0.72

Figure 1. Selected coals for flash hydrogenation studies

<u>Component</u>	<u>Corr. variable</u>	<u>Corr. coefficient</u>	<u>σ</u>
Methane	$0.17V + 0.58(PV+E+R)$	0.9811	0.67%
Ethane	$0.08V + 0.05(PV+E+R)$	0.7661	0.52%
BTX	$0.08V + 0.127(PV+E+R)$	0.427	0.92%

Figure 2: Correlations applied to individual components

THE FORMATION OF BTX BY THE HYDROPYROLYSIS OF COALS

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ABSTRACT

The pyrolysis of British coals has been studied at hydrogen pressures of 50 to 150 bar in single- and two-stage, tube reactors at heating rates of up to 30 K s^{-1} . In the single stage reactor, hydrolypyrolysis of a high-volatile coal gave up to 4.5% single-ring aromatics; the results suggested that the evolution of volatiles and their cracking to benzene were sequential reactions. This was confirmed using a two-stage reactor in which the coal was heated at a controlled rate and the volatiles cracked in a separate zone at constant temperature. Yields of up to 12% benzene were obtained from a high volatile coal in hydrogen (similar to the yields obtained by various workers from American coals by flash pyrolysis) without very rapid heating of the coal. Hydrolypyrolysis of model compounds showed that benzene was a major product of the cracking of polynuclear aromatics under hydrogen pressure.

1. INTRODUCTION

The carbonisation of coal under hydrogen pressure is known as 'hydro-pyrolysis'. A review of published work¹ showed that flash hydrolypyrolysis of coal, which involves heating rates of hundreds of K s^{-1} , can give appreciable yields of light aromatic hydrocarbons such as benzene, toluene and xylenes (BTX). The present paper is concerned with studies of both single-stage and two-stage hydrolypyrolysis of coals aimed at producing single-ring aromatics, especially benzene, from coal. In the single-stage reactor the carbonisation and cracking zones are heated by the same source, while in the two-stage reactor there is independent control of the carbonisation and cracking zones.

2. MATERIALS

2.1. Coals

The analyses of the coals used for hydrolypyrolysis are given in Table 1. The coals were ground, sized +251 -500 μm and dried at 373 K in vacuum.

2.2. Model Compounds

Hydrolypyrolysis experiments were also carried out on six aromatic hydrocarbons: benzene, toluene, p-xylene, naphthalene, anthracene and phenanthrene. Where possible, 'ANALAR' grade chemicals were used without further purification. As the hydrolypyrolysis reactor was only suitable for solids, 1g of compound was either absorbed on or mixed with 9g of active carbon (NCB Anthrasorb).

3. SINGLE-STAGE HYDROPYROLYSIS

3.1. Experimental

The design of the reactor is based on that used by Hiteshue and co-workers at the USBM². A 1830 mm long x 8 mm ID stainless steel, pressure tube in which about 10g of coal were secured between degreased wire wool plugs was heated by passing a large current (up to 1600A) through its wall. The heating rate was controlled by switching tappings on a transformer. The pyrolysis

vapours were swept out of the reaction zone by pressurised hydrogen at up to 150 bar, some of the liquid products collecting in the ice-cooled trap. The remaining liquid products and gases were reduced to atmospheric pressure through a needle valve, which was also used to control the flow rate, before being collected for analysis. The products in the trap were weighed and then washed from the trap and adjoining tubing with chloroform. The residual char in the reactor was weighed and analysed.

3.2. Product Analysis

Both gaseous and liquid products were analysed by chromatography. The hydrocarbon gases were measured on an alumina column with a flame ionisation detector, and the permanent gases on a molecular sieve 5A column with a katharometer detector. The liquids were measured using a silicone SCOT column with a flame ionisation detector. Water was estimated by titration with Karl Fisher reagent. Proximate and ultimate analyses were carried out on selected char samples.

3.3. Results

The effect of variations in the final heat-treatment temperature and in the vapour residence time on the yields of single-ring aromatics formed by hydrolysis of high-volatile Linby coal was investigated using heating rates in the range 7 to 30 K s⁻¹, a pressure of 150 bar and zero solids residence time at maximum temperature.

3.3.1 The effect of final heat-treatment temperature

The effect of the final carbonisation temperature on the yields of benzene, toluene and xylenes (BTX) and phenol, cresols and xylenols (PCX) is shown in Figure 1, where it can be seen that for a vapour residence time of approximately 10 s the yields of both BTX and PCX passed through a maximum at a temperature of about 1000 K. The maximum yield of single-ring aromatics was approximately 4.5%, being composed of about equivalent amounts of BTX and phenolics.

3.3.2 The effect of vapour residence time

The effect of vapour residence on the yields of BTX and PCX at heating rates of 10, 20 and 30 K s⁻¹ to a final heat-treatment temperature of 1000 K is shown in Figures 2a and b. The yield of BTX increased steadily over the range of residence times investigated and was little affected by the heating rate. In contrast, the yield of PCX passed through a maximum at a residence time of 3 s and was markedly affected by the heating rate, at the two higher heating rates the PCX being almost completely destroyed after 8 s. Dehydroxylation of the PCX to BTX at the longer residence times only partly explains the fate of the PCX since the decrease in PCX is considerably greater than the increase in BTX.

4. TWO-STAGE HYDROLYSIS

4.1 Modification to Apparatus

The modification to the hydrolysis apparatus to enable the carbonisation and cracking zones to be separated is shown in Figure 3. The upper portion of the stainless steel tube reactor, which served as the cracking zone, was thermostatically controlled at temperatures up to 1273 K using two muffle furnaces; the lower portion which contained the coal was electrically heated as previously.

4.2 Experimental

The samples (coals, coking coals plus coke and model compounds on active carbon) to be pyrolysed were placed, as before, in the lower section of the tube. The flow of hydrogen through the reactor was established to give the required vapour residence time with the upper section maintained at the cracking temperature. Current was then passed through the lower section to heat it and the sample to the carbonisation temperature. The products were collected and analysed in the same way as with the single-stage reactor.

4.3. Results

4.3.1 Effect of carbonisation time, temperature and heating rate

The effect of varying the carbonisation time is shown in Figure 4. The methane increases monotonically with time and the benzene yield reaches a limit of about 11% w/w on d.a.f. coal at 9 minutes. Thus, to achieve optimum benzene yield with minimum methane formation, the residence time of the coal should be controlled.

Varying the final carbonisation temperature from 848 to 973 K (at a carbonisation time of 9 minutes) while cracking the products at 1123 K gave the results plotted in Figure 5. Methane increases monotonically with increase in final carbonisation temperature whereas ethane and benzene pass through broad maxima at about 923 K, the benzene yield peaking at 12% w/w on d.a.f. coal (13.4% C on C). The lower benzene yield at 973 K suggests that, at this temperature, some of the benzene is destroyed during the carbonisation stage. The volatile matter content of the char decreased from about 16% at a carbonisation temperature of 750 K to 5.5% at 923 K.

The results of tests on the effect of heating rate show that, at a carbonisation temperature of 750 K, increasing the heating rate of the coal from 1 to 25 K s⁻¹ has no significant effect on benzene yields, although the methane and ethane yields are reduced by the higher heating rate.

4.3.2 Effect of cracking temperature and residence time

The yields of gases and liquids were determined after cracking at temperatures from 773 to 1223 K using the relatively low carbonisation temperature of 750 K and a carbonisation time of 15 minutes.

The yields of methane, ethane, benzene and tar are given in Figure 6. Above 900 K, increasingly severe cracking of the carbonisation vapours gives continuously increasing yields of methane, whereas the ethane and benzene pass through broad maxima. The yield of tar decreases with increasing temperature, suggesting that tar vapours are the precursors of much of the ethane and benzene, themselves being hydrogenated to methane under more extreme conditions.

The effect of varying the hydrogen flow rate and hence the gaseous residence time was also investigated. The carbonisation temperature was 873 K and the pressure was 150 bar. The results are summarised in Figure 7 and show that, as the hydrogen flow was increased, the yields of ethane and benzene increased and the benzene passed through a broad maximum. At the lower hydrogen rates, the volatiles were overcracked to give high methane yields. The lowest hydrogen rate of 0.85g min⁻¹ (equivalent to a flow of 0.01 m³ min⁻¹ at room temperature and pressure) gave a gaseous residence time of about 7 s in the cracking zone at 150 bar and 1123 K.

4.3.3 Effect of pressure

Tests at 50, 100 and 150 bar in which the vapour residence time was maintained constant by using a constant linear hydrogen velocity gave the results shown in Figure 8. Methane and ethane yields increased linearly with pressure but the benzene yield increased less than proportionally to pressure.

4.3.4 Effect of coal-rank

The results on the effect of coal-rank are summarised as yields versus carbon content of coal in Figure 9 and suggest that the maximum ethane and benzene yields are obtained from the CRC 800 coals. Anthracite, as expected, gave less volatile hydrocarbons, and the coking coals tended to cake in the carboniser and would therefore be difficult to process continuously. The high volatile brown coal contained 24.8% oxygen and the oxygen appeared mainly as water rather than carbon oxides. The Lady Victoria coal gave comparatively low benzene and high methane yields, probably reflecting the high aliphatic content of this coal.

4.3.5 Model compounds

Table 2 gives the results of the hydrolysis of the aromatic compounds listed in Section 2.2.; only the aromatic products are listed. The cracking temperature was varied from 823 to 1173 K at a constant vapour residence time of about 5 s. As might be expected, the extent of decomposition increased with increasing temperature, and the percentage remaining undecomposed at 973 K was taken as a measure of thermal stability. The stability sequence in order of decreasing stability was as follows: benzene = naphthalene > phenanthrene > p-xylene > anthracene. It should however be stressed that the order depends on the temperature. Thus, at 1073 K toluene and p-xylene are less stable than anthracene.

The yield of benzene at three temperatures (973, 1073, 1173 K) from the model compounds is shown as a bar chart in Figure 10. Benzene survives both as a feedstock and as a product of the cracking of toluene, p-xylene and polynuclear hydrocarbons. It is interesting that naphthalene, anthracene and phenanthrene give benzene as a major product at the two higher cracking temperatures.

5. DISCUSSION

In line with the various groups of American workers²⁻⁵ who have studied hydrolysis, the carbonisation of coal under hydrogen pressure has been shown to give much higher yields of light aromatics, in particular benzene, than are obtained by conventional carbonisation, i.e. at atmospheric pressure in an inert atmosphere.

The results of the experiments carried out in a single-stage reactor similar to that used by Hiteshue, Anderson and Schlesinger² are in good agreement with their published data. With this apparatus which employs relatively slow heating rates (up to 30 K s^{-1}) a maximum yield of 4.5% single-ring aromatics can be expected from a low-rank coal.

In these single-stage reactors the temperature cycle of the reactor together with the hydrogen flow rate through it determine the conditions for both the pyrolysis of coal and the hydrocracking of the volatiles produced. Thus, it is impossible to optimise simultaneously both the carbonising and cracking conditions. However, in the two-stage hydrolysis reactor, the carbonisation and cracking processes have to a large extent been separated and it is therefore possible to optimise separately the conditions for each.

The present work with the two-stage reactor shows that yields of over 10% benzene can be obtained from a low-rank coal without the need for heating at very high rates (up to 1000 K s^{-1}). From the point of view of the design of a hydrolysis plant, a process employing a moderate heating rate should be preferable since it is likely to be difficult to achieve very fast heating on an industrial scale.

6. CONCLUSIONS

The present study has:

- (i) confirmed that hydrolysis of coal produces appreciable yields of single-ring aromatics, especially benzene, and has shown that a benzene yield in excess of 10% can be obtained without heating the coal very rapidly;
- (ii) shown that the benzene yield depends on the temperature of the cracking zone and the residence times of the volatiles in this zone;
- (iii) demonstrated the potential of a two-stage reactor whereby the pyrolysis and cracking stages can be independently controlled, and which should make it simpler to optimise the yields of desired products.

7. ACKNOWLEDGMENTS

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Table 1: Analyses of Coals

Colliery or Coal Type	NCB CRC No.	Grade	Proximate analysis		Ultimate analysis					Maceral analysis			Coking Test			
			Moisture a.f.	Ash d.b.	V.H. d.a.f.	C	H	N	O	Total Cl S	Vitrinite	Exinite	Inertinite	Grey King Coke Type	Swelling No.	
																d.m.m.f.
Coed Bach	101	Washed duff	2.5	5.6	5.7	93.9	3.1	1.25	0.9	0.8	0.08	62	0	38	A	0
Garw	203	Washed smalls	0.8	10.1	17.9	91.6	4.7	1.55	1.6	0.8	0.01	71	Tr.	29	F	7
Detwent-haugh	301b	Washed smalls	0.5	5.3	29.7	87.6	5.5	1.75	4.3	0.8	0.04	N.D.	N.D.	N.D.	C ₉	8½
Bersham	402	Washed + 2 in.	1.9	2.0	38.3	85.9	5.6	1.75	6.8	1.0	0.39	87	3	10	G ₉	8½
Annesley	602	Washed doubles	4.5	2.4	38.6	84.3	5.5	1.9	7.2	0.8	0.49	73	9	18	G ₄	6½
Linby	802	Washed doubles	8.3	5.8	39.1	82.4	5.3	1.95	9.0	1.0	0.46	79	6	15	C	1
Daw Hill	802	Smalls	9.3	11.7	39.7	80.6	4.9	1.4	11.9	1.65	0.23	63	11	26	C	1
Cotgrave	902	Blend A	8.5	14.2	41.5	82.5	5.7	1.85	9.2	0.65	0.26	N.D.	N.D.	N.D.	A	1
Lady Victoria	-	Cannel	2.0	2.9	52.2	84.4	6.8	1.5	5.8	1.3	0.19	26	21	53	E	1
German brown	-	-	13.5	7.6	52.8	69.7	4.6	0.9	24.8	0.25	0.03	N.D.	N.D.	N.D.	A	0

N.D. = Not determined.

Table 2: Yields of Aromatics from Two-stage Hydropyrolysis of Aromatics

Feedstock	Cracking Temperature, K	Calc. vapour residence time, s	Yield % w/w on feed					
			Benzene	Toluene	Xylenes	Naphthalene	Anthracene	Phenanthrene
Benzene	973	5.2	92					
	1023	4.9	101					
	1073	4.6	95					
	1123	4.4	71					
	1173	4.3	18					
Toluene	823	6.1	20	66				
	873	5.7	21	42				
	973	5.2	59	32				
	1023	4.9	54	1				
	1073	4.6	73	0				
	1123	4.4	61	0				
	1173	4.3	18	0				
p-xylene	773	6.5	4	21	97			
	873	5.7	4	6	76			
	973	5.2	14	23	21			
	1023	4.9	56	7	8			
	1073	4.6	67	0	0			
Naphthalene	773	6.5	1	0.2	0	99		
	973	5.2	4	0.8	0	93		
	1023	4.9	5	2	0	80		
	1073	4.6	24	1	0	52		
	1123	4.4	41	0.4	0	8		
	1173	4.3	23	0.3	0	0.2		
Anthracene	773	6.5	0.5	0.4	0	3	16	
	873	5.5	0.5	0.4	0	2	14	
	973	5.2	2	0.7	0	8	9	
	1073	4.6	15	0.4	0	20	7	
	1173	4.3	16	0.1	0	0.6	2	
Phenanthrene	773	6.5	0.4	0	0	0	0	37
	873	5.7	0.5	0	0	0	0	36
	973	5.2	0.9	0	0	0.9	0	42
	1073	4.6	4	0.1	0	2	0	18
	1173	4.3	21	0	0	0.1	0	0.7

Condition: 1g of feedstock with 9g of active carbon
 Carbonised at 750K with 15 min. solids residence time
 Heating rate 1 K s^{-1}
 8 mm ID carboniser and cracker
 Hydrogen 0.85 g min^{-1} at 100 bar.

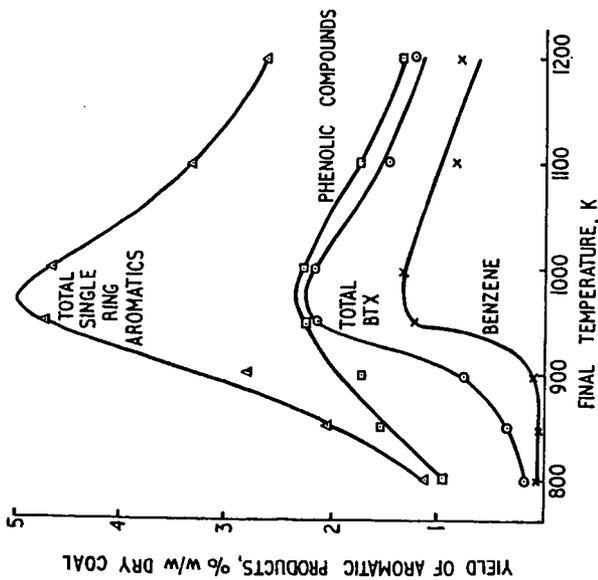


FIGURE 1. EFFECT OF FINAL TEMPERATURE ON YIELD OF PRODUCTS

HEATING RATE 7Ks^{-1} , PRESSURE 150 BAR, SOLIDS RESIDENCE TIME 0s , VAPOUR RESIDENCE TIME 11.5, 10g OF 251 TO 500 μm LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.

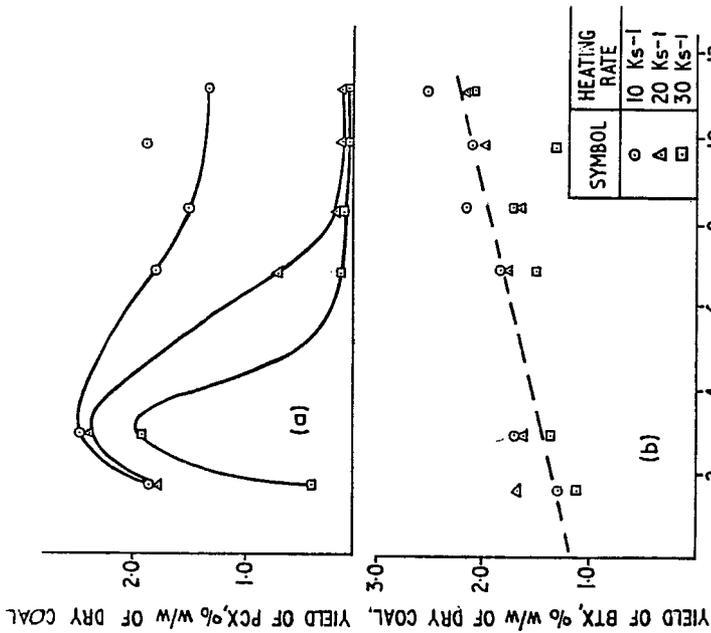


FIGURE 2. EFFECT OF VAPOUR RESIDENCE TIME AND HEATING RATE

ON YIELDS OF (a) PHENOL, CRESOLS AND XYLENOLS (PCX) AND (b) BENZENE, TOLUENE AND XYLENES (BTX)

FINAL TEMPERATURE 1000K, HEATING RATE 7Ks^{-1} , PRESSURE 150BAR, SOLIDS RESIDENCE TIME 0s , 10g 251 TO 500 μm LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.

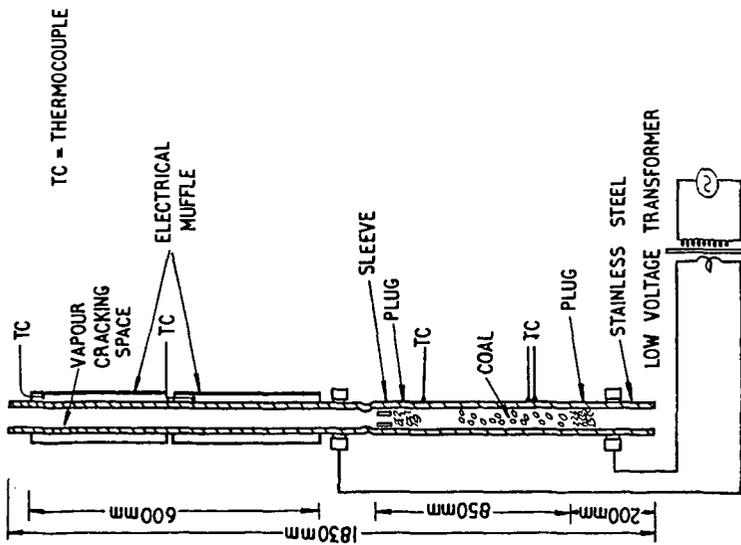


FIGURE 3. DETAILS OF C.R.E. TWO-STAGE REACTOR WITH TEMPERATURE CONTROL OF VAPOUR SPACE

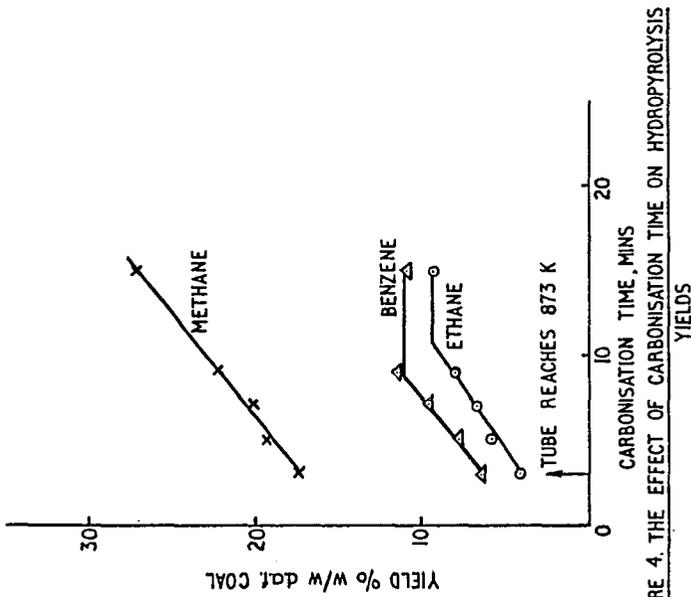


FIGURE 4. THE EFFECT OF CARBONISATION TIME ON HYDROLYSIS

CONDITIONS: HEATING RATE 5Ks^{-1} , CARBONISATION TEMPERATURE 873K , CRACKING TEMPERATURE 1123K , HYDROGEN 1.44g min^{-1} , PRESSURE 150 BAR , $10\text{g LINBY COAL } 251$ TO $500\mu\text{m}$, 8mm ID CARBONISER AND CRACKER.

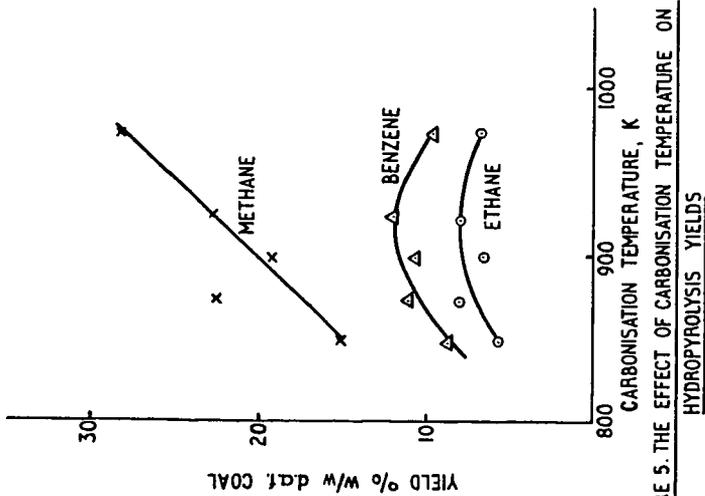


FIGURE 5. THE EFFECT OF CARBONISATION TEMPERATURE ON HYDROPYROLYSIS YIELDS
 CONDITIONS: HEATING RATE 5Ks^{-1} , CARBONISATION TIME 9 min, CRACKING TEMPERATURE 1123K , HYDROGEN 1.44g min^{-1} , PRESSURE 150BAR , 10g LINBY COAL 8mm ID CARBONISER AND CRACKER.

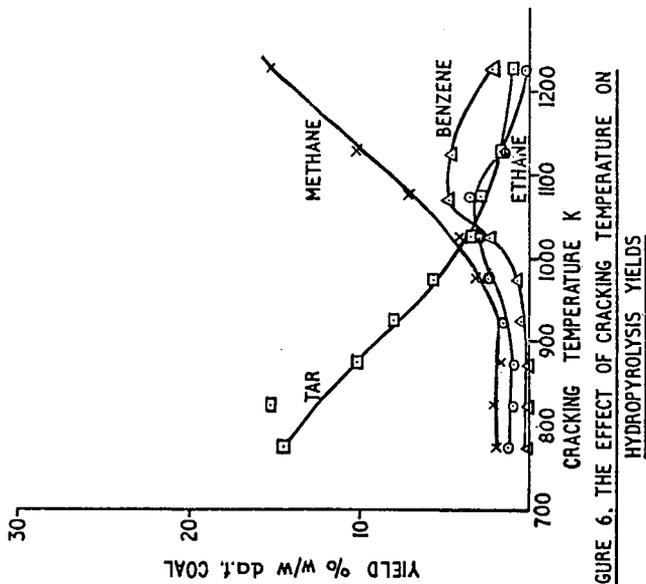


FIGURE 6. THE EFFECT OF CRACKING TEMPERATURE ON HYDROPYROLYSIS YIELDS
 CONDITIONS: HEATING RATE 1Ks^{-1} , FINAL CARBONISATION TEMPERATURE 750K , CARBONISATION TIME 15 min, HYDROGEN RATE 0.85g min^{-1} , PRESSURE 100BAR , 10g OF 251 TO $500\mu\text{m}$ LINBY COAL, 8mm ID CARBONISER AND CRACKER.

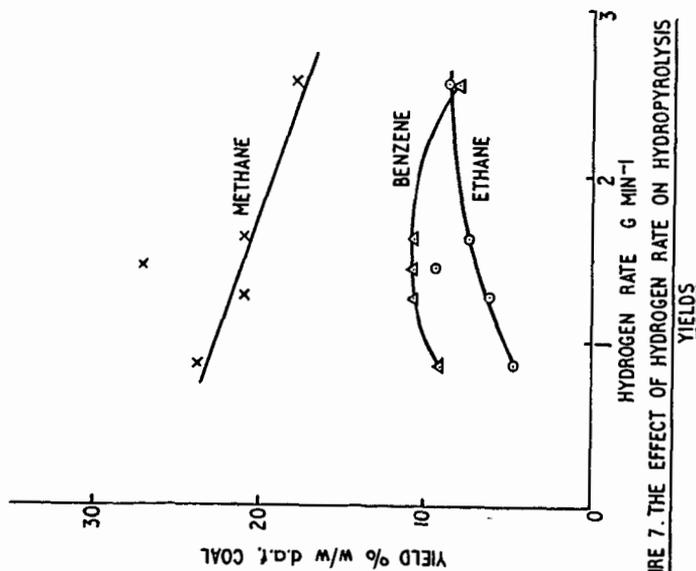


FIGURE 7. THE EFFECT OF HYDROGEN RATE ON HYDROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks^{-1} ; FINAL CARBONISATION TEMPERATURE 873K , CARBONISATION TIME 15min , CRACKING TEMPERATURE 1123K , PRESSURE 150BAR , 10g OF 251 TO $500\mu\text{m}$ LINBY COAL, 8mm ID CARBONISER AND CRACKER.

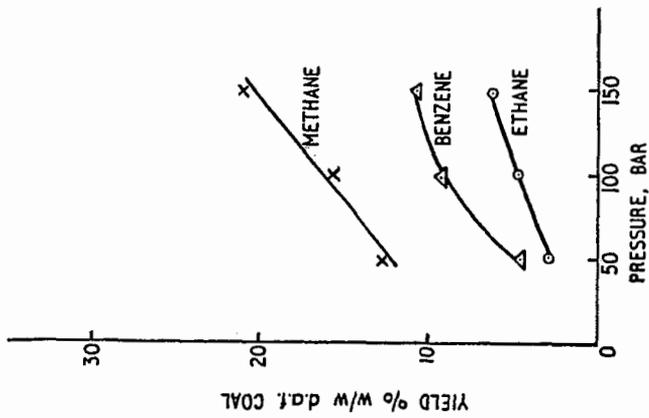


FIGURE 8. THE EFFECT OF PRESSURE ON HYDROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks^{-1} , CARBONISATION TEMPERATURE 873K , CARBONISATION TIME 15min , CRACKING TEMPERATURE 1123K , 10g OF 251 TO $500\mu\text{m}$ LINBY COAL, 8mm ID CARBONISER AND CRACKER.

FIGURE 10. YIELDS OF BENZENE AT VARIOUS TEMPERATURES - FROM MODEL COMPOUNDS

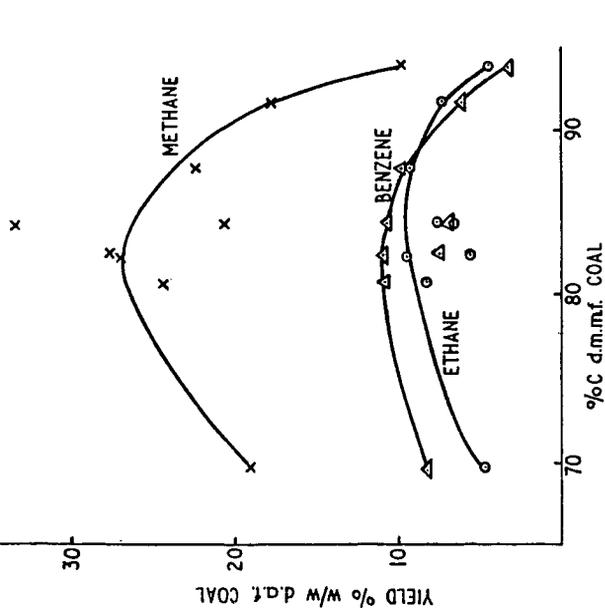
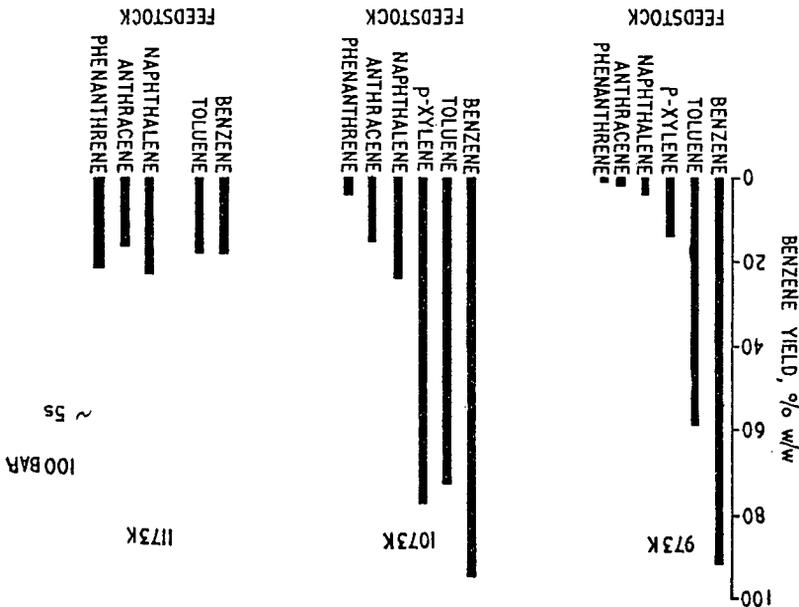


FIGURE 9. THE EFFECT OF COAL RANK ON HYDROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks^{-1} , FINAL CARBONISATION TEMPERATURE 873K , CARBONISATION TIME 15min , CRACKING TEMPERATURE 1123K , HYDROGEN 1.44g min^{-1} , PRESSURE 150BAR , 10g FEEDSTOCK, 8mm ID CARBONISER AND CRACKER.