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FLASH HYDROGENATION OF COAL

City University of New York PH.D. 1982

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Flash Hydrogenation of Coal

by

Wei-Yin Chen

A dissertation submitted to the Graduate Faculty in Chemical Engineering in partial fulfillment of the requirements for the degree of Doctor of Pilosophy, The City University of New York.

1981

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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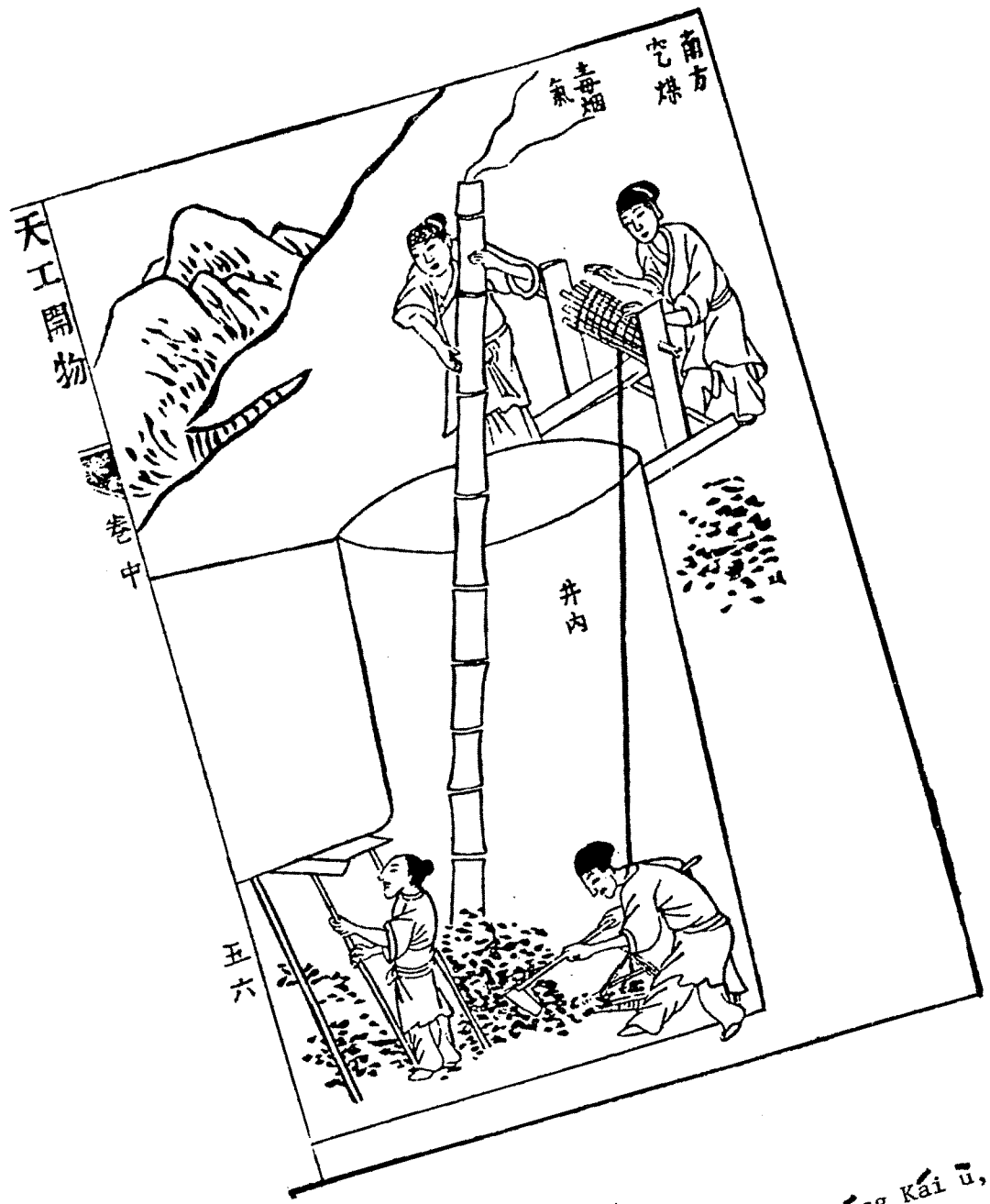
This thesis is dedicated to my 95 year old grandfather, Dr. Ta-Chi Chen, who fully understands the similarity we share.



Mining in 17th Century China; from Tien Gung Kai u,
by Sung Ying Xing (1637).

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Adviser: Robert A. Graff

Summary

Flash hydrogenation is a process approach for converting coal to liquid and gaseous fuels. It is distinguished from other conversion techniques in that raw coal is contacted with hydrogen at elevated pressure under conditions of rapid heating and control of vapor product residence time. The objective of the work reported here is to expand the experimental base for evaluating the potential of the approach and guiding pilot scale development.

The first part of this dissertation (Chapter 2) is a review of previous work on flash hydrogenation, in particular the effects of process variables on yield structure. It also reviews adjacent technical areas important to developing an improved understanding of the process. Prospects for kinetic modeling, reactor design, and catalysis are discussed.

Experimental studies have been carried out using the flash tube reactor system developed at City College. A ten to twenty milligram batch sample of ground coal is rapidly heated in flowing hydrogen at pressures up to 100 atmospheres. Yields of compounds up to xylene are determined with an on-line mass spectrometer. In the usual procedure, reaction with hydrogen is followed by combustion and the carbon content

of the residual char determined by carbon dioxide. Heavy liquid yield is calculated from a carbon balance. For the collection of liquids, a trap cooled in liquid nitrogen is inserted immediately following the reactor. This allows liquids to be directly measured and to be subjected to analysis. For studies in two-stage flash hydrogenation, a separate vapor hydrocracking zone was introduced downstream of the reactor allowing independent control of devolatilization and vapor hydrocracking temperatures. A series of experiments conducted with flash tubes gold plated on their interior surface gave the same results as unplated tubes; the experiments are evidently free of catalytic wall affects (section 4.7.1).

Only a handfull of different coals, mostly lignites, had previously been tested in flash hydrogenation and these in experimental systems with widely varying characteristics. It was therefore important to study a broad range of coals in one experimental apparatus under identical conditions. This would help establish the variations in performance to be expected in the process from different coals, provide a data base for the development of predictive correlations, and remove differences in experimental apparatus as an uncertainty in the comparison.

Such a comparative study was carried out with a suite of eight coals selected from the Pennsylvania State University coal bank as broadly representative of the U.S. spectrum (section 4.1). These were augmented by data for three additional coals from other sources. A very high degree of variability is observed, particularly in total volatiles yield (41 to 69% carbon conversion) and total liquids yield (13 to 42% carbon conversion). Even coals of the same rank show wide differences

in yield, and it is quite clear that this rather than equipment is the more important cause for discrepancies among investigators.

Using dmmf carbon content (as an index of rank) proves wholly inadequate for the purpose of correlating yields. More success is obtained with maceral content, which contains an interesting result. In this correlation the coefficient for exinite content is too high if exinite were simply to contribute its carbon to the yields of the various products. Rather, exinite appears to stimulate yields from other macerals, a result readily explained by exinite's highly aliphatic structure.

This suite of coals was subjected to Fourier Transform infrared spectroscopy for further characterization. It was found possible to bring together not only flash hydrogenation data from various coals, but also vacuum pyrolysis yields and certain liquefaction data in a single correlation with aliphatic hydrogen and oxygen content as the independent variables.

For the purpose of predicting yields of individual products from various coals empirical correlations were developed. These were obtained by stepwise regression from a field of sixteen variables. In each case, equations in only two independent variables correlate the yields within experimental error.

A more detailed comparison was made of the performance of two bituminous coals, Illinois No. 6 and Pittsburgh No. 8 (section 4.2). Even though these coals are very close in rank, Pittsburgh No. 8 coal yields 10 to 12% more liquid. The liquids from both coals were trapped and subjected to SESC fractionation. The increased liquid yield from Pittsburgh No. 8 is found to be mostly in the heavier, more highly

functional molecules. The heaviest (THF soluble) fraction is totally absent from liquids derived from Illinois No. 6 coal. This certainly suggests that the quantity and character of the liquid product in flash hydrogenation is highly dependent on the structure of the parent coal.

There is, of course, no inherent necessity of conducting the two stages of flash hydrogenation - devolatilization and hydrocracking - at the same temperature. Higher yields of desired compounds might be attainable if the temperatures of the two stages can be separately adjusted. The equipment was modified as described above and a series of tests conducted at various temperatures and residence times in the hydrocracking zone. No advantage was found over single stage flash hydrogenation in terms of maximum attainable yields of either light aromatic liquids or total yield of heavier species. This contrasts with the results of other workers using low heating rates in the devolatilization step. The experiments provided a set of data for the devolatilization of a caking coal in hydrogen which is successfully modeled using an exponential decay function for the residence time distribution of bubbles within a particle.

The effect of hydrogen pressure on yield was determined on a sample of Illinois No. 6 coal (section 4.4.1). Yields show a much weaker pressure dependence than those measured previously on a closely related sample of the same coal. Oxidation or local variations in organic structure may be responsible. In either case, the results illustrate that pronounced differences in yield structure can arise from subtle differences in sample character.

In a commercial process, the reaction gas will contain reaction products, and some idea of their effect on yield is needed. The

addition of methane to hydrogen (section 4.4.2) reduces total volatile yield and specifically BTX. Carbon monoxide addition (section 4.4.3) also reduces BTX yield.

The action of hydrides as promoters for flash hydrogenation was briefly examined (section 4.5.1). Sodium hydride, perhaps acting through the release of hydrogen atoms, gives increased yields of methane at the expense of single ring aromatics and char. Titanium hydride appears to act as a catalyst, increasing the heavy liquid yield at temperatures below 800°C.

Mixing coal with kaolin increases the yields of total volatiles, particularly liquids and ethane (section 4.5.2). Kaolin is likely inert, and this effect is a result of reduced agglomeration during the plastic transitory phase.

In spite of the well recognized sensitivity of coal to oxidation, no effect on yield was found after 2½ months exposure of ground coal to ambient air (section 4.6.2). It was also ascertained that vacuum drying of lignite at 110°C does not affect yield (section 4.6.1).

Passage of volatiles through a bed of char suppresses methane yields but not that of other light species, including single ring aromatics. The results suggest that heavy liquids are lost by deposition on char (section 4.7.2) and this has undesirable consequences for commercial reactors when char and volatiles are not promptly separated.

Liquids obtained from short contact time solvent refining of coal respond similarly to whole coals in flash hydrogenation (Chapter 4.8). Yields are slightly higher than for whole coals. Taken together with

the insensitivity to oxidation, noted above, these results suggest that flash hydrogenation chemistry involves the rupture of stronger bonds than the low temperature processes of liquefaction or pyrolysis.

Samples of char produced in the flash hydrogenation of Pittsburgh No. 8 coal showed substantial reductions in nitrogen and sulfur content. From a coal containing 1.4% maf nitrogen and 6.5% maf sulfur, chars containing 0.6 to 1.1% maf nitrogen and 1.6 to 2.6 maf sulfur were obtained. This enhances their value as boiler fuel.

Conclusions

Here we summarize the most significant results of this research and call attention to some of the important uncertainties.

1. U.S. coals vary considerably in their response to flash hydrogenation - even coals very close in rank. Low rank coals are more suitable for the production of light gases; methane yields from lignites are about 40% higher than from hva bituminous coals. For the production of liquids high rank bituminous coals are most suitable. While the variation among coals of nearly the same rank (as measured by dmmf carbon) is very large, liquid yields in the 30-37% range are readily obtainable.
2. Total yields in flash hydrogenation, vacuum pyrolysis, and liquefaction in tetralin are all correlated by a single linear equation in oxygen and aliphatic hydrogen content (see section 4.1.3c).
3. Empirical equations are given for predicting the yields of methane, ethane, propane, carbon oxides, BTX, and heavy liquids at 800°C, 0.6 sec vapor residence time (see section 4.1.3d).
4. Exinite is a promoter for the production of liquids from other macerals, probably because of its highly aliphatic character.

The above conclusions are all circumscribed by the small number of samples tested in the comparative study. Clearly, a far larger number of samples would be required for a proper statistical study of U.S. coals.

5. The high liquid yields from Pittsburgh No. 8 coal are mostly attributable to heavier, more functional species when compared to the liquids from Illinois No. 6 coal. It is not known to what extent this is valid for other coals which are high liquid producers.
6. Two-stage flash hydrogenation offers no improvement in yields over the single stage process provided coal is rapidly heated to a temperature between 850 and 965°C. The reverse is true for heating rates of about 7°C/sec.
7. Coals may respond strongly or weakly to changes in hydrogen pressure and the effect is sensitive either to oxidation or organic structure.
8. The presence of methane or carbon monoxide in the reaction gas reduces BTX yield.
9. Hydrides act as promoters for flash hydrogenation. Sodium hydride increases methane yields, perhaps by decomposing to release hydrogen atoms. Titanium hydride, acting as a catalyst, greatly enhances liquid yields below 800°C.
10. Yields of volatiles are increased if the effects of agglomeration are reduced. Experiments were conducted by mixing coal with kaolin, but the result is likely obtainable with any inert material.
11. Neither drying in vacuum nor air oxidation (2½ months) under ambient conditions affects flash hydrogenation yields.
12. Continued contact of volatiles with char after their release from a coal particle results in loww of heavy liquids. This result was not obtained directly, but inferred from a reduction

in rate of methane production from coal hydrogenation when char is contacted with flash hydrogenation volatiles.

13. Short contact time solvent refined coal responds similarly to whole coals in flash hydrogenation, the yields being only slightly higher than for whole coal. This together with item 11 implies that stronger bonds are involved in flash hydrogenation as compared to liquefaction and other low temperature processes.
14. Flash hydrogenation chars are substantially reduced in sulfur and nitrogen content.

1. Introduction

Flash hydrogenation is a potential route for the production of valuable fuels and chemicals from coal. The important factors defining flash hydrogenation are:

(a) raw coal,

(b) high hydrogan pressure,

(c) high heating rate, and

(d) controlled vapor residence time.

Forty years ago (Dent, 1944), workers at the U.S. Bureau of Mines showed that high Btu gases could be generated in one step using dry hydrogen at high pressure. This was anticipated on thermodynamic grounds. The effect of heating rate on yield structure involves almost all the chemical and physical processes involved in a complex kinetic mechanism. As a result, theoretical studies have been inconclusive. High heating rates, however, have come into increasing use over the last decade. In most cases, the yields obtained under high heating rate (above several hundred °C/s) have been higher than the proximate volatile matter obtained at several °C/s. Recently, vapor residence time has also been found to be a dominant parameter in determining yield structure mainly because valuable single ring aromatics are lost by hydrocracking to light paraffins within a few seconds. Hydrogen consumption is consequently lower than in long residence time processes.

The reactant, coal, is a highly heterogeneous material containing a complex organic matrix and mineral matter. The structure of coal is even now a subject of considerable controversy. Rank and petrographic

composition are the most commonly used classifications. Rank represents coalification history (age, temperature, etc.) and petrographic composition reflects its origin. Young coals are low in carbon. Old coals, on the other hand, have high aromaticities and are low in hydrogen. Coals of "middle age" are most suitable for hydrogenation. Among them, bituminous coals soften, swell and show mass transfer controlled kinetics; they are called "caking" coals. Lignites and subbituminous coals are non-agglomerating and they generally do not show mass transfer limitations. The major petrographic components (macerals) are three: vitrinite, exinite and inertinite. Exinite has the highest hydrogen content and is the most reactive maceral. Inertinite is highly aromatic and generally resistant to hydrogenation. Vitrinite, in general, is the most abundant maceral in coal, especially in U.S. coals, and it has medium reactivity. Mineral matter contains four major components: clays, oxides, carbonates, and sulfides and sulfates. This mineral matter is oxidized on pyrolysis and release CO_2 and H_2O. The effects of mineral matter on hydrogenation are, in some instances, catalytic but generally are not well understood.

Hydrocarbons predominating in hydrogenation volatiles include methane, ethane, propane, single ring aromatics and other heavier liquids. The residual solid contains organic char and mineral matter. Carboxyl and hydroxyl oxygen in coal is converted to CO_2 and CO, respectively. The third functional group containing oxygen, ether, is converted to CO or is inert upon hydrogenation. Sulfur, which can be either organic or pyritic, yields H_2S. The only other major element, nitrogen, appears in the product gas as HCN.

Processing variables which have a dominant effect on yield structure are: temperature, hydrogen partial pressure, heating rate, coal contact time and, vapor residence time. For the caking coals, since the hydrogenation is mass transfer controlled, yield structures also vary with particle size and total pressure. One of the difficulties of coal kinetics research is that the variables often interact. For example, the effects of pressure, heating rate and particle size usually combine with chemical reactions and are difficult to investigate independently. Considerable work has been carried out on the study of hydrogenation kinetics in the last decade, and the implications of these studies will be reviewed in the next section.

Different experimental arrangements are sometimes a source of discrepancies. Surface-to-volume ratio determines the rate of carbon deposition. Slip velocity controls the reaction between volatiles and char. Flow patterns affect particle agglomeration. A proper understanding of these factors would not only unify the hydrogenation theory, but would also provide a basis for reactor design.

Kinetic modeling, reactor design, and catalysis are major research areas for the near future. Recent developments are discussed in the next section. While from a commercial point of view economic analysis determines the feasibility of a hydrogenation process, such considerations are outside the scope of the work presented here.

The largest part of this study is concerned with a survey of U.S. coals. Direct correlations between yields and coal properties are developed and these have important chemical implications. An example is the linear relation between total volatiles yield and aliphic hydrogen and oxygen content. Differences between two bituminous coals,

Illinois No. 6 and Pittsburgh No. 8, are discussed in detail in section 4.2. Coal hydropyrolysis and vapor phase reactions are studies with two independent temperatures. A mass transfer controlled model is presented, but the vapor phase correlation is not yet complete. Other subjects under this investigation include pressure effect, hydrogenation with additives, effect of drying and oxidation, secondary reactions in the vapor phase (volatiles-wall, volatiles-char), short contact time solvent-refined coal and char composition.

2. Literature Review

2.1 General Scope

Energy is basic to the world economy. All other industries depend on it. In a report by the International Energy Agency published two years ago (Lantzke, 1979), it was suggested that world coal production must at least triple by the end of this centure if energy supplies are to accommodate even moderate levels of economic growth. Leaders of seven major industrial nations concluded, after the Venice Economic Summit Meeting (New York Times, June 24, 1980), that coal production and use should be doubled by 1990. Coal can become the most significant substitute for the worlds dwindling oil supply.

Coal reserves are abundant and widely dispersed. The uses of coal, however, involve difficult questions - from production to transport to eventual use. The chemical engineers' contribution to the solution of these problems will inevitably be to develop new techniques for producing synthetic gas and liquid fuels. Considerable effort is presently being directed toward development of processes for coal conversion.

Routes to the production of clean liquids, gases and solids from coal are shown in Figure 2.1 (Bodle and Vyas, 1975). Of these, gasification is in the most advanced stage of development. The gasification processes of Lurgi, Winkler, and Koppers-Totzek are in commercial use. In this approach, the reaction of coal with air and steam gives a mixture of carbon monoxide, nitrogen, hydrogen, methane and products of combustion. The process produces low

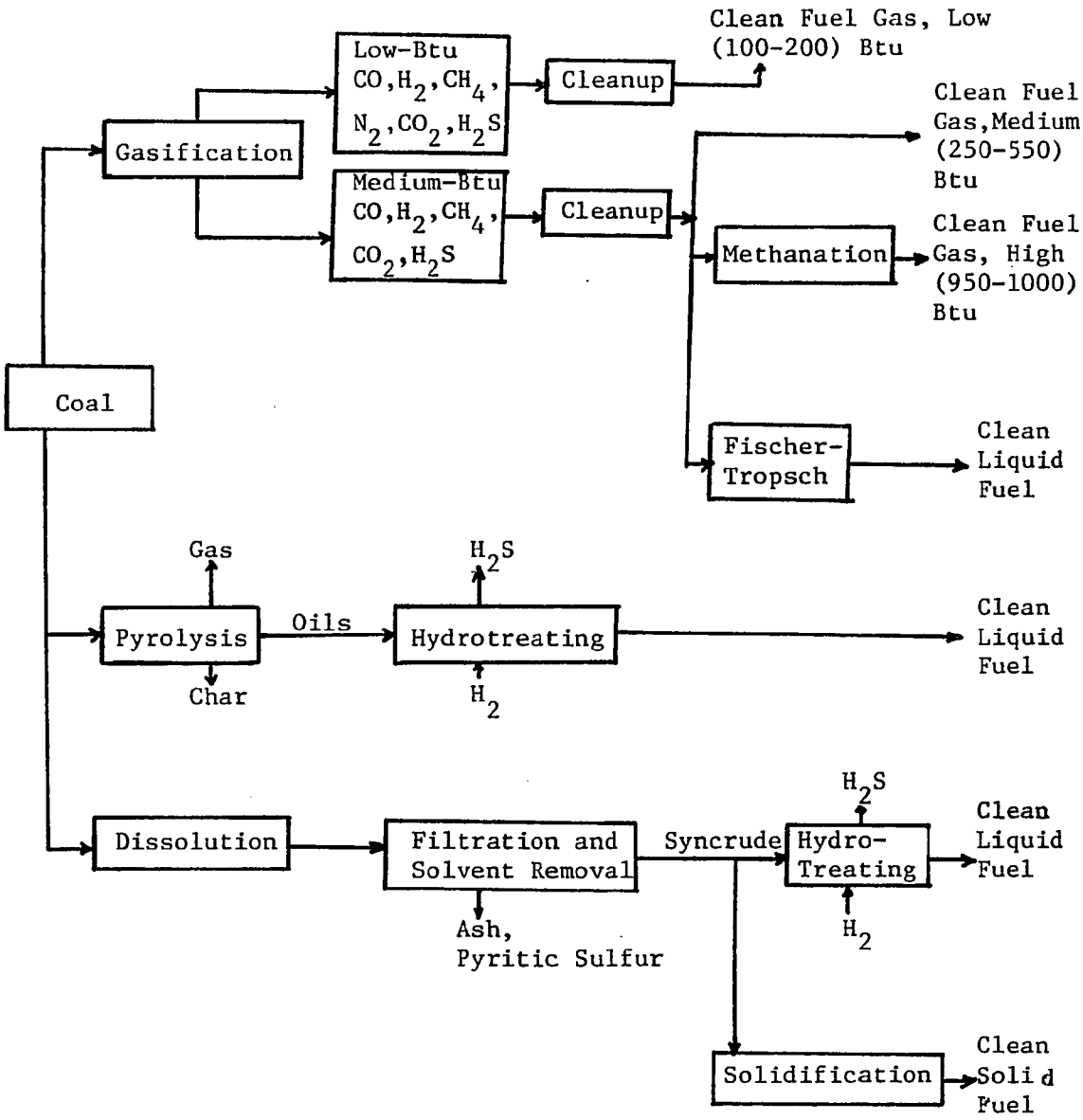


Figure 2.1 Clean Fuels from Coal (Bodle and Vyas, 1975)

(100-250 Btu/CF) heating value gas. An alternative is the processing of coal with oxygen-steam mixture to give a medium (250-550 Btu/CF) heating value or even high (950-1000 Btu/CF) heating value product gas. The latter can be converted to supplement pipeline quality natural gas (SNG) by reacting appropriate proportions of CO and H_2 (synthesis gas) over an appropriate catalyst. Gasification is usually carried out at 600-1000°C and 1-100 atm pressure.

A second route, pyrolysis, involved heating coal in an inert gas to give volatiles, and then treating the product oil with hydrogen for quality improvement and desulfurization. It is also called "devolatilization" for the volatile yield and "carbonization" (or "dehydrogenation") for the solid char. Pyrolysis is generally carried out at 600-1000°C and a few atmospheres pressure. Pyrolysis processes produce significant quantities of by-product char which must be disposed of economically.

A third route to clean liquid fuel involves dissolving the coal in a solvent and filtering out ash matter which contains pyritic sulfur. After removing solvent, the resulting heavy crude oil is treated with hydrogen to remove organic sulfur and at the same time, to improve its quality. The liquefaction processes are usually carried out at 400-500°C, at hydrogen pressures generally greater than 100 atm, and much longer residence times than that of gasification or pyrolysis. Although the three conversion processes described above use different reacting gases and processing conditions, they have one key factor in common: converting the coal to higher hydrogen to carbon ratio volatiles.

The atomic hydrogen to carbon ratio of coals of potential commercial interest for conversion processes is typically 0.6 to 1.0, which is substantially less than the value for liquid and gaseous fuels commonly used (H/C = 1.2 ∿ 4.0). Therefore, the primary requirement of any coal conversion scheme is either to add hydrogen or to reject carbon, thereby upgrading the hydrocarbon fraction. To achieve this purpose, the choice of atmospheric gas for the conversion process is one of the variables which keeps the research so active. Hydrogen is probably the most direct answer to this question. Hydrogen is expensive, but can be obtained from various routes (Berry, 1980): natural-gas reforming, electrolysis, and coal gasification. Replacing the inert gas by hydrogen in pyrolysis is called hydrogenation or hydropyrolysis. Though it is not a new idea, the research on coal hydropyrolysis did not receive a great deal of attention until the 1970s, except in a program with low funding carried on at the U.S. Bureau of Mines. Some authors also use the term "hydrogenation" to refer to the slurry liquefaction process, but the discussion here is confined to direct coal-hydrogen reaction without solvation. From the chemical point of view, coal hydrogenation is closely related to pyrolysis followed by hydrogenation of volatiles. Pyrolysis is the initial stage of thermal reaction, no matter what the ambient gas or solvent is. The word "Pyro-lysis" is a combination of two originally Greek words which take the meaning, fire and loosening. Following this meaning exactly, the very first step in coal pyrolysis is the rupture of the extended, complex coal skeleton to smaller fragments which include gas, liquid and solid. This thermal decomposition step, in theory, is independent of the atmosphere. However, since pyrolysis is extremely

fast (< 1 sec), secondary reactions of char or volatiles with the atmospheric gas or liquid is generally microscopically coupled with this initial reaction. Hydrogenation of coal takes advantage of this feature and completes the pyrolysis and hydrogenation of volatiles in one stage.

Flash hydrogenation of coal, by definition (Graff, 1977), has the following special features:

- raw coal,
- high temperature (> 600°C) and high hydrogen pressure,
- controlled vapor residence time, and
- high heating rate.

Early work by Dent (1944) showed that rapid heating of raw coal can give substantial yields of gaseous hydrocarbons at high temperature and hydrogen pressure. Birch, et al. (1960) demonstrated the existence of an initial rapid reaction stage in coal hydrogenation. Also, Hiteshue, et al. (1962a, 1962b, 1964) and Moseley and Paterson (1967) showed that volatile yields far in excess of the proximate volatile matter content could be achieved in hydrogen.

Several recent reviews are available. Anthony and Howard (1976) and Suuberg (1977) discussed flash hydrogenation of coal from a broad scientific point of view. Greene, et al. (1980) summarizes the process engineering and economics of a conceptualized facility based on flash hydrogenation reactor operation with a lignitic coal. The Institute of Gas Technology published an in-depth review (Pyrcioch, et al., 1972) of its extensive coal gasification research including a brief recapitulation of some of the most important hydrogasification studies. A classic, encyclopedic volume, edited by Lowry (1963), covered coal's origins, properties, analyses, and reactions to various utilizations in great detail. In that work, Howard (1963) reviewed coal pyrolysis

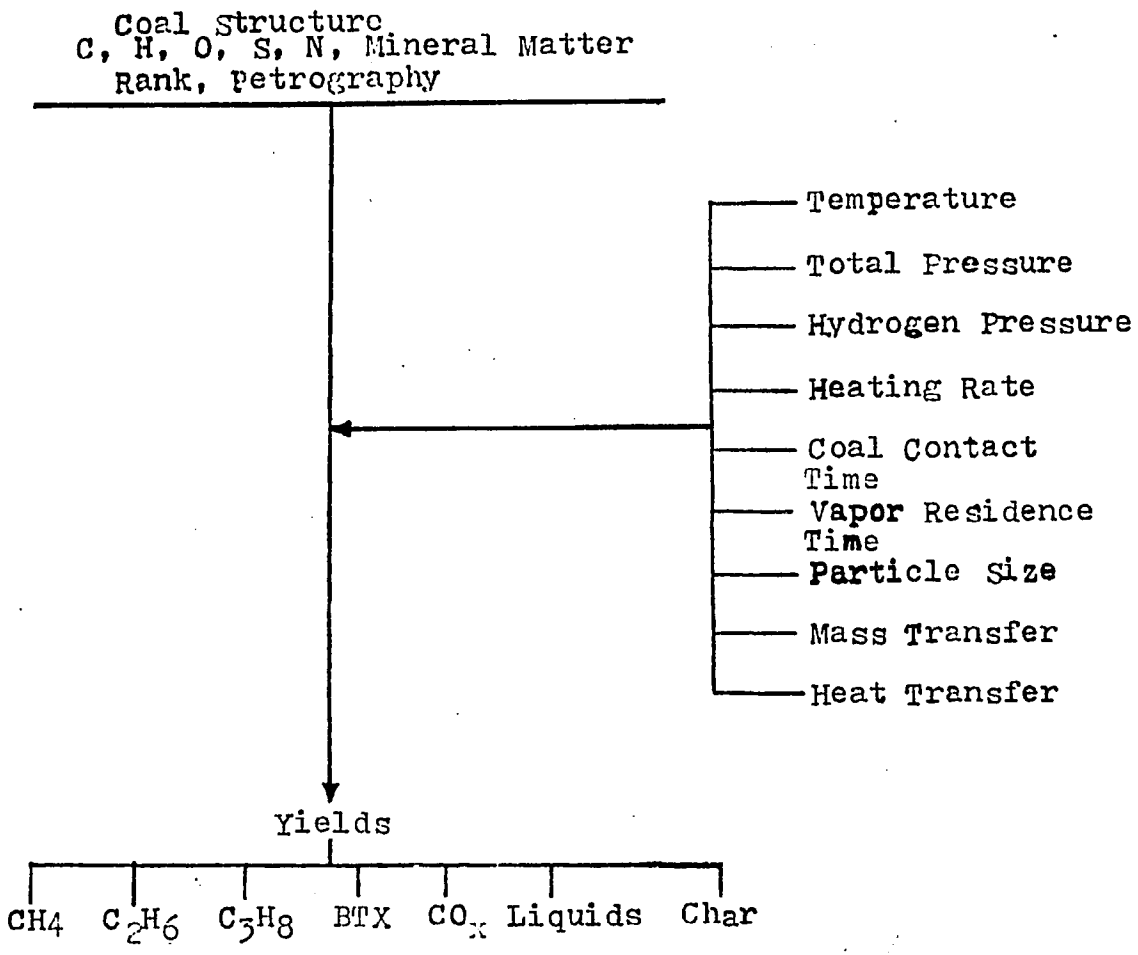
reaction under slow heating, and Von Frederdorff and Elliott (1963) reviewed the state-of-the-art in coal gasification. Tingey and Morrey (1973) have reviewed the chemical aspects of coal reactivity and structure.

Figure 2.2 is a simplified schematic representation of the flash hydrogenation process. The reactant, coal, is a highly heterogeneous, organic-rich substance originating from different plant forms mixed with inorganic sediments. Its structure depends not only on its origin, but also on its coalification history: the nature of the topographic depression, the nature of the underlying rock and soil, the climate and the physiography. Rank and petrography are commonly used for the classification of coal and they are reviewed by van Krevelen (1961), Parks (1963), Tingey and Morrey (1973), Stach, et al. (1975), Waddell, et al. (1978), and Neavel, et al. (1980).

The hydrocarbon products from coal flash hydrogenation include methane, ethane, propane, benzene, toluene, xylene, carbon oxides, liquids and char. In addition, a great proportion of sulfur in coal is emitted as H_2S. These volatile species are profoundly affected by the coal nature and processing conditions. These processing variables include almost every possible variable in chemical kinetics: temperature, total pressure, hydrogen pressure, heating rate, coal contact time, vapor residence time, particle size, and transport limitations.

The measurement of flash hydrogenation products with different coals under various operating conditions in the laboratory provides data for kinetic analysis, process evaluation and pilot plant design. In addition, it provides the coal scientist with more information about the

Figure 2.2 Schematic Representation of the Flash Hydrogenation Process



nature of coal.

Several physical and chemical methods are available for the direct measurement of coal properties. IR spectra measure the concentration of each functional group. X-ray diffraction provides information on the size of aromatic lamellae and the aromaticity of coal. NMR spectra also give coal aromaticity. The methods of selective oxidation by various agents are used to assess the ratio of aromatic to aliphatic hydrogen. Such techniques were reviewed by Sunberg (1977). An investigation of the flash hydrogenation of various coals can provide complementary information on coal structure.

In addition to the present limits of our knowledge of coal structure, the interpretation of coal hydrogenation data faces a second difficulty. In the laboratory, some of the operative processes mentioned above are coupled. As an example, pressure, particle size and transport phenomena are important, and none of these can be studied independently of the other two.

Research publications on coal devolatilization and hydrogenation over the last ten years are tabulated in Table 2-1. Several types of reactor have been used. The fixed bed, used the The City College of New York, can achieve high heating rate and also provide a thermal hydrocracking zone for volatiles. The quenching rate is slow (about 20°C/s), but no significant effect is expected, due to the relatively slow methanation of char in comparison to coal devolatilization. For the electric grid technique, utilized by MIT, CIT, UTRC, and CSIRO, there is little interparticle mass transfer. The cold atmosphere minimizes vapor phase hydrocracking and liquid products condense on the reactor wall. The basket or thermal balance reactors can provide

Table 2.1. Experimental Techniques and Conditions

Author, Date Institution	Reactor	Capacity	Temp. (^{o}C)	Press. (atm)	Heating Rate (^{o}C/s)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Squires, et al. (1975) Graff, et al. (1976) Dobner, et al. (1976) Chen, et al. (1978) Chen, et al. (1979a) Chen, et al. (1979b) Chen, et al. (1979c) [The City College of New York]	Ring or Fixed Bed in Hot Rod	10 mg	600-1000	H_2, N_2 25-100	650	10-60	0-6	$\leq$ 44	
Kobayashi (1976) Kobayashi, et al. (1977) [MIT]	Entrained	2.5 mg/s	727-1827	1, Ar	10^4-2 x 10^5	0.01-0.22	---	38-45	
Anthony (1974) Anthony, et al. (1974) Suuberg (1977) Suuberg, et al. (1978, a,b)	Elect. Grid	10 mg	400-1100	0.001-100 N_2,H_2,He	100-12000	0.1-30	0	53-1000	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (°C)	Press. (atm)	Heating Rate (°C/s)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Howard, et al. (1977) [MIT]									
Growcock and MacKenzie (1976) [Brookhaven]	Injected Fixed Bed	3 mg	550-850	10-276 H_2	> 10^4	5-300	0.32-9.7	37-44	
Steinberg and Fallon (1975) Steinber, et al. (1976) Fallon and Steinberg (1977) Steinberg, et al. (1978) Fallon, et al. (1979) [Brookhaven]	Entrained	0.5 lb/hr	700-900	34-170 H_2	2000-3000	1-10	1-10	$\leq$ 150	
Oberg, et al. (1977) Combs, et al. (1978) Oberg, et al. (1978)	Jet-mixing	0.25-1 T-D	815-1040	34-100 H_2	---	0.01-4.0	0.01-4.0	25-175	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (^{o}C)	Press. (atm)	Heating Rate (^{o}C/s)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Ranier, et al. (1979) Combs (1979) [Rockwell]	(see previous page)								
Johnson (1975) Johnson (1977) Beeson, et al. (1979) [IGT]	Helical Entrained	50-500 g/h	480-870	18-68 H_2,N_2	28 or fast	5-14	5-14	74-89	
Greene (1977) Greene, et al. (1978)	Entrained	5000-10000				0.05-10	0.05-5		
Hainshar, et al. (1978)	Helical	1500-35000	700-950	20-170	> 50000	0.05-10	0.05-5	---	
Oko, et al. (1979) [Cities Service]	Free-Fall	100-300 lb/hr-ft^2				0.1-4	2-30		
Solomon and Colket (1978) Solomon (1979a) Solomon (1979b) Solomon, et al. (1979) [UTRC]	Elect. Grid	200 mg	300-1250	vacuum	600	3-78	0	150	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (°C)	Press. (atm)	Heating Rate (°C/s)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Durai-Swamy, et al. (1979)	Entrained	1 kg/hr	540-760	1.2,N_2	> 62400	1.5, 3	1.5, 3	---	
Che, et al. (1979) [Occidental]	Entrained	3 T/D	510-707	1.2,N_2 CO+H_2O	> 6240	1.5, 3	1.5, 3	---	char/coal = 10
Nsakala, et al. (1977a) Scaroni, et al. (1979) [PSU]	Entrained	1 g/min	700-1000	∿ 1,N_2	> 10000	0.05-0.4	0.05-0.4	.75 x 220 to 38 x 50	
Chambers and Yavorsky (1978) [PERC]	Free-Fall	9-47 lb/hr	900	68,H_2	---	∿ 0.8	---	< 150	
Weimer and Ngan (1979) [Air Prod.]	Ther. Bal.	3 g	25-1000	1.0,He	0.7-2.7	---	0	175-833	
Finn, et al. (1979) [National Coal Board]	Fixed Bed	10 g	550-750 (1st) 500-1000 (2nd)	49-148 H_2	< 30	900	1-11	251-500	
Campbell and Stephens (1976) [LLL]	basket	50 g	110-1000	1.0,Ar	0.056	---	0	1680-3350	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (°C)	Press. (atm)	Heating Rate (°C/s)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Gray, et al. (1974) [PSU]	Crucible	0.25-3 g	950-1200	1.0, N_2	0.3-20	420	0	< 200	
Hamilton, et al ()1979) Hamilton (1980)	Elect. mesh	< 10 mg	1000	N_2	10^{-1} - 10^4	1.0	0	100	
Tyler (1979) Tyler (1980)	Fluid Bed	1-3 g/h	450-900	H_2,He,Ne	----	> 0.7	0.7	76-104	
Young (1980)	Basket (coal)	10-20g	500-1000	N_2	0.08	3600 + heating p.	----	300-1000	
	Silica boat (char)	500 g 1 g	1000 925	N_2	1.5-4.5	900	----	----	Char Carboniza-tion
Wailes, et al. (1980) [CSIRO]	Packed Bed	29-35 g/h	400-450	138-172 H_2	---	8 hr	----	----	Tar Hydro. Cat. Ni/Mo
Coates, et al. (1974) [Brigham Young]	Entrained	1-416/ hr	650-1370	1.0, H_2, H_2O	-----	0.012-0.34	0.012-0.34	< 74	
Ubhayaker, et al. (1976) Ubhayaker, et al. (1977) [Avco]	Entrained	2g/s	1500-2000	1.0 CO_2 H_2O,N_2	$\leq$ 130000	0.007-0.07	0.007-0.07	70% < 74	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (°C)	Press. (atm)	Heating Rate (°C/sec)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Nsakala, et al. (1977b) [PSU]	Fluid-Bed	50 g	800	1.0,N_2	0.17	0	----		
	Fix-Bed	0.25-4	750-1150	1.0,N_2	0.5-22 or larger	540	0	< 200	
Juntgen and van Heek (1968, 1969, 1970, 1979) [GmbH]	Fixed Bed	----	400-1100	1-70 He,H_2, H_2O	$1.7x10^{-5}$-1.7	10^3-10^6	---	< 50	
	Elect. Brid	0.01 mg			$16_4$7-1.7x 10^4		0		
Gavalas and Wilks (1980) Gavalas and Oko (1978) Cheong/et al. (1975) Cheong (1976) [CIT]	Elect. Grid	200 mg	< 1000	0.01-2,He	600	∞	0	323-417 88-124	
Kershae, et al. (1980) [Fuel Re. Inst.]	Fixed Bed	25 g	450	250,H_2	3.3	900	---	250-590	$SnCl_2$ $ZnCl_2$
Morris and Keairns (1979) [Westinghouse]	Fluid	0.27 g	760-1000	10,N_2	---	---	---	500-3350	
Peel, et al. (1979) [Univ. Estradual]	Batch	10 g	470	200,H_2	0.17	10800	10800	100	

Table 2.1. Experimental Techniques and Conditions (continued)

Author, Date Institution	Reactor	Capacity	Temp. (°C)	Press. (atm)	Heating Rate (°C/sec)	Solid Contact Time (sec)	Vapor Resid. Time (sec)	Particle Size (μm)	Comments
Gardner, et al. (1974) [Case U.]	Basket	< 6 g	0-1000	0-68, H_2	---	< 3000	0	---	$ZnCl_2$ K_2CO_3 $KHCO_3$ (char hydrogenation)
Wood and Wiser (1976) [Utah]	Entrained	90-273 g/min	500-700	102-136 H_2	----	1-6	∿ 0.8	150-351	$ZnCl_2$
Cypres and Soudan-Moinet (1980) [Libre de Bruxelles]	TGA	4 g	0-1000	He	$3x10^{-3}$ ∿ 0.26	----	-----	pellet made from 250-400	coal and iron oxides
Butler and Snelson (1980) [IIT]	Quartz Container	0.03 g	300-400	41-69, H_2	---	3600	3600	---	$AlCl_3$ MCl_x
Sato, et al. (1979) [Nat Res. Inst.]	Autoclave	0.06 g	500-600	50-150 H_2	---	< 15	< 15	----	
Menteer, et al. (1974) [PERC]	Elect. Grid	0.25 mg	400-1200	vacuum	8250	0.05-0.15		0	44-53

direct kinetic information, but mass transfer effects cannot be ignored and data are usually collected under low rates of heating. Entrained and fluidized beds are continuous processes and close to large scale operations. Their long coal-volatile contact time makes the data analysis more complex than the captive sample techniques previously mentioned.

In the following sections, the effects of coal nature and each processing variable on product distribution will be discussed.

2.2 Coal Nature

Coal is a heterogeneous material composed principally of different organic macerals, subordinately of minerals, and containing water and gases in submicroscopic pores. For the organic portion, the formation of coal from large plant masses via biochemical and geochemical processes is called coalification. The extent of coalification determines the degree to which the original plant material approaches the structure of pure carbon. Thus, the rank classification of coal is a measure of the coalification process, i.e., it designates the metamorphism from plant debris to various coal types. On the other hand, a second classification based on the composition of different organic macerals originating from various sources is called petrography. The historical development and the definitions of various terms used in rank and petrographic classifications were recently reviewed by Penn State University scientists (Waddel, et al., 1978). In the following sections, the interrelationships among classifications, chemical structure and reactivity will be discussed. In addition, the structure and reactivity of the inorganic part of the coal, or the mineral matter, will be briefly discussed.

2.2.1 Rank

It is generally accepted that coalification occurs in two stages. The first stage involves biological-bacterial processes and is termed biochemical coalification. This is primarily a diagenetic process. The second stage begins at the formation of lignite and is termed geochemical coalification. The results of early geochemical

coalification are said to be primary "physico-structural" changes due to overburden pressure associated with increasing depth of burial (Teichmüller and Teichmüller, 1968). The main process acting at this stage is dewatering and decreasing in porosity. Chemical changes also occur and these include decarboxylation (-COOH), dehydroxylation (-OH), and loss of other edge groups rich in oxygen from the chemical structure. These processes result in an enrichment of carbon, an increase in calorific value, and a decrease in both moisture content and oxygen. The second phase of geochemical coalification begins in the high volatile bituminous rank range. Most of the oxygen is said to have been lost by the time this stage is reached, leaving mainly hydrogen-rich edge groups. The loss of hydrogen in the form of methane becomes the main process of coalification. The results of coalification at this stage are a decrease of hydrogen and volatile matter, and an increase in reflectance. Quantitatively speaking, rank can then be a monotonic function of hydrogen content, oxygen content, carbon content, volatile matter, moisture content, reflectance, H/C ratio or O/C ratio. The interrelationships among these variables were discussed by van Krevelen (1961). All of these variables, except reflectance, are provided by the proximate and ultimate analyses. Ultimate analysis gives elemental composition. Proximate analysis provides the weight fractions of moisture, volatile matter, ash (or mineral matter), and fixed carbon under a given set of conditions. The conditions and chemical reactions for determining the elemental and proximate analyses are defined by ASTM Standard (1976), and Table 2.2 is an abstract of these definitions. Some of the important properties of coals of various ranks are shown in Table 2.3. Anthracites have the highest carbon

Table 2.2

Definitions of Coal Analysis

Analyses	Description
Proximate	Moisture - weight loss in drying, air oven, 104-110°C
	Volatile matter - weight loss upon slow (7 min) pyrolysis in crucible to 925-950°C
	Ash - weight loss of solid residue after combustion at 750°C
	Mineral Matter - weight of unaltered minerals in raw coal as determined by acid demineralization or radiofrequency ashing
	Fixed Carbon - dry ash free (DAF) or dry mineral matter free (DMMF) basis, 100-volatile matter
Ultimate	Percent carbon, hydrogen, oxygen, nitrogen and sulfur as determined by ASTM chemical methods, DAF or DMMF basis.

Table 2.3

Classification of Coals by Rank (A.S.T.M. - D. 388-38), Tingey and Morrey (1973)

Class	Group	% Fixed Carbon Range (DMMF)	% V.M. Range	BTU Content/LB	Requisite Physical Properties
Anthracitic	Meta-anthracite	98-100	0-2		
	Anthracite	92-98	2-8		
	Semi-anthracite	86-92	8-14		Non-agglomerating
Bituminous	Low-volatile	78-86	14-22		
	Medium-volatile	69-78	22-31		
	High-volatile A	<69	>31	14,000	
	High-volatile B			13,000-14,000	
	High-volatile C			11,000-13,000	Either agglomerating or non-weathering
Subbituminous	A			11,000-13,000	Both weathering and non-agglomerating
	B			9,500-11,000	
	C			8,300-9,500	
Lignite	Lignite			<8,300	Consolidated
	Brown Coal			<8,300	Unconsolidated

content, give little volatile yield and do not agglomerate. Bituminous coals give a high yield of volatiles and their chars usually swell and agglomerate under rapid heating. Lignites and subbituminous coals also give high volatiles yield, but the chars do not agglomerate. It is one of the objective of this research to investigate the elemental change in char compositions under hydropyrolysis.

Figure 2.3 shows some of the basic structure and functional groups in coal. The fundamental carbon structure is the polynuclear aromatic; hydroaromatic and aliphatic structures account for most of the hydrogen. The hydroxyl (-OH), carboxyl (-COOH), and carbonyl (=CO) forms are the major oxygen functional groups; lower rank coals may also contain ether, quinone, methoxyl and heterocyclic oxygen structures. Sulfur and nitrogen occur as substituted aromatics or heterocyclics. The elemental analysis, aromaticity, and the distribution of functional groups are the basis for the study of coal chemical structure. However, these are not enough, partially because coal rank is an average of the heterogeneous characteristics of coal. Two coals with the same rank may exhibit markedly different chemical characteristics. Several model coal molecules have been postulated in the literature: Fuchs and Sandhoff (1946), Given (1960), Hill and Lyon (1962), Mazumdar, et al. (1962), van Krevelen (1963), Wender (1975), Wiser (in Wolk, et al., 1975), and Heredy and Wender (1980). The objectives of these studies are (Heredy and Wender, 1980):

1) to incorporate into the model new structure information that has become available in recent years,
2) to derive additional input data for the model molecule by

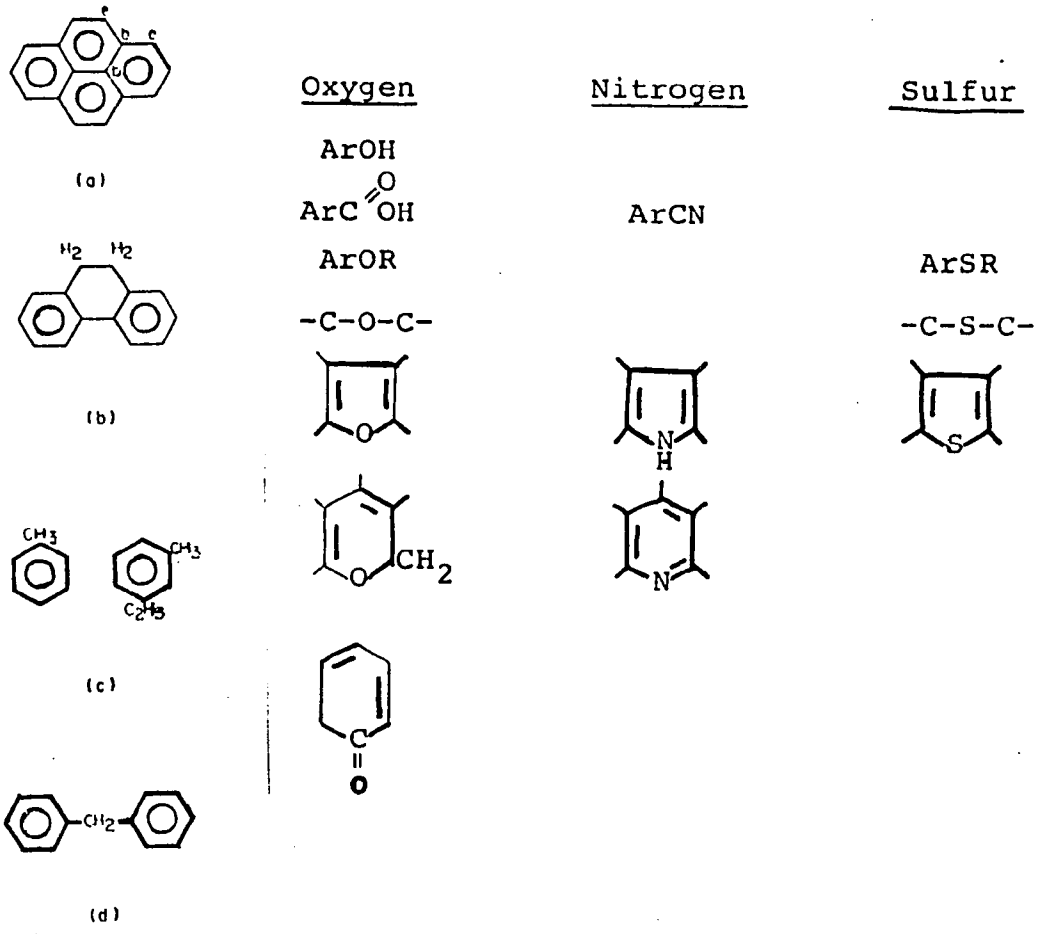


Figure 2.3 Basic Chemical Structure and Functional Groups in Coal

means of a mathematical analysis, and,

3) to test the model by comparing the experimentally observed behavior of a specific coal in a number of chemical reactions with the expected behavior of the model molecule in the same reactions.

Gavalas and co-workers (Oko, et al., 1976; Cheong, 1977) have recently taken an interesting approach to modeling coal pyrolysis, based on a statistical model of coal structure statistically degrading. It is the author's personal opinion that their model can be extended to a synthetic coal structure which contains various species. The composition of these species is the result of their different origins and stochastic coalification history. The coalification process may be stochastic in nature due to the lack of exact information about coalification history of which makes the process appear random. The mathematics of stochastic processes is well developed and can be found in several texts: Seinfeld and Lapidus (1974), Papoulis (1965) and Karlin and Taylor (1975).

2.2.2 Petrographic Composition

The development of coal petrology in recent years has added a new approach to studying and classifying coals. Stopes (1919, 1935) was the first to classify coals on the basis of microscopic and petrographic composition, and to relate composition to chemical and physical properties. She proposed the term "maceral" as the organic counterpart of "mineral" to designate the organic components of coal. Cady (1942) also discussed the fundamental chemical differences in the

three kinds of coalified materials: vitrinite, fusinite, and "wax-resinoid phyterals" (liptinite). He suggested that the chemical differences in the petrographic components may be important in coal utilization. This three-component classification of macerals is useful for many purposes. The basic chemical differences in the three groups are that the liptinite-group macerals are relatively rich in hydrogen and are the most aliphatic in chemical structure; the inertinite-group macerals are relatively rich in carbon and are highly aromatic in chemical structure; and the vitrinite-group macerals are relatively enriched in oxygen and are intermediate in degree of aromaticity and aliphatic structure. Van Krevelen (1961) uses the atomic H/C versus O/C ratios for the maceral groups to indicate different lines of development during coalification. Given, et al. (1960), also studying the chemistry of macerals, cites experimental evidence that the macerals of the liptinite group are more aliphatic than are the vitrinite-group macerals, and that the macerals of the vitrinite group are enriched in hydroxyl groups. The three maceral groups are known to behave differently from one another in certain technological processes. Under devolatilization conditions, vitrinite and exinite groups are considered reactive macerals because they become plastic, and volatilize, respectively. The degree to which these macerals are reactive depends on the rank of the coal. The inertinite macerals (fusinites, macrinite, micrinite, and sclerotinite) receive their name because they are relatively inert to the devolatilization process. Discussion of maceral properties and of systems developed for predicting coke strength are given by Ammosov, et al. (1966), Benedict, et al. (1968b), Harrison, et al. (1964), Brown, et al. (1964a), Brown, et al. (1964b). Studies

relating maceral composition and conversion yields in liquefaction processes indicate that macerals of the vitrinite and liptinite groups are probably reactive in liquefaction processes, and the inertinite group macerals are probably inert in the processes (Fisher, et al., 1942; Davis, et al., 1976; Mitchell, et al., 1976).

Several systems have been developed for classifying the organic constituents of coal. Thiessen (1920) developed a method for use with transmitted-light microscopy. The classification schemes most widely in use today are adaptation of the Stopes-Heerlen System (International Committee of Coal Petrology, 1971, see also Table 2.4) for reflected light microscopy which is based on morphology, reflectance and behavior in technological processes. In this system, coal macerals are grouped into three main classes as discussed above, and each component is composed of macerals with unique identifying characteristics of morphology, tenture, and reflectance. Some modifications have been made to the classification scheme. For instance, Benedict, et al. (1968) have subdivided vitrinite into "reactive" vitrinite and "pseudovitrinite" based on slight differences in reflectance, morphology, and behavior. Brown, et al. (1964c) also subdivides vitrinite into two components: vitrinite A and B. Teichmüller (1974a,b) has added three new members to the liptinite maceral group based on observations of fluorescence in blue light.

2.2.3 Mineral Matter

Mineral matter is the inorganic fraction of coal. Direct determination by chemical methods is available but complex (Miller, et al., 1979; Given and Yarzab, 1979; Padia, 1976) and still

Table 2.4. Modified Stopes-Heerlen maceral classification

Maceral Group	Maceral	Origin		Appearance		Chemistry	Technological Behavior	
		Source	Process	Thin Section	Reflected Light		Carbonization	Liquefaction
VITRINITE	Telinite (cell walls) Collinite (cell fillings, structureless vitrinite	Woody tissues, bark, leaves, etc.	Mummification	Red-brown	Intermediate grey	Intermediate hydrogen content and volatiles	Principal reactive constituent in coking coal	Susceptible to Liquefaction
LIPTINITE (OR EXINITE)	Resinite	Resins	Resistant remains	Yellow	Dark grey	Higher hydrogen content and volatiles; more aliphatic	Reactive during carbonization	Susceptible to Liquefaction
	Sporinite	Spore exines						
	Cutinite	Cuticles						
	Alginite	Algae						
	Fluorinite	Plant Oils, Fats			Black			
	Bituminite	Bacterial lipoids, Fats, Proteins	Migration		Between Vitrinite & Sporinite			
	Exudatinite	Exudates from Liptinite & Vitrinites			Black			
INERTINITE	Micrinite (massive & granular	Plant materials	Degradation products	Opaque	White, yellowish, light grey	Lower hydrogen content and volatiles; more aromatic	Generally inert during carbonization	Generally resistant to liquefaction
	Fusinite	Woody tissues, etc.	Fire; biochemical oxidation					
	Semifusinite	Woody tissues, etc.	Intermediate between vitrinite and fusinite					
	Sclerotinite	Fungal sclerotia, hyphae	Resistant remains					

faces some difficulties for the low rank coals (Given and Spackman, 1978). It can also be estimated by substituting the ASTM ash content and other analytical data into the empirical equations available in the literature (Parr, 1932; Given, et al., 1975; Padia, 1976; Neavel, et al., 1980). A classical review on mineral matter in coal was written by Ode (1963). Recent research on the identification of mineral matter is emphasized because of several practical interests:

1) the catalytic or poisonous effects of a mineral element in conversion processes,
2) pollution control, and
3) ash filtration and disposed problems.

According to Gluskoter (1975) and O'Gorman and Walker (1972), four major mineral types have been found:

1) aluminosilicates (clays), such as kaolinite [$Al_2Si_2O_5(OH)_4$] and illite [$KAl_3Si_3O_{10}(OH)_2$] - 50% by weight of mineral matter;
2) oxides, such as silica [SiO_2] and hematite [Fe_2O_3] - 15%;
3) carbonate, such as calcite [$CaCO_3$], siderite [$FeCO_3$], dolomite [$CaCO_3 \cdot MgCO_3$] and ankerite [$2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$] - 10%;
4) sulfides and sulfates such as pyrite [FeS_2] and gypsum [$CaSO_4 \cdot 2H_2O$] - 25%.

Mineral matter is converted to oxides, CO_2 and H_2O under heating during pyrolysis gasification or combustion. The major reactions include:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O\ (g)$$

$$CaCO_3 \rightarrow CaO + CO_2\ (g)$$

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \ (g)$$

$$CaSO_4 \rightarrow CaO + SO_3 \ (g)$$

$$FeS_2 + 7/2\ O_2 \rightarrow Fe_2O_3 + 2SO_2 \ (g) \text{ (oxidation only)}$$

The products from these reactions include both solid and gas. The "ash" content of coal is determined by the amount of solid oxides, and the gases, CO_2 and H_2O, causing weight loss during the high temperature ashing. It is therefore of interest to have a simple correction equation for the calculation from ash and other analytical data. Early work by Parr (1932) is widely used in the ASTM system of coal classification for converting parameters of volatile matter, fixed carbon, and calirific value to a mineral-matter-free coal basis. The Parr empirical formula is as follows:

$$MM = 1.08 * (Ash) + 0.55 * (sulfur)$$

Several other authors also made attempts to develop correlations. King, Maries and Crossley (KMC) (1936) proposed an equation involving six analytical terms. Brown, et al. (1952) made a statistical study that showed certain components were interrelated. They simplified the KMC formula and the new equation required fewer analytical determinations. Fereday and Flint (1953) devised another formula which allows calculation to a sulfur-free ultimate analysis by including the organic sulfur as part of the mineral matter. Given, et al. (1975) modified Parr's formula based on mineral matter determinations by acid demineralization. Padia (1976) derived a stoichimetrically based relationship between mineral matter and ash composition. Neavel, et al. (1980) proposed another stoichimetric formula which includes a correction term for the organic oxygen appearing in the ash as alkali salts. Even though their measurement requires a relatively more complex

analytical procedure, good correlation was obtained for coals of all ranks.

Direct determination of mineral matter content by acid demineralization with HCl and HF is general recognized as a reliable procedure (Bishop and Ward, 1958), even for low rank coals. Frazer and Belcher (1973), however, claim that some of the organic matter is solubilized by acid treatment. Miller, et al. (1979) have established a procedure for determining the mineral matter content of coals of bituminous and high ranks, based on low-temperature ashing (LTA) under closely specified conditions. LTA involves oxidizing the organic material in coal with an oxygen plasma at a temperature no higher than 180°C, presumably leaving the mineral matter intact. The procedure as specified is not valid for lignite and subbituminous coals, because most or all of the organic sulfur is fixed in the ash as sulphate. The Penn State University researchers also suggest that a pretreatment with acid to remove ion-exchangeable cations before LTA will most probably give acceptable results. Neavel, et al. (1980) verified this proposal by showing that low rank coals with oxygen contents greater than 16% have higher LTA mineral matter contents than the calculated values obtained by the equation they postulated in the same paper. They also showed that the modified LTA with acid pretreatment will significantly improve the result for these high-oxygen coals.

In addition to the dmmf and daf classifications, the behavior of mineral matter upon coalification and conversion processes is probably more important from a practical point of view. However, it is not well understood so far. Upon hydrogenation, its mineral matter gives both chemical and physical effects. Gray's study (1978) indicated that the

mineral matter appears to be acting in a physical capacity as an internal diluent, reducing agglomeration of the coal particles. This decrease in agglomeration allows more effective diffusion of hydrogen to the site of bond rupture and of products away from the coal particles as well as maintaining a higher overall surface area for reaction. It is surprising to note that the conversion was brought up from 50 to 65 wt% by adding kaolin. It may just be a result of the particular South African coal, which has extremely high semifusinite content (62%) and low vitrinite content (18.3%), but the study did indicate the potential of the effect of mineral matter on volatile transport in coal particle. In an earlier report, Mukherjee and Chowdhury (1976) also found that the conversion of an Indian bituminous coal was improved by impregnating it with titanium oxide or kaolin. However, this trend was not found in a study by Jackson, et al. (1979) with Australia brown coal. Instead, they found only iron (Fe_2O_3) has a major effect on conversion yields when impregnating coal with its principal inorganic constituents. Ouchi, et al. (1973) discovered that H_3PO_4, $FeCl_3$, $ZnCl_2$, and $AlCl_3$ are catalysts for the coal depolymerization.

A comparison of the hydrogenation behavior of raw and acid demineralized coals is an approach to the mineral matter effect other than impregnation. However, this fails to isolate the effects of individual inorganic components and the process of demineralization may in itself significantly alter the coal structure (Kuczyaski and Andrzejak, 1961; Schafer, 1972), and thus the behavior of the coal during hydrogenation.

The large scale use of coal draws attention to the possible expulsion of harmful quantities of trace materials. Mercury is one such

metal which has received attention during recent years. Other elements such as arsenic, selenium, and radium also should be of concern. Ruch, et al. (1973) reported the occurrence and distribution of potentially volatile trace elements in coal, most of which were from the State of Illinois.

2.2.4 Rank-Petrographic Composition-reactivities

For the last two years, the statistical stepwise regression method has been used to investigate the interrelationships among coal reactivities and their chemical and physical properties. Multilinear models have been tested (except in some cases, ratios of H/C and of O/C were included) because of their simplicity. Nonlinear models will require more sophisticated chemical and physical information.

Though the author's contribution on this subject will be detailed later in this thesis, the highlights of his results will be briefly reviewed here as a comparison. It will be shown in Chapter 4.12 that rank alone is not sufficient to predict the yield of volatiles from a coal during flash hydyrogenation. Using stepwise regression with 16 rank and petrogrhic variables (Chapter 4.1.3.d), it is found that the best correlation is

$$VM = 3.93 * (E) - 0.49 * (M) + 54.5$$

where E = exinite content (dmmf wt%)

M = mineral matter (Dry wt%), and

VM = volatiles (dmmf carbon %)

The strong correlation of total volatile with exinite content indicates that exinite may provide the internal hydrogen required for stabilization of light free-radical species from other kinds of

macerals. Exinite is high in hydrogen and is generally aliphatic in structure. This result led to an IR analysis for the coal samples and volatiles is found in good correlation with oxygen and aliphatic hydrogen contents (Solomon, et al. 1979).

$$VM = 0.8 * (O) + 15.0 * (H_{AL})$$

It is found that this correlation fits the experimental data from three major conversion processes: coal hydrogenation, vacuum pyrolysis and liquefaction. Accordingly, Neavel, et al. (1980) found the best correlation for ASTM volatile matter yield is

$$VM_{ASTM} = 1.281 * (O) + 12.345 * (H) + 1.915 * (S_{org}) - 42.251$$

where O, H, and S_{org} are the dmmf oxygen, hydrogen and organic sulfur contents in coal, wt%.

It is interesting to note that the coefficients of oxygen and hydrogen (or aliphatic hydrogen) are in the same of order of magnitude in the above two equations. The chemistry behind these numbers remains as a question. It will be shown in Chapter 4.1.3.d that most of the results from the direct correlation between reactivities and coal properties are neither quantitatively nor qualitatively explainable, but it is the author's opinion that these results will provide a new and valuable basis for coal structure studies in the future. Traditionally, elemental analysis, aromaticity and fractions of each function group, form the basis for the modeling of coal structure. The predicted structure is then evaluated by heat of formation and some reaction kinetics for support or screening.

Penn State University studied the dependence of liquefaction behavior of 104 bituminous coals on coal characteristics (Yarzab, et al., 1980). For the whole set of coals, volatile matter and vitrinite

reflectance have the highest correlation coefficients with conversion. However, tests showed that the sample set contained more than one population. Cluster analysis partitioned the set into three reasonably homogeneous populations. A factor representing sulfur content was the major contributor from a set of variables in separating the coals into groups, with smaller contributions from factors related to rank and petrographic composition. Each of the groups contained samples mostly from one geological province, but 11 coals of relatively high sulfur content from the Eastern province were clustered in a group that contained also 25 coals from the interior province. The range of conversions are distinctly different for the three groups, and the three regression equations developed for correlating conversion each required a different set of coal properties.

Penn State University (Waddell, et al., 1978) and Exxon Research and Engineering Co. (Neavel, et al., 1980)developed a computerized coal data base and investigated the interrelationships among coal properties. Their correlation equations provide empirical tools that are useful for predicting coal characteristics and may have significant value for the study of coal structure in the future.

2.3 Temperature

Temperature is the most important processing variable in hydrogenation. Hydrocarbon yields from Illinois No. 6 coal hydrogenation under flash heating to temperature were reported by Graff (1977). Methane, ethane, propane, CO_x and BTX yields during hydrogenation were determined and the char left in the reactor was then

determined by in situ combustion to permit a carbon balance calculation. The carbon deficit, observed at lower temperatures is attributed to species heavier than xylene. Figure 2.4 is a summary of the City College's study. Char yield is not shown on the figure, it is the difference between 100 and the sum of the five curves. The carbon oxides are less than 3% and they are also not presented. The features of these yields are:

- Each species shows a bell-shaped curve, providing the temperature region is extended to both directions, ($CH_4 \rightarrow C + 2H_2$ occurs at higher temperature), and
- Heavier species form at lower temperatures than light species.

This information suggests that a series of consecutive reactions occur during hydrogenation. If the heavy liquid products are considered as one component, the following reactions occur:

$$\text{Heavy Liquids} \rightarrow \left\{ \begin{matrix} \text{BTX} \\ C_2H_6 \\ C_3H_8 \end{matrix} \right\} \rightarrow CH_4 \qquad 600°C < \text{Temp} < 1000°C$$

It is interesting to note that this reaction scheme matches closely a classical work by Chermin and van Krevelen (1957):

$$P \rightarrow M \rightarrow \begin{matrix} R + G_1 \\ \searrow \\ S + G_2 \end{matrix}$$

where P denotes the original coal, M the metastable intermediate product, R the semi-coke, S the coke, G_1, the primary gas and G_2 the secondary gas.

Early work hardly involved volatile analysis; the abstract terms "metastable intermediate", "semi-coke" therefore were utilized for kinetic analysis.

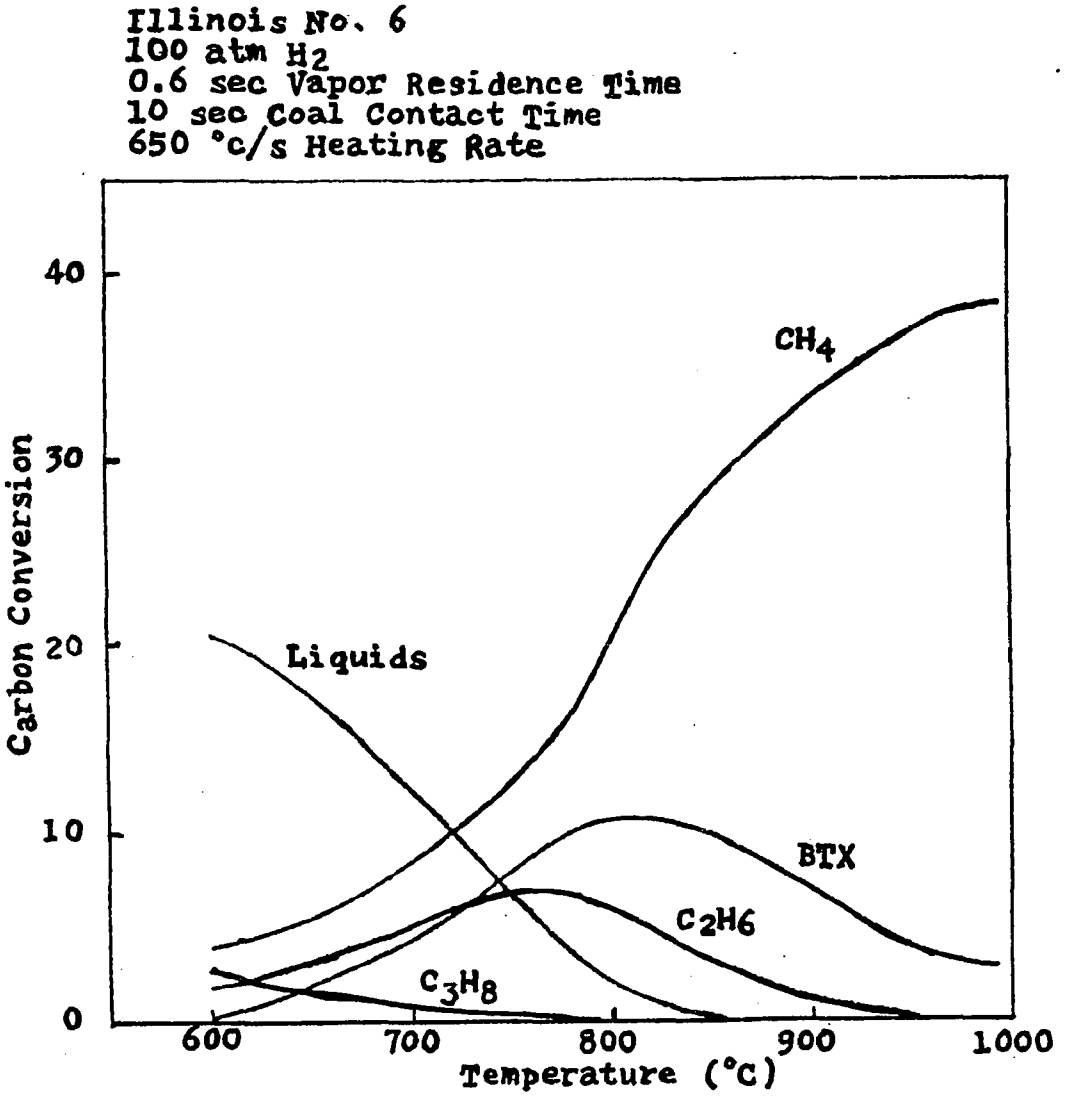


Figure 2.4. Effect of Temperature on Coal Hydrogenation

The actual coal hydrogenation mechanism is, however, much more complex than the one proposed above. Coal is heterogeneous and it has a complex structure. Each species may be involved in a set of parallel and/or consecutive, independent and/or competitive reactions. The model mentioned above is valid only for an overall description, and for the downstream vapor phase hydrocracking reactions which are relatively well understood. In order to trace dynamic behavior, many pyrolysis studies have focused upon obtaining time-temperature resolved rates of production of various volatile species from coal (Juntgen and van Heek, 1968, 1979; Campbell and Stephens, 1976). In the acquisition of very rapid processes data, two major problems are likely to occur. The data to be measured are distorted by some portion of the equipment or the signal is too fast to be measured. In the second case, the signal has to be spread out in time, and the result from this process is measured. Hahn and Wendt (1978) suggested that a technique based on the numerical inversion of the Laplace transform could be used to interpret the distorted signal accurately. Exact knowledge of the residence time distribution of the specific reactor is required to use this method.

2.4 Pressure

Figure 2.5 shows the pressure effect on yield structure of Illinois No. 6 coal in hydrogenation (Graff, 1977). The figure is presented in a cumulative way and the unmarked area in the lower left is the heavy liquid yield. Features of this figure are:

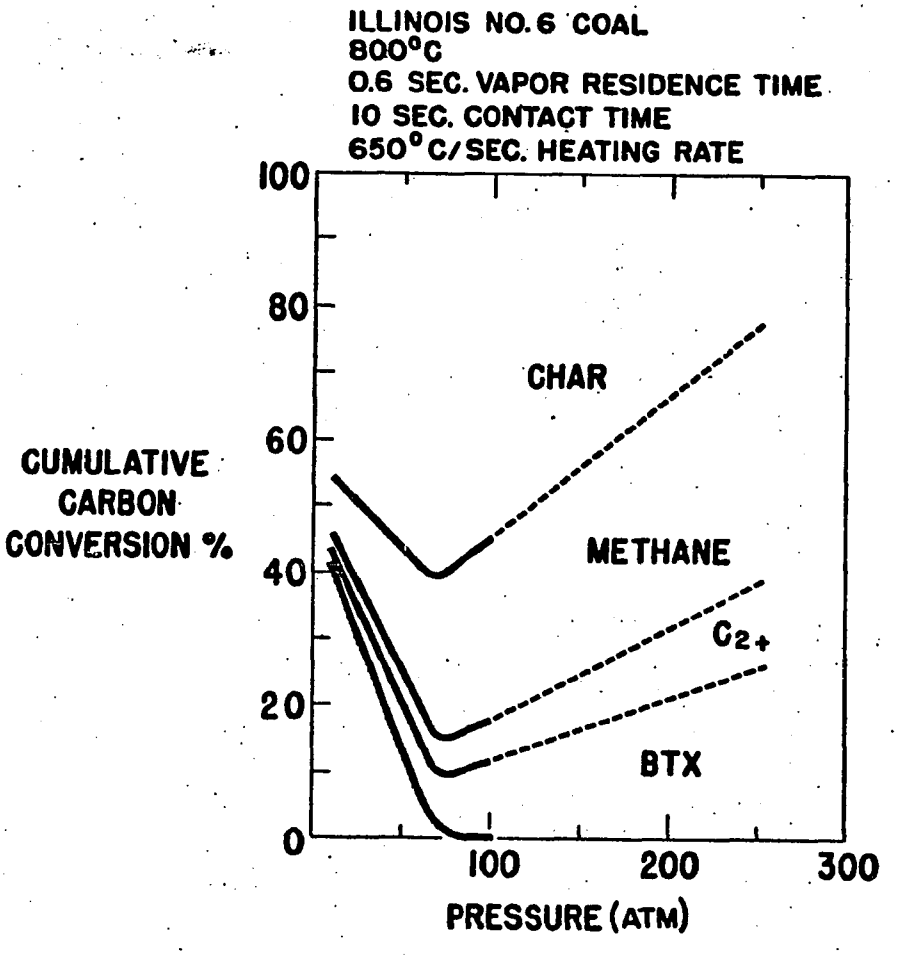


Figure 2.5. Effect of pressure on the yield structure of Illinois No. 6 coal in flash hydrogenation.

- the light species, C_1, $C_2 + C_3$, and BTX, increase with increasing hydrogen pressure,
- the heavy liquid species decreases up to a pressure of about 69 atm, and
- char yield is a maximum at a pressure where heavy liquid yield is totally suppressed.

Since volatiles have a higher hydrogen to carbon ratio than the starting coal, the first point is consistent with thermodynamic law. The results for heavy liquids and char may be explained by the interplay of two effects. The first is the effect of increased pressure in retarding the evolution of volatiles from the coal particle. In an inert gas atmosphere, secondary reactions result in redeposition of these volatiles, especially heavy liquids, within the particle. Hydrogen, however, retards condensation reactions (perhaps by stabilizing active free radicals) allowing them to crack further to BTX and light gases which escape from the particle more easily.

The behavior observed here may be specific to caking coals. A maximum in char formation has been reported at 10 to 20 atm of hydrogen for Pittsburgh No. 8 coal (Anthony and Howard, 1976) while no effect of pressure on total yield was reported for a lignite (Gray and Sprouse, 1977).

Caking and noncaking coals behave quite differently during hydrogenation. For a caking coal, the particle first softens and then distends and fuses to other particles (Waters, 1962). During the same period, product gases form within the particle as bubbles and the coal viscosity varies (Fitzgerald, 1956, 1965). Coal softening is related to its oxygen content (Tingey and Morrey, 1973). Oxygen content of

bituminous coals is too low to provide sufficient cross-linking to fix the coal and it therefore becomes mobile upon heating. Swelling is probably caused partially by the density change after secondary cracking reactions in the bubbles, and partially by the surface tension induced bubble migration. Particles of a noncaking coal, however, can not support any strain when volatiles form and will consequently burst in fragments. A film from Germany (Bergbau-Forschung Co., GmbH, 1976) showed that the bubbling process for caking coal is much longer than the bursting process for noncaking coal. This implies that mass transfer and internal secondary reactions are more important for caking than noncaking coals.

The importance of mass transfer controlled secondary reactions is reinforced by the observation that for caking coal, volatiles yield decreases with increasing size of particle (Anthony, 1974) or of crucible sample (Nsakala, et al., 1977; Gray, et al., 1974). The effect of particle size will be discussed in Section 2.8.

Anthony and Howard (1976) also investigated the pyrolysis behavior of caking Pittsburgh No. 8 coal. Total volatiles yield was found to decrease monotonically, from 54 to 37% of original coal weight, with increasing helium pressure. It does not increase, as in the case of hydrogen, at any pressure up to 100 atm. Though their work did not include volatiles analysis, comparison with the City College data strongly suggests that heavy liquids are most subject to mass transfer effects. The finite limiting value of total volatiles in Anthony and Howard's pyrolysis study indicates that the mass transfer effect on light species is limited, or even insignificant. It is also interesting to compare this result with Occidental Research's study (Che, et al.,

1979) on the effect of carrier gas on tar yield. ORC found that char provides active sites for the adsorption of tar vapor, and tar either polymerizes or cracks on the char surface.

Gray (1978) found that perticle agglomeration can be reduced and volatiles yield increased by adding kaolin to coal. As mentioned in Section 2.2.3, his result is valid only a for a particular coal and petrographic composition. However, reducing particle agglomeration seems to be an important research area for both coal chemists who want to optimize yield and processing engineers who want to avoid reactor choking. Siegell (1976) related agglomeration rate to flow patterns and operating conditions in fluidized beds. Two approaches are therefore presently available for minimizing mass transfer effects in coal hydrogenation:

- proper use of processing variables or even reactor design,
- proper use of additives.

2.5 Vapor Residence Time

Volatiles produced from the coal-hydrogen reaction are swept by the hydrogen gas along the reactor. Three types of reactions may take place in the vapor zone:

- reactions among volatiles,
- volatiles-char reactions, and
- volatiles-wall reactions.

The reactions among volatiles can be catagorized into three types:

- hydrocracking to light species,
- formation of aromatic compounds, and
- interactions among each component.

Though the reaction network is complex, in most respects the evolution of products in the vapor residence zone is relatively well understood and easier to describe than that in the devolatilization.

A maximum in BTX yield occurs at an optimum vapor residence time (Graff, 1977; Finn, et al., 1979; Greene, et al., 1978). This optimum vapor residence time varies with temperature, pressure, hydrogen to hydrocarbon ratio, ...etc., and ranges from a fraction of a second to about ten seconds, perhaps more. Some of the reactions mentioned above may be insignificant within the VRT. A careful examination of reaction velocities is needed.

Brooks (1966, 1967) examined the hydrogenation behavior of selected pure hydrocarbons, representatives of those occurring in light petroluem distillate, with varying hydrogen to hydrocarbon ratio and at pressures up to 100 atm. He found that carbon deposition can be reduced at high initial hydrogen to hydrocarbon ratio, high pressure, low temperature, or by using additives such as H_2S. Little is known about the exact mechanism of carbon formation. Brooks (1966, 1967) found the following trend in tendency for carbon deposition: olefins > aromatics > aliphatics. This trend may be different under different reaction conditions (La Cava, 1977), but single ring aromatics at any conditions have strong carbon-forming tendencies. Since benzene is the aromatic hydrocarbon in highest concentration in the flash hydrogenation process, its carbon forming tendencies are very relevant to the present research.

Two mechanisms for carbon formation from benzene have been proposed. One model involves the breakage of benzene ring to $C_4H_3^{\cdot}$ and $C_2H_3^{\cdot}$ and follows an addition of $C_4H_3^{\cdot}$ to benzene to form napthalene, to napthalene to form anthracene or phenanthrene, ... etc. (Thompson and

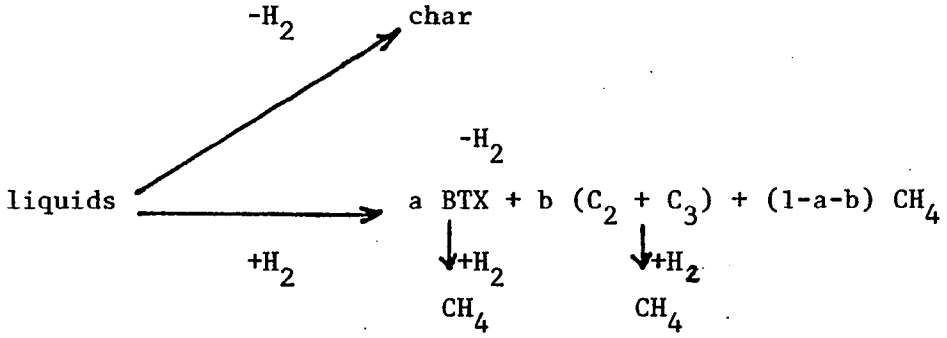
Brooks, 1973). Since the breakage of a benzene ring takes a large amount of energy, it is expected to be valid at high temperature. Another model proceeds through diphenyl as the intermediate (Thompson and Brooks, 1973; Kinney and Delbel, 1954; Virk, et al., 1974).

Based on the information outlined in the previous paragraphs, heavy liquids and BTX seem to be the major sources of deposited carbon in coal hydrogenation. The City College study (Figure 2.6, Graff 1977) showed that about 4% carbon is formed in 5 sec vapor residence time. Among the operation variables, the high hydrogen pressure and high hydrogen to volatiles ratio inhibit carbon formation, while the high temperature and high surface to volume ratio favor it. Systematic study is required for the understanding of vapor phase reactions. The unknown structure and composition of heavy liquids are major sources of difficulty.

The secondary reactions between volatiles and char are also poorly understood. Generally speaking, char provides adsorption sites for volatiles cracking and polymerization. The effects of char on these two reactions depend not only on the processing variables, but also on the char's history, structure and mineral matter. In addition, the presence of product gases, especially the active species H_2S, H_2O and CO_2, may also have profound effect on the char surface. Che, et al. (1979) found, from their pyrolysis studies, that char catalyzes tar cracking. Ganwal and McMicheal (1980) found that coal-derived materials having high ash content show significant catalytic enhancement of the vapor phase cracking of benzene and alkylated benzene compounds. Lahaye and Aubert (1977) found that coke-tar interactions depend on the hydrogen bonding between the two components and that above a critical value surface-chemical-function content has no influence on coke-tar interactions.

Hydrocracking of volatiles is the most important reaction in the vapor zone. Moignard and Stewart (1958) used an essentially aromatic free light hydrocarbon feed and found that BTX yield is almost negligible when the hydrogen to hydrocarbon ratio is greater than 6.5 at 800°C, 10 atm and 10 sec residence time. Similar results were obtained by Brooks (1967) for aliphatic hydrocarbon feeds: n-butane, n-hexane and isobutane. Also, Shultz and Linden (1957) investigated the hydrogenation products of various aliphatic and aromatic hydrocarbons with a batch reactor at 650°C to 732°C, 2000 to 4400 psi, 80 to 169 min residence time, and at hydrogen to hydrocarbon ratio for total conversion to methane. They found that only trace amounts of unaccounted for aromatics formation and that the main product from benzene is methane.

Figure 2.6 shows the vapor residence time effect on volatiles from coal hydrogenation. Heavy liquids completely convert to light species and char. The latter consumes only a small portion of the heavy liquids. The gross effects can then be described as follows:



where a and b are the fractions of liquid converted to BTX and C_2^+, respectively.

This is a simplified model. The actual mechanism is different from devolatilization in the following aspects:

Illinois No. 6
700°C
100 atm H_2

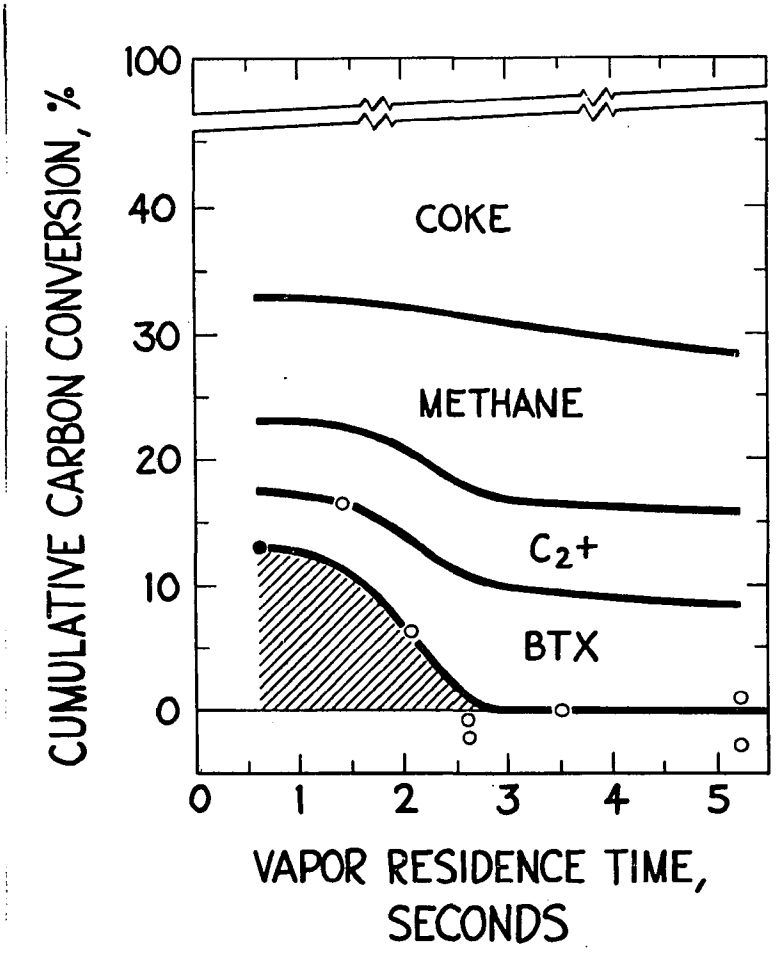


Figure 2.6. Effect of Vapor Residence Time on Coal Hydrogenation

1) The nature and composition of liquids are rather complex. In an earlier review (Rhodes, 1945), more than 300 components in the tar had been identified from low and high temperature carbonization. Two subsequent reviews contained broad discussions on tar characterization, properties, processing and utilization (Karr, 1963; Weiler, 1963). Recently, Fallon and Steinberg (1977) identified 32 species in coal hydrogenation liquids. Among them naphthalene, phenathrene and fluorene account for about 70% weight of the heavy liquids. Solomon (1979a) compared the infrared spectra of four coals and their vacuum pyrolysis liquids. The resemblance of the liquids and parent coals suggest that the liquids consist of "monomers" released from the coal "polymer." Most tar studies were made in connection with the liquefaction. Tens of thousands of paper, books and patents have been published. Among these references, Whitehurst, et al. (1976) report their study on the nature and origin of asphaltenes in processed coals using SESC fractionation in a most comprehensive way. Lytle, et al. (1979) reviewed 60 coal liquefaction processes. Recently, Squires, et al., (1977) developed F^{19} NMR technique as a tool for the identification and quantification of various organic functional groups.

2) More operating variables are adjustable in the vapor zone. In addition to the temperature and pressure, the vapor residence time, gas composition, surface to volume ratio solid nature are all adjustable as described earlier in this section.

3) Various studies indicate a remarkable lack of quantitative agreement on the hydrocracking rates of benzene and other possible components (Table 2.5). For example, Gangwal and McMichael's (1980) data showed a higher benzene hydrocracking rate on the order of 1 to 2 periods than that of Virk, et al. (1974) and Hou and Palmer (1965). Though Gangwal and McMichael claimed that their high rates might be due to the high surface to volume ratio (about 3-6 times those used in previous studies), their reactor size is very similar to that used by Hou and Palmer. They also found that the cracking activity appeared to increase rapidly with run time, reaching a steady-state value after an differences between various studies probably can not be explained without a study of kinetic mechanism and the effect of each operating variable on each reaction step. One such case appeared in Davis and Williamson's (1979) study on propane pyrolysis. They showed that the difficulty of attaching a single value of energy of activation to the decomposition of propane is related to the problem of product inhibition.

2.6 Solid Contact Time

Under flash heating, coal pyrolysis (or hydrogenation) may generally be regarded as occurring two stages with considerably different rates. The first stage, devolatilization, is extremely fast and is complete in one or two seconds (Anthony and Howard, 1976; Kobayashi, et al., 1977). The second stage is slow, the only important process being char methanation (Graff, 1977; Anthony and Howard, 1976).

Table 2.5. Kinetic Data of BTX, Propane and Ethane

Species	Rate	K_o	E	Source
Ethane	$K[C_2H_6]$	$10^{17.5}$	90000	Brooks (1967)
Benzene	$K[C_6H_6]$	1.4×10^9	52000	Hou and Palmer (1965)
Benzene	$K[C_6H_6]$	4.4×10^8	52600	Virk, et al. (1974)
Benzene	$K[C_6H_6]$	1.1×10^{10}	70587	Thompson and Brooks (1973), LaCara (1977)
Benzene	$K[C_6H_6]$	3.38×10^7	36510	Gangwal and McMichael (1980)
Toluene	$K[H_2][C_6H_5CH_3]$	$10^{11.44}$	58800	Brooks (1971)
Toluene	$K[C_6H_5CH_3]$	7.21×10^6	31250	Gangwal and McMichael (1980)
O-xylene	$K[C_6H_4(CH_3)_2]$	1.75×10^7	31830	Gangwal and McMichael (1980)
Propane		discussion in difference see		Davis and Williamson (1979)

Figure 2.7 (Anthony and Howard, 1976) shows the effect of coal contact time on caking Pittsburgh No. 8 coal and noncaking Montant lignite. A hot grid reactor was used for this experiment so that vapor cracking effect should be negligible. Devolatilization, coupled with hydrogenation, was complete at about 1 and 0.1 second for the bituminous coal and lignite, respectively. The pronounced difference suggests that the bubbling and swelling phenomenon does prolong the devolatilization process, even for particles as small as 70 μm. In a separate study, Morris and Keairns (1979) found that pyrolysis reactions were completed in about 8 sec in a fluidized bed when large particles (-1.40 mm + 1.00 mm) were used. The different pyrolysis time scales for Pittsburgh Seam bituminous coal and Montana lignite in Figure 2.7 can also be attributed to the different heating rate in their experiments. From their data, it takes 1.3 and 0.1 sec to heat the small particle from 25°C to 1000°C under 750 and 1000°C/sec heating rate, respectively. The actual pyrolysis time, therefore, depends on coal nature, heating rate and particle size. Figure 2.7 also indicates that second stage hydrogenation is much slower than the devolatilization and, in fact, no secondary reaction was found in a helium atmosphere.

Since devolatilization is completed in a short time under rapid heating and the remaining second phase reaction gives no significant increase in yield, the contact time is not an important controlling factor from the coal-hydrogen reaction point view. On the other hand, char-volatiles reactions may alter the yield structure significantly and this is a subject to be investigated.

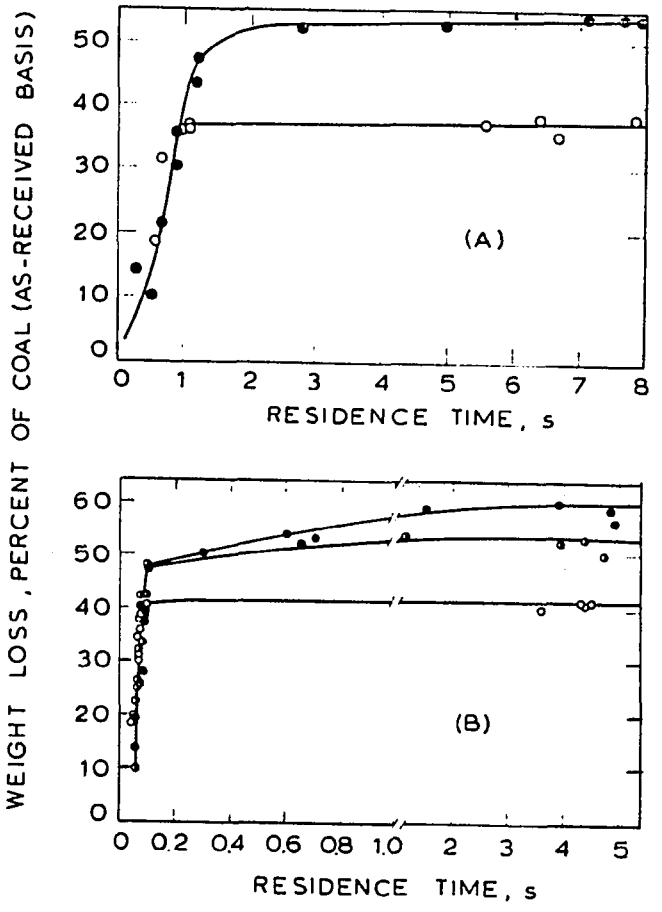


Figure 2.7. Effect of solid contact time on weight loss from coal heated in helium and hydrogen atmospheres [Anthony (1974); mean particle diameter, 70 μm. (A) Pittsburgh Seam bituminous coal (Ireland Mine); final (holding) temperature, 900°C; nominal heating rate, 750°C/x; pressure, 69 atm; (○) helium; (●) hydrogen. (B) Montana lignite (Savage Mine); final (holding) temperature, 1000°C; nominal heating rate 10000°C/s; (○) helium, 69 atm; (◑) hydrogen, 69 atm; (●) hydrogen, 103 atm]. (From Anthony and Howard, 1976).

2.7 Heating Rate

High heating rates in coal pyrolysis and hydrogenation have recently been emphasized partially because of the high volatiles yields found in some experiments and partly to meet the requirement of short vapor residence time for optimizing light liquid yield as mentioned in section 2.5. However, various experimental studies showed such divergent results that no unifying principle has been accepted. Johnson's data (1975) showed a higher volatiles yield at a high heating rate (several hundred °C/s) than the lower heating rate (28°C/s) for noncaking Montana lignite. Peters and Bertling (1965) and Sass (1972) showed the same trend when varying the heating rate in low temperature pyrolysis. Mentser, et al. (1974) and Badzioch and Hawksley (1970) found that the volatile yield from pyrolysis under 8250 ∿ 50000 heating rate is much higher than the ASTM volatiles. However, Graff, et al. (1976) showed a 17% decrease (of original carbon in the coal) in volatiles yield from heating rate 20°C/s to 650°C/s at 100 atm H_2 for caking Illinois No. 6, though the yield from 20°C/s heating rate is also higher than ASTM volatile matter.

The difficulties in analyzing heating rate effects arises both from coal's chemical kinetics and from its complex transport phenomenon. From the physical point of view, it is obvious that heating rate is associated with heat transfer problems. Volatiles transport in a coal particle should be described by mass and momentum transport equations. These conservation equations are coupled and involve phase change and moving boundaries. Some terms or even some equations are not significant in the process simulation under a specific set of conditions. It is essential to estimate the relative magnitudes of each

term before solving the equations. Russel, et al. (1979) compared three sorts of processes which are involved in establishing the temperature of a particle:conduction and convection to the particle's outer surface, conduction and bulk flow inside the particle, and energy absorption and evolution due to the various reactions. In a situation where a small particle is exposed to a high temperature gas, the heatup rate is characterized by the natural time scales of the internal and external processes. The time scale for heatup when the external resistance controls is $a(\rho C_p)_s/h$; $(\rho C_p)_s$ is the volumetric heat capacity of the particle, h the external heat transfer coefficient and a, the radius of coal particle. Inside the particle, the time scale for conduction is a^2/α_s; α is the thermal diffusivity. These two time scales are roughly the same order of magnitude, about 10^{-2} s for 100 μm particles at 600°C, showing that both external and internal processes are important in establishing the thermal response of a particle. Bulk flow, on the other hand, plays a very minor role. Heat transfer by bulk flow can be compared to the flux due to conduction in terms of the ratio:

$$\frac{k_o C_o RT}{P_o} \frac{a^2(\rho C_p)g}{\alpha_s(\rho C_p)_s} = \frac{\text{transfer by bulk flow}}{\text{conduction}}$$

which is small ($10^{-4} \sim 10^{-2}$) for particles 100 μm and smaller. In the above equation, P_o, k_o and C_o are bulk gas pressure, devolatilization rate constant and total molar density of reactive coal in particle. For larger particles (about 1000 μm), the ratio increases to become O(1) at roughly 100 atm.

Before applying the above analysis, two points should be noted:

(1) the overall heat transfer coefficient, h, was calculated assuming the particle was in a stagnant atmosphere.

The slip velocity between the particle and gas in some laboratory and pilot scale reactors will provide a higher heat transfer coefficient and consequently will also influence the particle heatup time.

(2) the particles were assumed to be in a constant temperature atmosphere. In cases of nonisothermal atmospheres, the process becomes more complex. Rectnely, Hamilton (1980) studied the char structure obtained from Liddell vitrinite pyrolysed at various heating rates (10^{-1} to 10^{4} °C/s). He found that the 100 μm particles heated at rates faster than 10^{-1}°Cs^{-1} showed an increase in plasticity with heating rate but the effects related to plasticity and volatiles evolution appeared to be approaching a limit. Little melting or swelling was observed when the particles were heated at 10^{-1}°Cs^{-1} for this highly "caking" vitrinite. Different char structures suggest distinct transport processes under different heating rates.

The kinetic mechanism of volatile-char and volatiles cracking reactions inside the char matrix is complex and very difficult to study experimentally. The char's role in this stage probably depends on both the coal structure and the mineral matter composition.

2.8 Particle Size

The particle size effect on coal hydrogenation was investigated at MIT (Figure 2.8, Anthony and Howard, 1976). The study shows that a reduction of particle diameter from 1000 to 70 μm increases the weight loss attained in 5 to 20 sec from 44 to 59% of the original bituminous coal at 69 atm hydrogen and 1000°C. The increase in yield

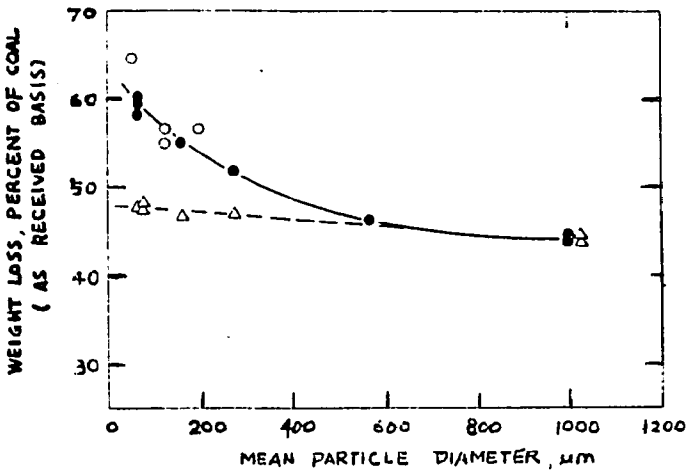


Figure 2.8. Effect of particle size on weight loss from bituminous coal heated in hydrogen and helium [(o) Maseley and Paterson (1967), Warwickshire coal, 175 atm H_2, 920°C final (holding) temperature, several s residence time. (•) and (▲) Anthony, et al. (1976), Pittsburgh Seam coal, 1000°C final (holding) temperature, 5-20 s residence time, 650-750°C/s nominal heating rate, 69 atm H_2 (•), 1 atm He (▲)]. (Anthony and Howard, 1976).

was found to be small in 1 atm helium. In the case of Montana lignite, no significant effect of particle size was observed in either hydrogen or helium.

The results for lignite are expected because it is noncaking, as discussed in sections 2.4 and 2.6. The mass transfer effect on bituminous coal in Figure 2.8 can be attributed to either gas absorption or the product desorption:

1) Gas absorption limitation: Anthony and Howard offered this explanation probably because the two lines in Figure 2.8 converge to the same value for large particles and because the difference between hydrogenation and pyrolysis for small particles is large.

2) Product desorption (especially tar) limitation: The evidence for tar transfer limitation has been discussed in section 2.4 where the tar yield decreases with increasing pressure. MIT also found a minimum volatiles yield and a monotonically decreasing yield with increasing hydrogen and helium pressures, respectively. However, they did not analyze the product. From another point of view, tar is more likely to be mass transfer-limited than hydrogen simply because of its large size and complex chemical structure. In addition, the characteristics of Figure 2.8 can also be explained by tar transfer limitation. The higher pressure of hydrogenation (69 atm) will make the caking period longer than that of low pressure pyrolysis (1 atm) and therefore enhance tar recondensation to char for the large particles. For the small particles, hydrogen enhances tar cracking and stabilizes light

species, therefore higher volatiles are found in hydrogenation. Gray, et al. (1974) and ya Nsakala, et al. (1977) also found that pyrolysis yields decreased with increasing sample size in crucibles. As in MIT's pyrolysis results, only a 3 ∿ 5% decrease in volatiles was found.

The above discussion is restricted to internal mass transfer. The following transfer resistances are also of potential importance under various processing conditions:

- external mass transfer,
- external heat transfer,
- internal heat transfer, and
- radiative heat transfer.

Several authors attempted to obtain empirical equations relating volatiles yield and particle size based on a certain transfer controlled mechanism. Results and some discrepancies were reviewed by Anthony and Howard (1976). Recently, Kalson and Briggs (1978) tabulated all the dimensionless characteristic numbers in the conservation equations with respect to the thermodynamic properties, processing variables, transport parameters and kinetic constants. Order-of-magnitude estimations of these characteristic numbers through the data in the literature has not been done, but will be valuable not only for unifying the experimental data but also for designing large scale hydrogenators.

2.9 Kinetic Modeling

While most of the progress in the last decade has been in the experimental determination of yield, parallel work has gone on in the

modeling of coal devolatilization and hydrogenation. The actual chemical and physical process is so complex, however, that every model has its limitations. For the purpose of correlating total volatiles yields, simple one-step irreversible kinetics have been widely used. Anthony and Howard (1976) reviewed the large discrepancies in Arrhenius constants and several modifications for this simple empirical equation. More complex kinetic mechanisms and models have been developed and they are listed in Table 2.6 and 2.7. Generally speaking, recent developments have the following characteristics:

(1) modeling individual components: Juntgen and van Heek's model (1968) which contained a set of parallel independent n-th order reactions offered a reasonable starting point for the purpose of modeling each component. It has recently been used by Sunberg, et al. (1977, 1978a, 1978b). However, they found difficulty in fitting bituminous coal data which may arise from tar recondensation and cracking reactions competing within the particle. In addition, some product species such as BTX and C_2H_6 are intermediates, rather than final products, in the series reactions. Therefore, better results can be expected by modifying the mechanism to a set of competitive consecutive reactions.

2) Distributed activation energies: Usually a three parameter model (activation energy, frequency factor and final yield) does not fit the complex coal hydrogenation data over the whole temperature range. Modifications used include either multistage kinetics or a temperature-dependent final yield (Stone, et al., 1954; Wiser, et al., 1967). However, these

Table 2.6 Kinetic Mechanisms Proposed in the Literature

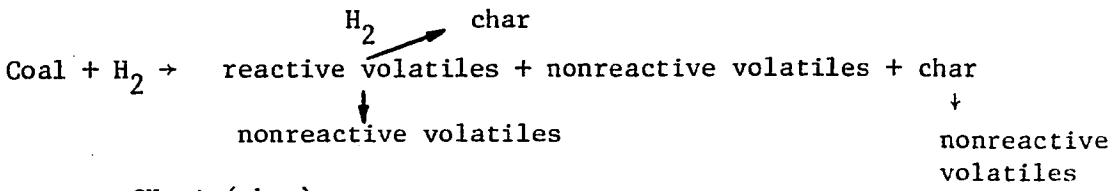
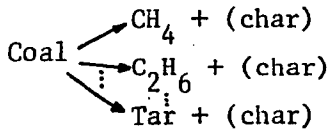
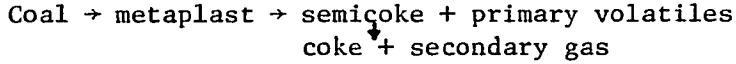
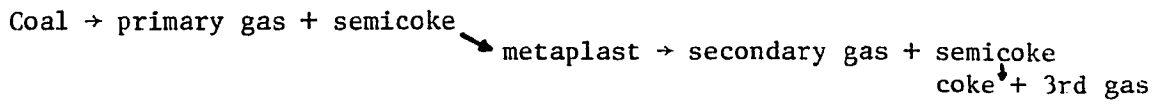
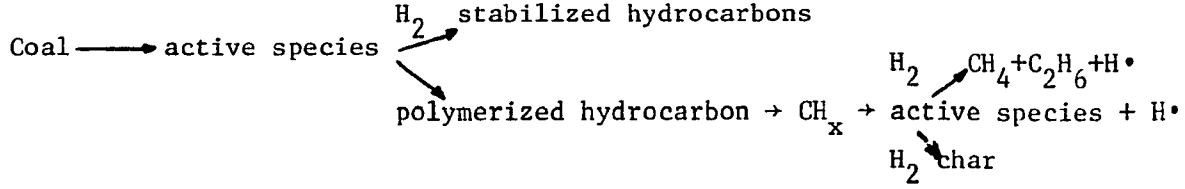
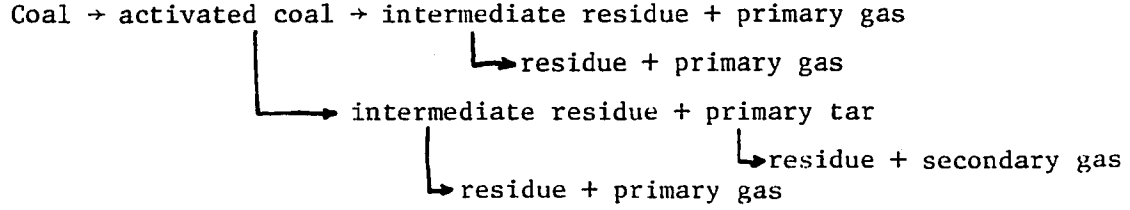
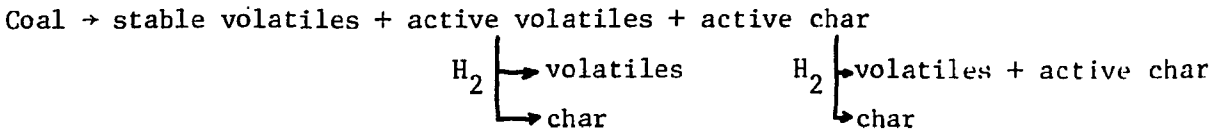
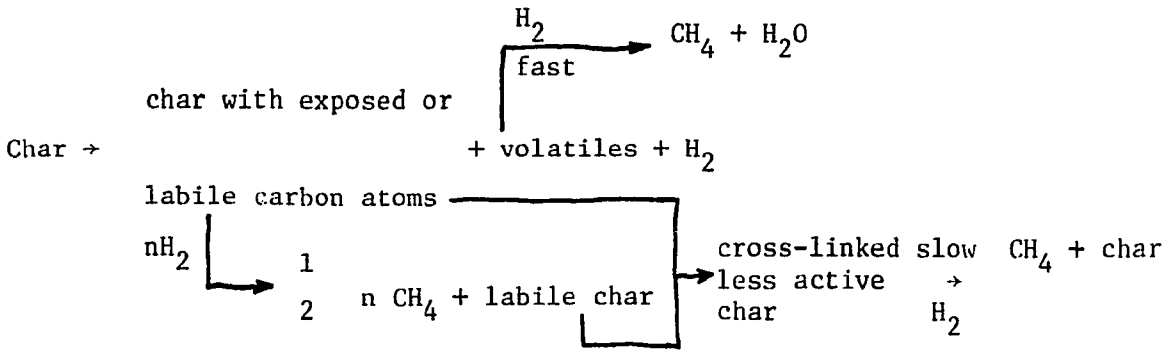
Anthony, et al., (1976)	
Juntgen and van Heek (1968) and Suuberg, et al. (1978a)	
Chermin and van Krevelen (1957)	
Mills, et al. (1975)	
Johnson (1975, 1977)	
Solomon and Colket (1978) Klein and Virk (1979) Cheong (1977)	Modeling Pyrolysis Products from Coal's Functional Groups
Reidelbach and Summerfield (1975)	

Table 2.6. Kinetic Mechanisms Proposed in the Literature (continued)

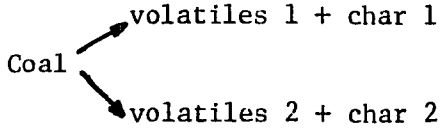
Russel, et al. (1979)



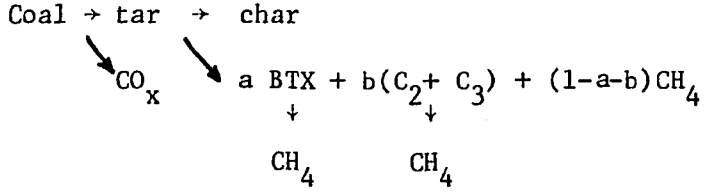
Moseley and Paterson (1965a)



Kobayashi, et al. (1977)



Chen (this study)



Zacharias and Howard (1979)

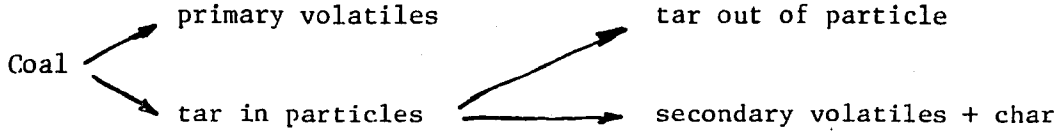


Table 2.7. Main Features in the Proposed Models

	T	P_{H_2}	P	M	SCT	VRT	Particle Size	Dist. E.	Transfer limitation	Modeled Compounds	Comments
Jüntgen and van Heek (1968)	Y	N	N	Y	Y	N	N	N	N	CH_4, C_2H_6	parallel reactions have no competition
Chermin and van Krevelen (1957)	Y	N	N	Y	Y	N	N	Y	N	T.V.	E is a uniform distribution
Johnson (1975, 1977)	Y	Y	N	N	Y	N	N	Y	N	CH_4, C_2H_6	Good stoichiometric analysis of methane, ethane and H_2
Mills, et al., (1975)	Y	N	Y	N	Y	N	Y	N	Y	T.V.	Mass, heat transfer and particle swelling were considered
Anthony, et al. (1976)	Y	Y	Y	N	Y	N	N	Y	Y	T.V.	One coefficient for mass transfer
Lewellen (1975)	Y	N	Y	Y	Y	N	Y	Y	Y	T.V.	Transported by bubble nucleation, growth and death
Suuberg, et al. (1977, 1978a)	Y	N	N	N	Y	N	N	Y	N	CH_4 CO_2 CO, H_2O BTX, Tar	Parallel reactions have no competition
Russel, et al. (1979)	Y	Y	Y	N	Y	N	Y	Y	Y	T.V.	Mass conservation applied to correlated pressure and particle size effects

Table 2.7. Main Features in the Proposed Models (continued)

	T	P_{H_2}	P	M	SCT	VRT	Particle Size	Dist. E	Transfer limitation	Modeled Compounds	Comments
Moseley and Paterson (1965a)	Y	Y	N	N	Y	N	N	N	N	CH_4	Active species model was later used by Johnson (1974) and Zahradnik and Glenn (1971)
Chen (this study)	Y	N	N	N	Y	Y	N	N	Y	CH_4, C_2+C_3 BTX, Tar CO_x	Simple residence time distribution assumed for volatiles in coal particles
Zacharia and Howard (1979)	Y	N	Y	N	Y	N	Y	Y	Y	C_1, C_2, CO_x H_2O, Tar	Langmuir (1961) equation used for mass transfer
Gavalas and Wilks (1980)	Y	N	Y	N	Y	N	Y	N	Y	Gas, Tar CO_x	

m : Heating Rate
VRT: Vapor residence time
SCT: Solid contact time

Y : Yes
N : No
T.V.: Total volatiles

modifications are neither mechanistically consistent with, nor mathematically amenable to the rate equations. Pitt's (1962) recognition of this problem led him to adapt Vand's (1943) treatment of a large number of independent parallel rate equations. The model has already been widely used (see Table 2.7) and the results show not only a good fit to experimental data (Sunberg, 1978a), but also shows higher activation energies which are consistent with expected bond energies.

3) Mass and heat transfer effects: Several different approaches have been tried to model the complex phenomena in the coal particle during hydrogenation (see Table 2.7). Anthony, et al. (1976) lumped mass transfer into one coefficient which followed the effect of pressure fairly well. Russel, et al. (1977) extended their kinetics to a shrinking core model which explained the particle size effect. Mills, et al. (1975) and James and Mills (1976) proposed a transport model for the swelling particle following the foaming law and incorporated a consecutive reaction scheme proposed by Cherwin and van Krevelen (1957). Lewellen (1976) developed a model of volatile transport in caking coals based on the concept that transport occurs primarily through nucleation, growth, coalescence and escape of volatiles-filled bubbles. All these models treated total volatiles, rather than individual species, as the product. Since the City College's data (Graff, 1977; see also section 2.4) showed that heavy species

are dominant in the transport process, further studies should emphasize these components. In addition, the difference between caking and noncaking coal should be emphasized. The models which treated transport as flow through porous media (Russel, et al., 1979; Zacharias and Howard, 1979; Gavalas and Wilks, 1980) are probably appropriate only for noncaking coal. Since the volatiles stay in a particle of a noncaking coal only for an extremely short period of time before the particle breaks into pieces (film by Bergbau-Forschung Co., GmbH 1976), it is doubtfall whether the volatiles flow within the particle of not. The results of pressure and particle size studies (section 2.4 and 2.8L) both showed little transfer resistance for noncaking lignite. Therefore transfer models are actually unnecessary for noncaking coals. On the other hand, a good model for caking coal should consider both the intraphase and interphase transfer phenomena and internal mass transfer includes the following items:

- bubble nucleation (Attar, 1978)
- bubble growth (Rosner and Epstein, 1972; Scriven, 1959; Moalem-Maron and Zijl, 2978; Johnson, 1977)
- bubble coalescence (Moalem-Maron and Zijl, 1978), and
- bubble departure (Johnson, 1977).

Although each of the bubble dynamics above is well understood, the combination of them with chemical kinetics is rather complex. The boundary layer around coal particles have also

been investigated by several authors. Sprouse (1979), Arri and Amundson (1978); Caram and Amundson (1979); Mon and Amundson (1978) and Mon and Amundson (1979). Only the first paper is related to hydrogenation, but others contain good discussions of gasification and combustion.

Qualitative analysis of various transfer limitations as functions of processing conditions are significant for understanding coal processing kinetics. The work is far from complete.

4) Secondary reactions of vapor products: These involve complex reaction schemes which include the hydrocracking of initial volatiles, reactions between each component, the reaction between vapor and remaining char and carbon deposition on the wall. Modeling the vapor phase reactions is a new research area and it involves solving a set of free radical reactions.

5) Coal nature: City College (Graff, 1977) has shown that rank alone is not sufficient to correlate or predict the hydrogenation volatiles yield. Statistical methods have been developed to investigate the relationships between volatiles and coal's physical and chemical properties. Some recent studies are discussed in section 2.2.4.

6) Heating rate: Any model which contains temperature as a variable can, theoretically, treat the transient heating rate effect. However, no systematic conclusion has been reached so far, even though heating rate, along with particle size, caking property and chemical reactions usually have a gross effect. The competitive reaction scheme proposed by

Kobayashi, et al. (1971; see also Table 2.6) is probably the simplest solution to this problem. Their model predicted that higher yields could be obtained at higher heating rate and it matches closely with their lignite and bituminous devolatilization behavior at various solid contact times (< 0.2 sec) and relatively high temperature (1000 ∿ 2100°K).

7) Functional groups: Modeling the pyrolysis behavior of each functional group in the coal is a new approach. Solomon and Colket (1978), Klein and Virk (1979) and Cheong (1977) have shown interesting results and difficulties.

8) Empirical formulas: Bechtel National has tried to fit yield data with a single empirical equation which contains almost all the important variables in hydrogenation: temperature, total pressure, hydrogen partial pressure, residence time and hydrogen to coal ratio (Epstein, et al., 1978). The City College tested Bechtel's equations with CCNY's data and large discrepancies were found. The difference may arise from the coal type.

2.10 Reactor Design

Four types of reactor have potential importance for processing coal: moving bed, fluidized bed, entrained bed and fast fluid bed.

1) Moving bed (Yoon, et al., 1978; Yoon, et al., 1979a; Wei, 1979; Yoon, et al., 1979b; Denn, et al., 1979; Stillman, 1979): The University of Delaware has made an in-depth examination of the thermodynamics, stoichiometric analysis,

design and parameter sensitivity of coal gasification in moving bed. The first moving bed, Lurgi reactor, was put into operation as early as 1936 in Germany. Coal is fed at the top of the reactor and moves downward by gravity flow, countercurrent to the upward gas flow. The advantages to a pressurized moving bed process when compared to fluidized and entrained bed processes are its relatively low pressure drop, high thermal efficiency, high carbon conversion and low entrainment of solids in the gas. Because of the countercurrent flow, the rich gas produced during devolatilization directly enhances the heating value of the products. The primary disadvantage of the moving bed reactor is the difficulty in processing highly caking coals without pretreatment. Since high hydrogen pressure and high heating rate for flash hydrogenation all enhance the caking tendency, a moving bed is generally not considered as a candidate for hydrogenation. Its only possible role in coal hydrogenation may be as a char gasifier suppling hydrogen.

2) Fluidized bed (Kayihan and Reklaitis, 1980; Sundaresan and Amundson, 1979; Fan, et al., 1979; Wen, 1979): Fluidized beds provide rapid circulation of solid in the bed so that isothermal conditions, excellent heat and mass transfer, minimum stagnant zones can be achieved in a compact reactor. In addition, fluidized beds are mechanically simple and suited to large scale operation (e.g., 30 ft in diameter is commonplace in other applications). Bubbles in the bed cause inhomogeneous contact between gas and solid which is a

disadvantage when compared with entrained and fast fluid beds. Scale-up is not simple since different regimes of fluidization tend to occur at different scales of operation. Large diameter beds exhibit circulation cells of solid and preferred bubble tracks. Recently, Wen (1979) reviewed the models and design principles for gas-solid reactions in fluidized bed. Fluidized bed has been applied to pilot scale Hygas and Hydrane processes.

3) Entrained bed (Wen and Chaung, 1979; Kane and Callister, 1978; Sprouse, 1979; Ubhayakar, et al., 1977; Oberle, 1979): Again, most of these studies are concerned with gasification except Sprouse's hydrogenation model. An entrained flow bed is basically a plug flow tubular reactor with small dispersed particles in a gaseous medium. Usually this gaseous medium is moving with enough velocity to keep injected particles entrained. The idea behind this entrainment concept is to provide the largest solid-gas surface area possible, so that chemical reactions between these phases are more rapid. In this way, chemical reaction times are shortened which means that reactor volume can also be minimized. This is important, economically, for high pressure reactors, where any reduction in size can substantially reduce capital equipment costs. The large gas-solid contact area also reduces char agglomeration. The ability to process all ranks of coal, irrespective of swelling and caking properties, has made entrained flow beds a major type of reactor in coal conversion technology. On the other hand, the concurrent flow gives small slip velocity and

little solid mixing so that heat and mass transfer are expected to be lower than in other reactors.

4) Fast fluid bed (Liss, et al., 1979; Yerushalmi and Cankurt, 1978; Yerushalmi, 1977): This type of reactor is characterized by a high slip velocity and extensive mixing, achieved in concurrent flow by increasing the solid content in the bed. A maximum slip velocity is reached by varying bed density, between the regimes of dilute entrained flow and bubbling fludized beds. In this condition the turbulent nature of a fluidized bed is retained and good solid mixing obtained. In a dilute entrained reactor fed with a caking coal, excess hydrogen serves the purpose of separating the molten particles. The same purpose can be served in fast fluid bed by refluxing char. The hydrogen requirement can be reduced to one-third or less of that typically used in an entrained bed. Since hydrogen has been shown (Pyrcioch, et al. 1972) to be the most important single cost factor (no fast bed was included in their analysis), the fast fluid bed has emerged as a promising reactor for flash hydrogenation of coal.

2.11 Catalysis

Catalytic hydrogenation of coal is likely to become an important research area in the next decade. The application can be discussed from three aspects:

1) Catalytic devolatilization: Dry, powdered coal (or char) mixed or impregnated with metal halides can be converted to

liquid and gas products (Wood and Wiser, 1976; Kershaw, et al., 1979; Ida, et al., 1979; Gardner, et al., 1974; Butler and Sudson, 1980). Low temperature (400-650°C) and long residence time (10 min to 8 hours) were used for higher liquid yield, except Wood and Wiser used 1-6 sec residence times because the catalytic effect is generally stronger in the early stages of devolatilization. The exact catalytic mechanism is not well known. Gray (1978) noted that catalytic and deagglomeration effects are, in some cases, difficult to distinguish for caking coals. The same result was also found in Cypres and Soudan-Moinet's study (1980) of coal pyrolysis with iron oxides. Catalysts are used in pyrolysis either to increase volatiles yield or to deplete the heteroatoms content of coal.

2) Catalytic liquids hydrogenation: The objectives of this study are to remove heteroatoms and to upgrade heavy liquids to selected species, such as single ring aromatics and low molecular weight cycloparaffins or branched paraffins needed for jet and diesel fuels. Polynuclear aromatics and high molecular weight heterocyclics contained in these fractions are difficult to convert to the desired molecules (breaking the polynuclear chain in a central ring instead of in a peripheral ring) and also cause rapid catalyst deactivation in naphtha reforming, hydrocracking, and cracking. Therefore, these fractions require severe hydrotreating before they can be processed by conventional petroleum technology. Such hydrotreating is costly because, being nonselective, it uses excessive amounts

of hydrogen. Dehydrosulfurization is relatively well understood. Practically all catalysts used commercially are oxides of cobalt, molybdenum, and nickel on supports of aluminum oxide or silica alumina which provide an extended surface. The catalyst can be in the form of pellets, beads, extrudates or microspheres. Even after decades of profound theoretical analyses of catalysts and the mechanisms involved in heterogeneous catalysis, there is no fundamental explanation for the preeminent choice of these metals on extended supports that permit desulfurization catalysts to function. Three reviews of dehydrosulfurization catalysis were published by Schuman and Shalit (1979), Ebel (1972), and Gates, et al. (1979). The oxygen removal from coal tar can be readily achieved with Co-Ni-Al type of catalyst (Mills, 1969). Dehydronitrogenation has just received attention (Satterfield, et al., 1975) and more research is expected for either catalytic or noncatalytic reactions of nitrogen because of air pollution problems.

3) Catalyst regeneration: Wood and Wiser (1976) found that catalyst recovery must be improved if the process is to become economically feasible, even with the most economical catalyst $ZnCl_2$. Generally speaking, catalyst regeneration will involve a series of chemical or physical separation processes.

A recent book by Cusumano, et al. (1978) contains a general survey of catalysis theory and its applications in the major coal conversion processes.

3. Experimental Arrangements

The experiments for this study were conducted in previously constructed equipment at City College (Graff, et al., 1976; see also Figure 3.1 for the reactor) though some modifications were needed to extend the range of reaction conditions. Figure 3.1 shows the reactor for contacting coal with hydrogen at pressures up to 100 atm and temperatures up to 1000°C. About 10 mg of powdered coal are packed between quartz wool plugs at a selected position in a reactor tube of 316 stainless steel, 6.35 mm o.d., 5.1 mm i.d. and approximately 300 mm in length. The more laborious technique, used in the past, of depositing a thin coal ring on the inner reactor wall is unnecessary since identical product yields have been found with both methods. Quartz wool is also placed in the downstream end of the reactor at the inlet of the cold zone to protect the pressure let down valve further downstream.

A metal screen is also placed downstream of the reactor to catch the quartz wool plug in the event of an inadvertant blowout. A thermocouple is spot-welded to the reactor tube at the location of coal sample.

Figure 3.2 shows the overall experimental arrangements. Flow of hydrogen is established at the desired pressure while the reactor and inlet system are at room temperature. At the time zero, electrical energy is supplied to the reactor tube from transformers at power levels of about 12 kw. The temperature of the reactor tube rises and at a preset temperature, as detected by a control thermocouple located

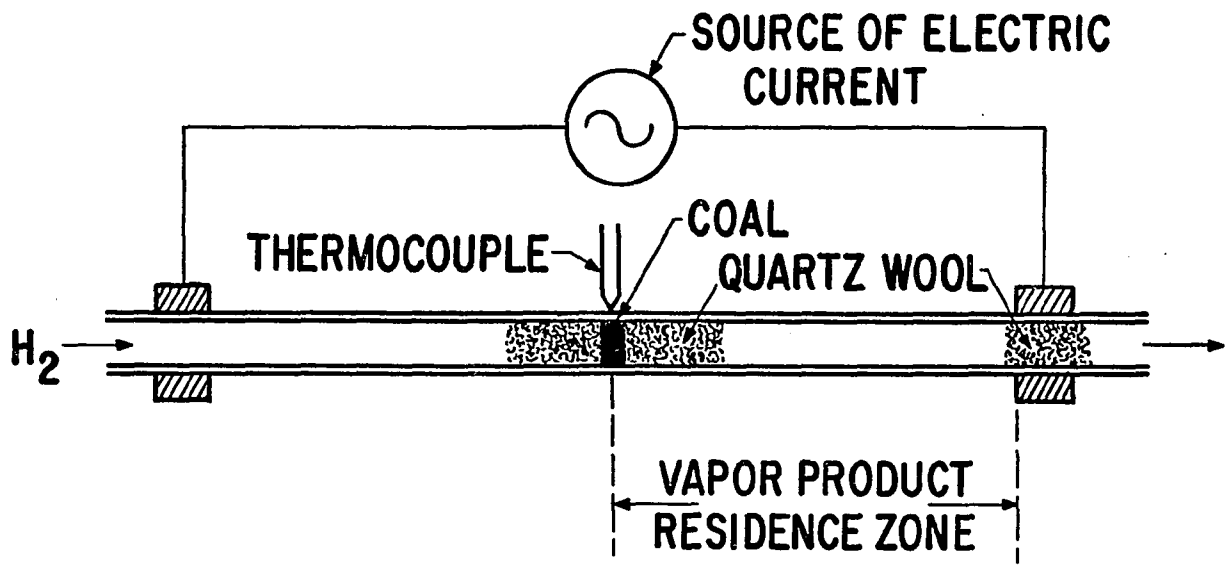


Figure 3.1. Reactor Tube for contacting coal with hydrogen under rapid heating and controlled residence time of vapor products.

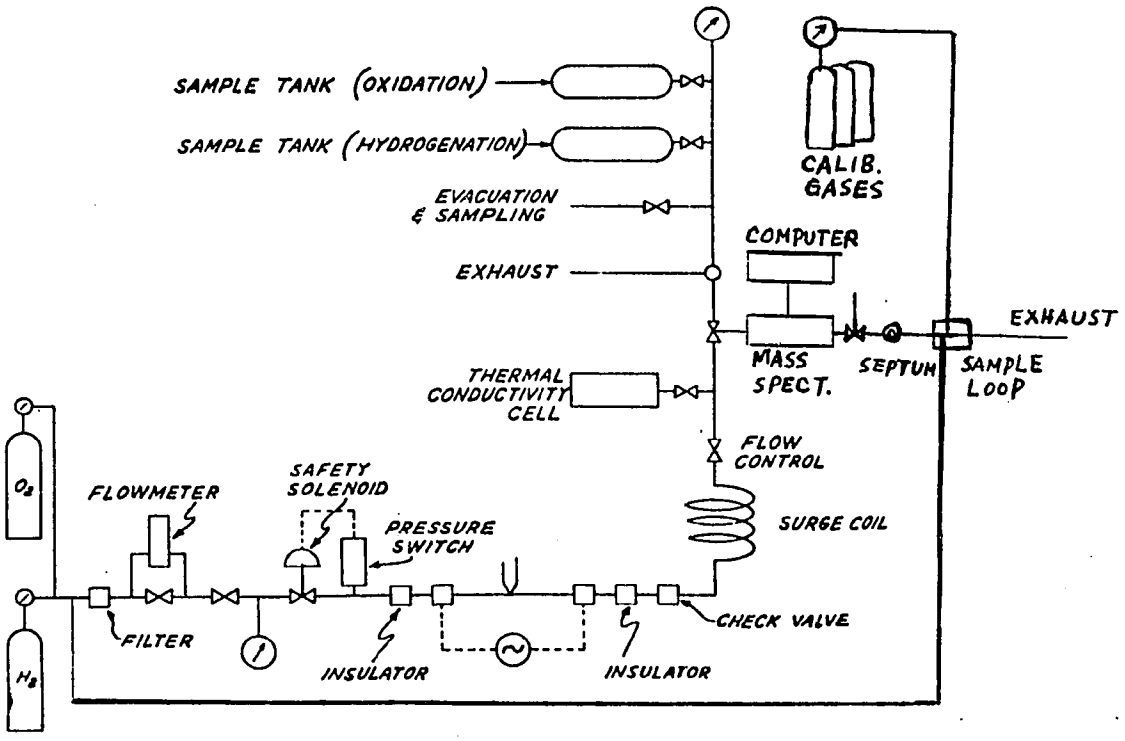


Figure 3.2. Overall experimental arrangement for study of reaction of coal with hydrogen under rapid heating and control of residence time of the vapor products.

halfway between the clamps, a control circuit switches off the heating current and switches on a holding current to maintain the desired temperature level for the duration of the experiment.

The temperature of the reactor wall at the location of the coal sample was measured with a second thermocouple on a stripchart recorder. No direct measurement of coal temperature was made in this work, the reported temperatures and heating rates are those measured by the external thermocouple.

Calculations (Appendix I) show that the flowing hydrogen comes to the temperature of the tube within less than 2 cm from the entrance. During heating, it follows the wall temperature with a time lag of only about 0.2 sec. The purpose of this calculation is to provide some assurance that volatiles enter an atmosphere at approximately the same temperature as the wall.

The vapor-product residence time in these experiments is the time required for the products evolved from the coal to be carried by the flow of hydrogen from the position of the coal to the righthand electrical lead. Because of its large mass, the lead stays at its initial temperature and serves as the quench point. In estimating the residence time, due allowance must be made for gas expansion during the rapid heat-up period.

If the reactor tube should burst, a pressure switch provided upstream of the reactor senses a drop in pressure and causes closure of the solenoid-operated safety valve to prevent continued flow of hydrogen and consequent risk of fire. A surge volume in the form of a coil is provided downstream of the reactor to prevent a reverse flow of gases over the coal sample when gases within the reactor expand during flash

heating. A check valve isolates this surge volume in the event of reactor rupture.

Tubing and valves downstream of the reactor are kept at about 150°C by heating tapes to minimize condensation or adsorption of heavier hydrocarbons. Analysis of products is either by an on-line mass spectrometer/computer or by gas chromatography. Since the former provides a more rapid analysis of products, most of the runs are performed with this system. In using the quadrupole mass spectrometer, two consecutive lines diverge from the main flow line through which the gases are exhausted to the atmosphere. The first one is evacuated by a pump and the flow is adjusted to 45 sccm. The second one, which goes to the mass spectrometer, diverges from the first branch and its flow is adjusted so that the pressure inside the ion source of mass spectrometer is 10^{-6} to 10^{-7} torr range. Selected mass numbers are monitored by the mass spectrometer at 10 millisecond intervals. Integrals over time of the response at each mass number are used to obtain yields by calibrating these responses with known amounts of pure substances.

Product species were identified on both the gas chromatograph and on the mass spectrometer. In the case of the gas chromatograph, a Poropak-Q and molecular sieve (5 Å) columns were used and products were identified with pure compounds on the basis of elution time. In the mass spectrometer, identification of products was by mass with confirmation by injection of pure compounds.

For quantitation, the integral response over time for mass j (Aj) is calculated by the summation

$$Aj = \Sigma_i \frac{I_{ji} - I_{ja}}{I_{si} - I_{bi}}$$

where I_{ji} = ith measured response at mass j

I_{ja} = average response for mass j calculated for the first ten seconds

I_{si} = ith measured response for the internal standard

I_{bi} = ith measured response at a blank channel.

The quantity I_{ja} establishes background at mass j and the summation is carried over only those points for which $I_{ji} - I_{ja}$ is larger than the standard deviation for the points used in calculating I_{ja}. The internal standard is a gas (argon or neon) premixed with the feed gas. Normalization on response to this standard compensates for variations in instrument sensitivity. A nearby mass, at which there is no response, establishes instrument baseline.

Quantitation is obtained by determining the integral response to known amounts of pure substances which are injected into the flowing gas. For gases, this is accomplished using a double sample loop. Liquids are injected into the line through a septum. After hydrogenation, the residual char is oxidized in place by oxygen at 5atm, and the combustion products are analyzed by similar methods. Carbon dioxide yield gives the char carbon content. The results allow a carbon balance to be constructed.

When gas chromatography is used to analyze the products, a thermal-conductivity cell operating on a bleed stream signals the arrival of products at the bleed point. At this moment the gas flow is

switched from exhaust to a previously evacuated sample tank and the tank is filled to a predetermined pressure. After allowance for mixing in the sample tank, a sample is withdrawn and analyzed by gas chromatography. Paropak-Q column and a flame ionization detector are used for all hydrocarbon analysis. After the hydrogenation, oxidation is carried out and the products are collected in a second sample cylinder. A thermal conductivity detector is used to analyze the carbon oxides. A carbon balance can then be constructed as before.

Figure 3.3 shows the electrical system of the flash hydrogenation reactor. The reactor heat is provided by two sets of transformers. The stepdown transformers and the two variable transformers supply the heat for the initial rapid heat-up period and for the isothermal stage, respectively. A timer and a temperature control serve as the two control devices which switch the electrical power from primary (rapid heating) to secondary (isothermal) stage, whenever the time or the temperature reaches its present value. The safety functions of the pressure switch, solenoid valve and relays have beem discussed earlier in this section.

This reactor system is designed for independent control of all the important process variables. It is, at present, the only bench scale reactor in which a vapor residence time is provided and can be independently controlled. Pressure, temperature and solid contact time are either predetermined or controlled during the runs. Heating rate can be adjusted either by changing the distance between the two electrodes or by changing the transformer. The left hand electrode is movable and a factor of 3 in the heating rate can be achieved. Therefore, a study of the most important processing variables over a

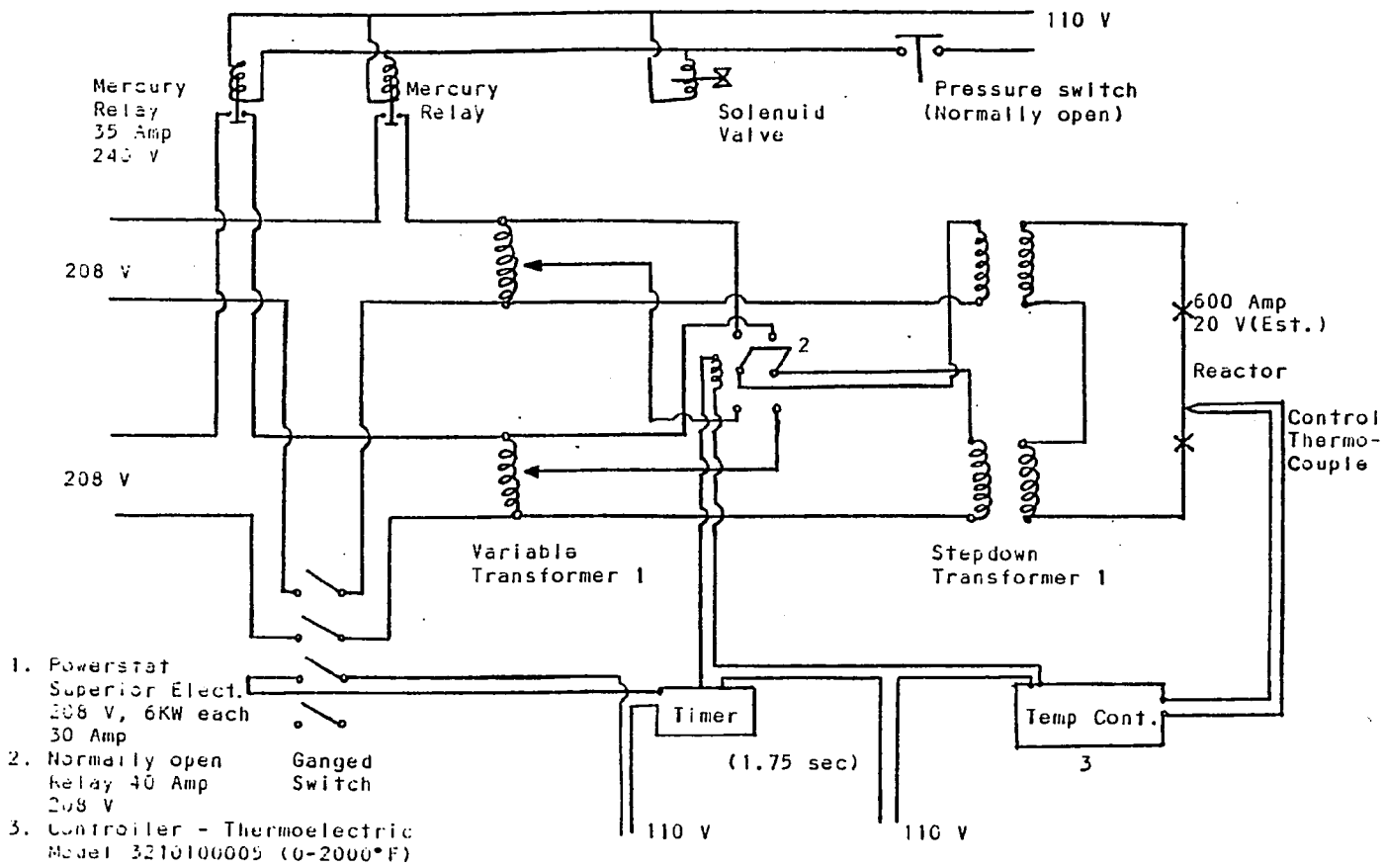


Figure 3.3. FLASH HYDROGENATION REACTOR ELECTRICAL SYSTEM

wide range of conditions can be carried out. This can be of great value not only in process development but may also improve our fundamental understanding of coal.

Eleven coals were used through this study. A suite of eight coals broadly representive of the U.S. spectrum were selected and prepared by Pennsylvania State University. These samples were used in the comparative study in Chapter 4.1 and their properties are shown in Table 4.1.1 and 4.1.2. Pittsburgh No. 8 coal was provided by Consolidated Coal Company and their proximate and ultimate is listed in Table 4.2.1. This coal was used for the comparative study of two bituminous coals in Chapter 4.2, and the hydrogenation study with hydrides in Chapter 4.5.1. Texas lignite was used for the study of drying effect in Chapter 4.6.1 and its analysis is shown in Table 4.6.1. Both Texas and Pittsburgh No. 8 coals were ground to -200 mesh in nitrogen and separated into vials with 2 g of coal in each. The vials were kept in a humidified, nitrogen pressurized (about 5 psig) desiccator sealed with paraffins. Most of the experiments were, however, carried out with the two samples of Illinois No. 6 coal. Both mined and collected on the same day. The first sample was crushed and air-ground to -325 mesh on the same day following collection, separated into small vials flushed with N_2 and sealed with paraffin. Its analysis is listed in Table 4.2.1 and was used for the comparative study (Chapter 4.2) hydrogenation with additives (4.5), secondary reactions of volatiles in the vapor zone (4.7) and char composition study (4.9). The second sample was kept as a large chunk. A two inch lump was broken off three years later and air ground and stored in the same manner as the first sample. Analysis of this sample was used for the two-stage hydrogenation (Chapter 4.3), and effect of pressure and gas composition (4.4).

4. Results and Discussion

4.1 Comparative Study of U.S. Coals

4.1.1 Experimental Conditions

This study was carried out on a suite of coals representative of the U.S. spectrum and from different ranks.

Eight coals were selected from the Pennsylvania State University collection and were subjected to flash hydrogenation in 100 atm of pure hydrogen, at 10 s solids contact time and 0.6 s gas phase residence time. Measurements were restricted to the temperature range of 750 to 850°C, where maximum yields of ethane and BTX are found. In all runs the temperature was reached at a heating rate of 650°C/s.

A summary of the properties of the coals is presented in Table 4.1.1 and the petrographic compositions in Table 4.1.2.

4.1.2. Results

The total carbon conversion to carbon contained in the volatiles evolved from the coal, is presented as a function of the rank in Figures 4.1. The overall trend observed is a decrease in the conversion to volatiles as rank increases. The trend, however, is affected by considerable scattering of the results and yields a low correlation coefficient. As a consequence, rank alone cannot be considered adequate to correlate differences in total yields given by different coals.

The conversion of coal to methane shows a clear negative correlation with carbon content as shown in Figure 4.1.2. Low rank

Table 4.1.1. Properties of Coals Used in the Comparative Study of Flash Hydrogenation (Penn. State Univ.)

Sample No.	Rank	Province	Age	State	Moist.	M.M. direct	C dmmf	O dmmf	S Dry	S Daf	H dmmf	N dmmf
PSOC 326	HVA	Eastern	Carb.	PA	2.21	21.18	84.49	5.56	4.36	5.28	5.86	1.54
PSOC 270	HVA	Eastern	Carb.	AL	1.27	17.72	85.15	4.85	2.34	2.77	5.54	1.79
PSOC 284	HVA	Interior	Carb.	IL	3.11	25.08	83.71	7.12	5.23	6.70	5.80	1.86
PSOC 314	HVA	Rocy M.	Cret.	UT	4.08	11.55	81.47	10.13	0.76	0.84	6.07	1.66
PSOC 280	HVC	Interior	Carb.	IN	11.32	18.31	81.58	9.51	3.78	4.50	5.73	1.92
PSOC 248	S. Bit. A	Rock M.	Cret.	WY	19.17	3.34	75.44	17.04	0.64	0.66	5.15	1.74
PSOC 240 B2	S. Bit. B	Pacific	Tert.	WA	19.73	16.47	73.96	18.98	0.50	0.60	5.05	1.41
PSOC 246	Lignite	North Gr. Plains	Tert.	ND	34.12	10.99	71.85	21.22	0.65	0.72	4.84	1.57

Table 4.1.2 Petrographic composition of the coals from the Pennsylvania State University collection used in this study. Note that compositions have been adjusted to a dry, mineral free basis.

PSOC Coal No.	Vitrinite	Pseudo-Vitrinite	Fusinite	Semi-Fusinite	Massive Micrinite	Granular Micrinite	Exinite	Resinite
326	69.4	7.6	3.2	7.3	2.0	6.0	4.4	0.1
270	68.1	3.2	8.6	4.6	0.6	9.0	5.0	0.9
284	78.9	8.2	3.8	1.6	0.3	4.4	2.7	0.1
314	73.3	8.8	4.5	4.7	2.1	0.7	5.2	0.6
280	92.1	0.0	1.2	1.1	0.0	2.7	2.1	0.7
248	68.2	8.1	0.7	11.8	0.0	9.5	1.2	0.4
240 B2	67.2	12.7	3.0	4.0	2.5	4.1	3.5	2.7
246	53.3	25.3	7.8	3.8	0.7	4.9	3.6	0.4

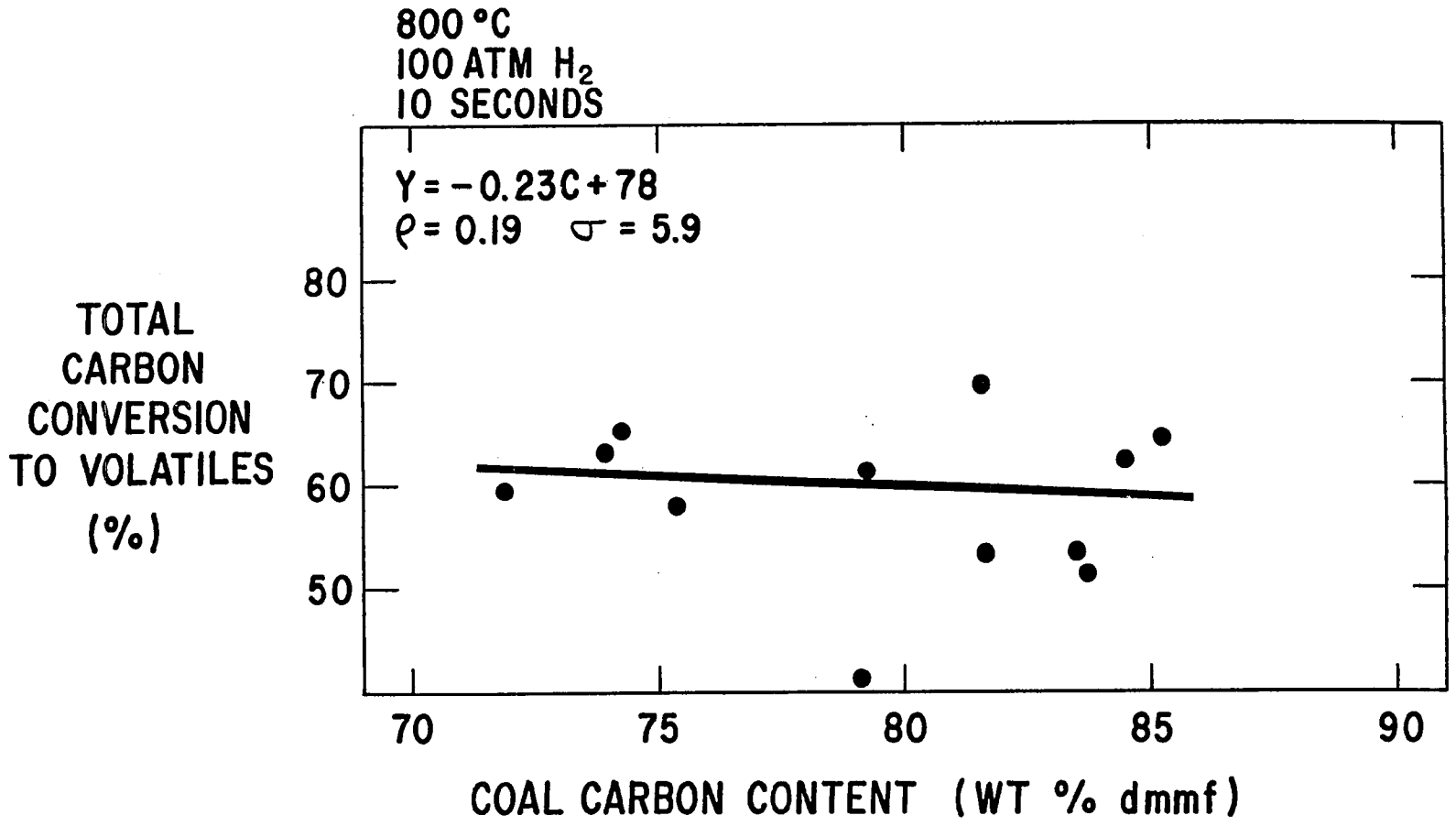


Figure 4.1.1. Total conversion to volatiles as a function of the coal rank.

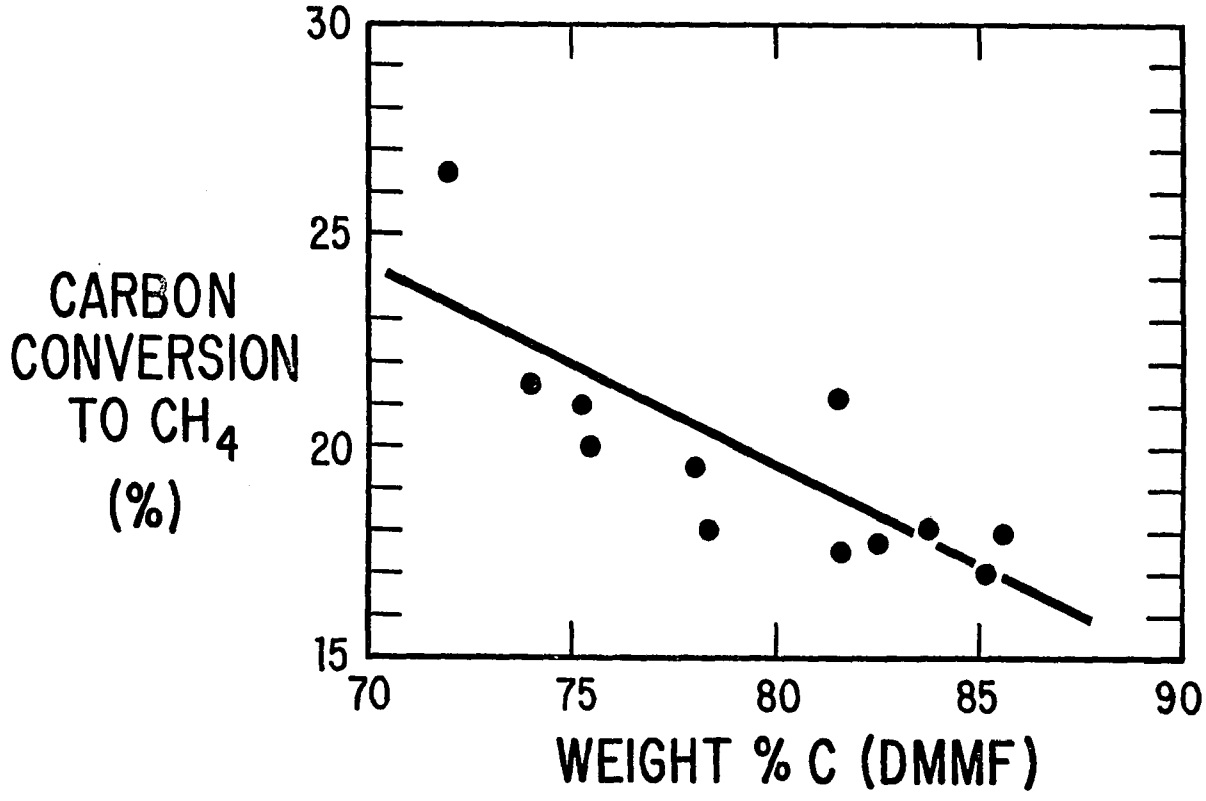


Figure 4.1.2. The Conversion of Carbon to Methane as a Function of Coal Rank.

coals give the highest yields of methane, but the conversion decreases rapidly with increasing rank.

The yields of ethane as a function of temperature are found, with all coals, to have a similar behavior to that reported by Dobner, et al. (1976) in the case of Illinois No. 6 coal. Ethane yields vs. temperature curves are bell-shaped, with a maximum whose position and amplitude depends upon the coal. Peak ethane yields range from 6.4 to 9 % carbon conversion, while the temperature of the maximum varies from 760 to 795°C. In Figure 4.1.2, a trend of decreasing peak yields and increasing peak temperatures with increasing rank is evident, though modest.

Oxygen, appearing as carbon oxides, is very nearly a uniform 70% of the coal oxygen content, as shown in Figure 4.1.4. In the low rank coals, 25% of the oxygen appears as CO_2, but this rapidly drops to zero for HVA coals. As a result of the relation between oxygen and carbon in coals of different ranks, there is a uniform decrease in carbon conversion to CO_x from about 13% in lignite to a few percent for HVA coals.

Liquid yields are a very important factor in the variability of carbon conversion in different coals. Both the total liquid yields and the yields of single ring aromatics (BTX) are plotted as a function of rank in Figure 4.1.5. Yields of BTX highest for coals of intermediate ranks (Subbituminous A) while decreasing towards lignites and towards higher rank coals.

However, the total liquids yield (which includes BTX and heavier liquids) increases with increasing rank and is found to be remarkably high for some coals (30 to 37%).

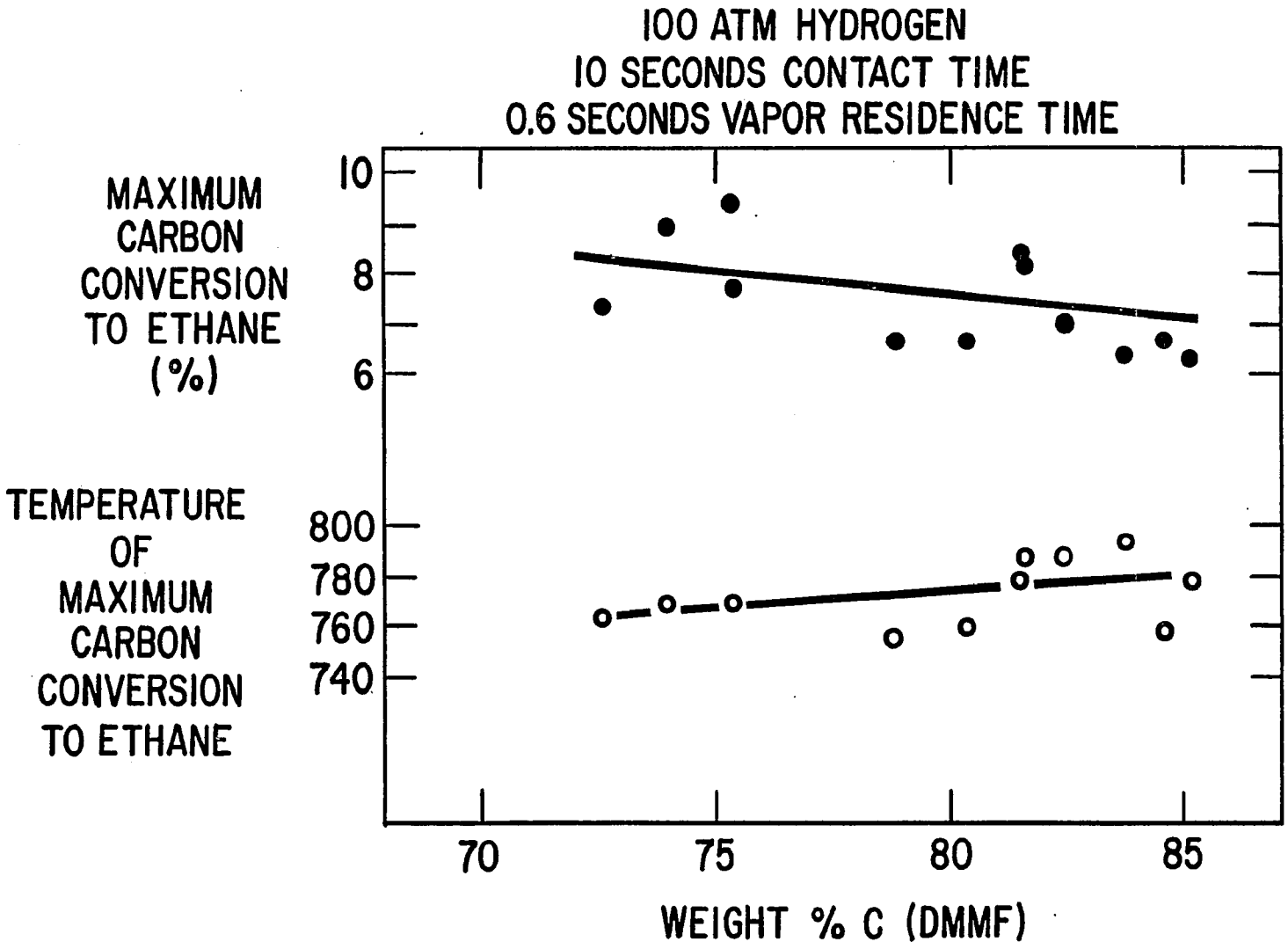


Figure 4.1.3. Maximum yields of ethane as a function of rank and temperature at which the masimum appears.

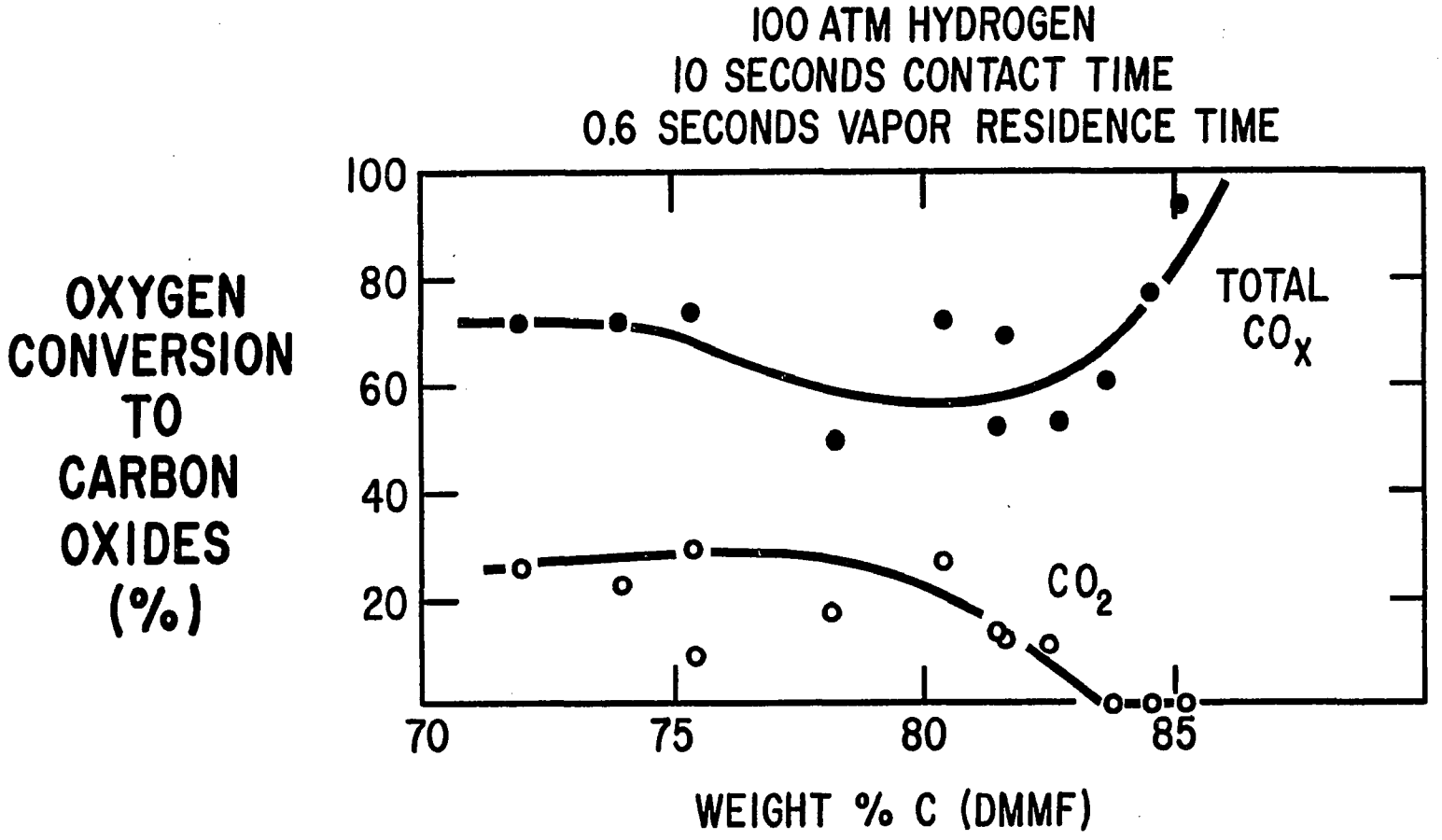


Figure 4.1.4. The conversion of total oxygen in coal to carbon oxides as a function of coal rank.

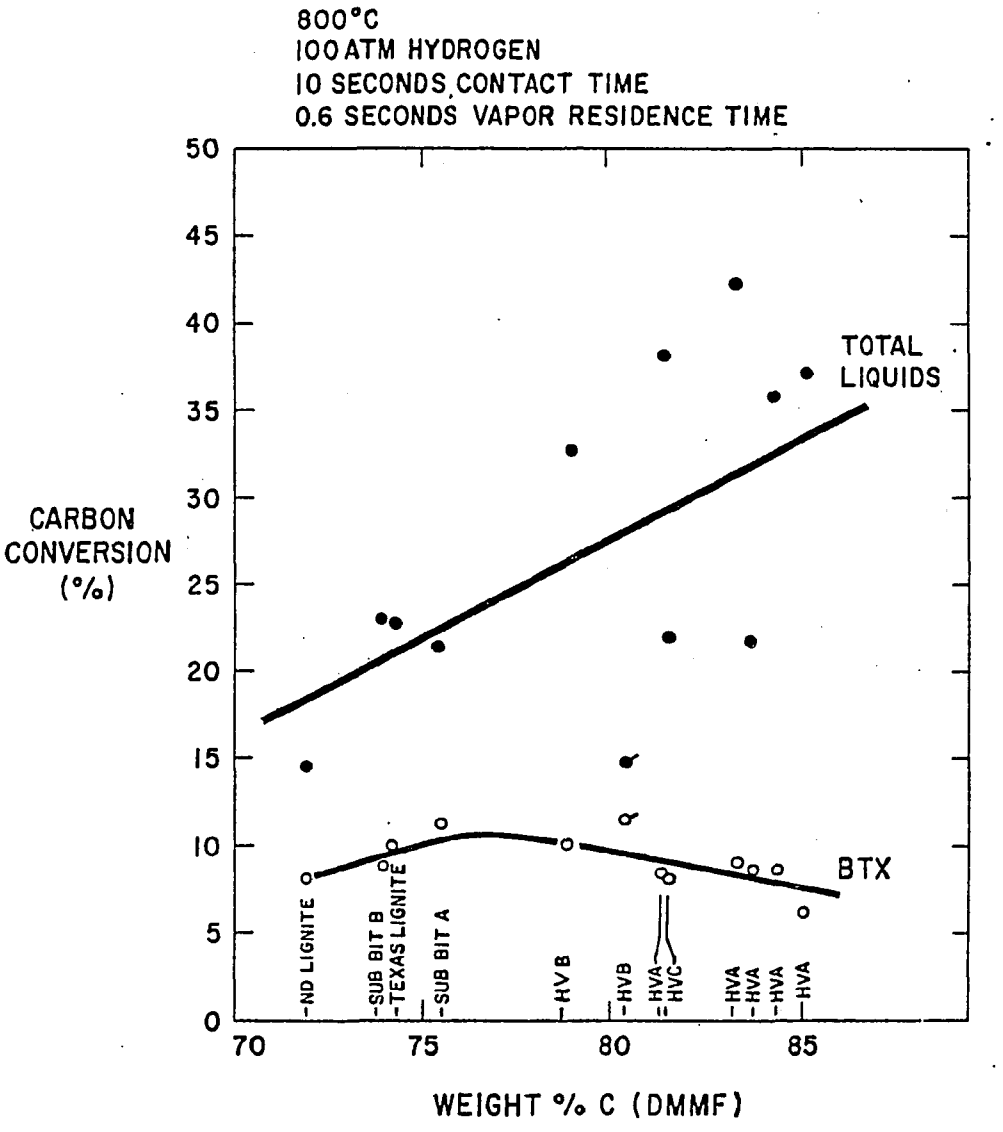


Figure 4.1.5. Conversion to total liquids and BTX as a function of the coal rank.

To summarize the results, there are general trends of variation with the rank of the coal that are followed by the products yields. The total yield of volatiles decreases slightly with increasing rank. The conversion to gases (methane, ethane, and CO_x) decreased markedly with rank, while the yield of total liquids increases noticeably with the rank of the coal. Yields of BTX are largest at intermediate values of the rank, decaying towards the extremes of the range of carbon content.

4.1.3 Modeling and Discussion

a. Rank correlation. The scattering of the experimental results observed in Figures 4.1.1 to 4.1.5 indicates that the rank alone is not adequate to characterize coals in the present context. This result seems obvious considering the complex chemical and physical structure of coal, which cannot be described with a single variable. Also, it is known from liquefaction (Abdel-Baset, et al., 1978; Neavel, 1979) that coals of the same rank can show a completely different behavior under reaction conditions. However, general trends are observed, and these deserve some discussion.

According to the classical study by Hirsch (1958), the average number of aromatic rings per cluster increases with increasing rank. Since the aromaticity of the cluster would increase, this would bring a decrease in the reactivity of the coal with increasing rank, as shown to occur as indicated by the trend in Figure 4.1.1. The smaller proportion of hydrogen with increasing rank gives also a smaller fraction of aliphatic groups in the average cluster. This will give us the result of decreasing in the light paraffin production in the coal with decreasing rank. Experiments follow this predicted trend, as shown in Figures 4.1.2 and 4.1.3.

In Figure 4.1.4, the CO_2 produced corresponds to 20% of the oxygen in the coals of low rank, and that is approximately the fraction of oxygen in carboxylic acid groups in such coals. At higher ranks, carboxylic acid groups in coals decrease and disappear (Tingey and Morrey, 1973). Also, from Figure 4.1.4, the yields of CO_2 approach zero at higher rank. Both observations suggest that CO_2 is produced from the carboxylic acid groups present in the coal.

It is interesting to notice that the total liquid yield increases with increasing rank, an increasing evolution of heavier species with increasing coal aromaticity. It is possible to expect that molecules of the coal "tar" would increase in aromaticity and average molecular weight with increasing rank and consequently show less reactivity towards thermal hydrocracking. Since the thermal hydrocracking of the tar molecule is believed to be the rate determining step in the formation of BTX (Section 4.3), this would explain the decay of BTX yields in the higher rank coals.

The high total liquids yields from flash hydrogenation, however, indicate a large potential for the production of synthetic liquid fuels, given an adequate treatment to the liquids produced.

b. Maceral correlations. Correlation of yield with maceral content is an alternative to the above approach. Petrography is a key to the origin, geologic history and chemical structure of coal.

It is simplest to assume a linear relation between yield and maceral content (Table 4.1.3). Such a relation is here applied to yield data from various coals but at fixed reaction conditions. The correlation is based on certain assumptions which are bound to be incorrect:

Table 4.1.3. Equation for Maceral Correlation

$$Y = \sum_{i=1}^{n} R_i C_i$$

Y = Yield (% of total coal carbon converted to product)

R_i = Reactivity of *ith* maceral

C_i = Carbon content of *ith* maceral (% of total coal carbon)

$$0 \leq R_i \leq 1$$

First: The reactivity R_i is assumed to be constant for coals of different origin and history. In fact quite the opposite has been demonstrated in studies 40 years ago with isolated coal constituents (Fisher, et al., 1939).

Secondly: The macerals are assumed to behave independently. That is, the presence of one maceral does not affect the yields from another and the vapor species from different macerals do not interact in the pores of the coal or in the vapor residence zone. R_i will then lie between zero and one. However, this cannot be expected to be rigorously correct and finding values of R_i greater than 1 would suggest an interaction effect.

In spite of these deficiencies, the small size of the data base does not permit a more elaborate model to be used.

A further difficulty is that maceral content is available as weight % of dmmf coal, X_i (Table 4.1.4). This can be converted to C_i, the carbon content of the ith maceral by multiplying by f_i, the weight fraction of carbon based only on material within that maceral, and dividing by f - the weight fraction carbon for the whole coal. This ratio (f_i) is incorporated into a new reactivity factor (r_i) based on weight % maceral content. Since f_i/f can be greater than 1, r_i can be greater than 1. But not by much; 1.3 is probably a generous upper limit for carbon-rich macerals.

A multilinear regression with six variables is shown in Figure 4.1.6. Since we have eight data points, the number of petrographic parameters was reduced from eight to six by assuming that the two forms of micrinite are inert. This allows two degrees of freedom. The resulting equation fits the data very well. E is exinite, R is

Table 4.1.4. Modified Maceral Correlation

$$Y = \sum_{i=1}^{n} - R_i C_i$$

$$C_i = \frac{f_i}{f} X_i$$

X_i = Coal maceral content (wt%, dmmf)

f = Coal carbon (dmmf)

f_i = Maceral carbon (dmmf)

$$Y = \sum_{i=1}^{n} r_i X_i$$

$$r_i = \frac{f_i}{f} R_i$$

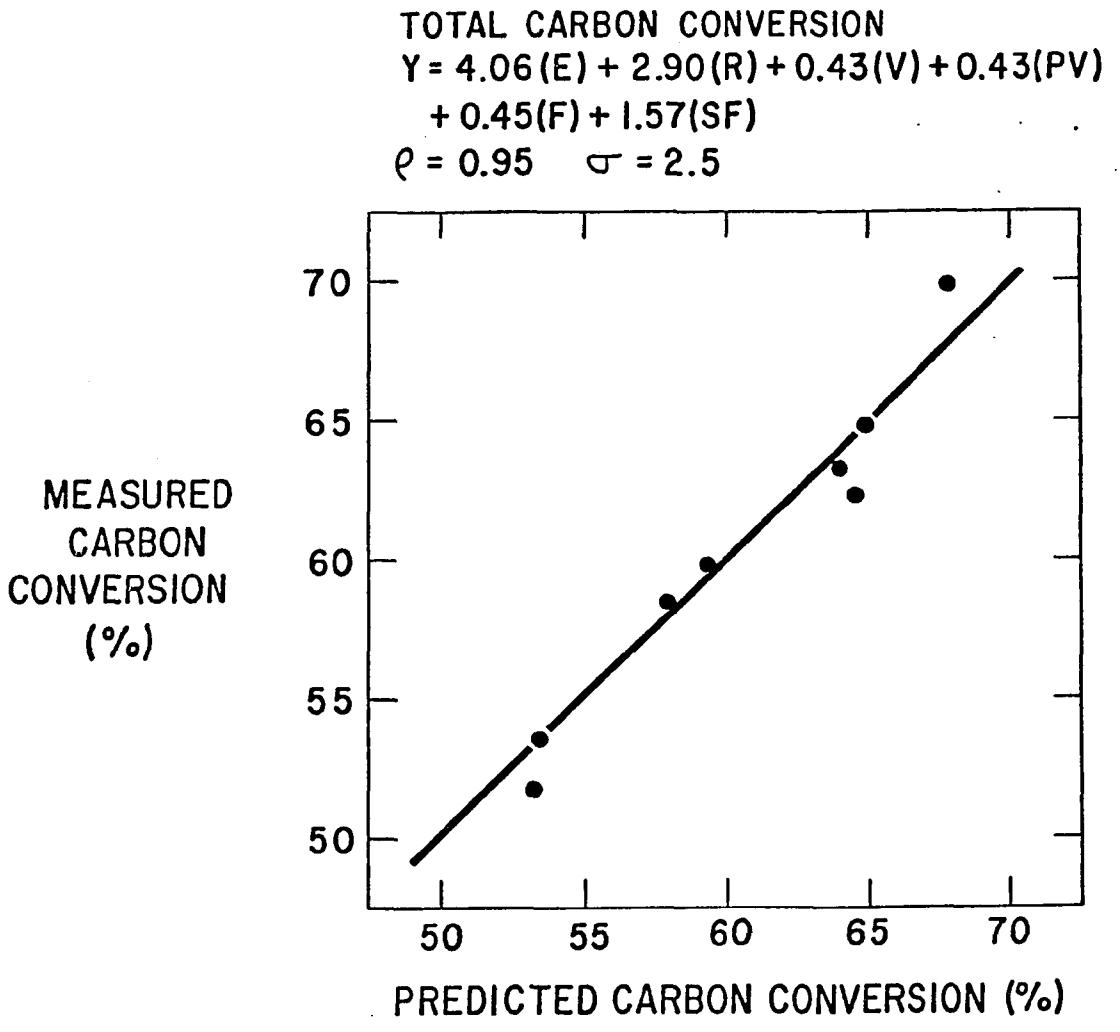


Figure 4.1.6. Comparison of the Total Carbon Conversion with the Predicted Value from Petrographic Composition.

resinite, V is vitrinite, PV is pseudo-vitrinite, F is fusnite and SF is semi-fusinite. The horizontal axis is the predicted yield and the vertical axis is the experimental value. The correlation coefficient is close to 1 and the standard deviation is small.

It is worth noting that the standard deviation is very close to the experimental standard deviation for the basic data. However, there are too many variables and some of the coefficients are much greater than 1.

Exinite, for example, has a coefficient of 4. This may be just a peculiarity of the small data set. For example, within this set exinite may be correlated with reactivity of vitrinite through its organic structure. Vitrinite is the major component in the coal and exinite is present only in small amounts. However, it is also possible that the coefficients - particularly for exinite - are significant.

In all of the correlations for total volatiles yield tested, exinite content always turns out to be the most important correlating parameter. Taken at face value, the reactivity greater than 1 suggests that exinite somehow enhances the yield obtainable from other macerals, particularly vitrinite. Since exinite is high in hydrogen and is generally aliphatic in structure, it may provide the internal hydrogen required for stabilization of light free-radical species.

The petrographic correlation was also applied to two sets of Penn State University liquefaction data (1978): one for the western and another for the interior and eastern coals. These correlations are tabulated in Table 4.1.5. For comparison, the two kinds of flash hydrogenation correlations are also included. One did not include the macrinite and micrinite in the correlations as explained above and another included them for a 8-equation, 8-variable exact solution. The results give the following ordering for maceral reactivities:

Table 4.1.5. Petrographic Correlations of CCNY's Hydrogenation Data and PSU's Liquefaction Data

	v	pv	f	sf	ma	mi	e	r	δ	ρ	Data Points	Comments
CCNY	0.43	0.43	0.45	1.57	0	0	4.06	2.90	2.47	0.95	8	ma and mi are forced to zeros
CCNY	0.39	0.52	-0.18	2.06	-4.16	-0.69	6.54	4.90	---	---	8	exact solution
PSU Western	0.67	0.82	0.28	0.83	1.42	0.59	0.92	1.82	4.89	0.49	30	
PSU (Interior and Eastern)	0.84	0.91	-0.65	1.63	-3.25	0.37	1.05	1.44	5.91	0.82	24	

v = vitrinite f = fusinite ma = macrinite e = exinite

pv = pseudovitrinite sf = semifusinite mi = micrinite r = resinite

exinite resinite semifusinite	>	vitrinite pseudo-vitrinite	>	fusinite micrinite

These results are consistent with the early report of Dryden (1963) except that semifusinite shows a higher reactivity than vitrinite. The causes of the large variations observed in fusinite, macrinite and micrinite are not clear, but may be associated with their inert nature.

c. Correlation with aliphatic hydrogen and oxygen. In order to obtain a more fundamental understanding of the relation between yield and the organic structure of different coals, we brought our samples to United Technologies Research Center (UTRC) for IR analysis. The correlation developed between yield, O content, and aliphatic H as determined by IR was not as good as other two-variable correlations we developed. However, in attempting the same correlation with other sets of yield data - vacuum pyrolysis yields from UTRC's experiments and liquefaction yields from Penn State - a parallel behavior was found which makes the relationship look more significant. A correlation of the form

$$Y = A\,[O] + B\,[H_{al}]$$

was tested for the three coal conversion processes listed in Tables 4.1.6 to 4.1.8. In the above equation, A and B are constants, O and H_{al} represent oxygen and aliphatic hydrogen contents, respectively. The Pennsylvania State University's liquefaction data were obtained after one hour in tetralin at 400°C. Tar yield was not determined and so is not listed. The coals which are listed are representative samples

Table 4.1.6. FLASH HYDROGENATION DATA (this work)

Coal	Analysis (wt % dmmf) C	O	H	H_{al}	Yields (wt % dmmf)* Total Liquids	volatiles**
PSOC 326	84.49	5.56	6.08	3.2	37	70.2
PSOC 270	85.15	4.85	5.45	2.8	37	71.2
PSOC 284	83.71	7.12	5.93	3.1	22	61.6
PSOC 314	81.47	10.13	6.06	3.9	38	74.5
PSOC 280	81.58	9.51	5.81	2.8	22	61.7
PSOC 248	75.44	17.04	5.15	2.6	25	63.8
PSOC 240	73.96	18.98	5.15	3.0	23	69.1
PSOC 246	71.85	21.22	4.84	2.1	15	65.4
Illinois #6	77.89	13.50	6.00	3.3	33	67.6
Pittsburgh #8	82.58	6.88	5.82	3.3	26	61.8
Texas Lignite	75.21	19.31	5.93	3.3	22	71.2

*Yields at 800°C, 100 atm H_2, 10 seconds solid contact time, 0.6 seconds vapor residence time.

**Wt % dmmf volatiles yields estimated from % carbon conversion using the Parr formula and the correlation wt % daf yield = 12.0 + 0.88 (% C conversion) obtained by fitting data in D.B. Anthony and J.B. Howard, AIChE Journal, 22, 625 (1976).

Table 4.1.7. VACUUM PYROLYSIS DATA
(United Technologies Research Center)

Coal	Analysis (wt % dmmf)				Yields (wt % dmmf)	
	C	O	H	Hal	Tar	Total volatiles
PSOC 268	86.25	6.13	5.24	2.7	28	42
PSOC 124	84.81	6.35	7.17	5.7	44	65
PSOC 103	82.99	10.04	5.11	2.6	22	44
PSOC 300	80.42	12.21	5.09	2.8	25	50
PSOC 170	81.75	9.12	5.37	3.1	35	55
Bu Mi 40660	79.93	11.74	5.32	3.3	35	55
PSOC 212	76.23	16.81	4.81	2.3	20	48
PSOC 308	74.04	18.14	5.11	2.8	26	52
Montana Lignite	65.15	29.44	3.60	1.7	11	45
Upper Cliff, AL	88.3	4.7	4.7	1.8	15.1	25
Rosa, AL	84.91	8.2	4.63	2.0	14	27
Black Creek, AL	86.35	5.7	5.73	2.8	26	42
TRW #2	83.87	8.3	5.29	2.6	28	41
UTAH	78.18	13.9	5.52	3.7	28	50
Beulah, N.D.	68.60	25.8	4.39	2.0	15	44
Scranton, N.D.	67.95	25.2	4.46	1.9	10	42
Savage, Montana	67.91	26.4	4.19	1.9	12	50

TABLE 4.1.8. LIQUEFACTION DATA
(Pennsylvania State University)

Coal	Analysis (wt % dmmf) C	O	H	H_{al}	Yields (wt % dmmf)* Liquids	Total Volatiles
PSOC 268	86.27	4.64	5.42	2.7	N/A	37.6
PSOC 357	87.75	4.71	5.45	2.6	N/A	38.5
PSOC 265	86.71	4.75	5.38	3.1	N/A	43.4
PSOC 270	85.15	4.85	5.44	3.0	N/A	43.8
PSOC 267	85.26	4.60	5.56	2.7	N/A	50.7
PSOC 299	86.86	4.73	5.53	3.3	N/A	52.4
PSOC 330	83.48	8.44	5.50	3.2	N/A	53.7
PSOC 316	79.07	12.64	5.48	3.3	N/A	53.8
PSOC 331	84.57	7.43	5.61	3.0	N/A	55.9
PSOC 341	85.99	5.28	5.79	3.7	N/A	58.6
PSOC 295	84.35	6.95	5.50	3.0	N/A	59.2
PSOC 326	85.46	5.56	5.71	3.2	N/A	60.2
PSOC 310	78.65	15.26	5.65	3.6	N/A	61.1
PSOC 401	82.52	7.85	6.52	3.3	N/A	61.4
PSOC 522	78.34	14.01	5.43	3.3	N/A	62.5
PSOC 314	81.47	10.26	6.06	3.9	N/A	62.9
PSOC 306	84.40	7.97	5.74	3.6	N/A	62.9
PSOC 437	80.21	11.78	6.13	4.2	N/A	72.0
PSOC 514	78.77	15.26	5.40	3.3	N/A	73.1

* Yields, obtained in tetralin at 400°C, 1 hour contact time, was defined as the gaseous yield plus the ethyl acetate soluble yield.

selected from PSU's Group 1 and Group 3 of the Eastern and Rocky Mountain Provinces, respectively. Coals in Group 2, the interior province, are particularly high in sulfur and show particularly high volatile yields. It is believed that sulfur is catalytic, an effect which is absent in the other two groups of coals and so these are not discussed.

The vacuum pyrolysis yields at 800°C for tar and total volatiles are listed in Table 4.1.7 with several properties of the coals. The total volatile yields are higher than that determined in proximate analysis since the thin bed used in vacuum pyrolysis typically promotes much higher tar yields than does the thick bed of the proximate analysis. Variations in tar yield cause the major differences in volatile yield from one experiment to another. The experimental arrangement for this study was developed at United Technological Research Center and was discussed elsewhere (Solomon and Colket, 1978).

The hydrogenation data were collected at the City College of New York and they were the same results used for rank and petrographic correlations described in the last two sections.

The results for the three groups taken individually and for all the coals taken together are shown in Figure 4.1.7. The equations determined for each case are listed together with the correlation coefficients. The yield calculated according to the determined equations plotted against measured yield. Considering how different the three experiments are, the yield equations show remarkably little difference. Examination of the data for all the coals taken as a group shows two coals which lie significantly off the center line. One is from the CCNY group. The other is from the UTRC group. Figure 4.1.8

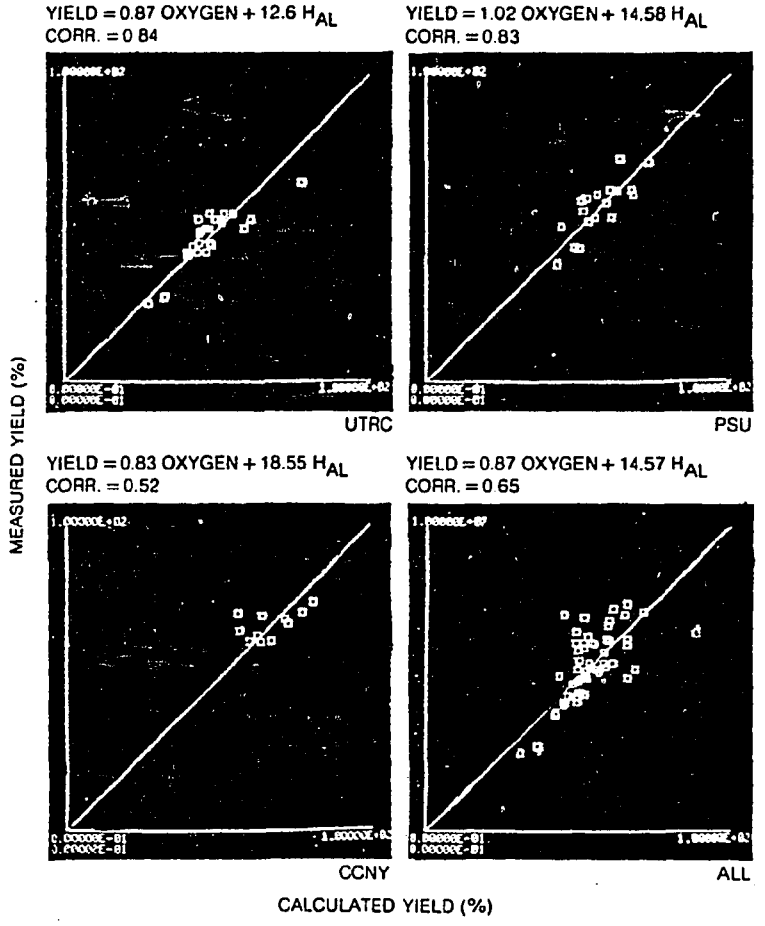


Figure 4.1.7. Correlation of Total Yields with Oxygen and Aliphatic Hydrogen Content (all data).

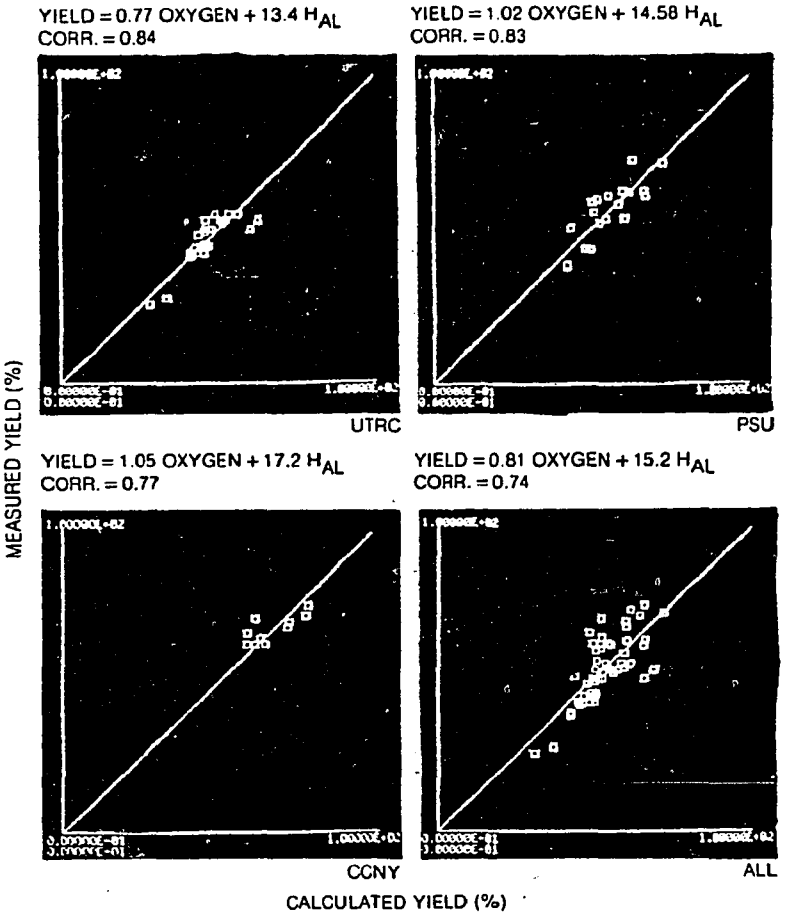


Figure 4.1.8. Correlation of Total Yields with Oxygen and Aliphatic Hydrogen Content (2 data points dropped).

shows the same analysis as in Figure 4.1.7 except for the elimination of these two coals. It is also interesting that when the coefficients

$$Y = A\ O + B\ H_{al} + C \qquad (1)$$

are evaluated, the coefficient, C, for the UTRC coals and all coals is very close to zero.

In order to understand how the total volatile yield varies with the properties of the coal, an examination was made of the factors which control the tar yield. The vacuum pyrolysis data suggest that the tar yield is a strong function of the aliphatic hydrogen content. This relationship can be understood in the following way. There is a strong resemblance between vacuum pyrolyzed tar and its parent coal. This resemblance is observed in chemical composition (Solomon and Colkedt, 1978), in the infrared spectra (Solomon, 1977; Orning and Greifer, 1956; Brown, et al., 1958) and in the NMR spectra (Solomon, 1977). It suggests that the tar consists of "monomers" released from the coal "polymer." The major difference observed between tar and parent coal is that the tar has a higher quantity of aliphatic hydrogen, especially methyl groups. This is presumably because the monomers abstract hydrogen to stabilize the free radical sites produced when the monomer was freed. Similar arguments were given for pyrolysis of model compounds by Wolfs, van Krevelen and Waterman (Wolfs, et al., 1960). Since the abstracted hydrogen is most likely to come from the aliphatic portion of the coal, it is reasonable to expect the tar yield to depend on H_{al}. In Figure 4.1.9, the tar yield in vacuum pyrolysis is plotted against H_{al} for a number of coals (circles). Also plotted are the

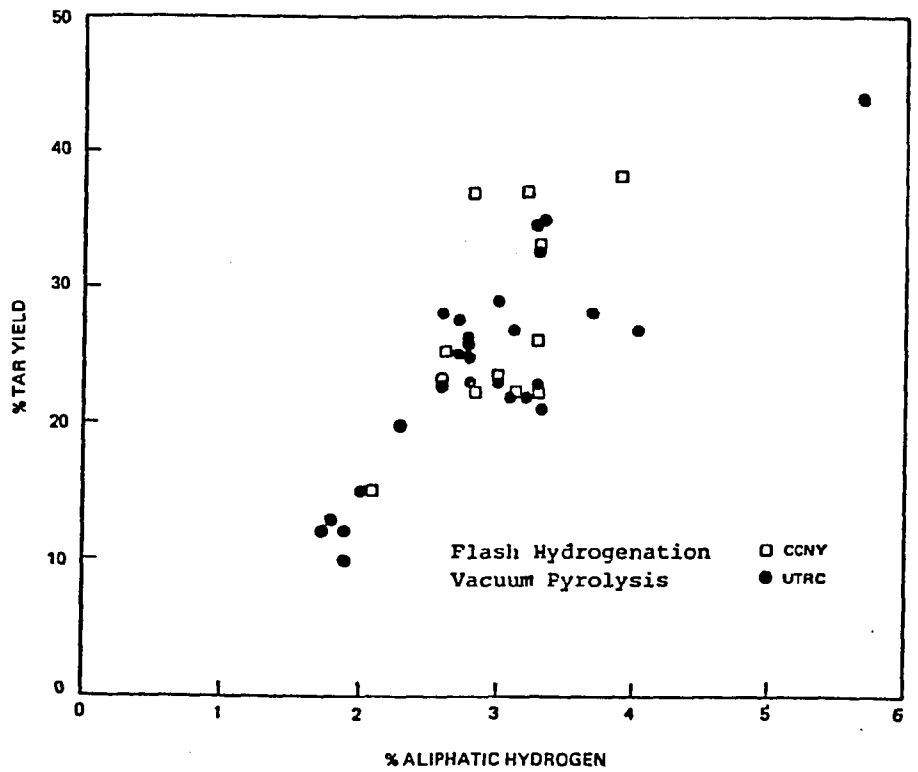


Figure 4.1.9. Correlation of Liquid Yield with Aliphatic Hydrogen Content.

yields of heavy hydrocarbons, (i.e., oils + BT) from hydropyrolysis (squares). Again the agreement is remarkable considering the variations in the experiments.

A discussion of the correlation of volatile yield with O and H_{al} is presented with reference to a pyrolysis model which has been reported in publications (Solomon and Colket, 1978). A review of the important features of the model is presented in Figure 4.1.10. The coal is represented as an area with X and Y dimensions (Figure 4.1.10). The Y dimension is divided into fractions according to the chemical composition of the coal. $Y^{\circ}(i)$ represents the initial fraction of a particular component (carboxyl, aromatic hydrogen, etc.) and $\Sigma Y^{\circ}(i) = 1$. There are two components for either since CO is typically evolved in two distinct steps. The evolution of each component into the gas (carboxyl into CO^2, aromatic hydrogen into H_2, etc.) is represented by the first order diminishing of the Y(i) dimension, $Y(i) = Y^{\circ}(i) \exp(-k_i t)$. The X dimension is divided into a potential tar forming fraction X° and a non-tar forming fraction $1 - X^{\circ}$ with the evolution of the tar being represented by the first order diminishing of the X dimension $X = X^{\circ} \exp(-k_x t)$. The kinetic rate constants and k_i and k_x are represented by Arrhenius expressions for which constants have been published previously (Maciel, et al., 1978). The same constants may be used for all coals. Some values for Y° are determined from quantitative infrared measurements (Solomon, 1979a), from ultimate analysis, and by difference. Values of X°, Y° (carboxyl) and Y° (ether loose) are fitted to the pyrolysis data. One half of the hydroxyl oxygen, O_{OH} has been included with ether-tight since it has been assumed that H_2O forms by

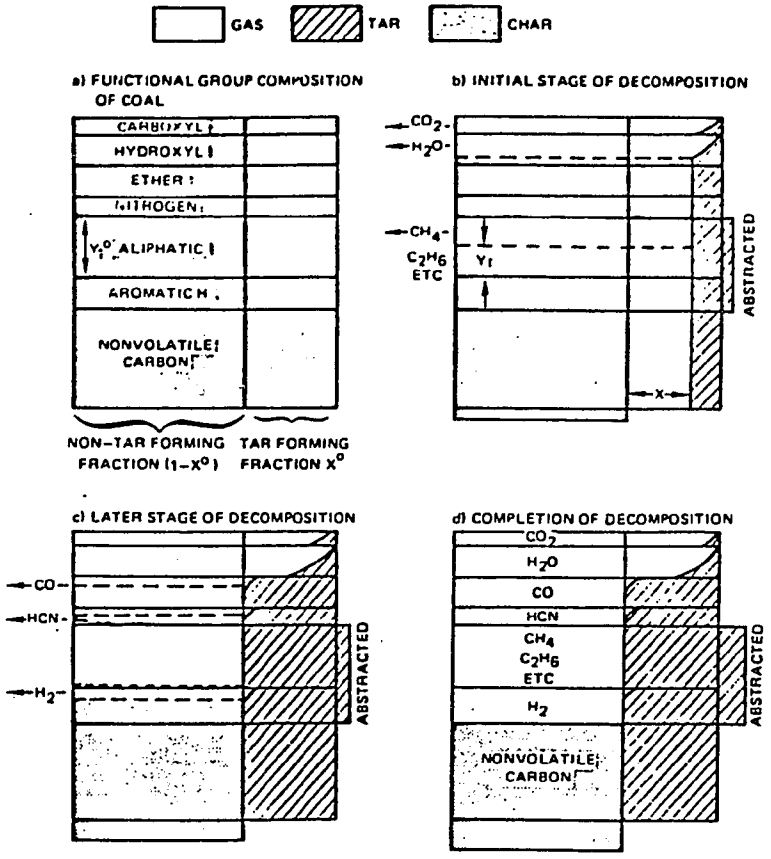


Figure 4.1.10. Progress of Thermal Decomposition According to Model a) Functional Group Composition of Coal, b) Initial State of Decomposition, c) Later Stage of Decomposition, d) Completeion of Decomposition

$$C\text{-}OH + C\text{-}OH = H_2O + C\text{-}O\text{-}C$$

The modeling of sulfur is complicated because of the presence of pyrite as well as organic sulfur and has not been included in recent versions of the model.

The three processes under consideration are vacuum pyrolysis and hydropyrolysis for short times (10-20 sec) at moderate temperature (800°C) and liquefaction for long times (1 hour) at low temperature (400°C). These cases are best represented by Figure 4.1.10. The volatilization of carboxyl, hydroxyl, ether-loose, aliphatics and tar has reached completion, while most of ether-tight, nitrogen and aromatic hydrogen remains in the char. The volatile yield is then represented by the equation

$$Y = 44/32\ O(\text{carboxyl}) + 9/16\ O(\text{hydroxyl}) + 28/16\ O(\text{ether-loose}) + 6.7\ H_{al} + 10\ H_{al}\ [C_{NVC} + 28/16\ O(\text{ether-tight}) + H_{al} + N] \quad (2)$$

In deriving the above equation it has been assumed that the stoichiometry of the aliphatics is $CH_{1.8}$ and (referring to Figure 4.1.8) that % tar = 10 $\%H_{al}$.

To evaluate the above expression, use has been made of data for 13 coals published by Solomon and Colket, 1978. The results give

$$Y = 0.77\ [O] + 14.1\ [H_{al}] \quad (3)$$

The result is in reasonable agreement with Equation 1.

It is surprising that all three processes may be represented by the same expression. It was expected that there might be some variation in the tar yield which would produce differences in the last term of Equation 2. Tar yields for vacuum pyrolysis in a thin bed are typically high. Thick beds and high pressures diminish the yield as is the case for proximate analysis. The results would indicate that the hydrogen donor potential of the tetralin in the liquefaction process and the hydrogen in the hydropyrolysis help maintain the tar yields at a high level.

d. Correlation with coal properties. Although yields of individual species during flash hydrogenation show some interesting trends with respect to coal rank and petrographic compositions, these correlations are not very useful as accurate correlations for predicting product distribution. For empirical purposes, correlations in two variables were developed using the technique of stepwise regression (Himmelblau, 1970).

The field of independent variables used to describe the properties of the coal were: a) the petrographic composition (dmmf), b) the elemental composition (dmmf), and, c) the mineral matter, volatile matter and the reactive maceral content (the sum of vitrinite, pseudo-vitrinite, exinite and resinite). These variables amounted to a total of 16.

The dependent variables of interest were: the total conversion to volatiles and the yields of the species: methane, ethane, CO_x, BTX and total liquids. In all cases the dependent variables were obtained from experiments performed at 800°C, 10 seconds contact time, 0.6 seconds

vapor phase residence time. Yields were expressed as percentage of the initial carbon present in the component considered.

The stepwise regression was carried out with all the dependent variables as a function of independent variables, assuming linear models. In all cases, two variables were necessary to yield correlations whose standard deviation was of the order of magnitude expected from the accuracy of the experimental data. The resulting relations, from all possible variable pairs, were compared according to their correlation coefficient (ρ) and standard deviation (σ) and the best fit chosen. The parameters obtained in the correlations are valid to predict yields under the reaction conditions employed in these experiments. The parameters are expected to change with the reaction conditions.

The best correlation for the total conversion of coal to volatiles was obtained with exinite content and mineral matter as independent variables. It shows a correlation coefficient close to one, and a standard deviation close to the standard deviation of the experimental data (see Figure 4.1.11). The content of mineral matter appears in the correlation with a negative coefficient, indicating that increased mineral matter will decrease the yield of total volatiles in flash hydrogenation. Although for the short residence times and high temperatures used in flash hydrogenation experiments, the catalytic effect of the mineral matter should be minimal (in contrast with the results obtained in coal liquefaction, at low temperatures and longer residence times), the presence of a negative effect is quite unexpected. Again, the strong correlation of the total yield of volatiles with the content of exinite in the coal indicates that this is the most important

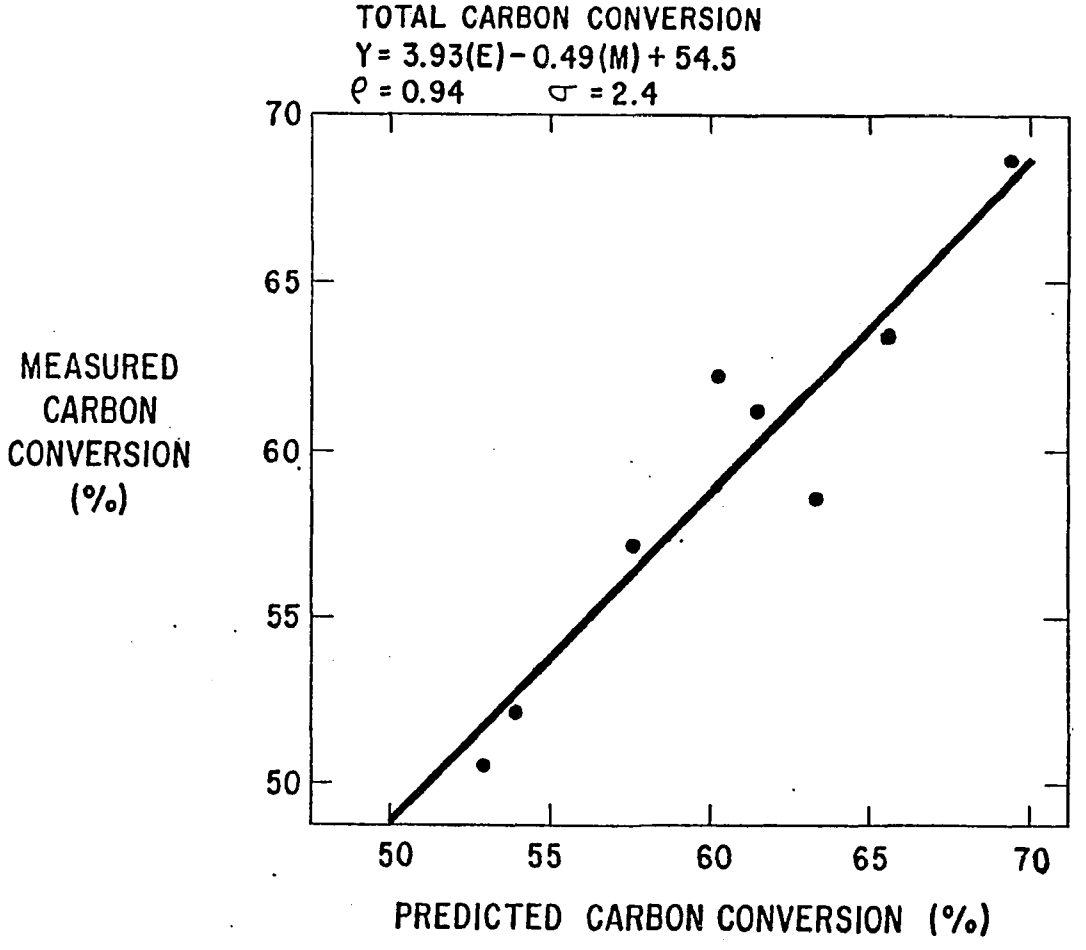


Figure 4.1.11. Comparison of Total Carbon Conversion with the Predicted Value from Coal Properties.

variable in the correlation. The possible explanation was given in the last section.

The technique of stepwise regression was also applied to the correlation of the individual species with coal properties. The correlations for the yields of methane, ethane, BTX, carbon oxides and heavy liquids are presented in Figures 4.1.12 to 4.1.16.

The best correlation for methane yields are with pseudo-vitrinite and sulfur. Sulfur, in the correlation, appears with a negative coefficient. This fact contrasts with the results from coal liquefaction (Abdel-Baset, et al., 1978) where a positive effect of sulfur content is observed.

Ethane yields correlate with vitrinite and sulfur content. Again, sulfur appears with a negative coefficient in the correlation.

BTX yields correlate with vitrinite and fusinite content. The coefficients for both macerals are negative.

The yields of carbon oxides correlate with oxygen and hydrogen content. In this case, the observed positive correlation with oxygen is to be expected, since in flash hydrogenation the only source of oxygen is what is contained in the coal. Hydrogen content appears to decrease the yields of carbon oxides.

The yields of liquids heavier then BTX correlated with exinite and pseudo-vitrinite. Again, exinite appears with a coefficient larger than one, indicating that it promotes the production of liquids.

A summary of the correlations obtained here is shown in Table 4.1.9. All correlation coefficients are about 0.9 or better, and the standard deviations are all quite low. The largest ones, σ = 2.4% for heavy liquids and 2.4% for total volatiles, are about the same as the

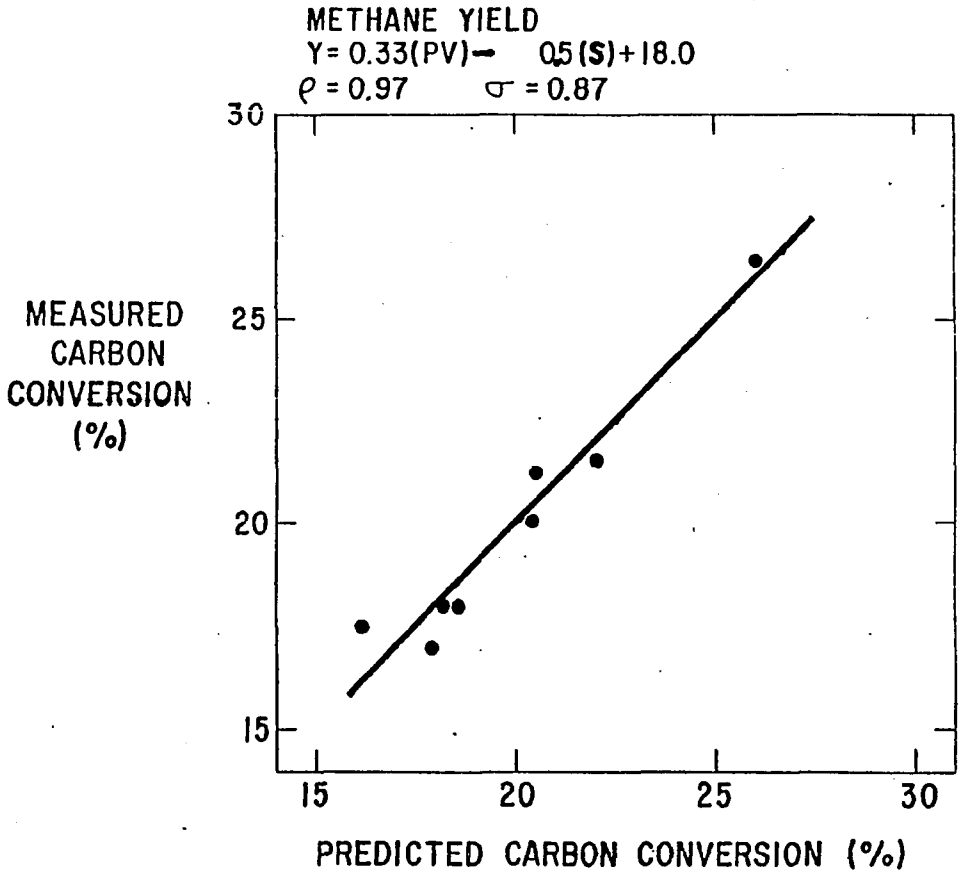


Figure 4.1.12. Comparison of Carbon Conversion to Methane with the Predicted Value from Coal Properties.

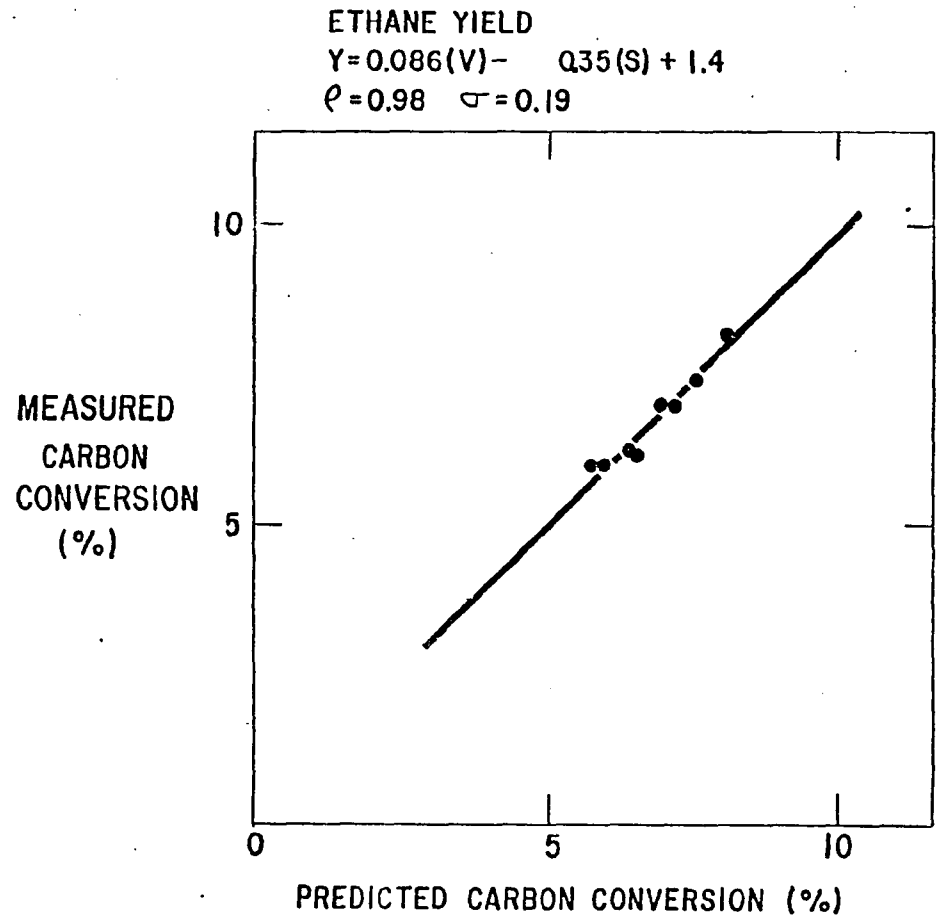


Figure 4.1.13. Comparison of Carbon Conversion to Ethane with the Predicted Value from Coal Properties.

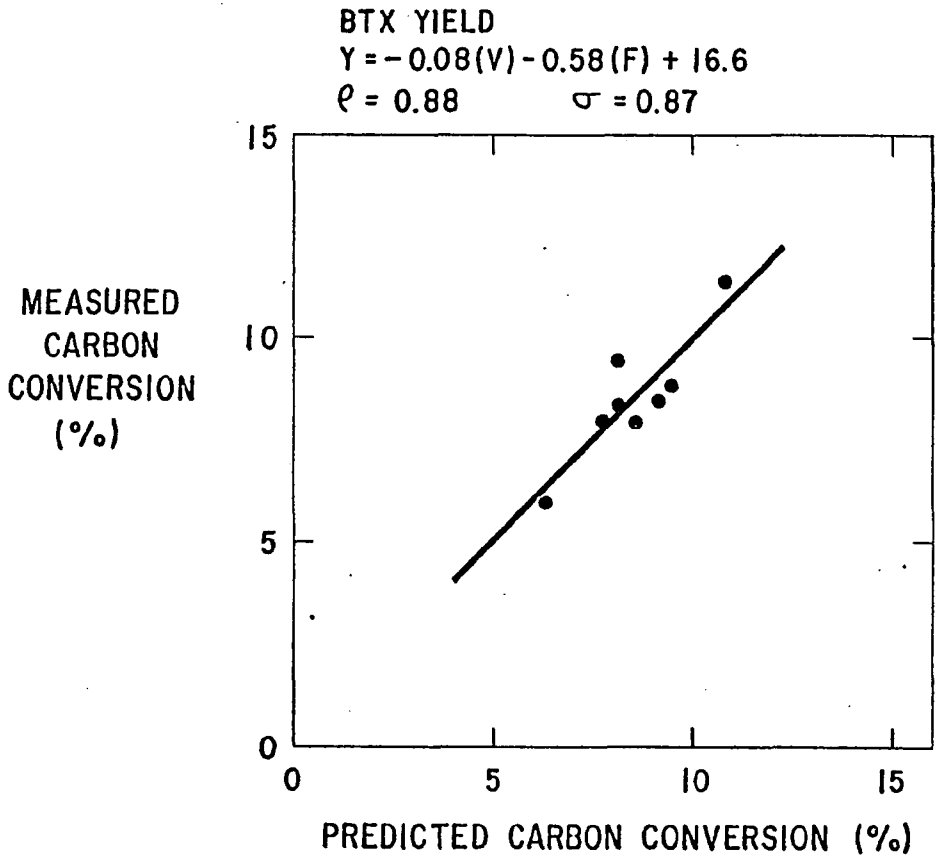


Figure 4.1.14. Comparison of Carbon Conversion to BTX with the Predicted Value from Coal Properties.

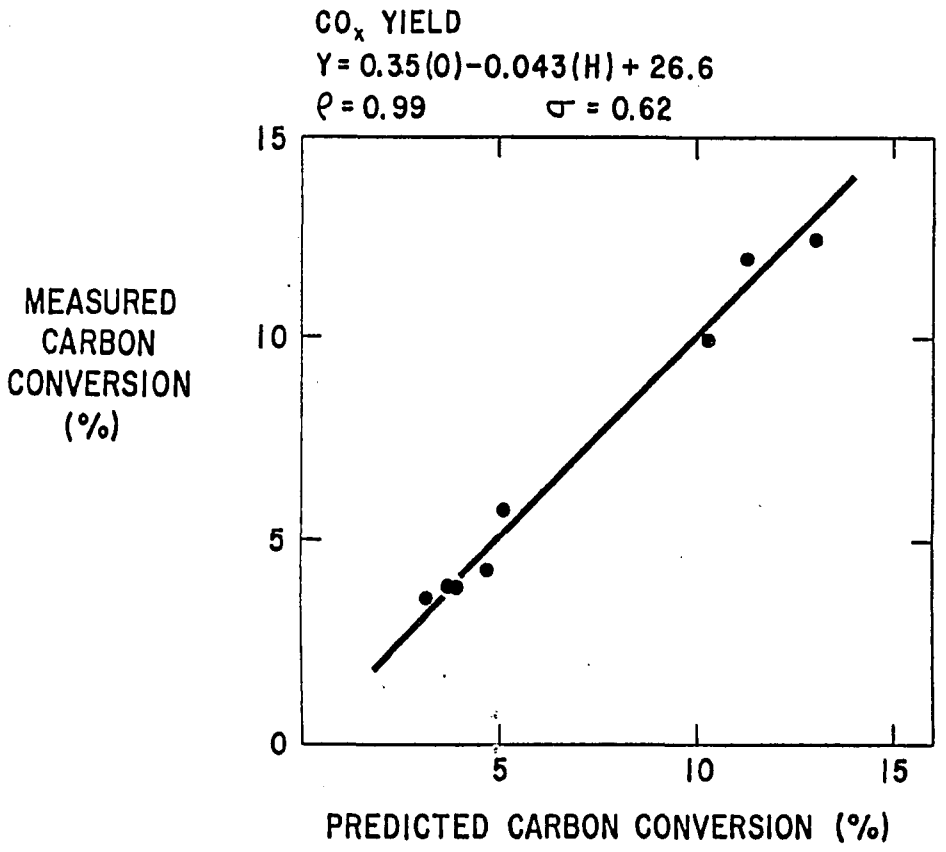


Figure 4.1.15. Comparison of the Carbon Conversion to CO_x with Predicted Value from Coal Properties.

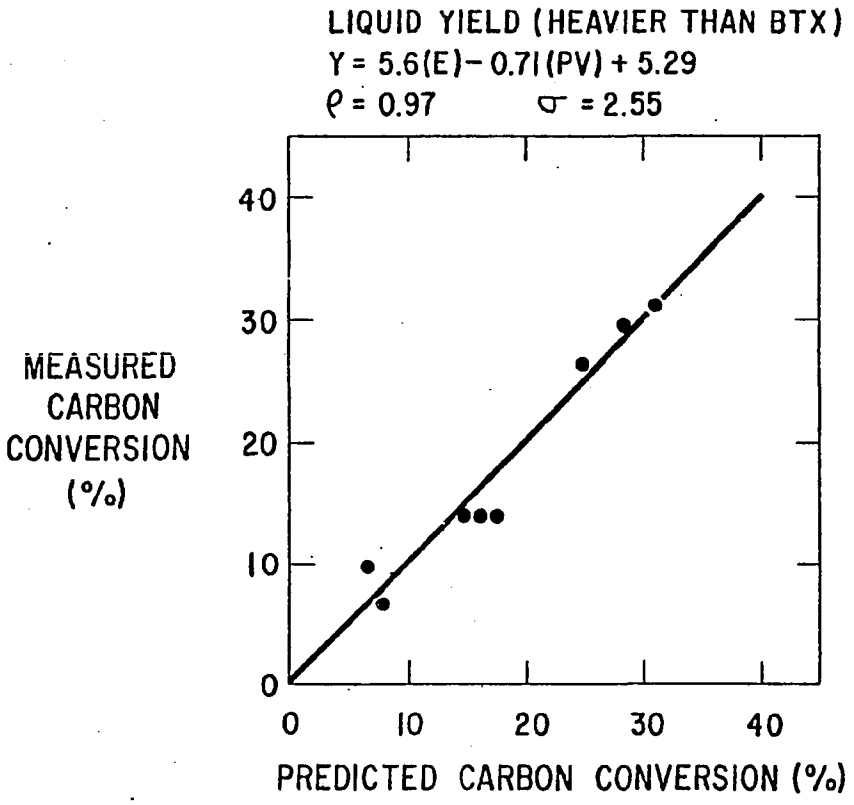


Figure 4.1.16. Comparison of the Carbon Conversion to Liquid with Predicted Value from Coal Properties.

Table 4.1.9. Summary of Correlations of Yields with Coal Properties

Fixed reaction conditions: 800°C, 100 atm H_2, 10 s solid contact time, 0.6 s gas residence time.

TOTAL VOLATILES = 54.54 + 3.93 (EXINITE) - 0.49 (MINERAL MATTER)

$\rho = 0.94$ $\sigma = 2.4$ %

METHANE = 17.97 - 0.5 (SULPHUR) + 0.33 (PSEUDOVITRINITE)

$\rho = 0.97$ $\sigma = 0.87$ %

TOTAL LIQUIDS = 2.35 (CARBON) - 4.2 (SULPHUR)

$\rho = 0.96$ $\sigma = 2.92$ %

CARBON OXIDES = 26.63 + 0.35 (OXYGEN) - 4.3 (HYDROGEN)

$\rho = 0.99$ $\sigma = 0.62$ %

BTX = 16.65 - 0.08 (VITRINITE) - 0.58 (FUSINITE)

$\rho = 0.88$ $\sigma = 0.87$ %

ETHANE = 1.44 + 0.086 (VITRINITE) - 0.35 (SULPHUR)

$\rho = 0.98$ $\sigma = 0.19$ %

LIQUIDS (TAR) = 5.29 + 5.64 (EXINITE) - 0.71 (PSEUDOVITRINITE)

$\rho = 0.97$ $\sigma = 2.4$ %

standard deviation obtained from the experimental scattering of the data for these two yields.

e. The empirical correlations and modeling. The reactions involved in coal flash hydrogenation can be visualized as occurring in two stages. In a first stage, in a solid or plastic phase coal decomposes thermally as in pyrolysis, yielding light gases and large fragments that are a part of the original coal structure. In the second stage, ocurring in the gas phase, the fragments undergo hydrogenation, and further hydrocracking to yield light gases and light aromatic species.

With this description of the sequence of the phenomena, it follows that flash hydrogenation may be modelled with the combination of a coal pyrolysis (or hydro-pyrolysis model) model, and a model of the thermal hydrocracking reactions in the vapor phase.

A model of coal pyrolysis, based on free-radical kinetics and a set of "structural parameters" for the coal, has been proposed by Gavalas and co-workers (Cheong, 1976). In this model, the structure of the coal affects the initial conditions used to start the integration of a set of nonlinear differential equations that describes the behavior of the chemical reactions involved in the model. The kinetic constants are assumed to be "universal," or to depend very little on other coal properties.

A more simplified model of coal pyrolysis was proposed by Solomon and Colket (1978). This model is based upon first order kinetics. It also contains a set of "structural parameters" as the coal, which are visualized as the initial content of chemical functional groups. These groups can be measured by different analytical techniques. Solomon's

structural parameters are used as initial conditions in the integration of the differential equations of his kinetic model, which also contains "universal" kinetic constants.

In both cases of the models described above, coal properties enter in the "structural parameters" of the coal, which are the initial conditions of the model differential equations. In both cases, it is possible to assume a linear relationship between the specified structural parameters and the properties of the coal, as measured by more conventional techniques.

With respect to the reactions in the gas phase, the simultaneous thermal decomposition and hydrogenation of hydrocarbons has been modeled using free-radical kinetics (LaCava and Trimm, 1978) and also using more simplified semi-empirical approaches (LaCava, 1977). The simplified approach, in the case of constant hydrogen pressure, leads to a system of first order reactions.

It is possible to build a flash hydrogenation model with a simplified pyrolysis model, such as the one proposed by Solomon and Colket, and a simplified gas phase reaction model. In this case, both chemical processes are modeled with first order chemical reactions and with "universal" kinetic constants. Thus, the model of coal flash hydrogenation will contain the properties of the coal in the initial conditions of the set of differential equations that represents the behavior of the coal.

It follows, using the general theory of first order kinetic networks (Wei and Prater, 1962) that under fixed reaction conditions the yield of each one of the individual species is a linear combination of the initial conditions, or more precisely, is a linear combination of

the coal properties. This important conclusion gives a theoretical basis to the empirical correlations given above.

A complete model, integrating coal properties and process conditions in flash hydrogenation, is very desirable. This model would be very useful in predicting yields for various coals and different operation conditions, knowing only the properties of the coals. .

4.1.4 Conclusion

A study of the effect of coal properties on product distribution in flash hydrogenation of a suite of eight coals, broadly representative of the United States spectrum was performed in a bench scale reactor.

The yields of total volatiles and of individual species show trends of variation with the coal rank (measured as the carbon content of the coal). These trends, however, are affected by considerable scattering, indicating that the rank is not the most important correlating parameter, i.e., is not enough to describe the properties of the coal and its reactivity.

Semi-empirical correlations, involving two coal properties were developed using the technique of stepwise regression to identify the most important pairs of parameters that will provide the best fit. As a result, correlations of yields of the individual products with coal properties are presented, valid for fixed reaction conditions. Finally, modeling considerations offer a theoretical basis for the empirical correlations presented.

4.2 Comparitive Study of Hydrogenation Behavior of Two Bituminous Coals: Illinois No. 6 and Pittsburg No. 8 (Ireland Mine)

4.2.1 Experimental

a. Coals. Pittsburgh No. 8 (Ireland Mine) and Illinois No. 6 coals were used in this study. Both the elemental analysis and the proximate analysis of the two coals are shown in Table 4.2.1.

b. Conditions. Runs were performed at a pressure of 100 atm of hydrogen, 0.6 seconds of vapor residence time and 10 seconds solids contact time. Usually about 10 mg of coal was used in each experiment. The reaction temperature, the principal parameter studied in this work, was reached at a heating rate of 850°C/sec.

c. The liquids composition. The liquid collection and separation were carried out by S.J. Shen under the supervision of Dr. A. I. LaCava. The appropriate portion of their work is included here to provide a unified account of this collaborative effort.

Figure 4.2.1 shows the arrangement used in the collection of liquids from flash hydrogenation. The reactor is the same that was used previously but the products are taken through a heated line into a silica gel packed tube immersed in liquid niitrogen. The efficiency of trapping of products by the device is measured in every run with the aid of a mass spectrometer.

The silica gel tube, containing the collected liquids is eluted by a sequence of solvents using the equipment shown in Figure 4.2.2.

The separation of the liquids into fractions using selective solvents is a modified version of the SESC technique reported by Whitehurst, et al., (1976). From the original sequence of Farcasiu

Table 4.2.1. Proximate and Ultimate Analysis of Illinois No. 6 Pittsburgh No. 8 Coals

Proximate Analysis

	Illinois No. 6		Pittsburgh No. 8	
	As Received	Dry Basis	As Received	Dry Basis
Moisture	3.30		1.25	
Volatile	39.10	40.44	39.85	40.35
Fixed Carbon	45.25	46.79	46.30	46.89
Ash	12.35	12.77	12.60	12.76
B.T.U.	11,464	11,855	12,665	12,825
Pyritic Sulphur	0.15	0.16	2.18	2.21
Organic Sulphur	3.00	3.10	3.43	3.47
Sulphate Sulphur	0.04	0.04	0.04	0.04

Ultimate Analysis

Moisture	3.30		1.25	
Carbon	64.11	66.30	68.73	69.60
Hydrogen	4.82	4.98	4.85	4.91
Oxygen	11.11	11.49	5.73	5.80
Nitrogen	1.12	1.16	1.19	1.21
Sulphur	3.19	3.30	5.65	5.72
Ash	12.35	12.77	12.60	12.76

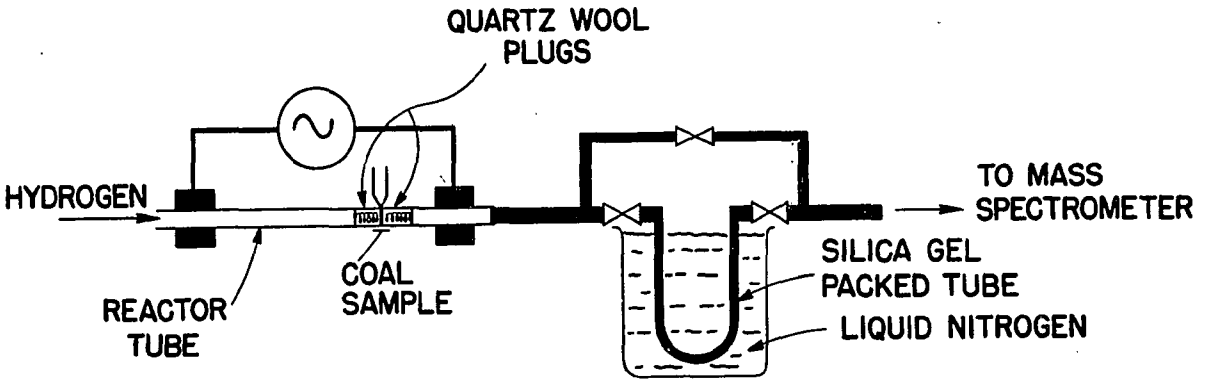


Table 4.2.1. Experimental arrangement used in the collection of liquids produced during Flash Hydrogenation.

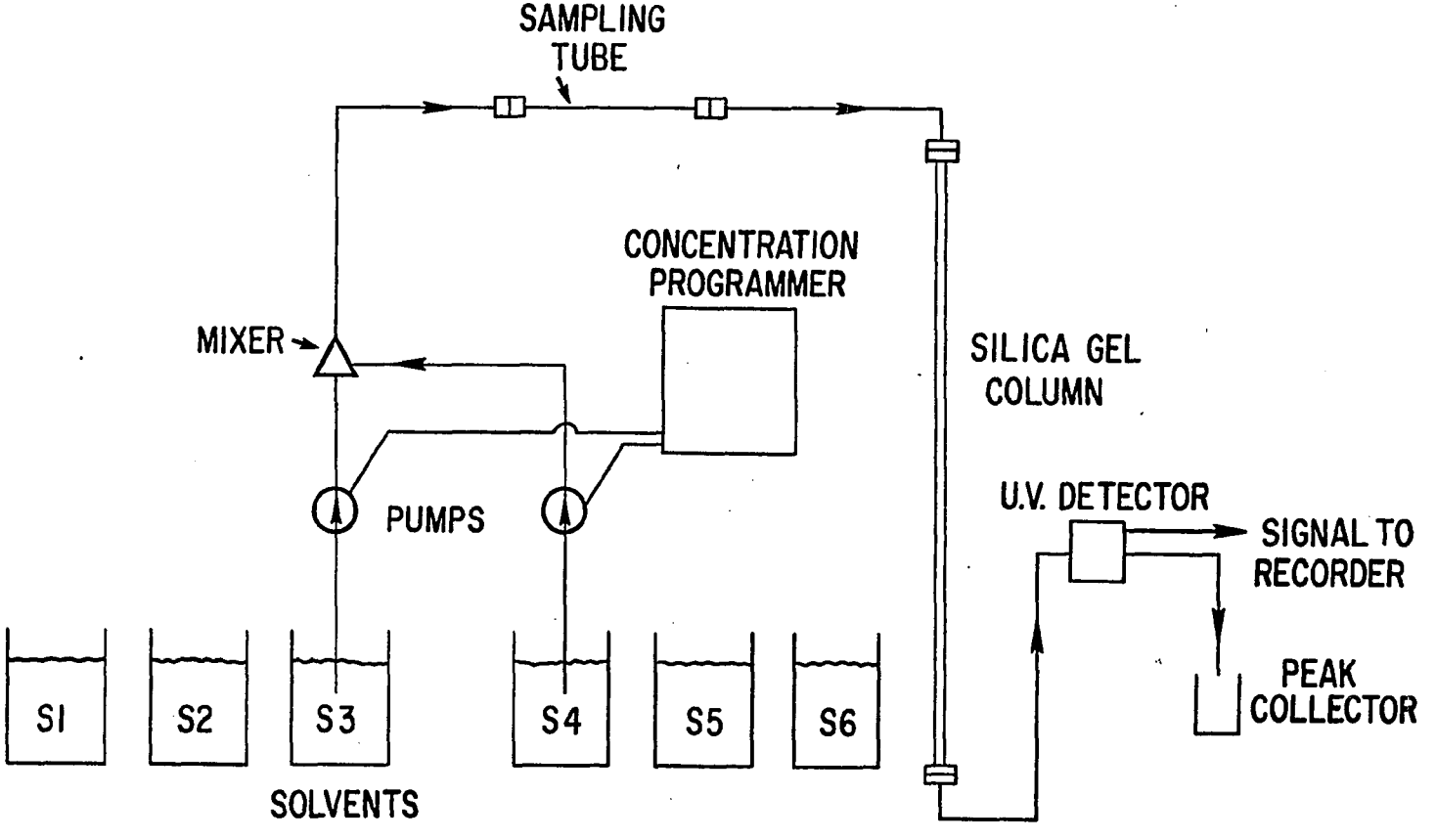


Figure 4.2.2. CONCENTRATION GRADIENT SESC EQUIPMENT

(1977), solvents that absorb in the U.V. range of the detector were eliminated. Also, instead of using a sharp front between solvents, a gradient concentration linear program is used to change from one solvent to another. This improves the separation. The peaks indicated by the detector are collected and the mass is measured by weighing, after the evaporation of the solvent under stream of nitrogen.

The concentration gradient SESC was built using an Altex Model 312 Gradient Research Chromatograph and a Silica Gel 60 Lobar Column.

Molecular weight distribution of the samples collected by SESC was determined by Gel Permeation Chromatography. A column of 1.20 m x 1 cm i.d. packed with Bio Beads SX-8 was used, with tetrahydrofurane as a solvent. The column was calibrated with polystyrene standards provided by Altex and with polycylic aromatics. An Altex model 153 UV-vis Detector was used as a sensor.

4.2.2 Results

In the following results, data corresponding to Illinois No. 6 coal was previously published (Dobner, et al., 1976). Curves representing these data are presented together with data for Pittsburgh No. 8, for comparison.

Figure 4.2.3 shows the carbon conversion to methane in both coals, as a function of the temperature. Yields of methane from Illinois No. 6 coal are slightly higher.

In Figure 4.2.4, carbon conversions to ethane and propane are presented. While conversions to propane do not show much of a difference, the temperature at which the maximum yield of ethane is obtained is higher for Pittsburgh No. 8 coal.

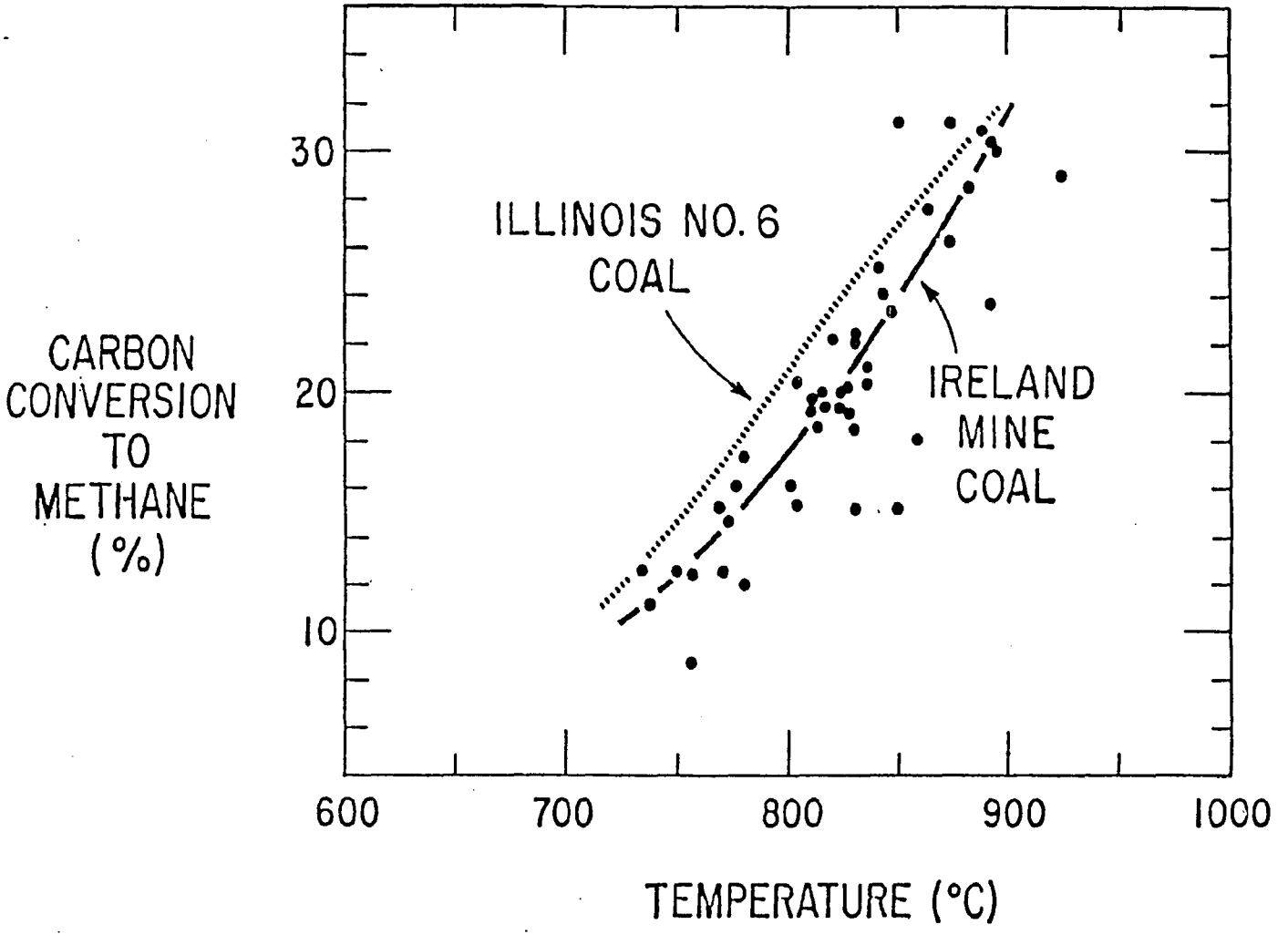


Figure 4.2.3. Carbon conversion to methane, showing slightly higher yields for Illinois No. 6 coal than Ireland Mine Coal.

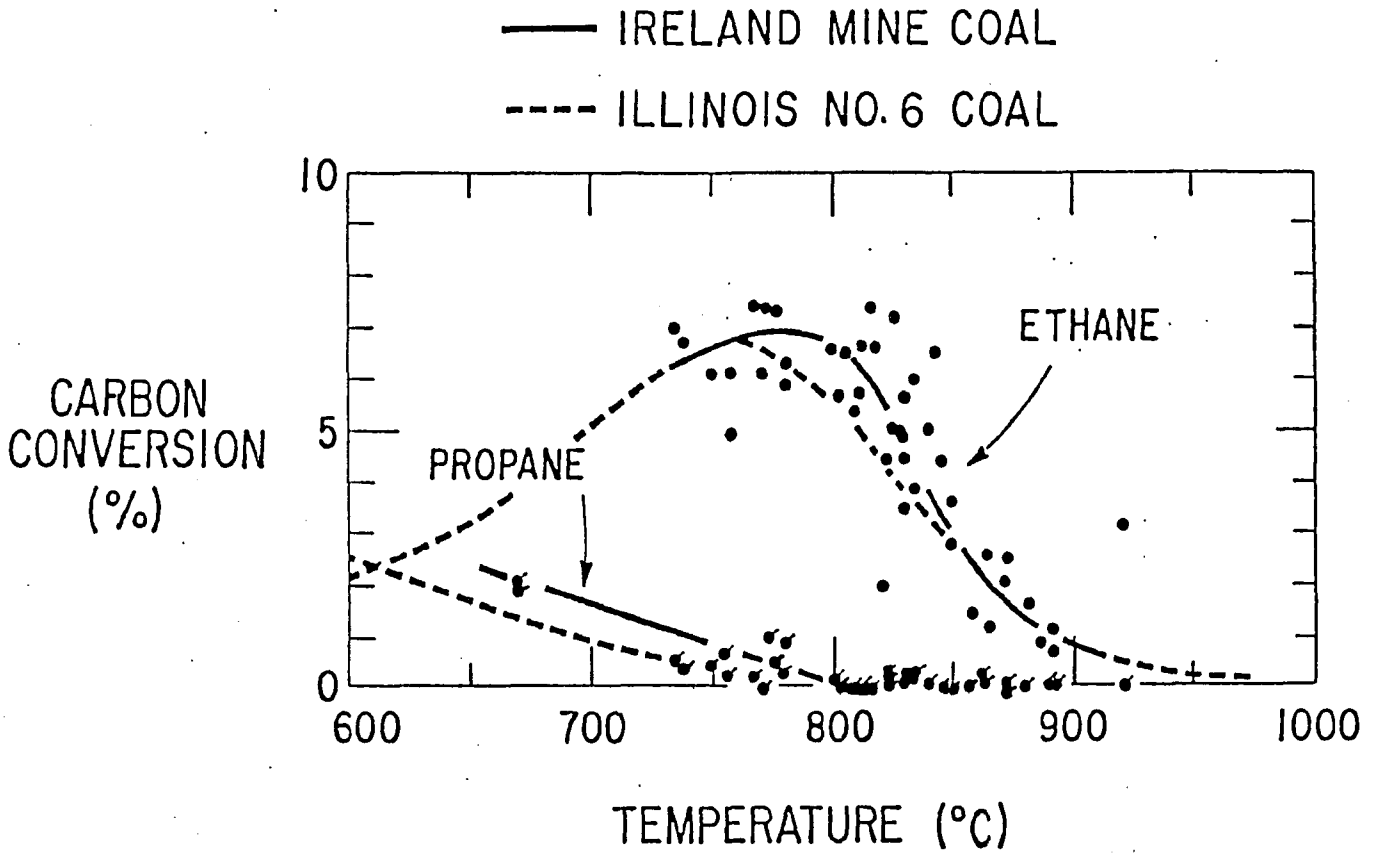


Figure 4.2.4. Carbon conversion to propane and ethane. The maximum yield of ethane is observed at higher temperatures in Pittsburgh No. 8 Coal.

Carbon conversions to BTX are shown in Figure 4.2.5. Although the data scatter considerably, the maximum yield of BTX attainable from Pittsburgh No. 8 coal is lower (about 2% lower). Also, the maximum appears at higher temperatures in this coal.

Figure 4.2.6 shows one of the more striking differences of behavior between both coals, in the way that yields of liquids heavier than BTX appear as a function of temperature. While for Illinois No. 6 coal the yield of heavy materials decays rapidly with temperature, in Pittsburgh No. 8 coal the yield has a maximum at about 800°C followed by a decay at higher temperatures.

Table 4.2.2 presents the weight percent distribution in the SESC fractions of heavy liquids obtained from reacting both coals at similar conditions. A comparison of yields of each fraction from the original coal can be established: the Ireland Mine coal tends to produce larger quantities of heaver material. (Fractions 3, 4 and 6.)

Table 4.2.3 gives an account of the molecular weight distribution of each fraction from both coals. Also, the possible chemical structure is indicated. The information on structure was obtained, for the case of fractions 1 and 2 by NMR analysis of our samples, and for the remaining fractions by comparison of the results obtained by Farcasiou (1977) in the SESC separation of several coal-derived liquids. With regard to the molecular weight of the different fractions, it may be noted that the molecular weights of the various fractions (except in fraction 2) are approximately the same.

Table 4.2.4 gives a detailed comparison of the product distribution from both coals at similar conditions. The yield of gases is approximately the same for both coals, the difference is more marked in

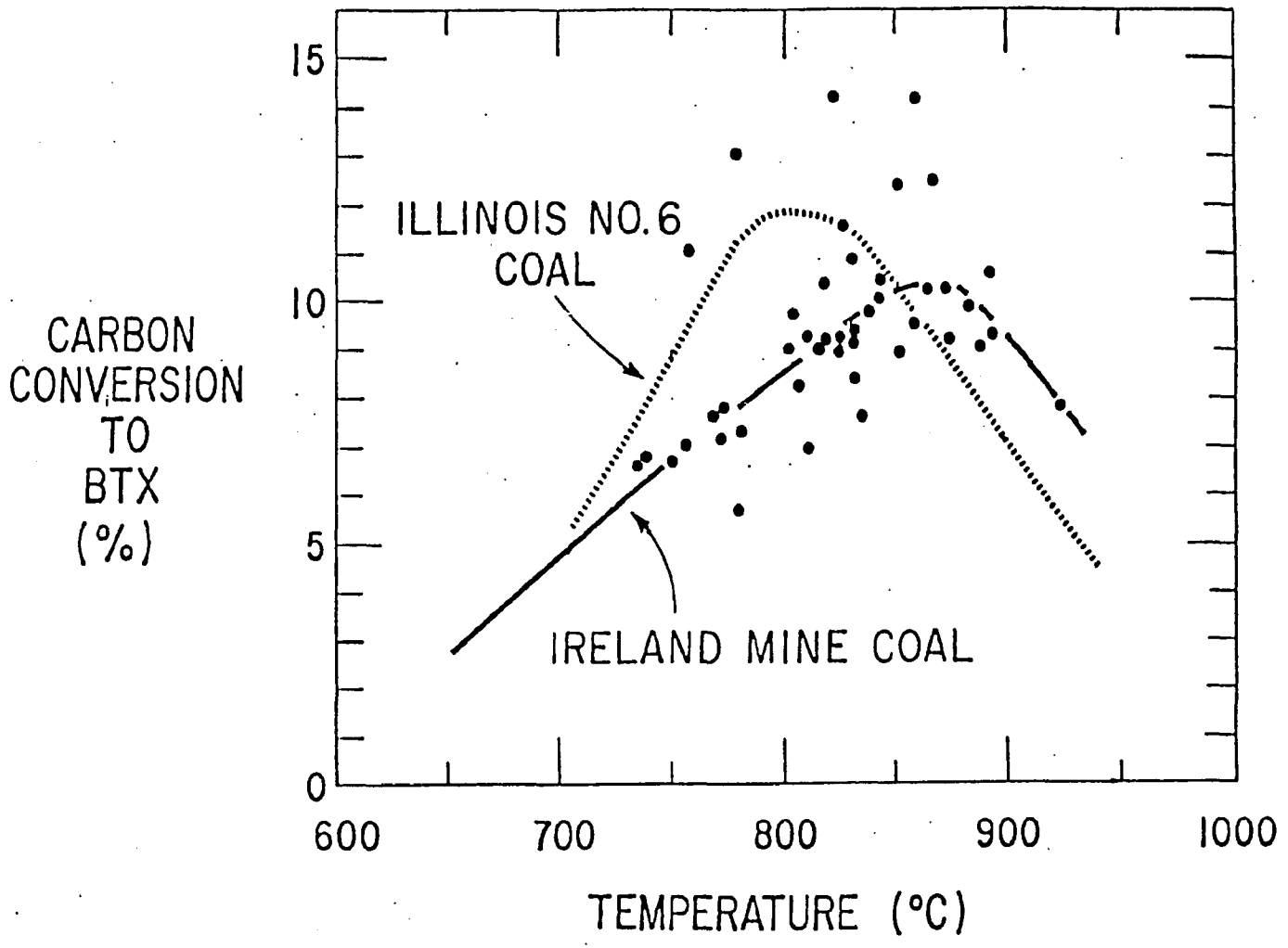
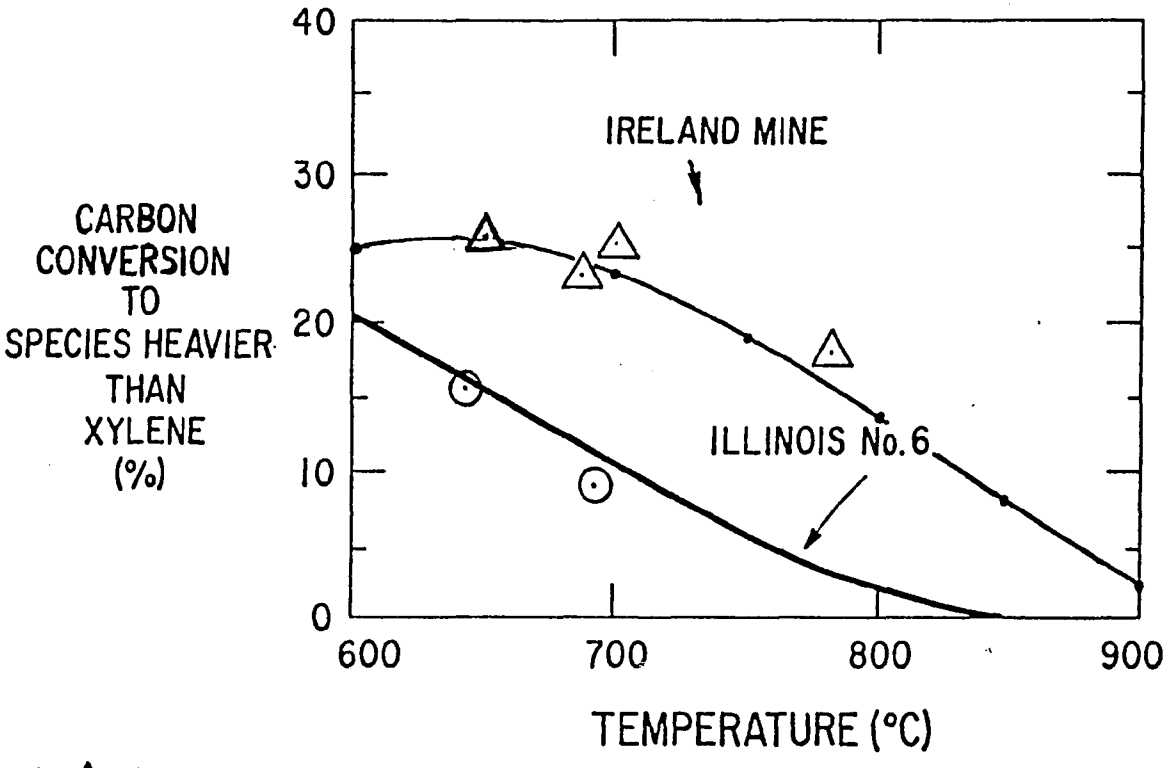


Figure 4.2.5. Carbon conversion to BTX. The maximum yield of BTX is obtained at higher temperatures in Pittsburgh No. 8 coal.



(△) From liquid collection experiments (Pittsburgh No. 8 coal)

(○) From liquid collection experiments (Illinois No. 6 coal)

Solid lines: average curves on values obtained from material balance.

Figure 4.2.6. Carbon conversion to species heavier than xylene. Species decay rapidly with temperature in Illinois No. 6, but present a maximum and decay at higher temperatures in Pittsburgh No. 8 Coal.

Table 4.2.2. Weight Percent Distribution of the Different SESC Fractions of Heavy Liquids from Pittsburgh No. 8 and Illinois No. 6 Coal.

		Pittsburgh No. 8 Coal, 685°C		Illinois No. 6 Coal, 678°C	
Fraction	Solvent	Wt% on Heavy Liquids	% Carbon Conversion	Wt% on Heavy Liquids	% Carbon Conversion
1	Hexane	2.1	0.46	10.0	0.75
2	Chloroform	4.2	0.93	5.0	0.38
3	Ether/3% Etoh	45.8	10.21	55.0	4.15
4	Methanol	37.5	8.35	10.0	0.75
5	Chloroform/3% Etoh	4.2	0.93	20.0	1.51
6	THF	6.2	1.4	0.0	0.0
		total	27.83	total	7.55

Table 4.2.3. Molecular Weights of the SESC Fractions of Heavy Liquids from Pittsburgh No. 8 and Illinois No. 6 Coals. GPC Results Indicate the Molecular Weight of the Maximum Peak, Accordingly to a Calibration of the Column with Polycyclic Aromatics and Polyestyrene Standards.

Fraction	Solvent Eluent	Chemical Structure (possible)	Molecular Weights (GPC)	
			Pittsburgh No. 8 Coal	Illinois No. 6 Coal
1	Hexane	Aromatics, Alkyl-Aromatics (NMR)	200	245
2	Chloroform	Aromatics, Polar Aromatics with -OH and $-CH_3$ Groups (NMR)	310	465
3	Ether/3% ETOH	Monophenols, Basic N, Heterocyclics (Farcasiou, 1977)	440	460
4	Methanol	Highly Functional Molecules, High Heteroatoms Content (Farcasiou, 1977)	435	425
5	Chloroform/3% ETOH	Polyphenols (Farcasiou, 1977)	640	640
6	THF	Increased O, Increased N, Bacicity (Farcasiou, 1977)	935	---

Table 4.2.4. Comparison of Products Distribution from Pittsburgh No. 8 and Illinois No. 6 Coals

	% Carbon Converted to Products	
	Pittsburgh No. 8 685°C	Illinois No. 6 678°C
Methane	6.0%	8.0%
Ethane	5.0%	5.0%
Propane	2.0%	1.5%
CO_x	2.7%	3.7%
BTX	4.5%	4.5%
Oils	1.4%	1.14%
Asphaltenes	10.2%	4.15%
Multifunctional	10.67%	2.26%
Char	58.0%	65.0%
Unaccounted for	-0.5%	4.7%
Total Conversion (by difference)	42.0%	35.0%
Maximum Conversion	60.0% (at 820°C)	45.0% (at 800°C)

the liquid fractions. Coal flash hydrogenation products from Pittsburgh No. 8 coal contain a large fraction of "asphaltenes" and "multifunctional" liquids. These differences, since the reaction conditions are the same, must arise from differences in the chemical structure.

4.2.3 Discussion and Conclusions

Although both coals behave similarly with respect to the production of gases and BTX, there are marked differences that have to be discussed further.

The heavy liquid fraction produced by Illinois No. 6 tend to disappear rapidly with increased temperature. This behavior can be explained by cracking and hydrocracking reactions occurring in the coal and in the vapor phase; as a result char, BTX and gases are produced.

Pittsburgh No. 8 coal, however, produces a heavy liquid fraction that starts disappearing only at higher temperatures. This behavior indicates that these liquids are more refractory and less reactive than those of Illinois No. 6. As a result, less char is produced and the maximum yields of BTX and ethane (products of the hydrocracking reaction) are obtained at higher temperatures.

From the SESC and steric exclusion analysis of the heavier liquid fractions in both coals we can advance an explanation for this difference in reactivity. From Figure 4.2.8 it is clear that tar from Pittsburgh No. 8 coal contains a lesser proportion of "oil" and a higher proportion of "polyfunctionals". The net result is a higher proportion of heteroatoms and polyfunctionals. These can be assumed to be more difficult to break down in the thermal hydrocracking of these fractions to BTX.

It is possible also to assume that the differences in the chemical structure are present in the original coals. One important difference is that the oxygen content is almost double in Illinois No. 6 coal. We have shown previously that oxygen and aliphatic hydrogen are important factors in determining the reactivity of a coal. Since the content of aliphatic hydrogen is approximately the same in both coals, we can assume that the increased amount of oxygen in the heavier liquids obtained from the flash hydrogenation of Illinois No. 6 coal could be responsible for its higher reactivity.

4.3 Two-stage Flash Hydrogenation

As previously remarked, flash hydrogenation occurs in two sequential steps. The first step is the devolatilization of coal in the presence of hydrogen. The species vaporized are predominantly heavy (even though light species down to methane are observed in significant amounts). In the second step, heavy species are hydrocracked in the vapor phase to more desirable light components. In the work described above, devolatilization and hydrocracking were carried out at the same temperature. This, however, is an unnecessary constraint. Providing a hydrocracking zone with independent temperature control makes available an additional degree of freedom for optimizing the process.

Experiments in two-stage hydropyrolysis have been conducted at the National Coal Board in England (Finn, et al., 1979)). In their experiments, ring aromic yields were increased from 5 wt% daf in single stage operation to 12% in two-stage operation at 150 atm pressure. The National Coal Board experiments employed a coal heating rate of 5°C per

second. A major difference is that here heating rates are much higher, about 1500°C per second.

4.3.1 Experimental Arrangement

The section of tubing between the flash tube reactor and expansion coil was lengthened and passed through an electric oven (see Figure 4.3.1). This provides a hydrocracking zone of 14 inch length whose temperature can be independently controlled. Devolatilization is carried out in the flash tube reactor as before but with a short vapor residence zone to minimize vapor phase reactions.

Illinois No. 6 coal was used for this study. Runs were carried out at 100 atm, 10 sec solid contact time, 1500°C/sec heating rate and 600 to 1000°C. Since a sharp temperature gradient exists near the two electrodes, a very short, nonisothermal vapor zone cannot be avoided. To verify that this region has no significant effect on yield structure, two vapor residence times, 0.05 and 0.1 sec were used by adjusting the hydrogen flowrate.

Runs were made with the second stage both at low and high temperatures. In the first part of this study, the second stage was operated at 150°C (to prevent BTX condensation) to obtain data on devolatilization alone. Runs were then carried out with second stage temperature at 850°C and 965°C. Two residence times, 0.6 and 1.2 sec, in the second stage were used at 965°C and 0.6 sec only was used at 850°C. The electric clamp between the two stages was kept at 200°C during the runs to avoid the liquid condensation. The residence time in this region is about 0.15 to 0.3 sec, depending on the flowrate used. In the second stage, the center temperatures were about 60°C higher than

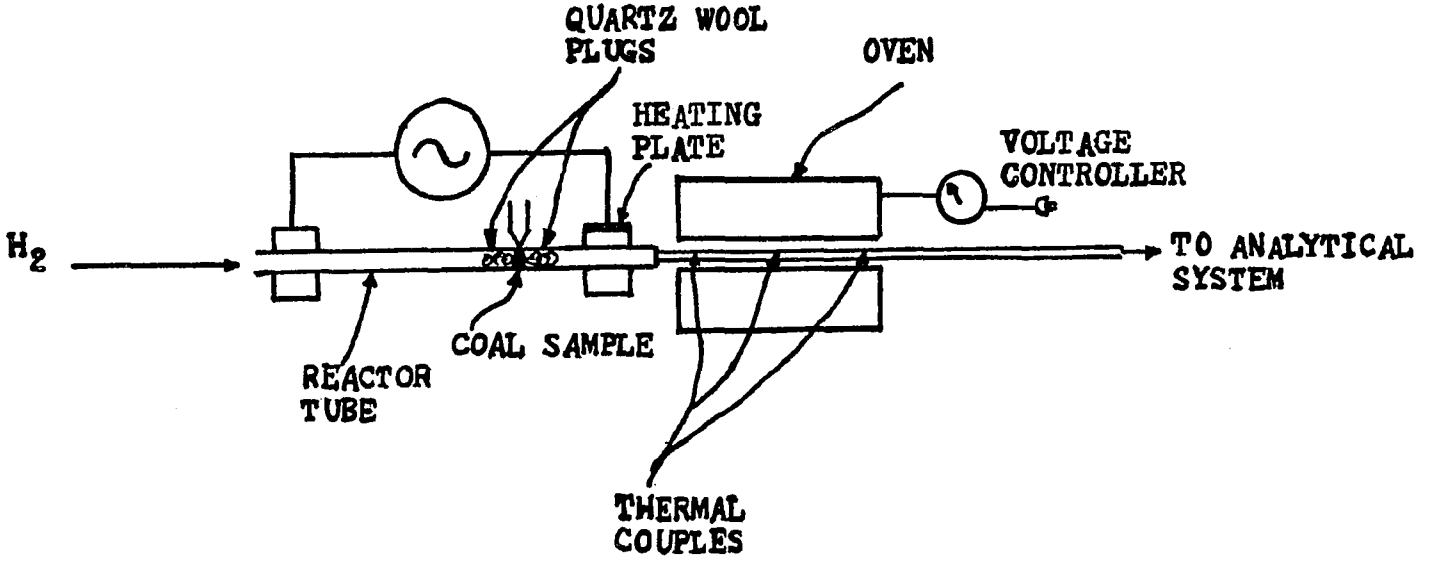


Figure 4.3.1. Experimental Arrangement for Two-Stage Coal Hydrogenation.

the two ends and the reported second stage temperature is that at the center.

4.3.2 Results

Yields from the first stage alone are shown in Figures 4.3.2 and 4.3.3. The six product species are represented by three different symbols with flagged and unflagged points differentiating the two residence times in the short nonisothermal zone. No difference in yield is found between these two residence time. The solid lines represent the correlated results which are discussed in the next section.

The results of complete two-stage runs are shown in Figures 4.3.4-4.3.9. Modeling is discussed in the next section.

4.3.3 Modeling

Film studies of individual particles have shown that caking coal soften and swell during pyrolysis (Bergbau-Forschung Co., GmbH, 1976). The time interval during which the coal is fluid may be termed the "caking period". During this caking period, bubbles containing product gases emerge on the surface. Bubble transport in the particle involves a series of processes including nucleation growth, coalescence and escape. The complete process is so complex that it seems to be statistical in nature. In traditional kinetics, the yield from a nonideal flow reactor is treated as an integral of the microscopic yield with a residence time distribution. This technique can be applied to model coal devolatilization. Each bubble in the caking coal particle can be assumed to be an ideal batch reactor where

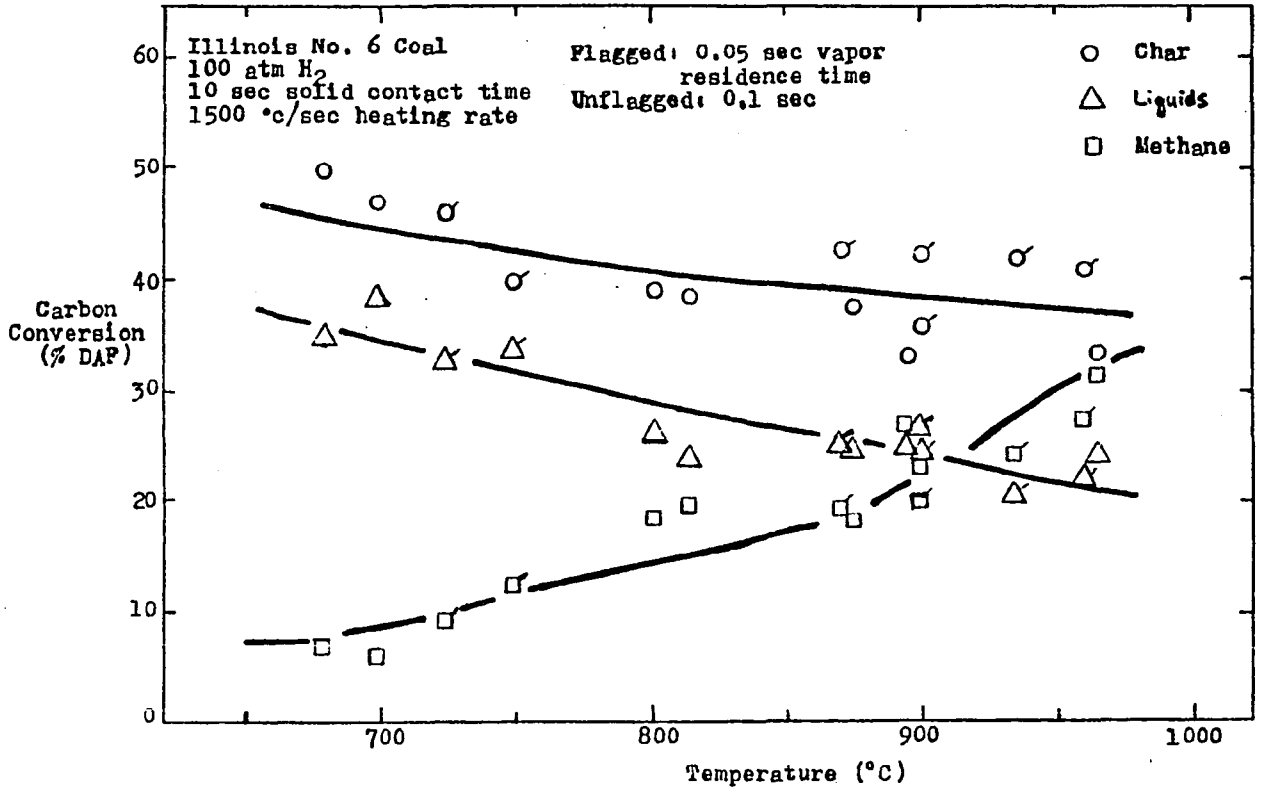


Figure 4.3.2. Carbon Conversion to Char, Liquid and Methane from the First Stage.

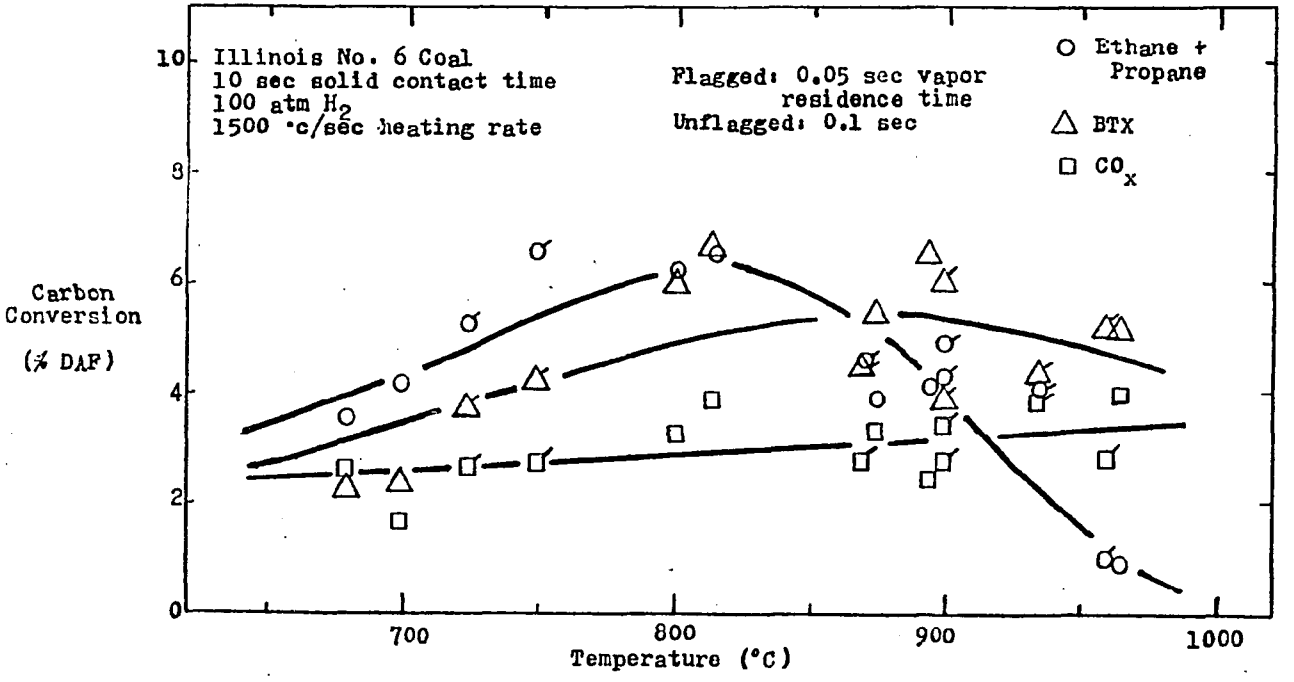


Figure 4.3.3. Carbon Conversion to Ethane, CO_x and BTX from the First Stage.

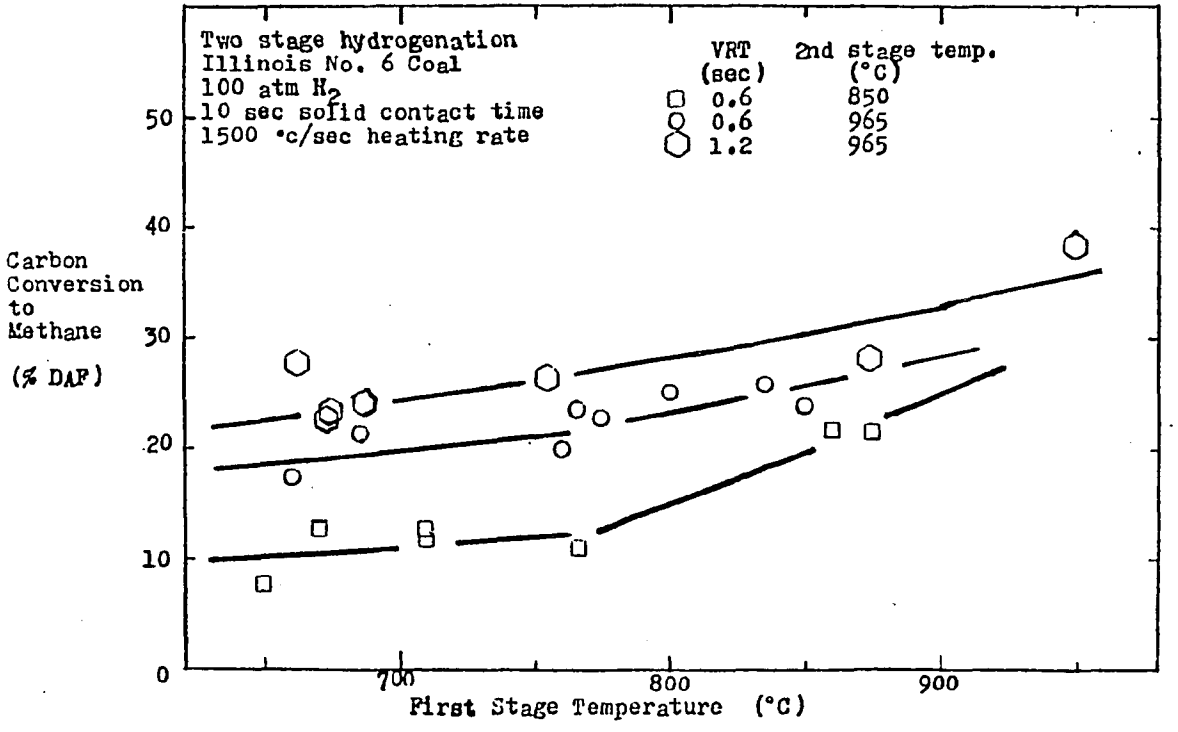


Figure 4.3.4. Methane Yields from Two-Stage Hydrogenation.

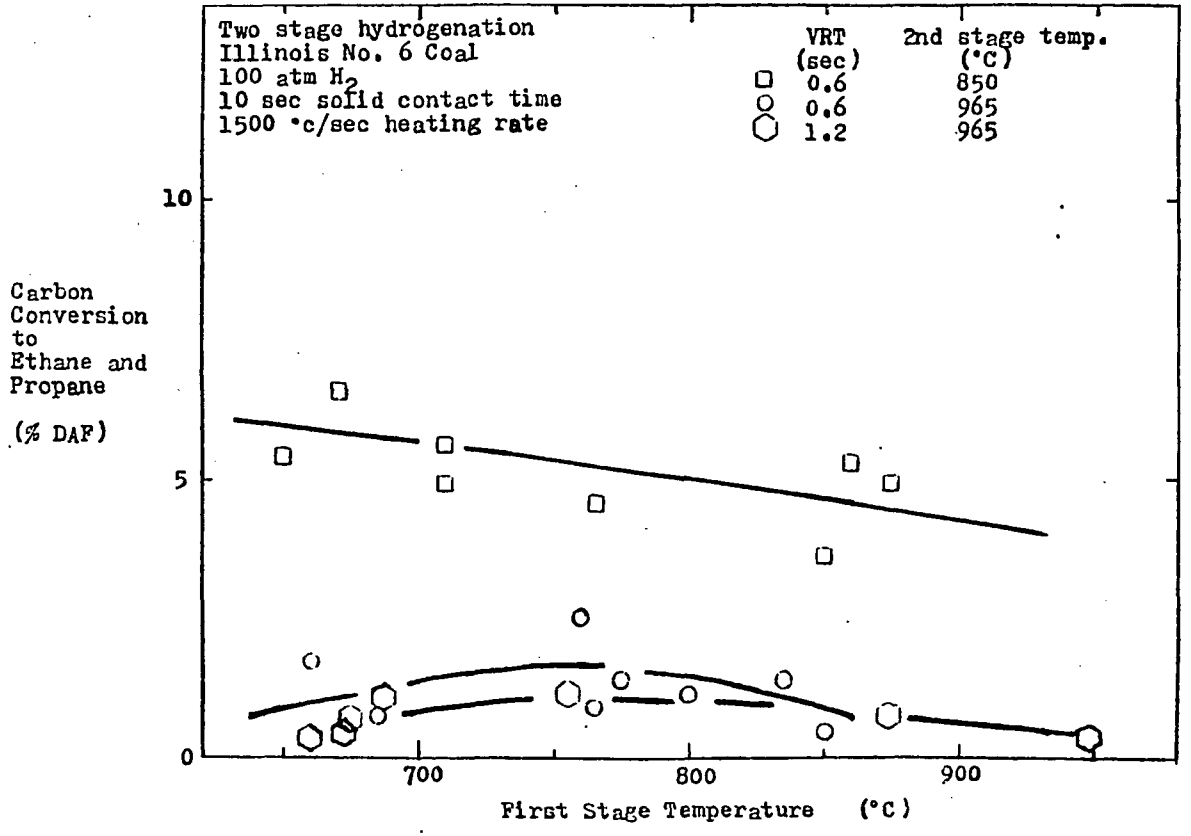


Figure 4.3.5. Ethane Yields from Two-Stage Hydrogenation.

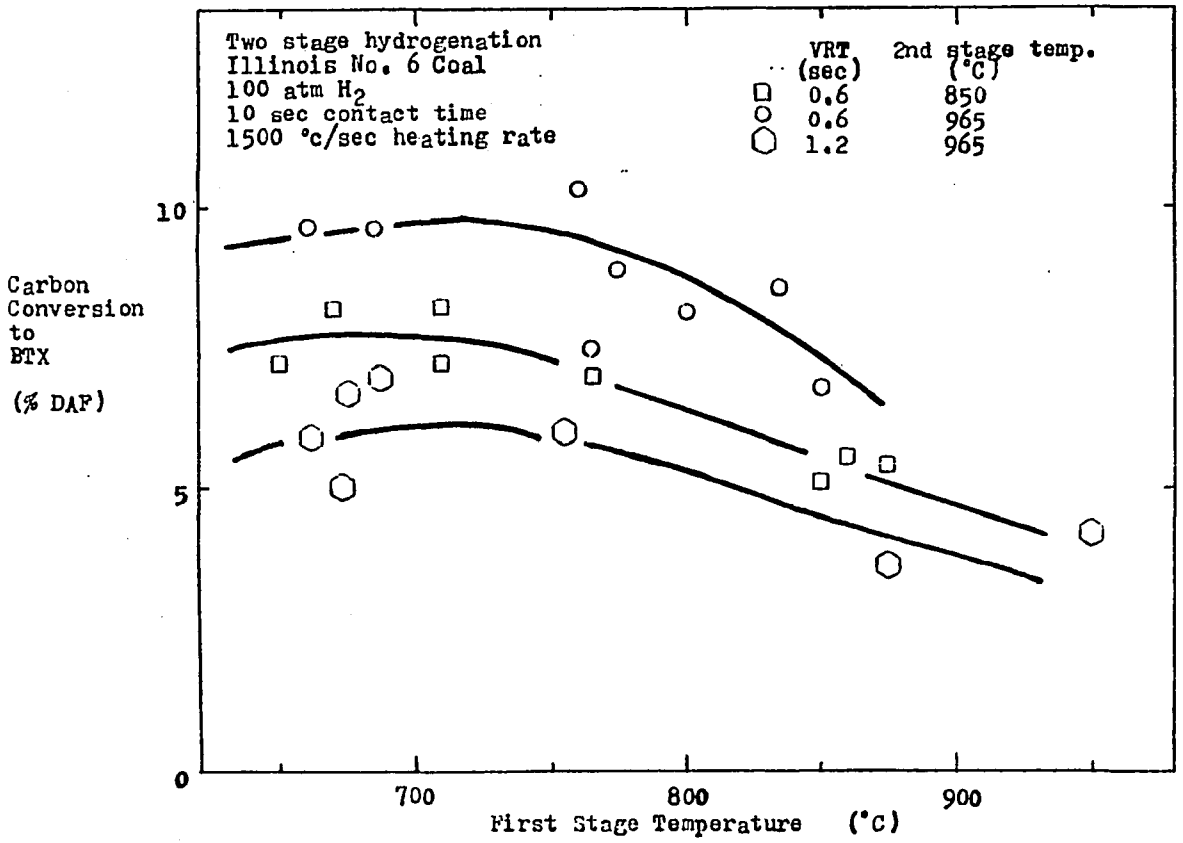


Figure 4.3.6. BTX Yields from Two-Stage Hydrogenation.

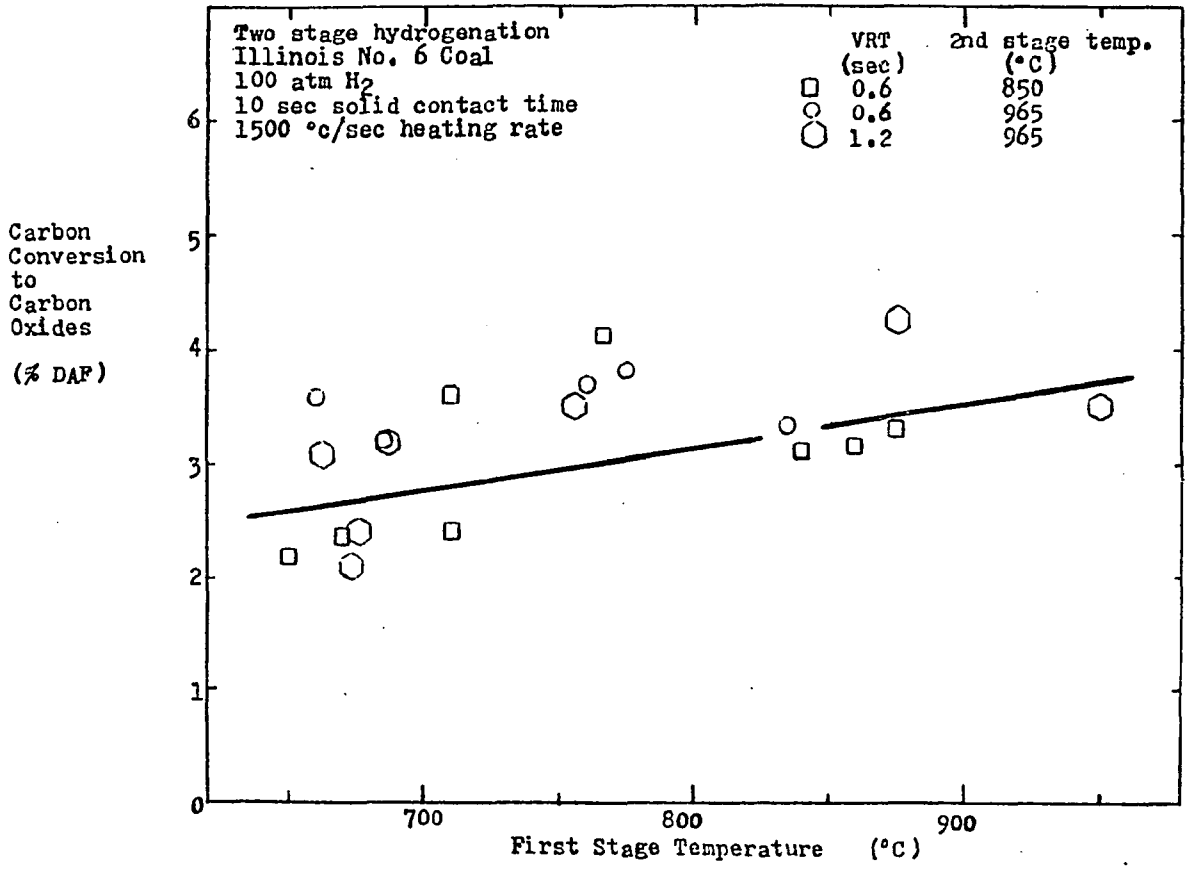


Figure 4.3.7. CO_x Yields from Two-Stage Hydrogenation.

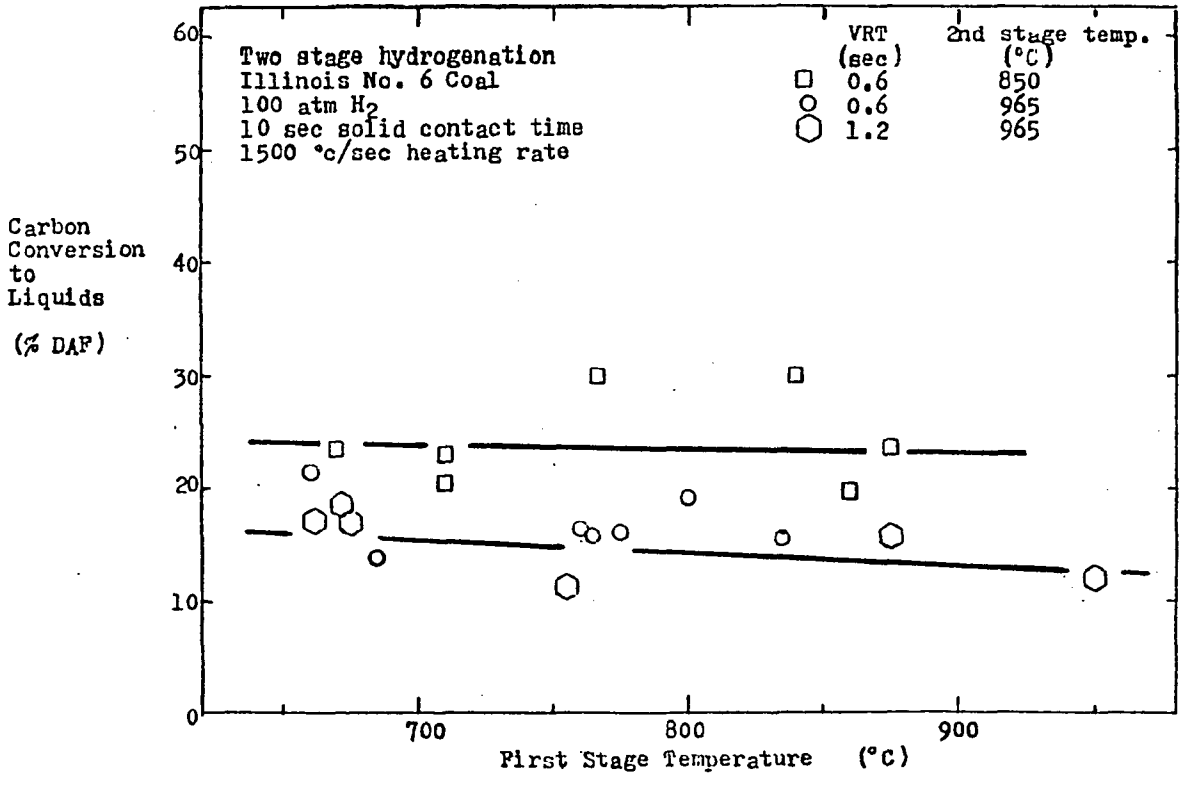


Figure 4.3.8. Liquid Yield from Two-Stage Hydrogenation.

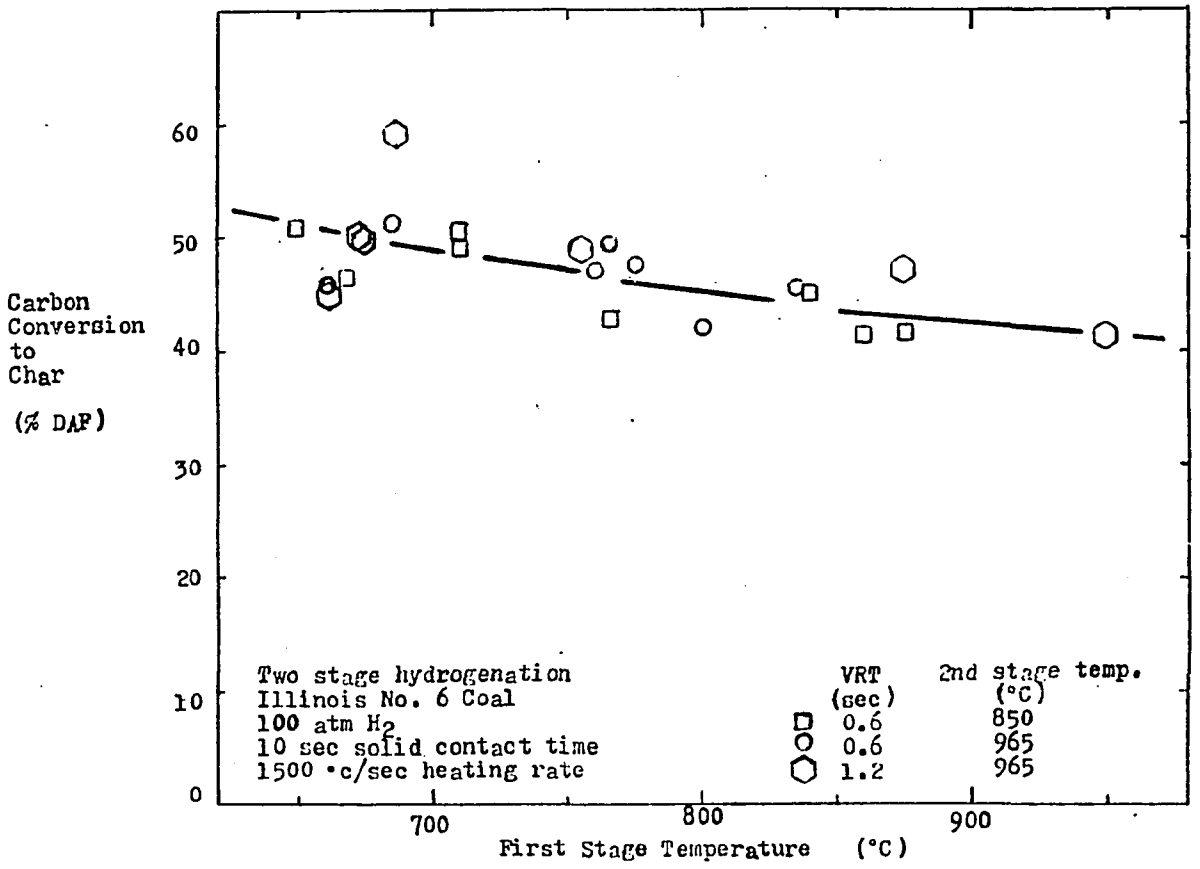


Figure 4.3.9. Char Yields from Two-Stage Hydrogenation.

volatiles undergo secondary reactions. The volatiles yield is, therefore, a summation of volatiles from each bubble. If a distribution is assumed for bubble residence time within a particle, the volatiles yield from coal devolatilization is

$$\bar{X} = \int_0^\infty X(t) \cdot S(t) \cdot dt \qquad (1)$$

where $\bar{X}$ = integral yield of a coal devolatilization component from all bubbles

$X(t)$ = yield of a coal devolatilization component in a bubble which has an age $\bar{t}$

$S(t)$ = residence time distribution of bubbles in the caking particle

This equation is similar to the complete segregation model in an ideal continuous stirred tank reactor (Aris, 1969) which consists of dispersed, independent droplets. Though the coal particle is not physically a CSTR, it can be treated with the same mathematical equation (1). The assumption of independent bubbles is bound to be incorrect because the bubbles coalesce during their transport. Furthermore, the boundary layer resistance around the particle is lumped into the above equation, though the relative magnitude of interphase and intraphase transfer limitations is not yet well understood. Implementation of Equation (1) requires a residence time distribution and a kinetic model.

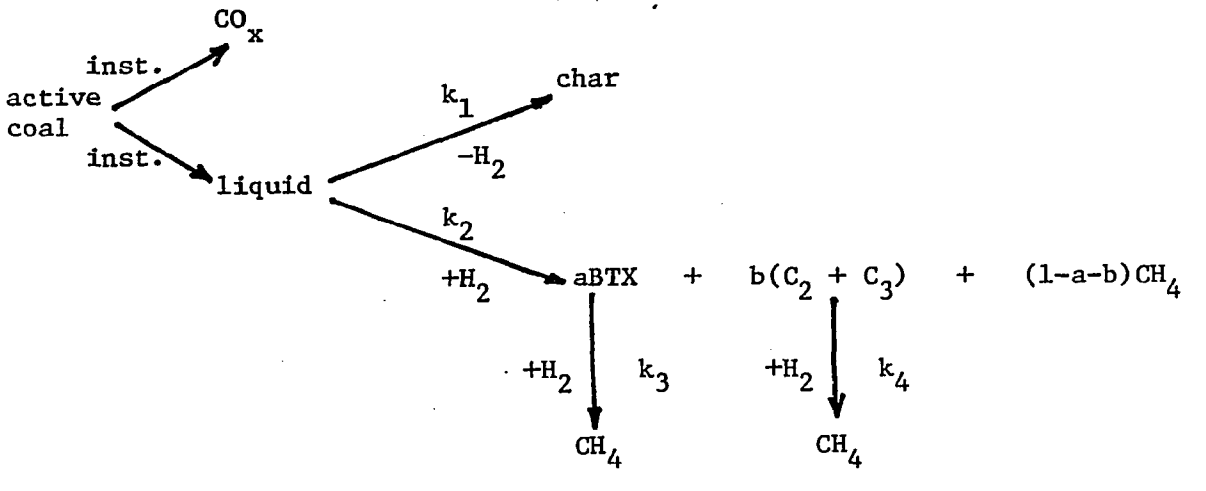
To avoid solving a set of differential equations, an exponential function is assumed for the residence time distribution

$$S(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}}$$

where $\bar{t}$ = mean residence time

Physically, the use of a decay function as a residence time distribution is justified by the following: an outer shell of the coal particle produces more bubbles than our inner shell of the same thickness, and bubbles in an outer shell escape more easily than those in an inner shell. Mathematically, the exponential decay function (2) is easy to handle because integral (1) becomes a well-known Laplace Transformation. Equation (2) contains only one parameter, $\bar{t}$, the mean bubble residence time in the particle. Since the caking process may depend on temperature, pressure, particle size, heating rate, etc., the parameter $\bar{t}$ is an implicit function of these process variables. In this study, pressure heating rate and particle size are kept constant in all runs and the parameter $\bar{t}$ is assumed to be temperature independent.

The following kinetic mechanism is used for coal devolatilization:



Carboxyl and hydroxyl bonds in coal are usually weak and upon heating, therefore, carbon oxides are among the first species emerging from coal.

At a temperature above 600°C, CO_X are assumed to be spontaneous products. The same assumption is made for liquids because the very first step in pyrolysis is the breakage of high molecular weight "organic rock" into smaller fragments and is complete much below 600°C. This theory is reinforced by a recent IR study of coals and their vacuum pyrolysis liquids (Solomon, 1979a). The resemblance of the liquids to their parent coals suggest that the liquids consist of monomers released from the coal "polymer." The instaneous liquid yield (denoted by A_o) is assumed to be independent of temperature based on the classical "fixed carbon" concept in proximate analysis.

Hydrocarbons usually undergo two categories of thermal reactions: Cracking to light species and formation of carbon. They are both free radical reactions and strongly depend on temperature, pressure and hydrogen to hydrocarbon ratio (Brooks, 1966). In the assumed mechanism (Equation 3) the liquid cracking and polymerization are competitive. Constants a and b are liquid fractions converted to BTX and $(C_2 + C_3)$ respectively in the cracking reaction. The bell-shaped BTX and $(C_2 + C_3)$ yields of Figure 4.3.3 indicate that BTX and $(C_2 + C_3)$ are intermediates between liquids and methane. This completes the kinetic mechanism of Equation (3). Carbon formation from BTX and light aliphatics are neglected in the model because the following mechanism (LaCava, 1977) is generally accepted:

$$\text{aliphatics} \overset{-H_2}{\rightleftharpoons} \text{olefins} \overset{-H_2}{\rightarrow} \text{simple aromatics} \overset{-H_2}{\rightleftharpoons} \text{aromatic polymers} \downarrow \overset{-H_2}{} \text{carbon}$$

According to this mechanism, the liquids (assuming they are mainly aromatic polymers) have the strongest tendency among the products to

form carbon. It is a first approximation to assume that only the liquids are important in carbon formation. In addition, "liquids" contain hundreds of species; treating liquids as one species is another approximation.

Hydrogen's role is complex in hydropyrolysis. It diffuses into the particle before the experiment. During the plastic period, hydrogen free radicals are released from C-H bonds and is consumed in free radical stabilization. In addition, interphase and intraphase transfer of hydrogen can be significant in controlling the reaction. Order-of-magnitude estimates of these terms are important but incomplete. Though our experiments were performed at 100 atm only, the kinetic constants in the model, A_o, $\bar{t}$ and the rate expression of each step in Equation (3) should be pressure dependent.

Assuming each step in Equation (3) is first order and irreversible reaction and that the rate constants follow the Arrhenius Law, the rate expressions are as shown in Table 4.3.1. These rate equations, can be integrated once to obtain the local conversion of each species in a bubble. Substituting these conversion equations and the residence time distribution (2) into the integral (1), we obtain the yields of coal hydropyrolysis shown in the right hand column of Table 4.3.1. Integral (1) is simply the Laplace transformation of the local conversion in the bubble so the yields in Table 4.3.1 are found in the standard texts.

The parameters in Table 4.3.1 were evaluated to fit the experimental data using a set of standard subroutines in the Marquardt Algorithm of the International Mathematical and Statistical Library (IMSL). Parameter values are listed in Table 4.3.1 and the correlations are drawn in Figure 4.3.1 and 4.3.2. The model is in good agreement

Table 4.3.1. Kinetic Equations and Correlation Results of the Proposed Coal Hydropyrolysis Model

Product	Symbol	Rate	Yield
Liquid	A	$\frac{dA}{dt} = -(k_1 + k_2)A$	$\bar{A} = \frac{A_o}{\bar{t}\,(k_1 + k_2) + 1}$
BTX	C	$\frac{dC}{dt} = ak_2A - k_3C$	$\bar{C} = \frac{aA_ok_2}{(k_1 + k_2 - k_3)}\left(\frac{1}{\bar{t}k_3 + 1} - \frac{1}{(k_1 + k_2)\bar{t} + 1}\right)$
$C_2 + C_3$	D	$\frac{dD}{dt} = ak_2A - k_4D$	$\bar{D} = \frac{bA_ok_2}{(k_1 + k_2 - k_4)}\left(\frac{1}{\bar{t}k_3 + 1} - \frac{1}{(k_1 + k_2)\bar{t} + 1}\right)$
CH_4	E	$\frac{dE}{dt} = (1 - a - b)k_2A + k_3C + k_4D$	$\bar{E} = \frac{A_ok_2}{k_1 + k_2}\left(1 - \frac{1}{\bar{t}(k_1 + k_2) + 1}\right) - \bar{C} - \bar{D}$
CO_x	Instaneous		$CO_x = f(\text{temperature in } °C) + g$
Char	B	$\frac{dB}{dt} = A_ok_1e^{-(k_1 + k_2)t}$	$\bar{B} = 100 - (\bar{A} + \bar{C} + \bar{D} + \bar{E} + CO_x)$

Parameters Evaluated from Experimental Data

$A_o = 68.7$	$k_{20} = 255.8$ sec^{-1}	$E_3 = 49500$ cal/gm-mole	$f = 3.6 \times 10^{-3}$
$\bar{t} = 0.71$ sec	$E_2 = 11400$ cal/gm-mole	$b = 0.25$	$g = 2.6 \times 10^{-2}$
$k_{10} = 0.631$ sec^{-1}	$a = 0.20$	$k_{40} = 0.85 \times 10^{17}$ sec^{-1}	
$E_1 = 0$	$k_{30} = 4.3 \times 10^{8}$ sec^{-1}	$E_4 = 90000$ cal/gm-mole	

with the experimental data. The magnitudes of the parameters have, on the other hand, some valuable kinetic implications which will be discussed in the next section.

Correlations of the two-stage data shown in Figures 4.3.4 to 4.3.9 have also been carried out. A mechanism similar to that used in the first stage was a reasonable starting point for the second stage:

$$\text{liquids} \rightarrow a'\ \text{BTX} + b'\ (C_2 + C_3) + (1-a'-b')CH_4$$
$$\downarrow \qquad\qquad \downarrow$$
$$CH_4 \qquad\qquad CH_4$$

where a' and b' are constants. Carbon formation from liquids is not included, as it was in the first stage, because the surface to volume ratio in the second stage is very much lower than that in a porous char particle. However, no satisfactory correlation has been obtained at the time of this writing. The difficulties may be from several sources:

a) Figure 4.3.9 indicates that char yield increases slightly with second stage temperature and vapor residence time. The increase may be from carbon deposited on the wall in hydrogenation and burned up during the subsequent oxidation step if the oxygen carries enough heat from the first stage. The oxidation runs were carried out at 5 atm, so that the residence time (about 0.01 sec) in the zone between the two stages was much shorter than the residence time in hydrogenation runs at 100 atm. In addition, the oxygen has a higher heat capacity than hydrogen.

b) Figure 4.3.8 shows little difference in liquid yield between the two vapors residence times of 0.6 and 1.2 sec when the second stage temperature is 965°C. This indicates that some portion of the liquids is too refractory to be cracked in the vapor zone.

c) The temperature profile is not constant along the second stage reactor tube.

d) The flow is in the laminar region, and it may be inadequate to treat the second stage as a plug flow reactor.

4.3.4 Discussion

Some kinetic implications of the parameter values determined in the first stage may be noted:

i) The mean residence time ($\bar{t}$) of bubbles in a caking coal is probably the most important parameter in the process. A long residence time can severely inhibit yields of some intermediates such as BTX. The correlated value, 0.7 sec, seems to be strikingly large for our -200 mesh coal samples. It should, however, be noted that the caking duration may depend on pressure. The high pressure of this experiment (100 atm) can prevent the volatiles from transferring out of the particles and therefore prolong the residence time. Particle swelling also makes the true particle size ellusive. On the other hand, the accuracy of the calculated residence time may be profoundly affected by one processing variable whose effect has not been well understood - heating rate. The heat-up time from 400°C (where coal devolatilization starts)

to 800°C (the mean experimental temperature) is 0.27 sec under our 1500°C/sec heating rate. Although it is shorter than the correlated residence time, 0.71 sec, the analysis is to some extent distorted by the existence of a nonisothermal period.

ii) The instaneous liquid yield (A_o = 68.7%) suggests that the chemical controlled carbon conversion to hydrocarbon volatiles is about 14% higher than the 55% total volatiles yield in Figuare 4.3.2.

iii) The potential BTX yield is only A_o x a = 68.7 x 0.2 = 13.4% of original carbon in the coal.

iv) The BTX and (C_2 + C_3) cracking rates are consistent with the reported data for benzene and ethane (Hou and Palmer, 1965; Brooks, 1967) implying that these reactions are not char-catalyzed.

v) The liquid polymerization has a zero activation energy (E_1 = 0) implying that it is a radical recombination reaction. This was not assumed; E_1 was kept as a parameter and converged to zero in the iteration procedure.

vi) The activation energy of liquid cracking reaction (E_2 = 11400) is lower than those of most organic compounds, implying that the mechanism involves a more complex network than a single cracking reaction.

vii) In Figure 4.3.10, the competitive polymerization rate k_1 and hydrocracking rate k_2 are plotted against reciprocal temperature. The two reactions change their magnitudes at 680°C. This implies that the cracking rate dominates at a temperature above 680°C and under a high heating rate so that

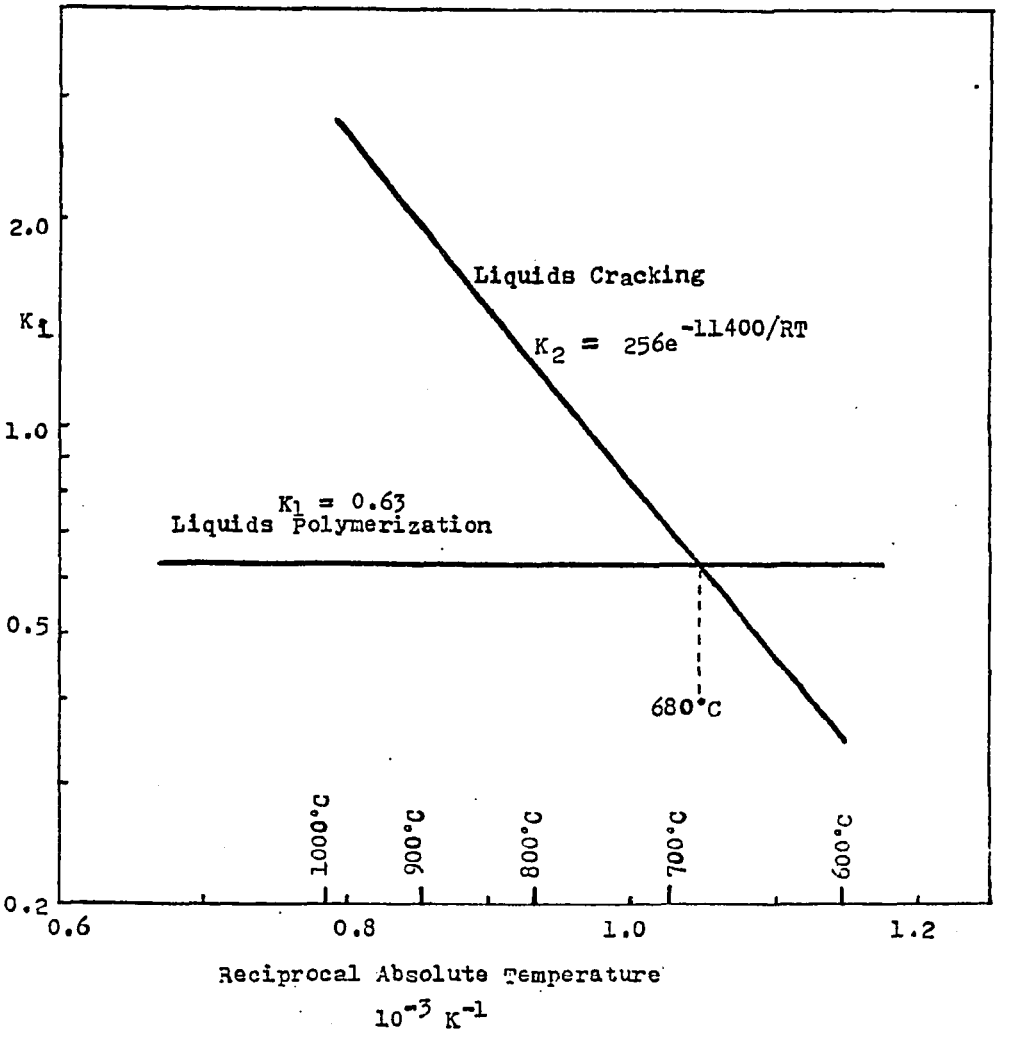


Figure 4.3.10. Comparison of Tar Cracking with Polymerization Rates.

the heat-up period is shorter than the caking period. Therefore, high volatiles yield can be achieved under high temperature and heating rate which is the basis for this and other recent research.

viii) Some discrepancies in the low temperature region (char and tar yields) may be due to the temperature-dependent nature of the mean residence time of volatiles in the particle. The caking period has been found to depend on heating rate (Anthony and Howard, 1976), but was assumed to be a constant in this model.

As for the two stage results, several points can be drawn for discussion:

i) Liquid yields decrease in the second stage. This may be due to both the hydrocracking to light species and polymerization to carbon. However, it seems to approach a limiting value at a specific temperature, as discussed in the last section. This indicates, perhaps, that the liquids cannot be treated as a single component. Only part of the liquids can be converted at a specific temperature and another portion of the liquids is refractory.

ii) Ethane, propane and BTX are intermediates between liquids and methane, therefore they have optimum yields within a few seconds.

iii) Methane is the hydrogenation product of every other species and its yield increases with temperature and residence time.

iv) Yields of carbon oxides remain the same in the vapor zone which implies that the liquids contain oxygen bonds which are very difficult to break.

v) Char yield increases slightly with temperature and residence time. This has been discussed in the previous section.

4.4 Effects of Hydrogen Pressure and Gas Composition

Pressure and gas composition are important process variables. In this section we describe tests to assess the effects of hydrogen pressure (using pure hydrogen) and of methane and carbon monoxide in hydrogen on yield structure.

The sample of Illinois No. 6 coal used in the studies described in this section is not identical to that used in previous experiments at City College or described in other sections of this work. For clarity, these samples are designated B (sample used in this section) and A (sample used in other sections of this report).

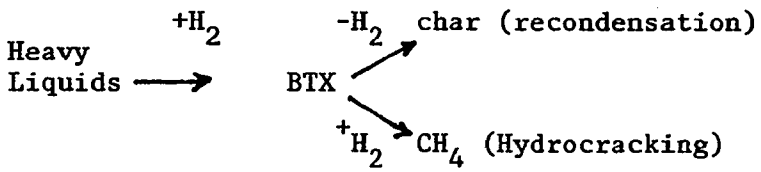
Both samples were prepared from chunks of coal fresh mined in 1974. Sample A was ground within a few days of collection and stored in sealed vials for use as needed. Sample B was ground from a large chunk stored under ambient conditions for four years.

It will be noted, in what follows, that the behavior of Sample B is different in substantial ways from that of Sample A. The analyses of these two coals are similar although B contains more oxygen and less sulfur. Oxidation during storage could explain the former. Local variation in composition is another possibility. It is also possible, because of local variations, that the organic structure of B is different than A, and that this difference is responsible for the observed differences in yield structure.

4.4.1 Effect of Pressure on Illinois No. 6 Coal Yield Structure

Flash hydrogenation of sample B was conducted over a range of temperatures at pressures of 100, 75, 50 and 25 atm of pure hydrogen. The results are displayed in Figures 4.4.1 to 8. Runs were carried out with samples ground to -325 mesh except in a few cases at 100 atm where -200 mesh samples were used. No significant effect of particle size was found. The pressure effect can be summarized as follows:

1. The yields of light species, methane, ethane and propane increase with increasing pressure, but they approach limiting values above 75 atm. Higher yields at higher pressure are expected because these light species are the terminal products in a series of consecutive reactions. The coal has a H/C atomic ratio equal to 0.9 while methane has a ratio of 4. The limiting values imply that the potential of heavy liquids for hydrocracking is limited.
2. BTX yield increases with pressure which indicates that hydrogen stabilizes single ring free radicals. The increase, however, is less at high temperature (and even is reverse at low pressure), which may be due to severe polymerization (to carbon) and hydrocracking (to methane):



Severe condensation and hydrocracking of BTX at high temperature will reduce the BTX yield. The former is a

Table 4.4.1. Ultimate Analysis of Illinois No. 6 Coal

Sample	A	B
C(maf)	77.6%	76.0%
H(maf)	5.8	5.7
O(maf)	10.6	13.2
N(maf)	1.2	1.4
S(maf)	4.8	3.8
Ash (mf)	12.1	12.8

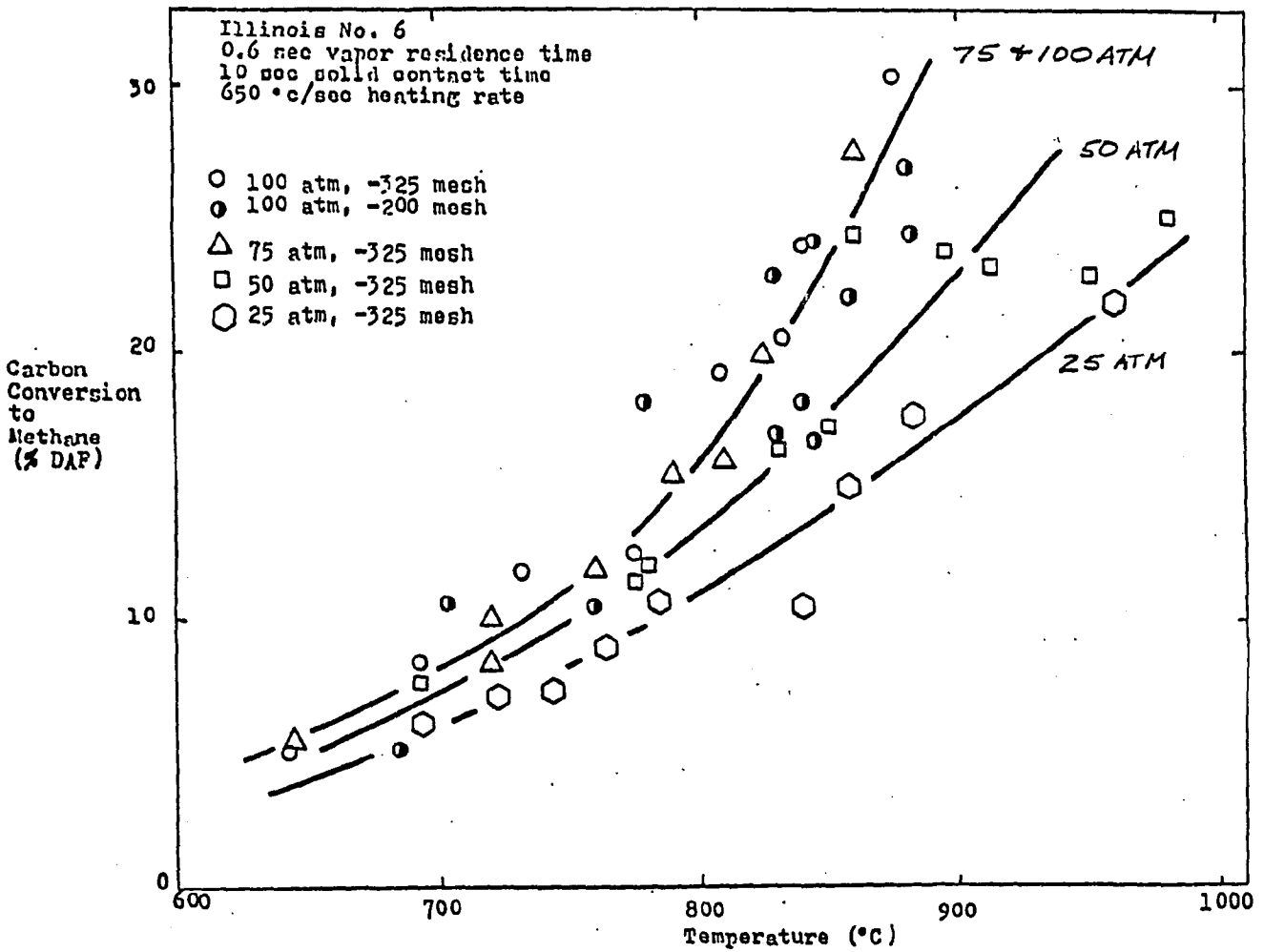


Figure 4.4.1. Effect of Pressure on Methane Yields

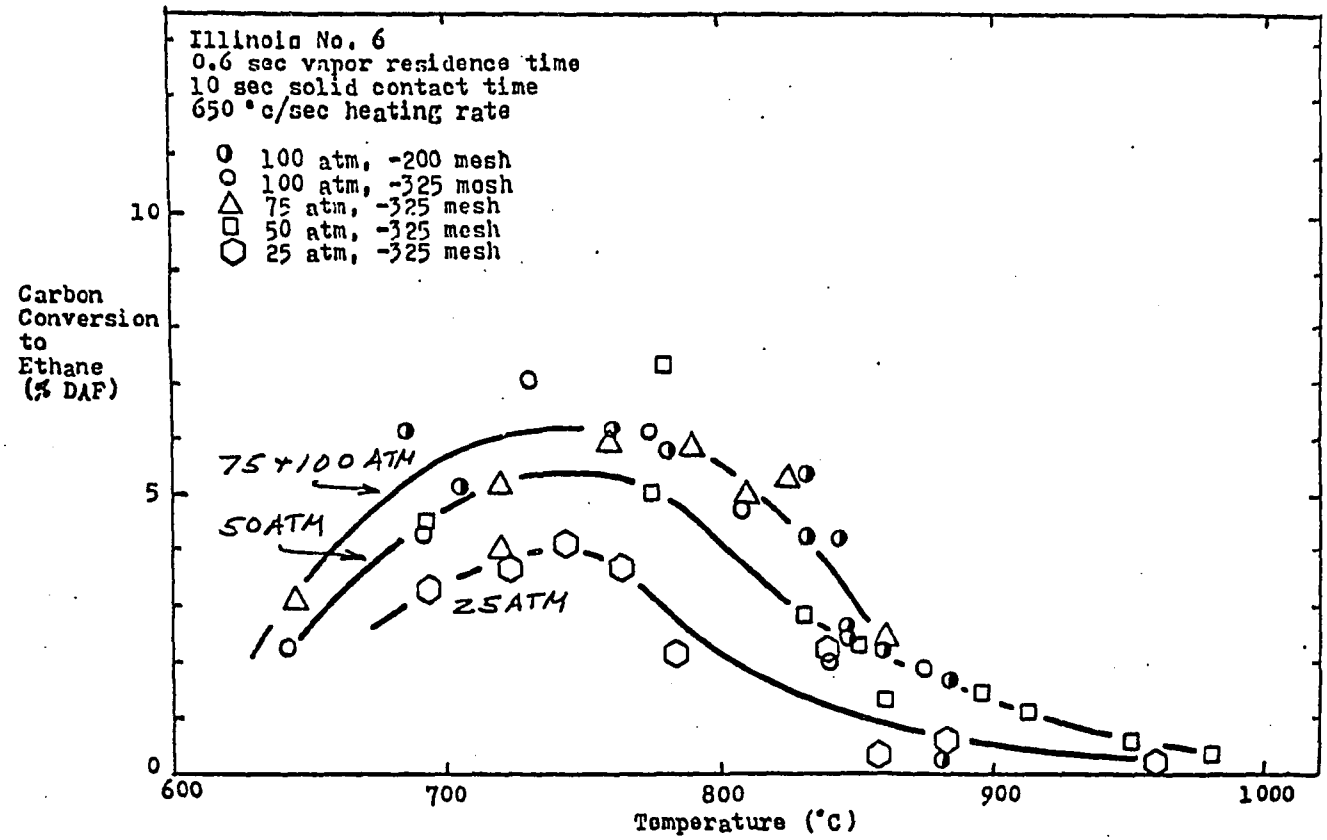


Figure 4.2.2. Effect of Pressure on Ethane Yields

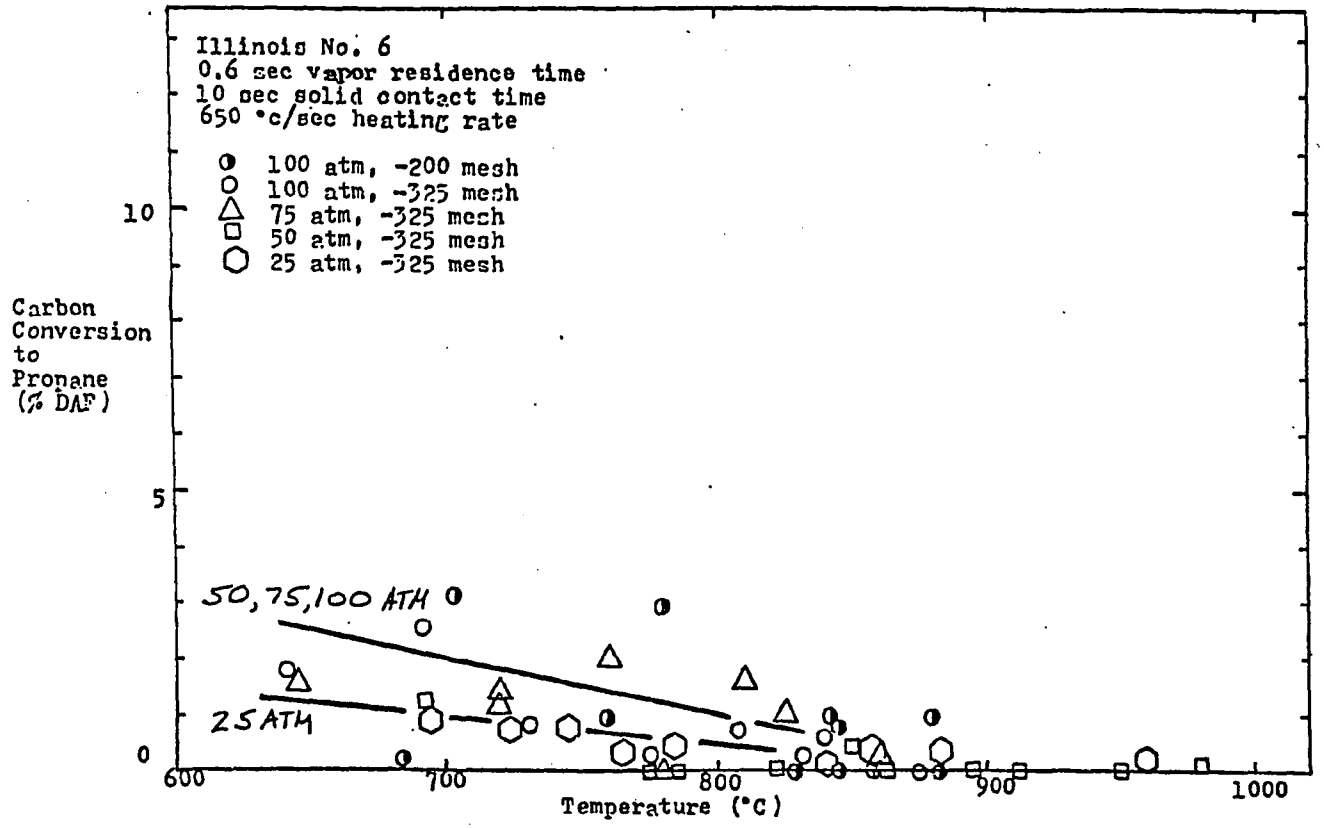


Figure 4.4.3. Effect of Pressure on Propane Yields

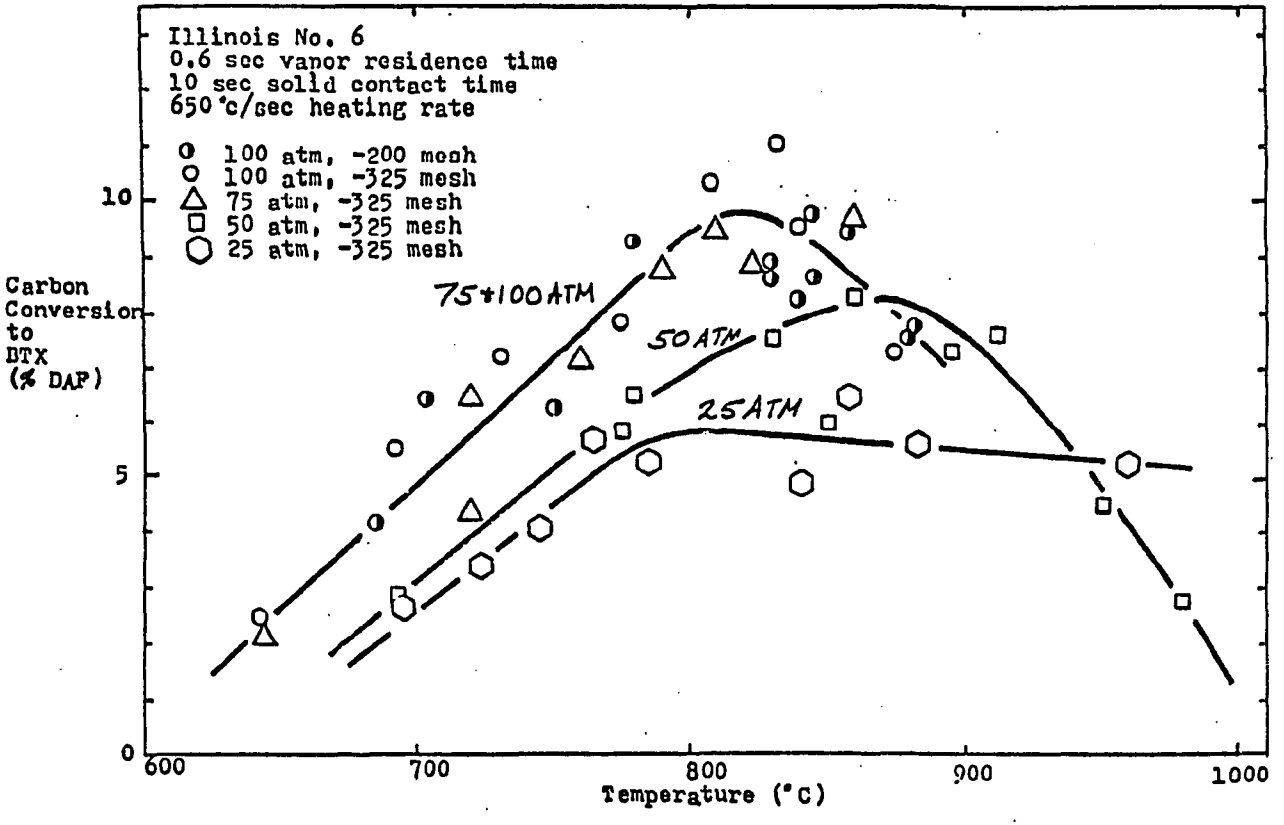


Figure 4.4.4. Effect of Pressure on BTX Yields

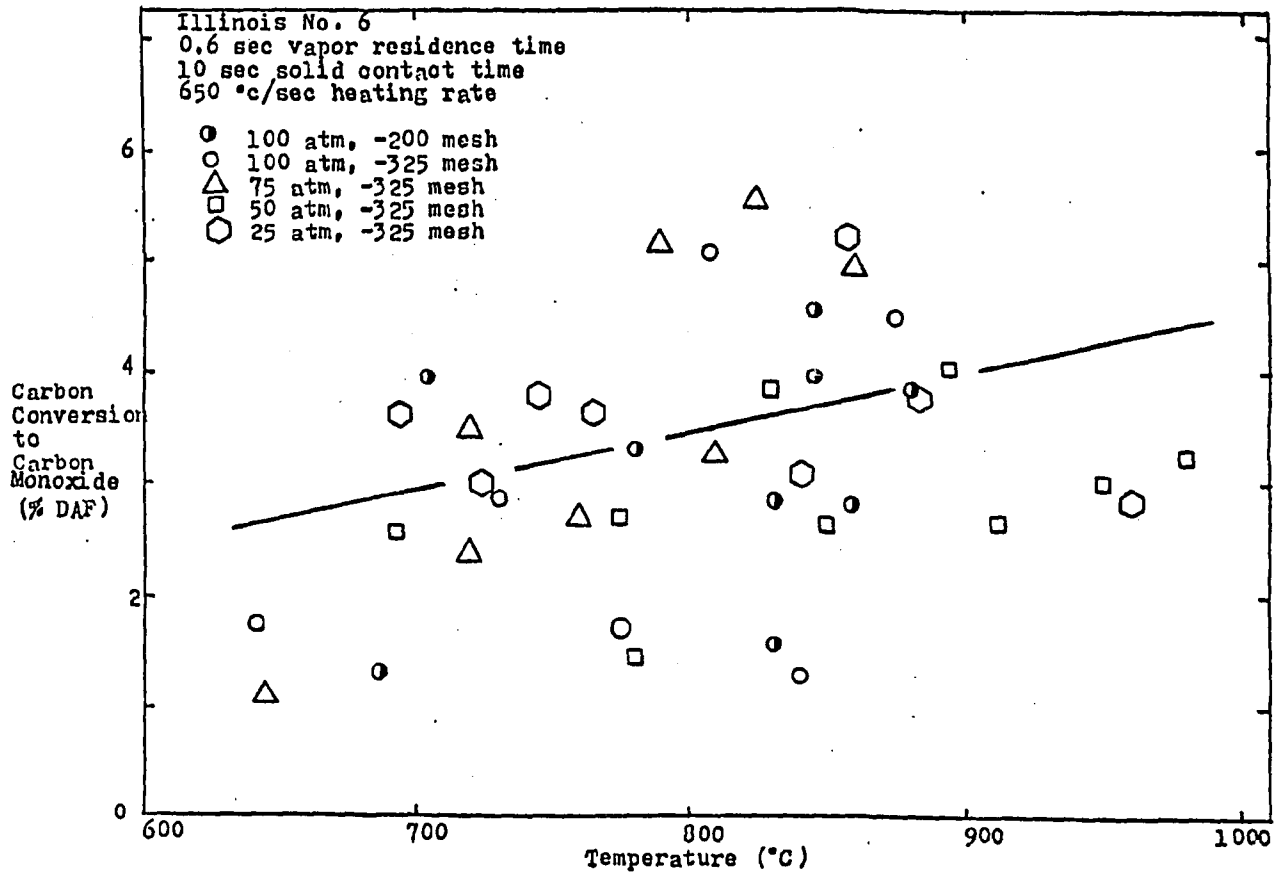


Figure 4.4.5. Carbon Monoxide Yields Determined at Various Pressure

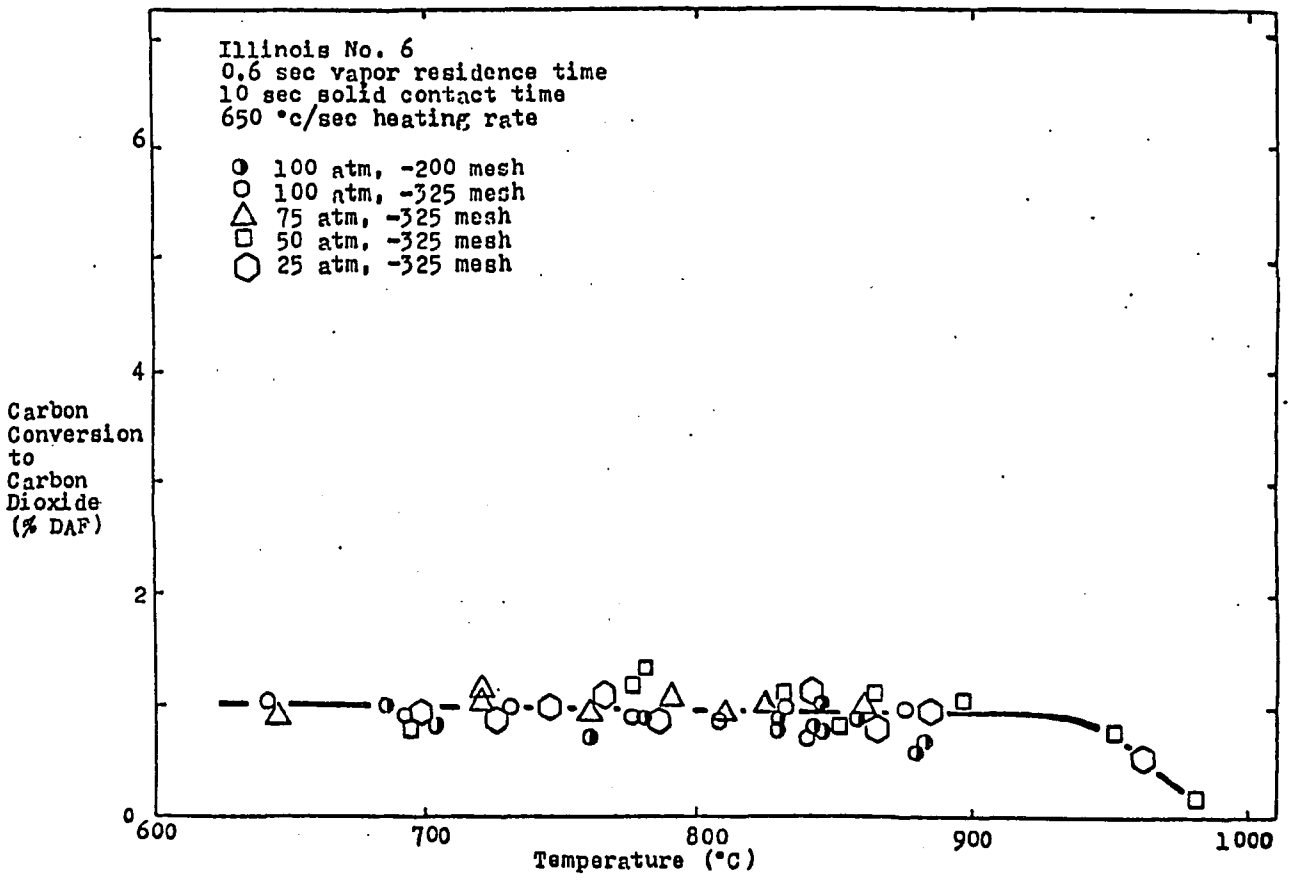


Figure 4.4.6. Carbon Dioxide Yields Determined at Various Pressures

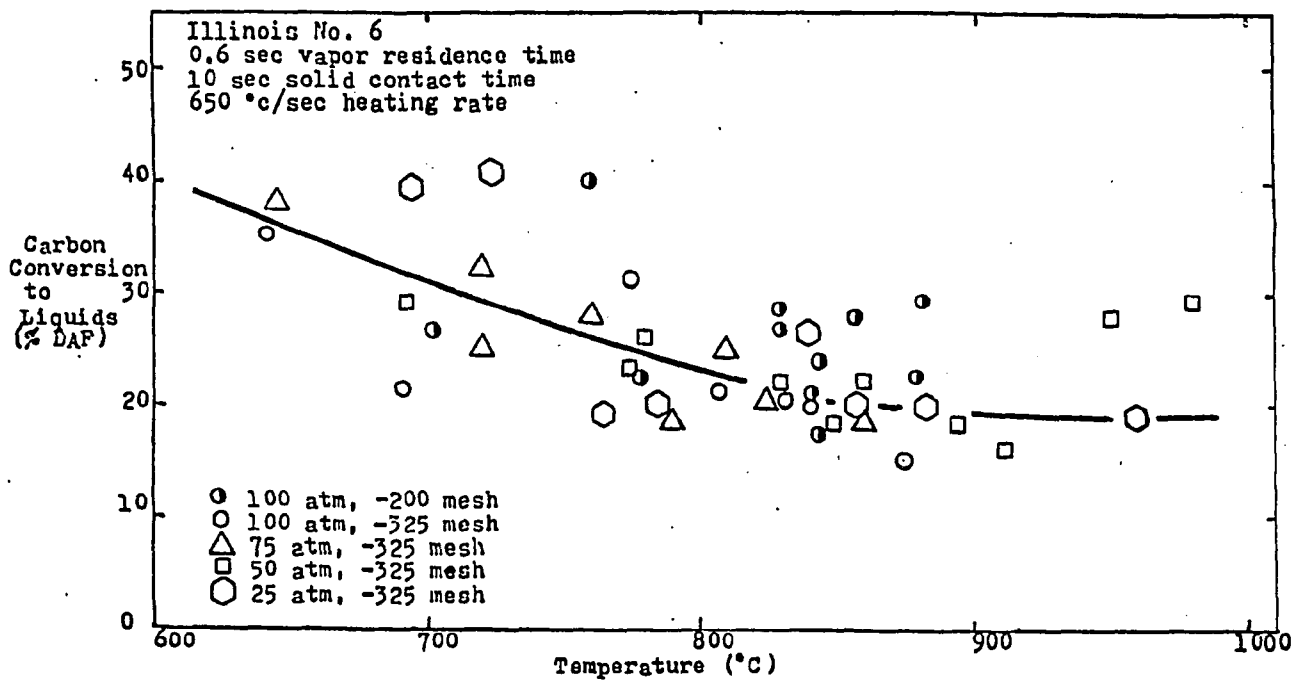


Figure 4.4.7. Heavy Liquid Yields Determined at Various Pressures

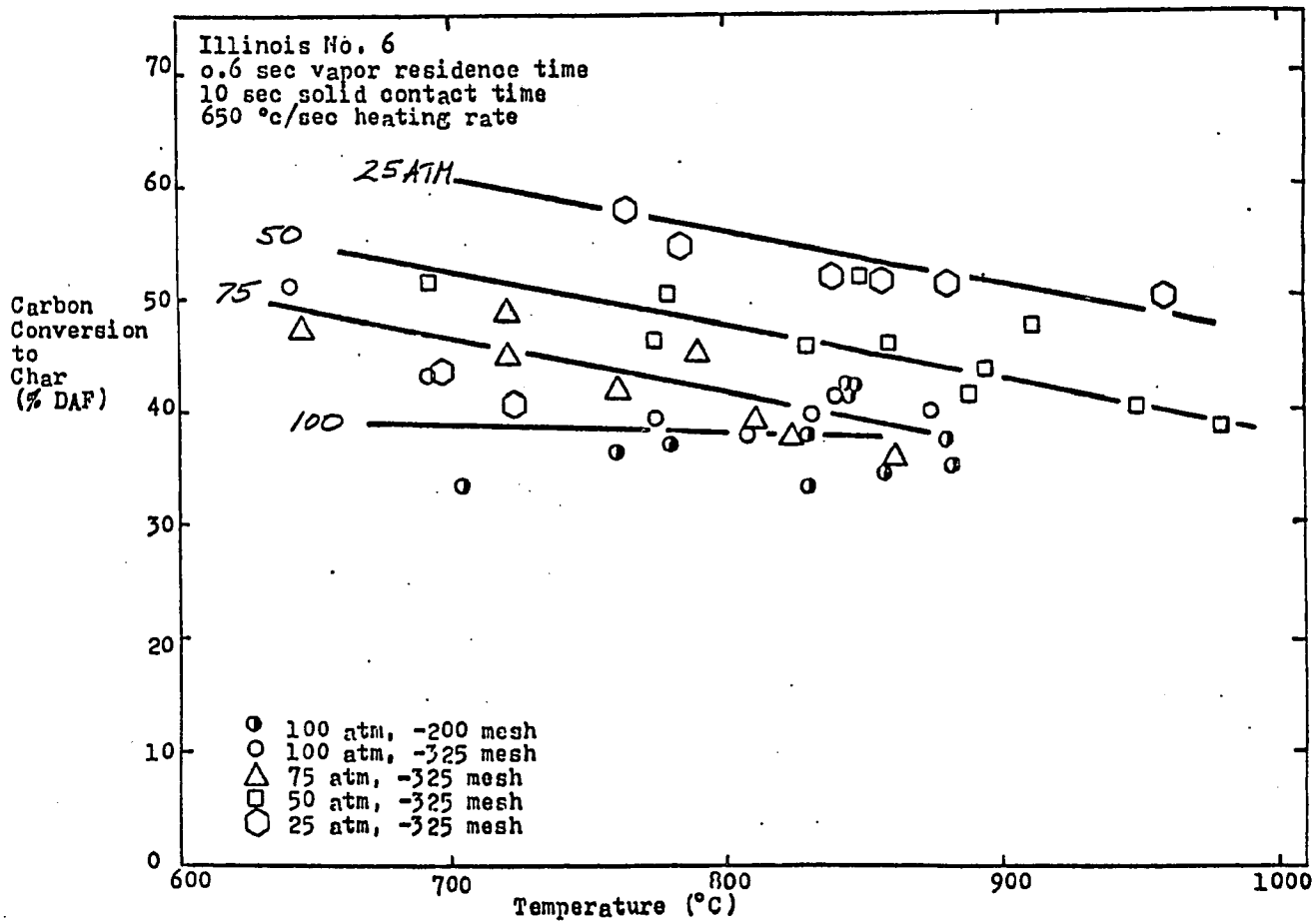


Figure 4.4.8. Effect of Pressure on Char Yield

dehydrogenation process and the latter consumes hydrogen. Therefore, the above factors combine in complex ways to produce either enhanced or reduced BTX yield at high temperature and pressure.

3. No significant pressure effect was found for CO and CO_2 yields. This is probably due to the weak oxygen bonds in the coal. Carbons are usually among the first products to be evolved upon slow heating of coal (Campbell and Stephens, 1976). The large scattering of CO yield is a result of the complex solution of a set of equations where CO is the final component in the calculation of experimental data.
4. The heavy liquid yields at various pressures are shown in Figure 4.4.7. No large pressure effect is evident. Similar to BTX, it presumably has a lower evolution rate. Intraphase mass transfer has two opposite effects on heavy liquid yield:

   · Higher pressure reduces evolution rate and therefore allows more time for reaction to char or light species.

   · Higher hydrogen pressure certainly enhances the stabilization of free radicals. The diffusion of hydrogen into coal is a most important factor in this process, but unfortunately, it is not well characterized at present.

The analyses of experimental data at high pressure for yields of intermediates are usually complex. They involve vapor phase reactions, intraphase and interphase mass transfer. The free radical chain reaction is also complex;

hydrocracking and recombination to polymeric materials are the two major reactions. At low pressure and temperature, higher yields of heavy liquids can be obtained because the mass transfer effect is small.

5. The char yield decreases with increasing temperature at all pressure levels, implying that high temperature enhances both hydrocracking of coal to heavy liquids and stabilization of those species. Since both hydrocracking and free radical stabilization consume hydrogen, the char yield decreases with increasing hydrogen pressure.

4.4.2 Effect of Methane in Hydrogen

Hydrogenation of Illinois No. 6 coal with a 25% methane and 75% hydrogen gas mixture was carries out at 100 atm total pressure, 0.6 sec vapor residence time, 10 sec solid contact time, 650°C/sec heating rate and 700 to 900°C experimental data are shown in Figures 4.4.9 to 4.4.12. These data are compared with the experimental results carried out at 75 atm hydrogen pressure reported in section 4.4.1 and represented by solid lines in Figure 4.4.9 to 4.4.12. The results indicate

- the char yield is increased about 10% (of original daf carbon) at high temperature,
- BTX yield suppressed,
- ethane, propane and carbon oxide yields are unaffected.

The methane yield could not be determined in these runs because of the large amount of methane in the gas supplied. Since heavy liquids are usually determined by the carbon deficit, their yield also could not be calculated.

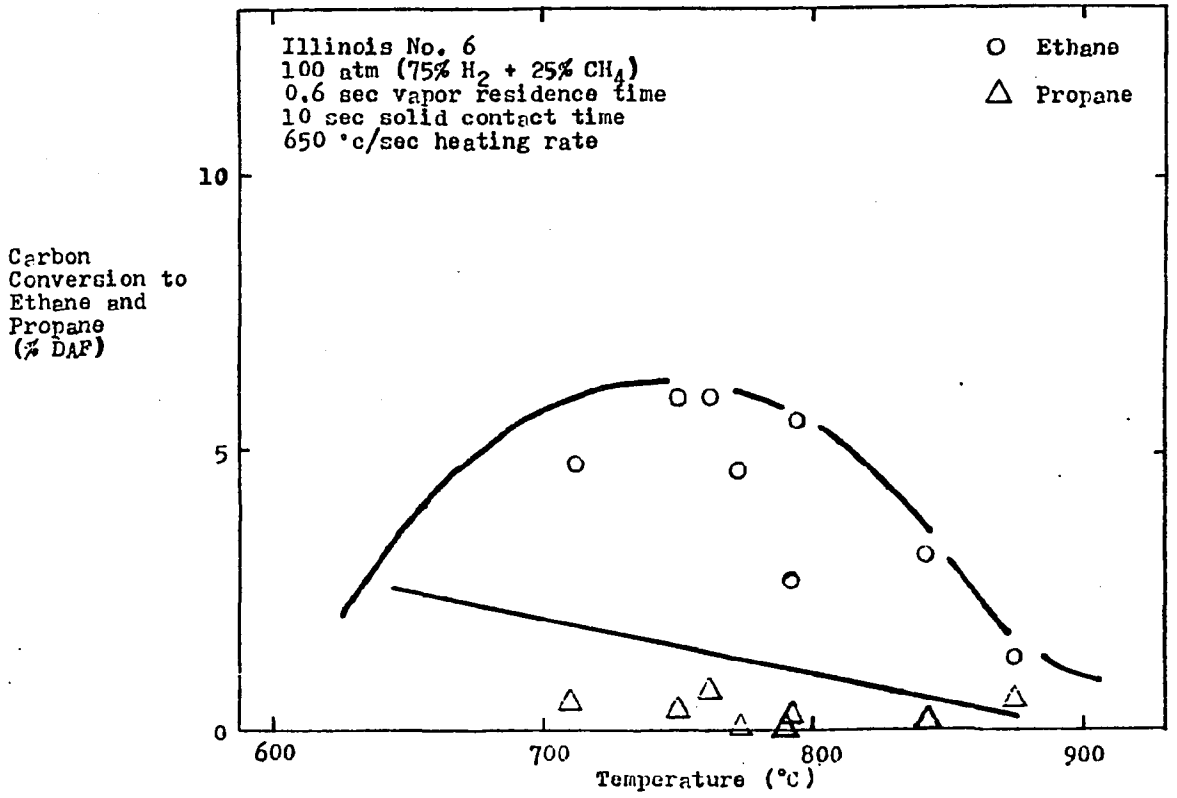


Figure 4.4.9. Ethane and Propane Yields from Coal Hydrogenation with a Hydrogen and Methane Mixture.

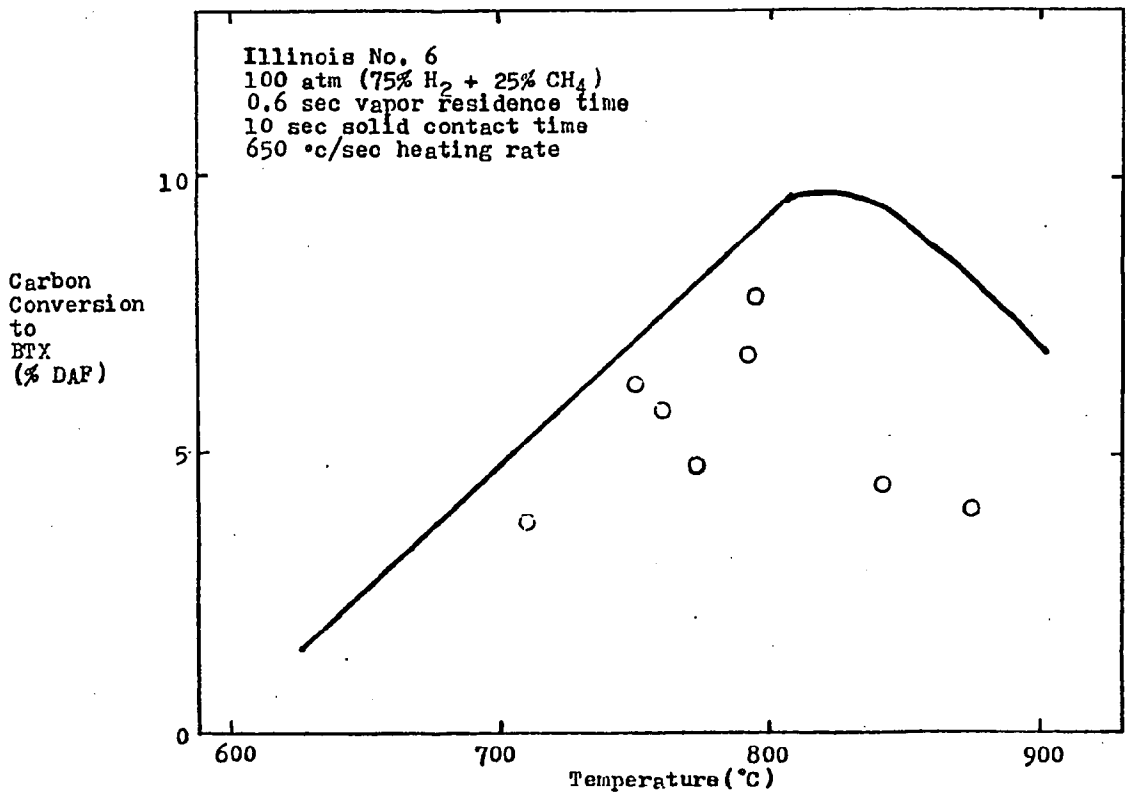


Figure 4.4.10. BTX Yield from Coal Hydrogenation with a Hydrogen and Methane Mixture.

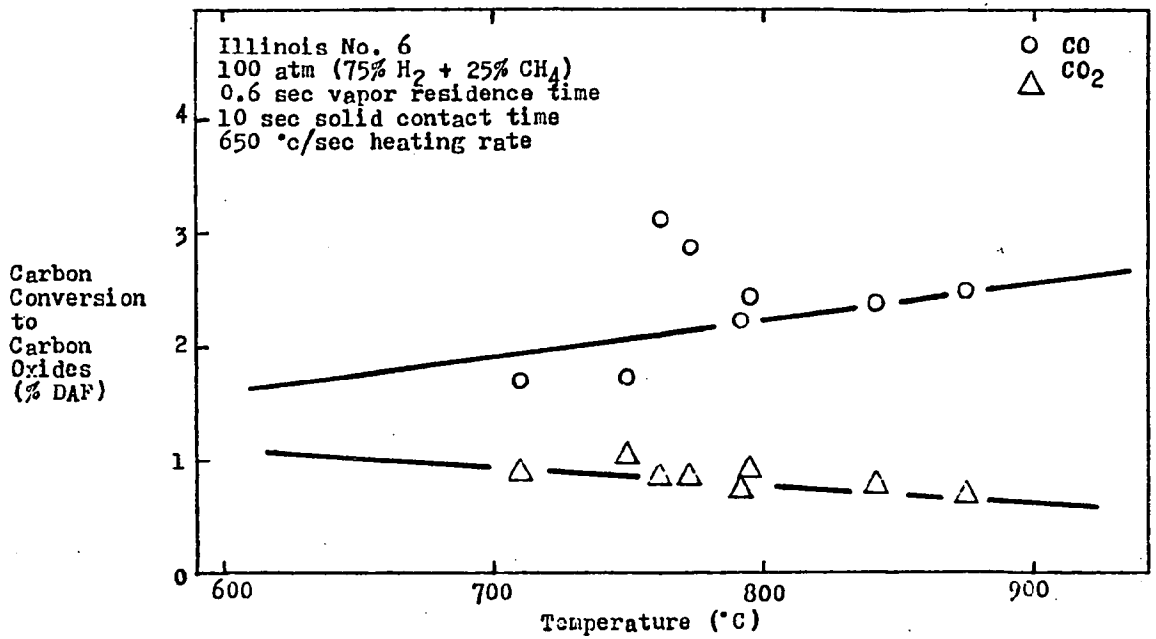


Figure 4.4.11. Yields of Carbon Oxides from Coal Hydrogenation with a Hydrogen and Methane Mixture.

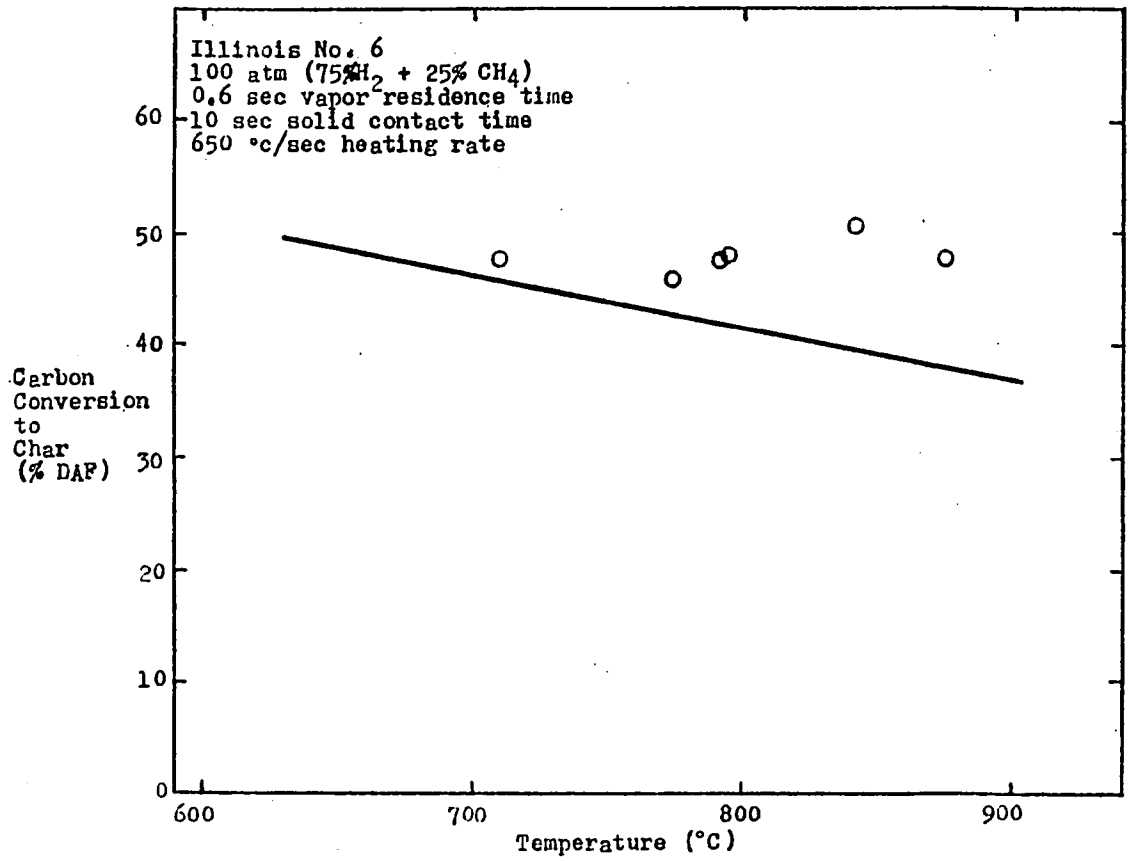
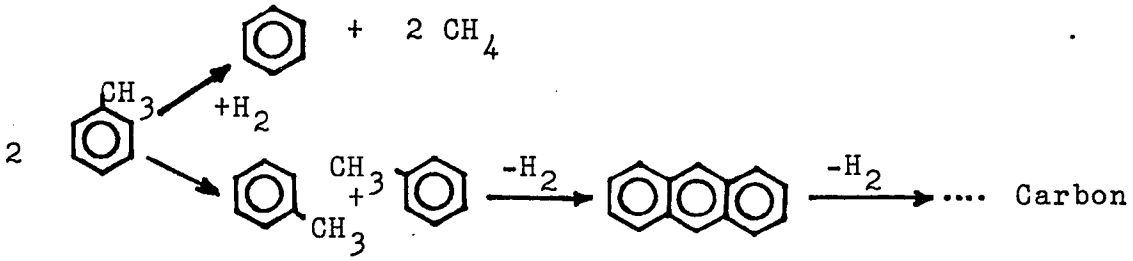


Figure 4.4.12. Char Yield from Coal Hydrogenation with a Hydrogen and Methane Mixture.

The increased carbon observed as char at high temperatures may result from either the deposition of volatiles or the decomposition of methane. Since BTX yield is suppressed at high temperature, carbon deposition may be the major source. Hydrogen's role in carbon formation may be as follows:



This mechanism indicates that lower hydrogen partial pressure favors aromatics formation, and therefore the carbon formation. The internal char surface may provide active sites for this reaction. In addition, the reactor surface may also catalyze carbon formation.

The absorption of methane and H_2 in Illinois No. 6 coal was recently studied by Yang and Liu (1979) at near atmospheric pressure, 17°C, and with 178 to 249 μm particle size and 30 min absorption time. They found about 0.05 c.c./mg-coal of gas was absorbed. This is equivalent to 2×10^{-9} g-mole/mg-coal absorption and it is not a significant quantity for our 10 mg samples. However, their data depend strongly on pressure; the absorption of methane at our high pressure and temperature experiments can be much higher than the results obtained by Yang and Liu. On the other hand, our oxidation was performed at 5 atm oxygen pressure, the methane absorbed the char during hydrogenation can be assumed completely desorbed before oxidation. Therefore, the carbon contribution from methane absorption in the char can be neglected.

Although methane yield could not be determined in our experiment, its yield may be reduced according to the above analysis because:

1) Methane is consumed in the carbon formation, and

2) BTX produces less methane during hydrocracking,

Tar is intermediate in two reactions -

$$\text{coal} \xrightarrow{+H_2} \text{tar} \xrightarrow{+H_2} \text{light species}$$

$$\text{BTX} \xrightarrow{-H_2} \text{tar} \xrightarrow{-H_2} \cdots\cdots \xrightarrow{-H_2} \text{pure carbon}$$

therefore, it is not possible to preduct methane yield with existing data.

4.4.3 Effect of Carbon Monoxide in Hydrogen

Experiments were carried out with a gas mixture containing 75% H_2 and 25% CO. The primary interest of this study is to investigate the effect of CO which would be present in recycle hydrogen and in two-stage reactors where hydrolysis of char in the first stage provides hydrogen-rich gas for coal hydrogenation in the second stage. Illinois No. 6 coal, sample B, (see Table 4.4.1) was tested at 100 atm total pressure, 0.6 sec vapor residence time, 10 sec solid contact time and 650°C/sec heating rate.

The experiments, however, suffered from several instrumental and operating limitations:

1) large amounts of CH_4 and carbon deposition resulted from Fischer-Tropsch reactions, and

2) CO in the gas stream saturated the peak of mass 28 and in mass spectrometry therefore precluded the analyses of gases which had mass fractions 28 and 29. These components include C_2H_6, C_3H_8, CO and CO_2.

In order to determine the net Fischer-Tropsch yield in our system, runs without a coal sample were carried out. Mass spectrometry indicated that CH_4 is the only product in the analysis up to mass 106. However, the CH_4 data were not quantitatively reproducible probably because of the effect of carbon formed in the tube downstream.

As a result, the only reliable data are the BTX yields shown in Figure 4.4.13. The experimental data is compared with the BTX yield at 75 atm hydrogen pressure, which was discussed in section 4.4.1 and is shown in Figure 4.4.13 with a solid line. It indicates that the BTX yield is suppressed, which may be due to the carbon formation from BTX.

Figure 4.4.14 shows the char yield from coal and (H_2 + CO) reaction. Again, the solid line represents the yield at 75 atm hydrogen pressure which was reported in the last section. It is not clear how much of the increase in char yield is due to the original coal and how much comes from the Fischer-Tropsch reaction.

The thermodynamic calculation of carbon formation by Fischer-Tropsch reactions is generally considered to be determined by equilibrium of the following reactions:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (a)$$

$$3H_2 + CO \rightleftarrows H_2O + CH_4 \qquad (b)$$

$$H_2O + C \rightleftharpoons H_2 + CO \qquad (c)$$

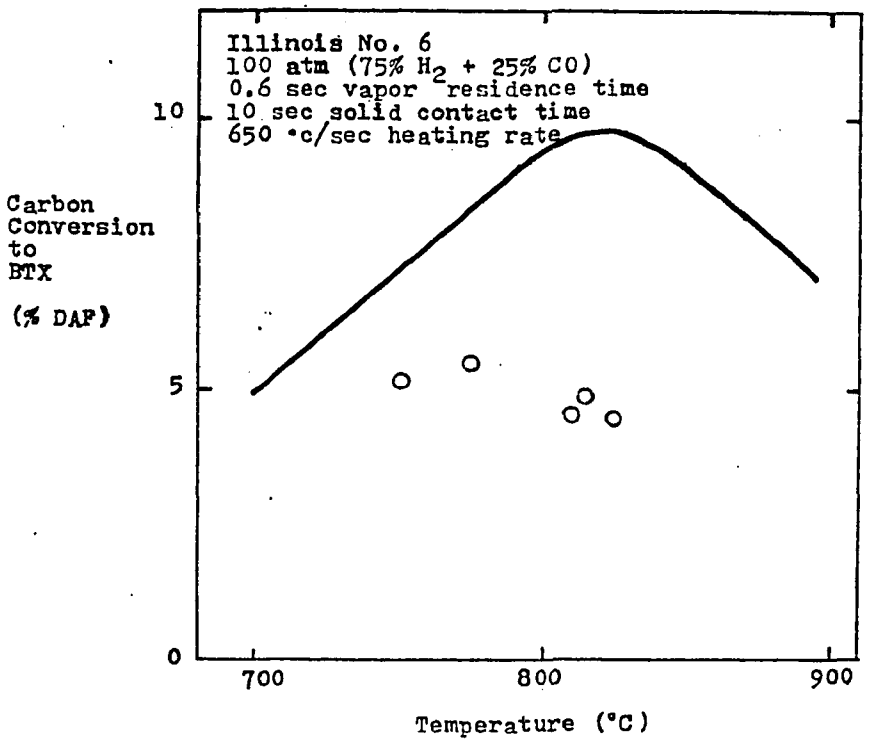


Figure 4.4.13. BTX yield from coal hydrogenation with H_2 and CO mixture.

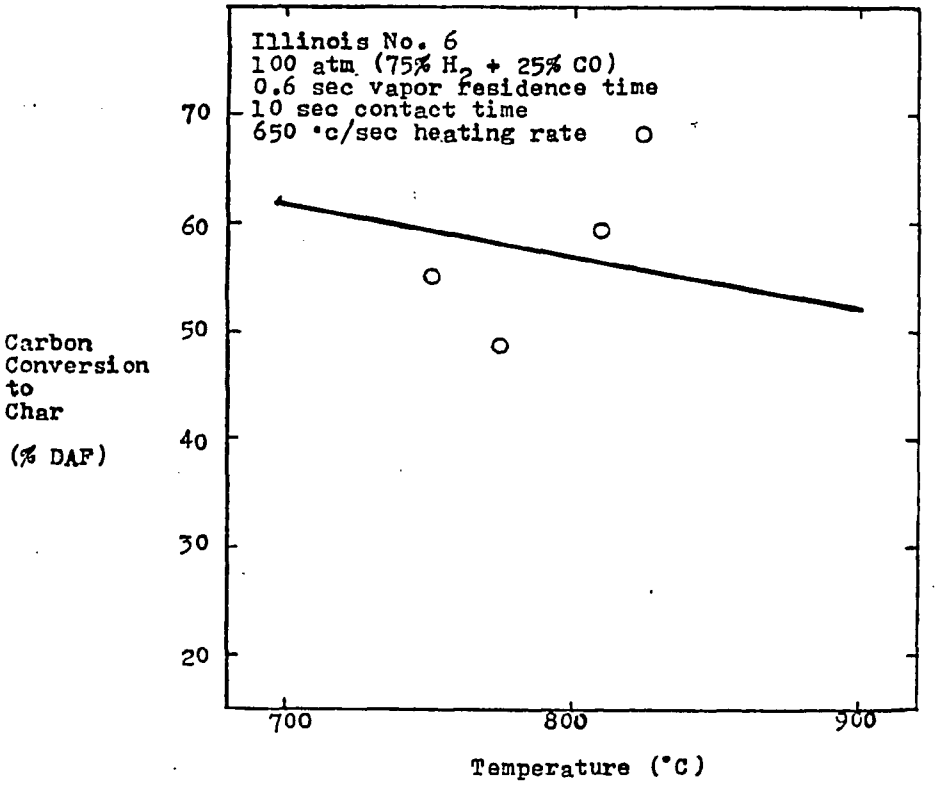


Figure 4.4.14. Char yield from coal hydrogenation with H_2 + CO mixture.

However, at conditions where the residence time is short and kinetic limitations prevent these reactions from proceeding to equilibrium, such thermodynamic predictions are tenuous. Reaction (b) predicts that about 11% of the original gas mixture ($CO + 3H_2$) can be converted to CH_4 and H_2O at equilibrium at 100 atm and 800°C. Experimental yields, on the other hand, show only 0.1% conversion.

Two mechanisms of carbon formation from benzene have been proposed. One involves the breakage of the benzene ring to $C_4H_3^{\cdot}$ and $C_2H_3^{\cdot}$ followed by addition of $C_4H_3^{\cdot}$ converting benzene to napthalene, to anthracene or phenanthrene, etc. (Thompson and Brooks, 1973). Since the breakage of the benzene ring takes a large amount of energy, it is expected to be invalid at low temperatures. Another model proceeds through diphenyl as the intermediate (Thompson and Brooks, 1973; Kinney and Delbel, 1954; Virk, et al., 1974). The role of CO in the carbon formation from BTX remains an interesting subject for study.

We also carried out several runs with 75% CO and 25% H_2 as reacting gas. Excessive carbon formation prevented the collection of consistent data. This is expected because the stoichiometry ($CO:H_2 = 3:1$; the previous experiment with $CO:H_2 = 1:3$) favors the carbon formation reaction (c) mentioned above, instead of the methanation reaction (b).

4.5 Hydrogenation with Additives

4.5.1 Promotion with Metallic Hydrides

While the details of the interaction of hydrogen with coal and volatiles in providing enhanced yields of light products in flash hydrogenation are not known, we speculate that hydrogen atoms may

be more effective in these processes than hydrogen molecules. Thermal decomposition of metallic hydrides can provide a convenient source of hydrogen atoms in experimental work.

Because of their ready availability, the hydrides of sodium and titanium were used for a few quick exploratory trials. At 100 atm, the decomposition temperature (calculated from the JANAF tables, Dow Chemical Co., 1962) of NaH is 637°C and of TiH_2 1173°C. TiH_2 and possibly NaH are hydrogenation catalysts at lower temperatures. For these trials, the reactor charge was made up of approximately equal volumes of Pittsburgh No. 8 coal (10 mg) and the hydride. Runs were made in 100 atm of pure hydrogen with a heating rate of 650°C per second and a vapor residence time of 0.6 seconds. To provide a direct comparison, runs with the hydride were interspersed with runs containing no additive; twenty-three runs were made in all. The results of coal-TiH_2 mixture are shown in Figure 4.5.1 to 4.5.6 and that of coal-NaH mixture are shown in Figure 4.5.7 to 4.5.12.

Pronounced effects with NaH are observed only above about 800°C. The methane yield increases substantially (e.g., rising from 20 to 50% at 810°C.) On the other hand, the BTX yield decreased to half its value. Char yields are lower. The yields of other compounds are not substantially altered.

Rather different results are found with TiH_2. The effects of this compound are observed below 800°C, increasing with decreasing temperature. Species heavier than xylene increase in yield. At 800°C the yield increases from 20 to 30%, at 710°C the increase is from 30 to 50%. This is accompanied by a corresponding decrease in the residual char, but no other yields are affected.

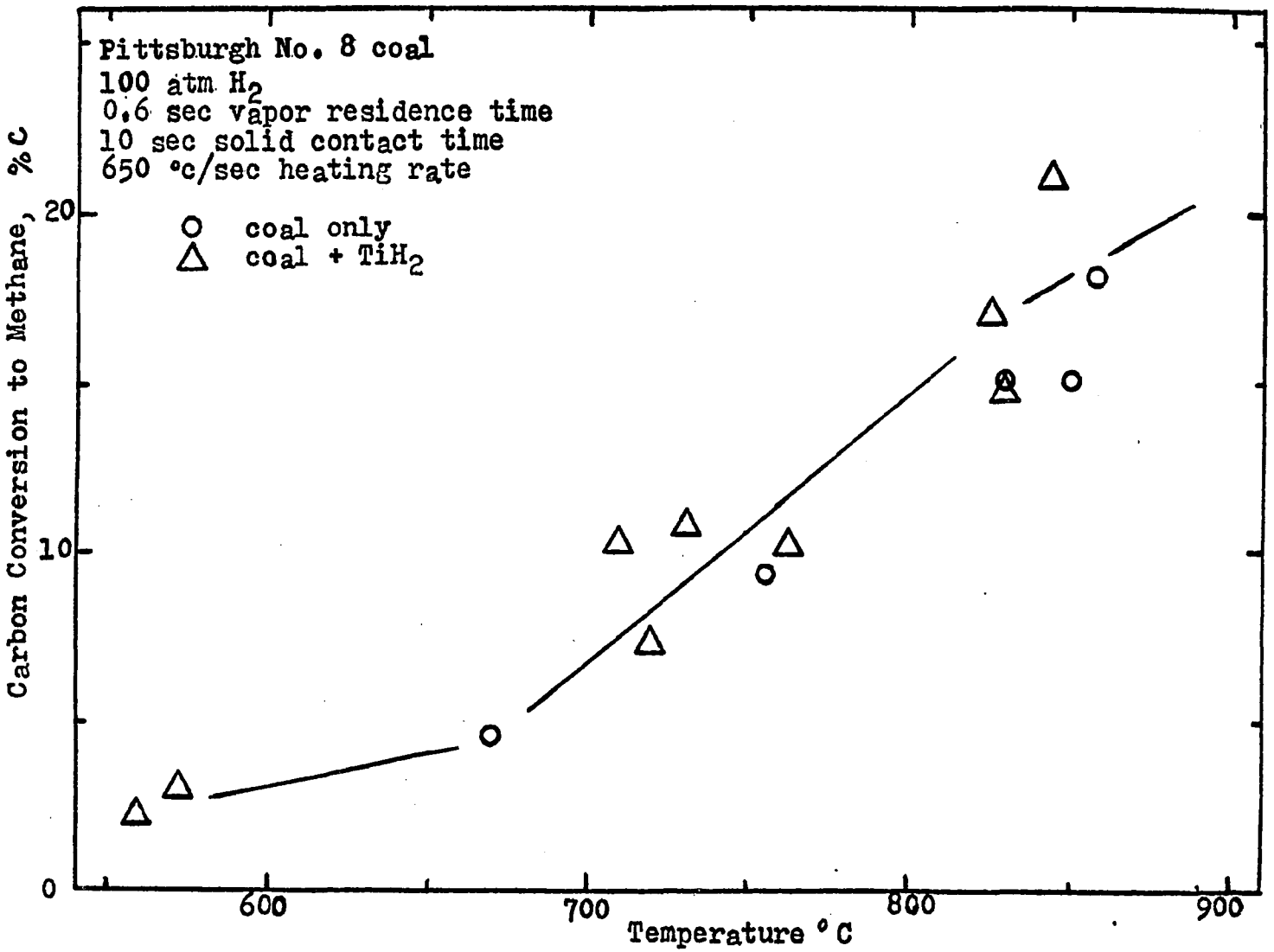


Figure 4.5.1. Methane Yield from Hydrogenation of Coal and TiH_2 Mixture.

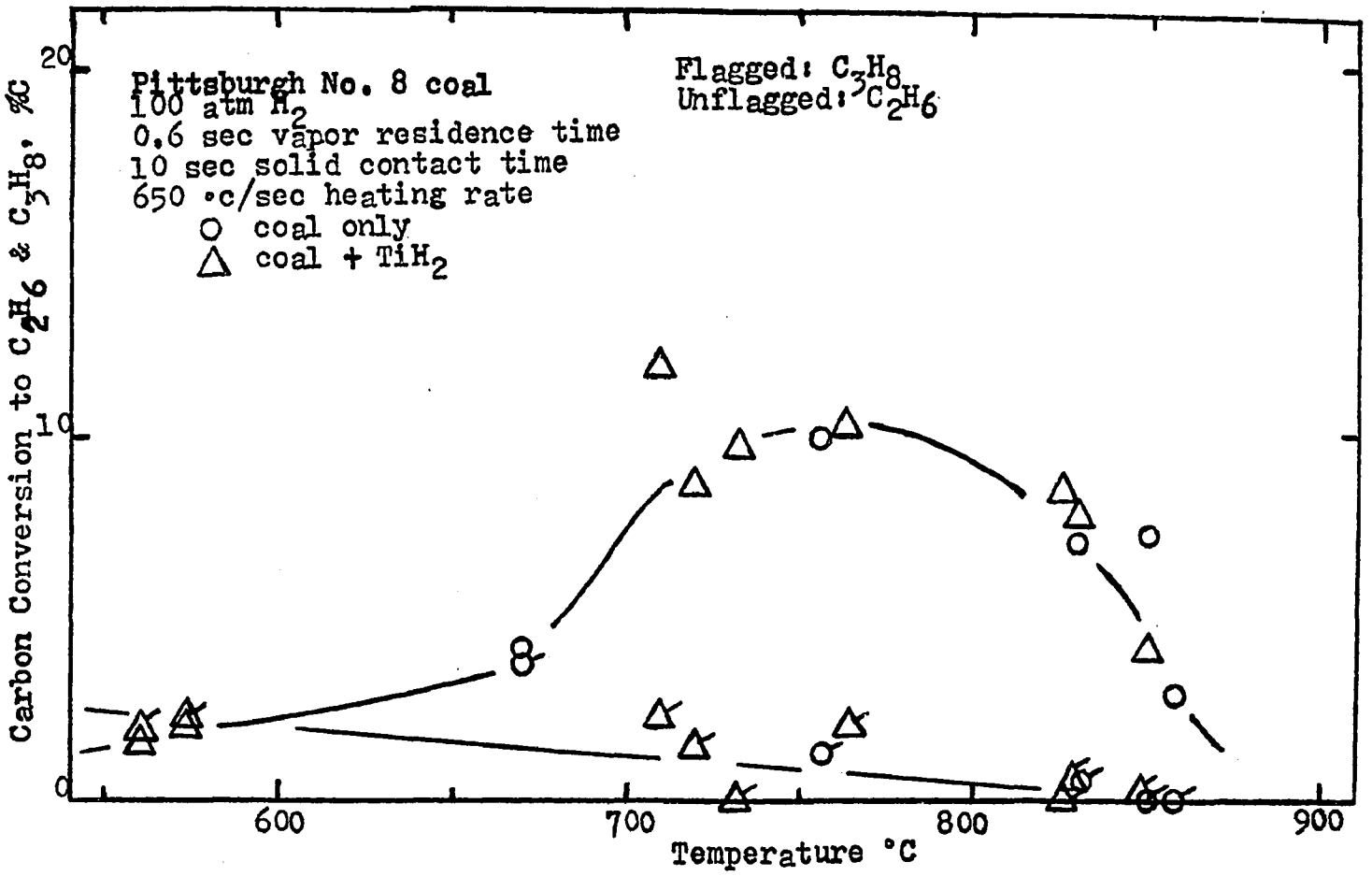


Figure 4.5.2. Ethane and Propane Yields from Hydrogenation of Coal and TiH_2 Mixture.

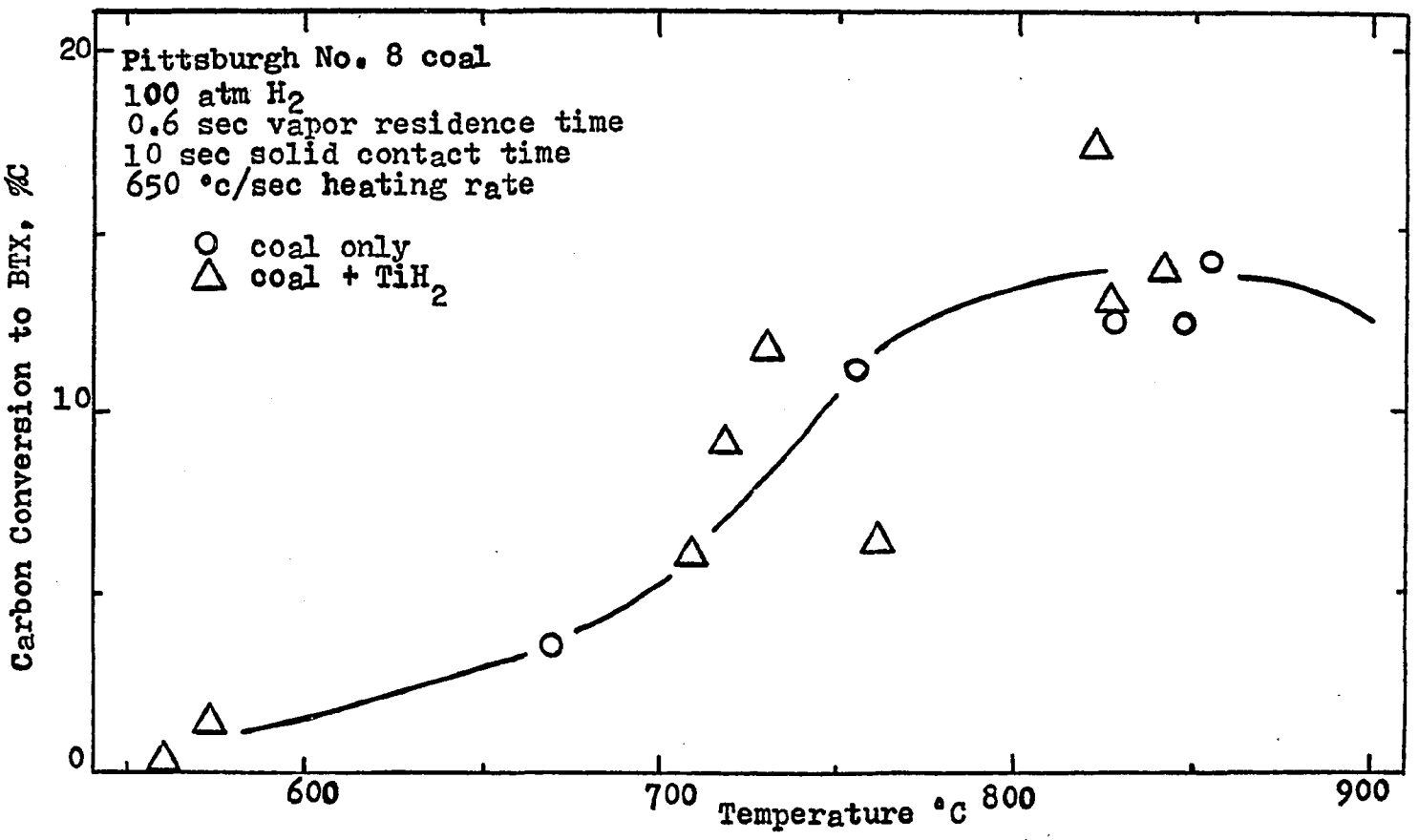


Figure 4.5.3. BTX Yield from Hydrogenation of Coal and TiH_2 Mixtures.

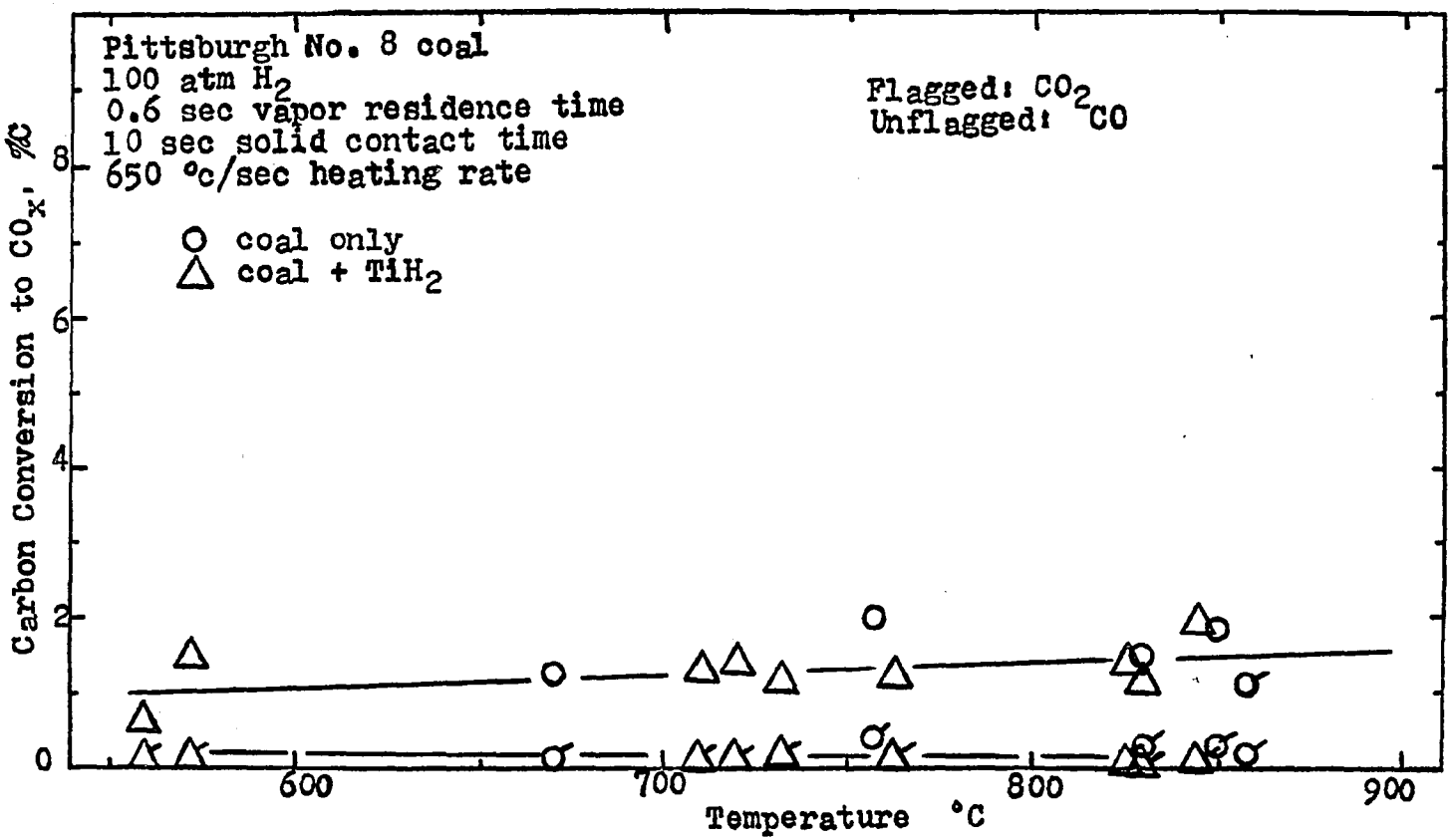


Figure 4.5.4. Yields of Carbon Oxides from Hydrogenation of Coal and TiH_2 Mixtures.

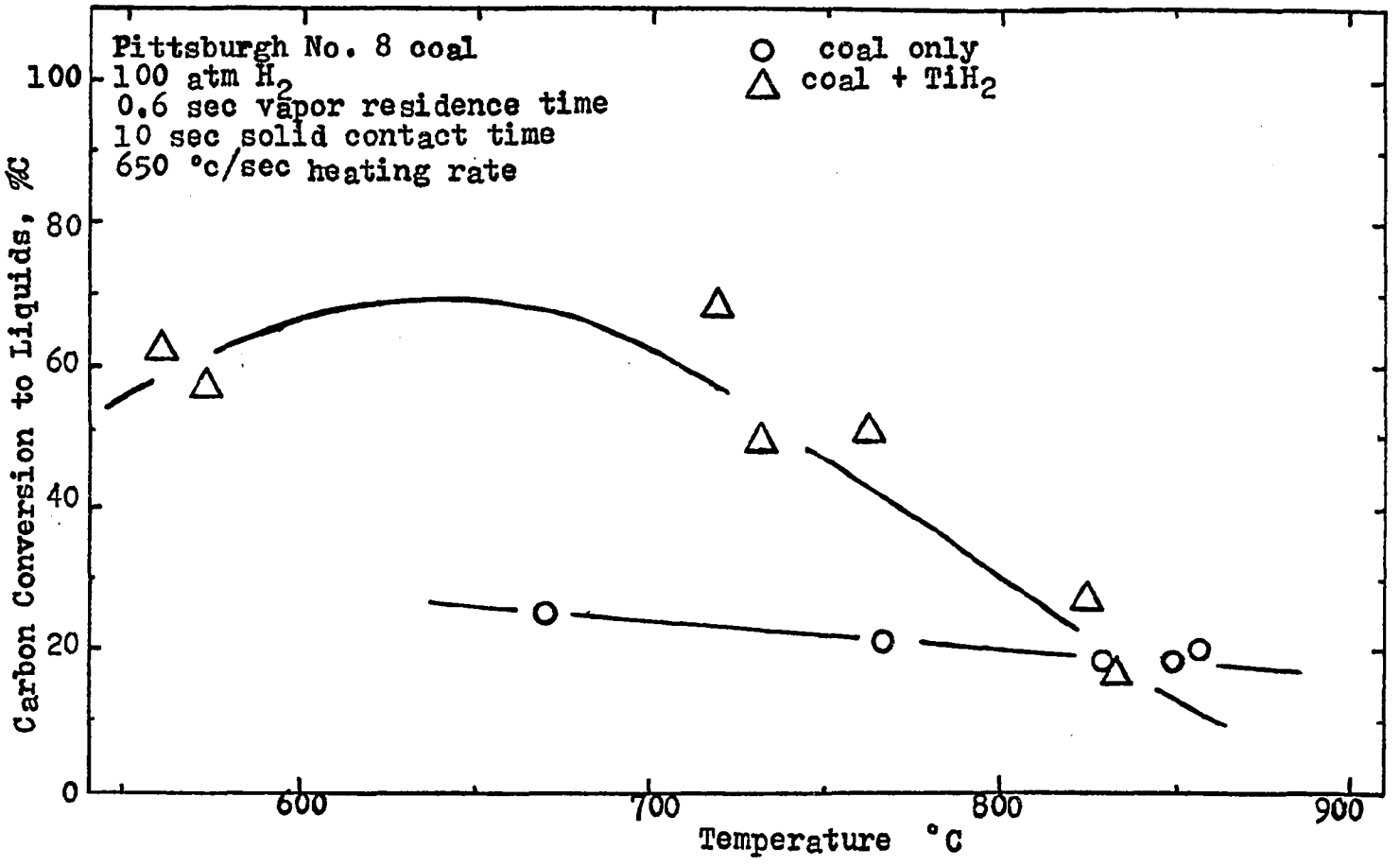


Figure 4.5.5. Liquid Yield from Hydrogenation of Coal and TiH_2 Mixture.

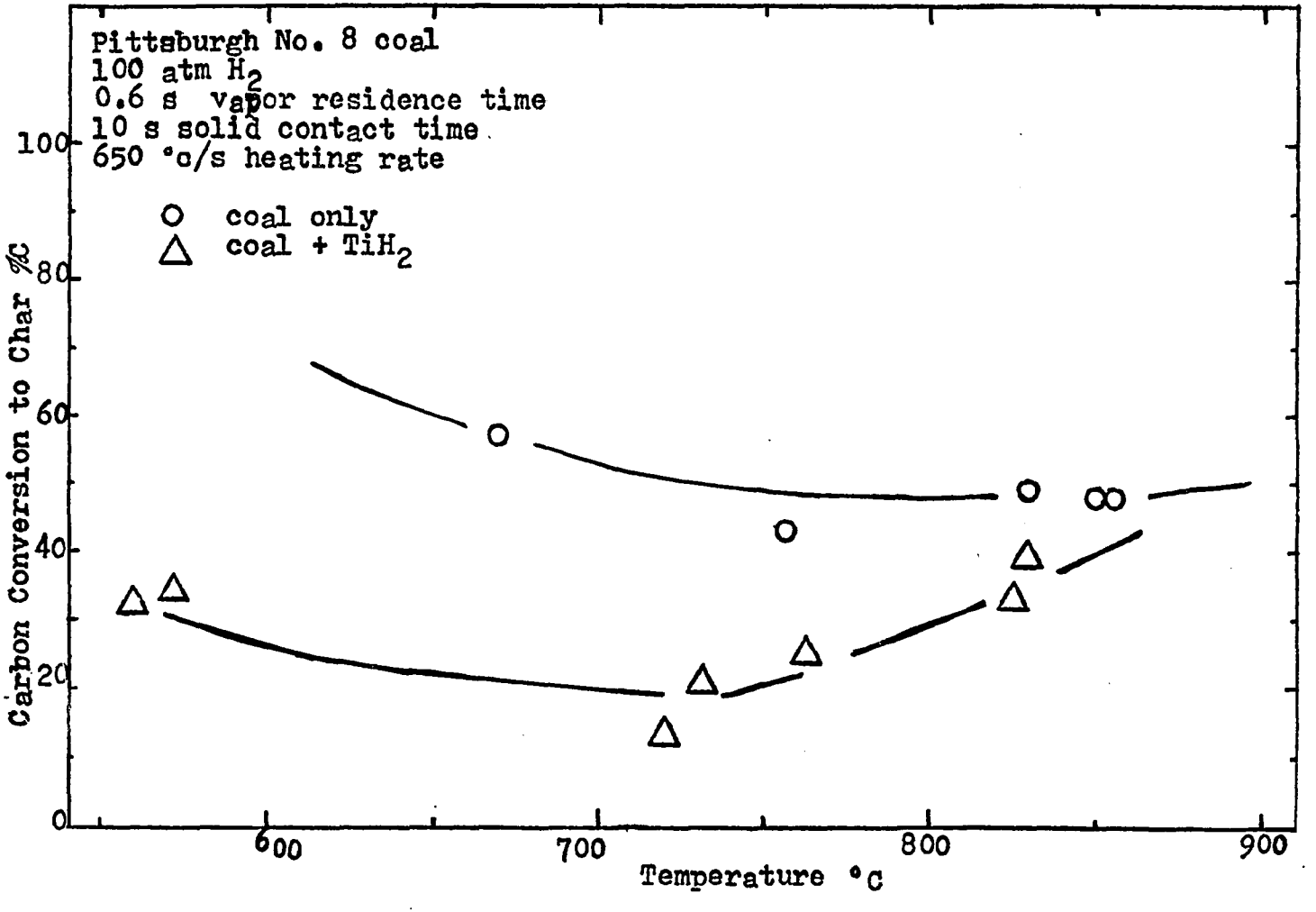


Figure 4.5.6. Char Yield from Hydrogenation of Coal and TiH_2 Mixture.

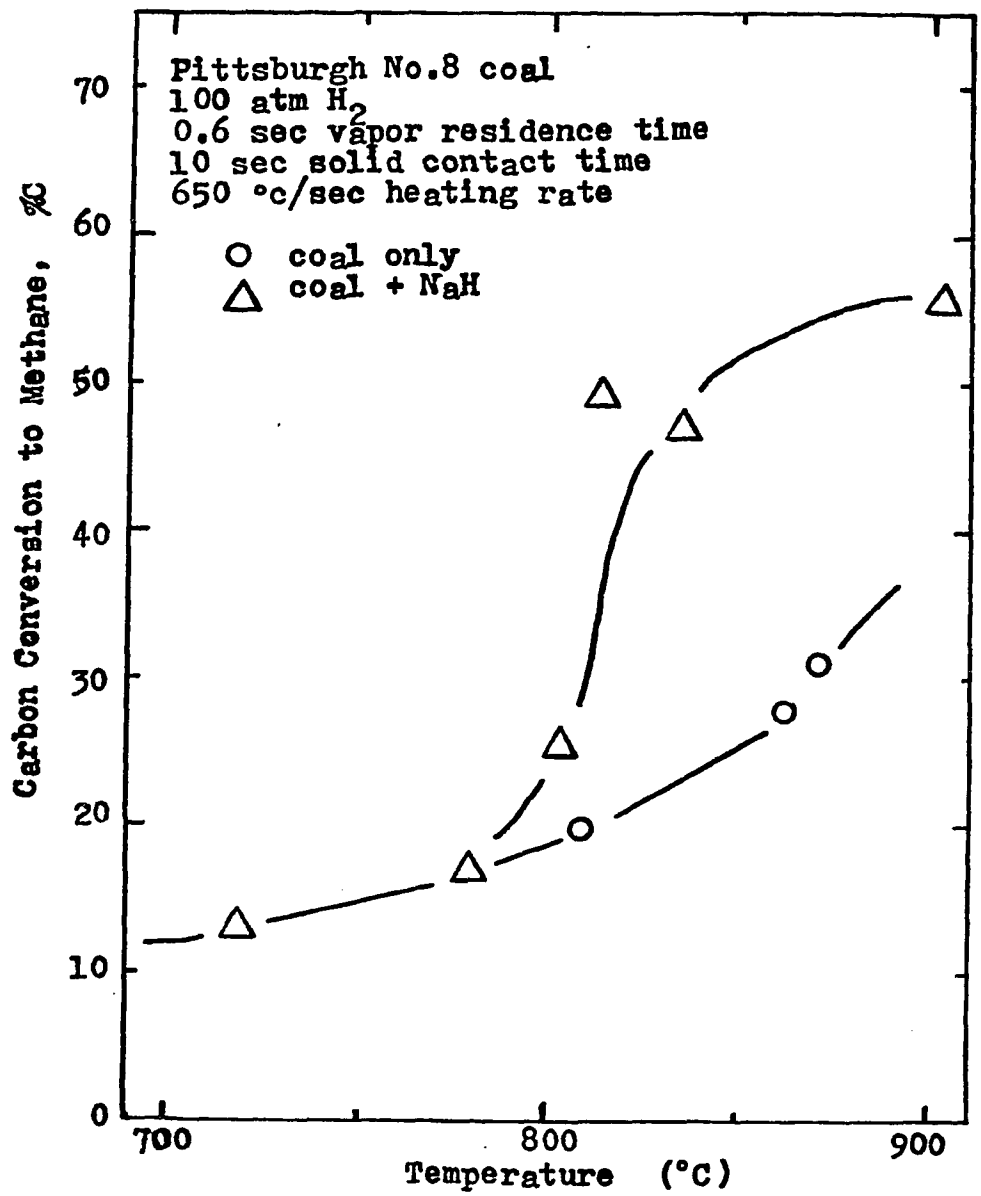


Figure 4.5.7. Methane Yield from Hydrogenation of Coal and NaH Mixture.

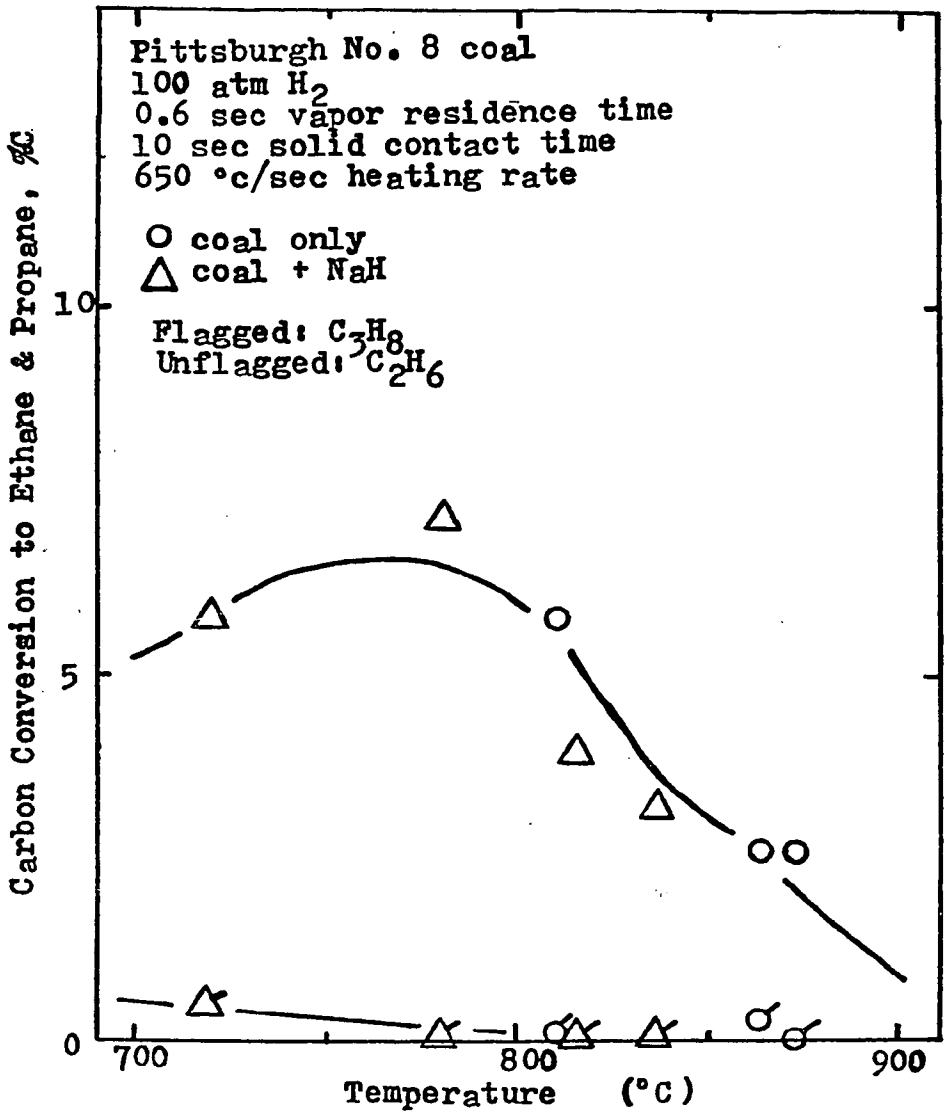


Figure 4.5.8. Ethane and Propane Yields from Hydrogenation of Coal and NaH.

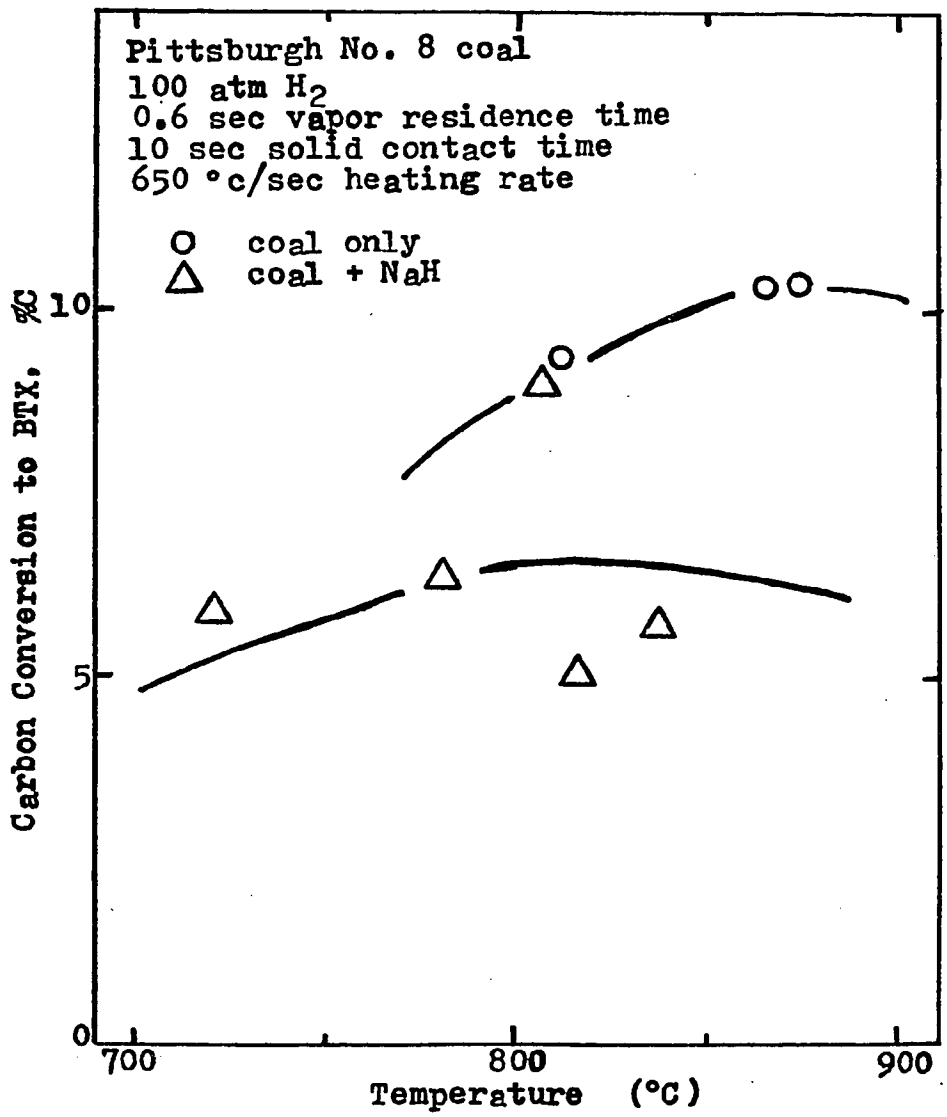


Figure 4.5.9. BTX Yield from Hydrogenation of Coal and NaH Mixture.

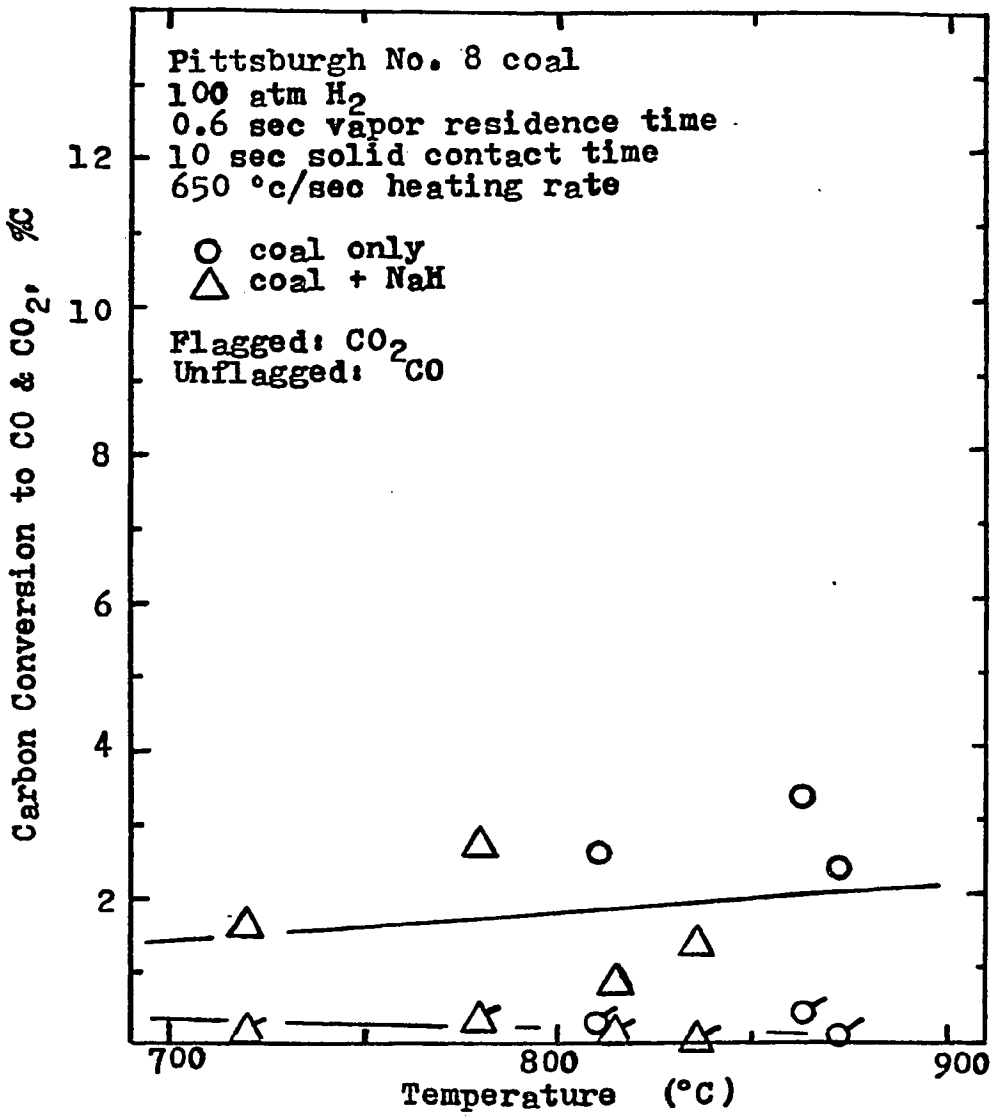


Figure 4.5.10. Yields of Carbon Oxides from Hydrogenation of Coal and NaH Mixture.

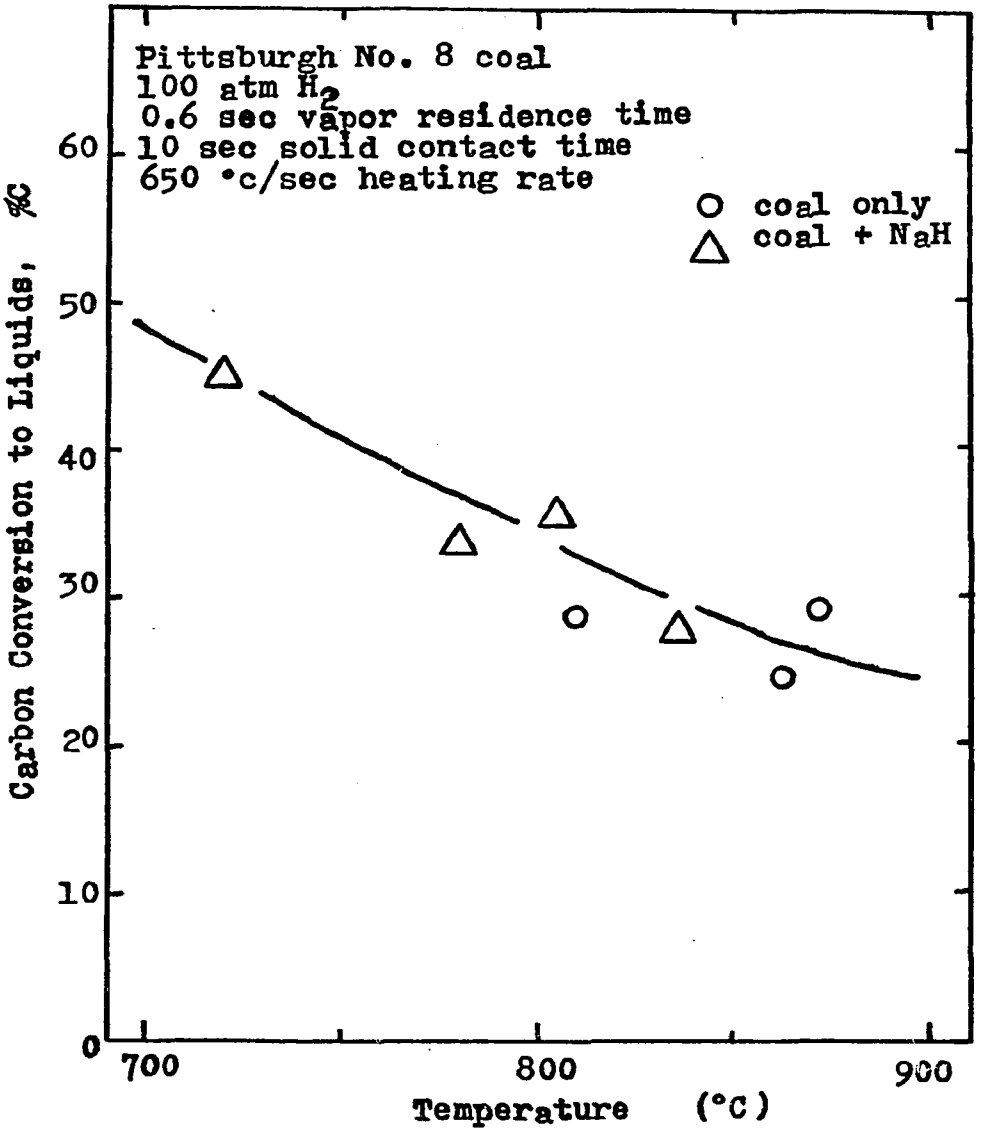


Figure 4.5.11. Liquid Yield from Hydrogenation of Coal and NaH Mixture.

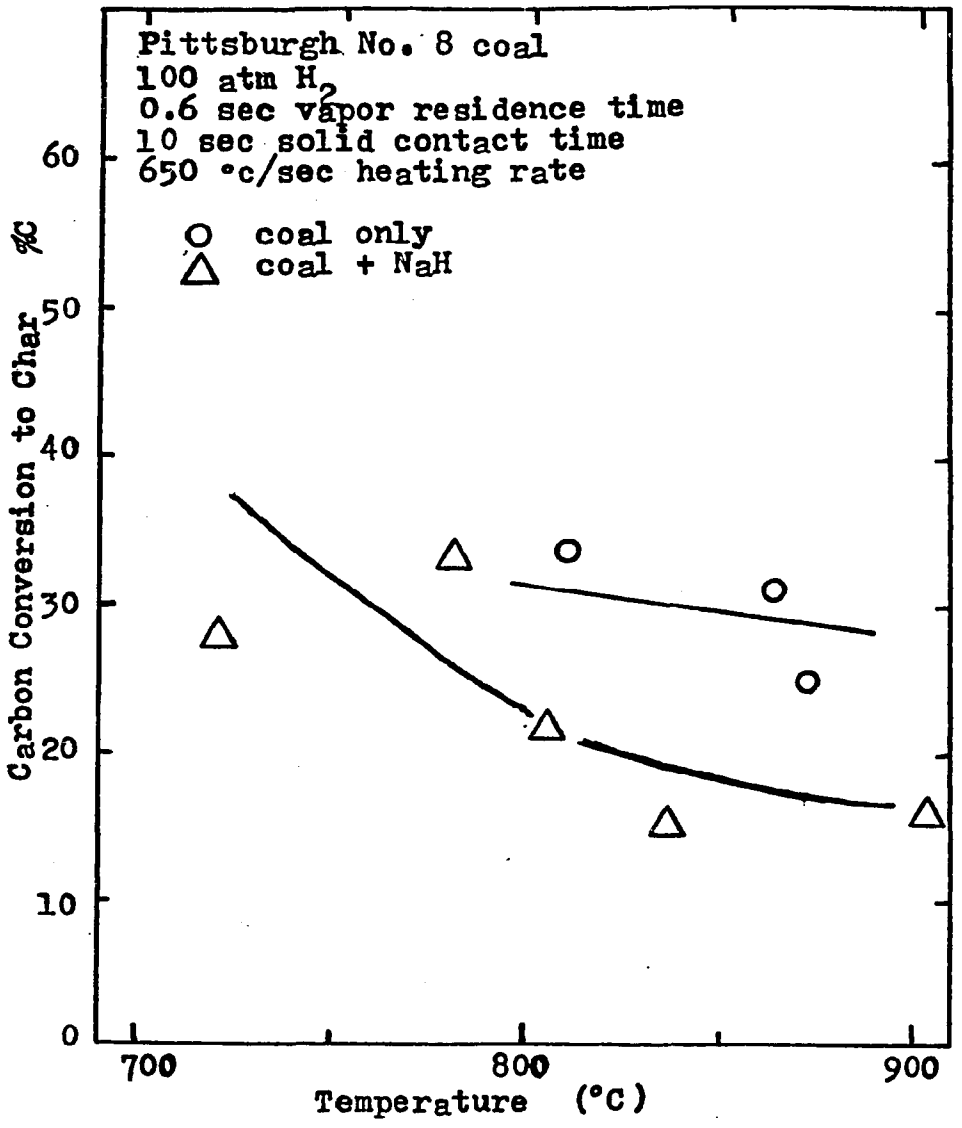


Figure 4.5.12. Char Yield from Hydrogenation of Coal and NaH Mixture.

In view of its high decomposition temperature, TiH_2 is not likely to have undergone dissociation. It appears to be acting as a catalyst which has the power to provide a dramatic increase in liquid yield. The mode of action may be through the hydrocracking of large molecules to more stable smaller species. It is noteworthy that the effect of this catalyst is to increase the selectivity toward liquids at the expense of residual char. Sodium hydride, on the other hand, is likely to have undergone decomposition. The hydrogen atoms it provides appear to react with the decomposing coal, enhancing methanation at the expense of the single ring aromatics.

4.5.2 Hydrogenation of Coal and Kaolin Mixture

In order to reduce coal agglomeration and therefore the secondary reactions of volatiles within a char particle, coal was mixed with kaolin at ratios 2:1, 3:1 and 5:1. Hydrogenation experiments were performed with Illinois No. 6 coal at 100 atm hydrogen pressure, 10 sec solid contact time, 0.6 sec vapor residence time, 650°C /sec heating rate and about 800°C. The results are compared with the similar experiments without kaolin at 100 atm hydrogen pressure which was reported in section 4.4.1. Figure 4.5.13 to 4.5.18 show the differences between these two studies for each component. The solid lines represent the results for hydrogenation of coal alone and the marked points are for mixtures with kaolin. The most interesting result in this set of Figures is the high carbon conversion to volatiles from coal and kaolin mixtures. The increases in yields appear in ethane and liquids, while BTX and CO_X drop slightly and methane and propane remain unchanges. The effects of kaolin dilution is particularly significant at coal to kaolin

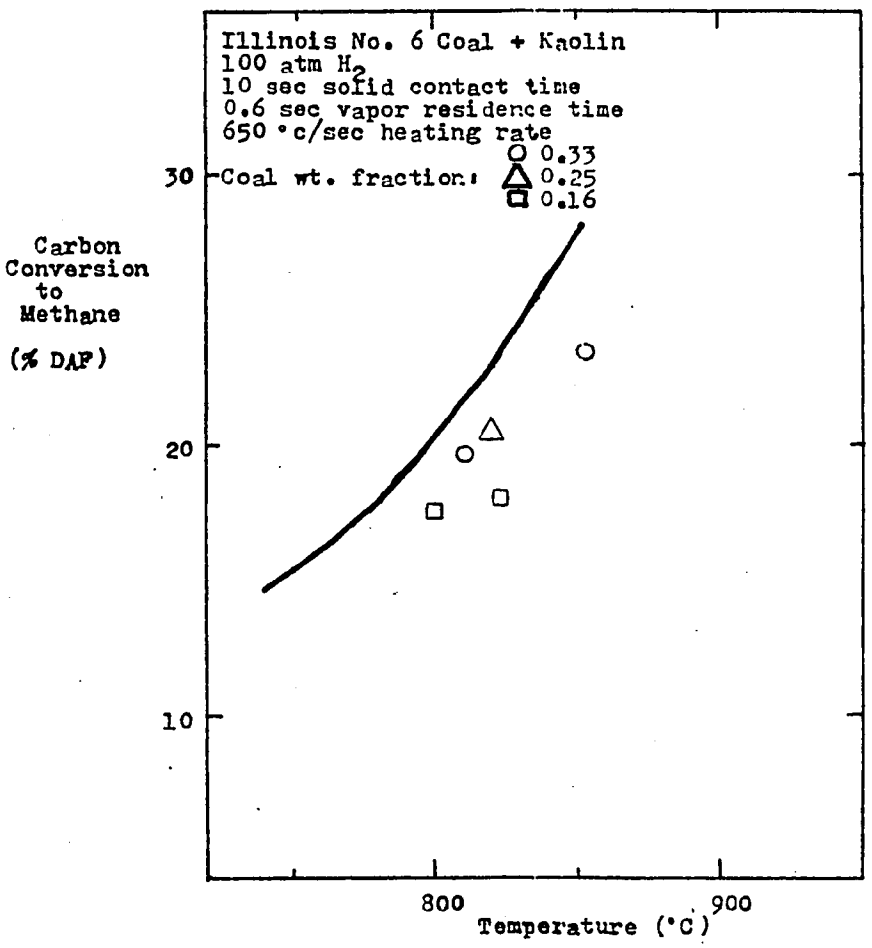


Figure 4.5.13. Methane Yield from Hydrogenation of Coal and Kaolin Mixtures.

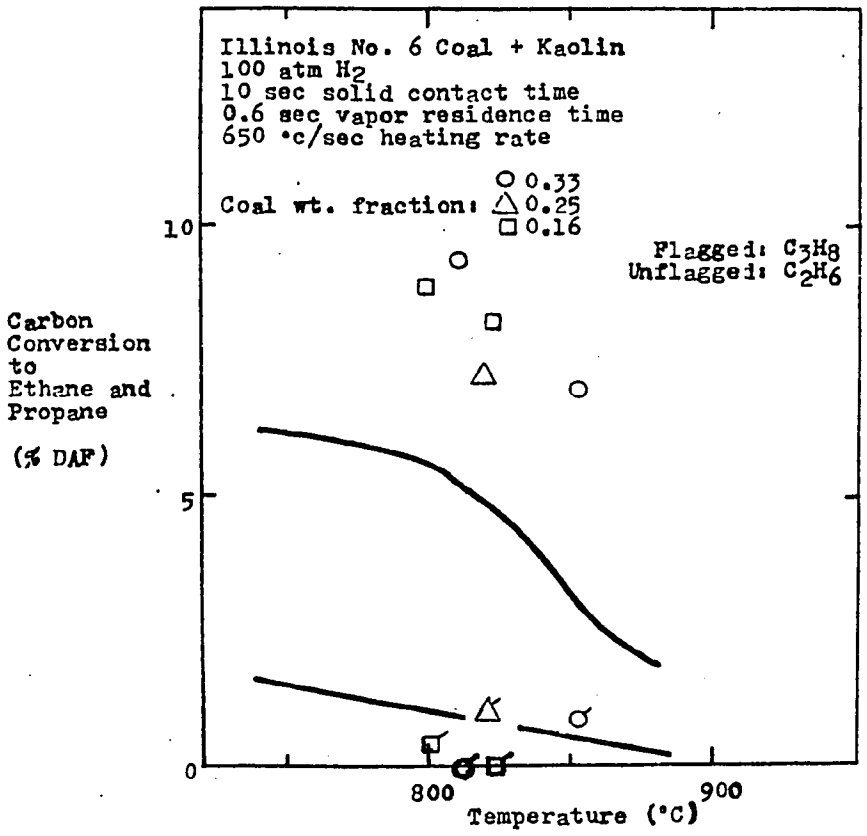


Figure 4.5.14. Ethane and Propane Yields from Hydrogenation of Coal and Kaolin Mixtures.

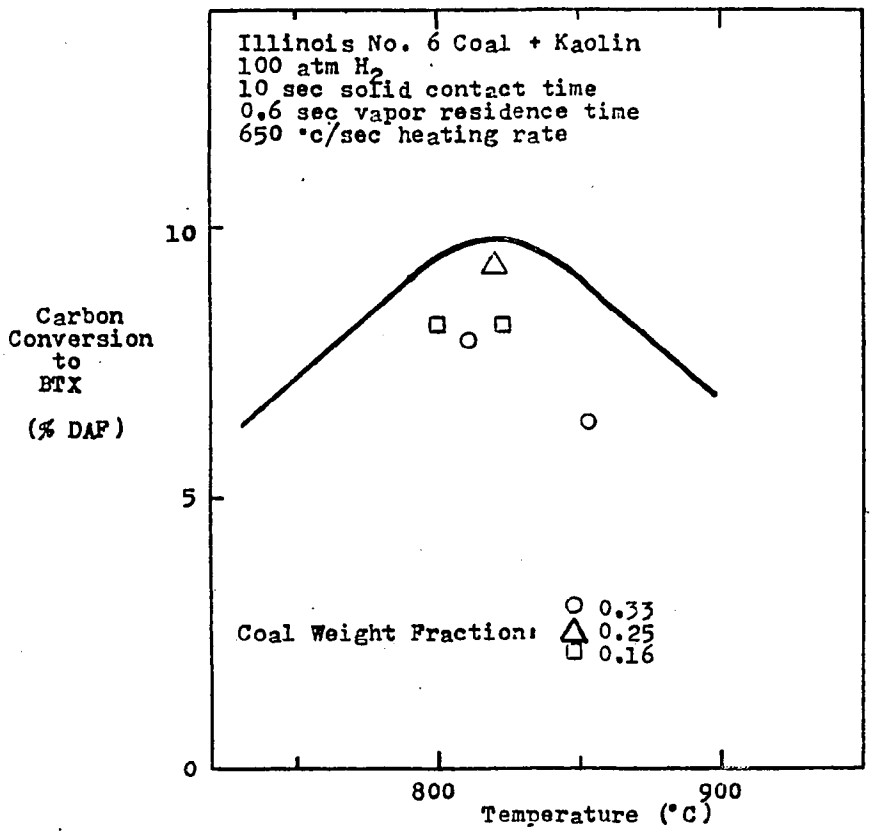


Figure 4.5.15. BTX Yields from Hydrogenation of Coal and Kaolin Mixtures.

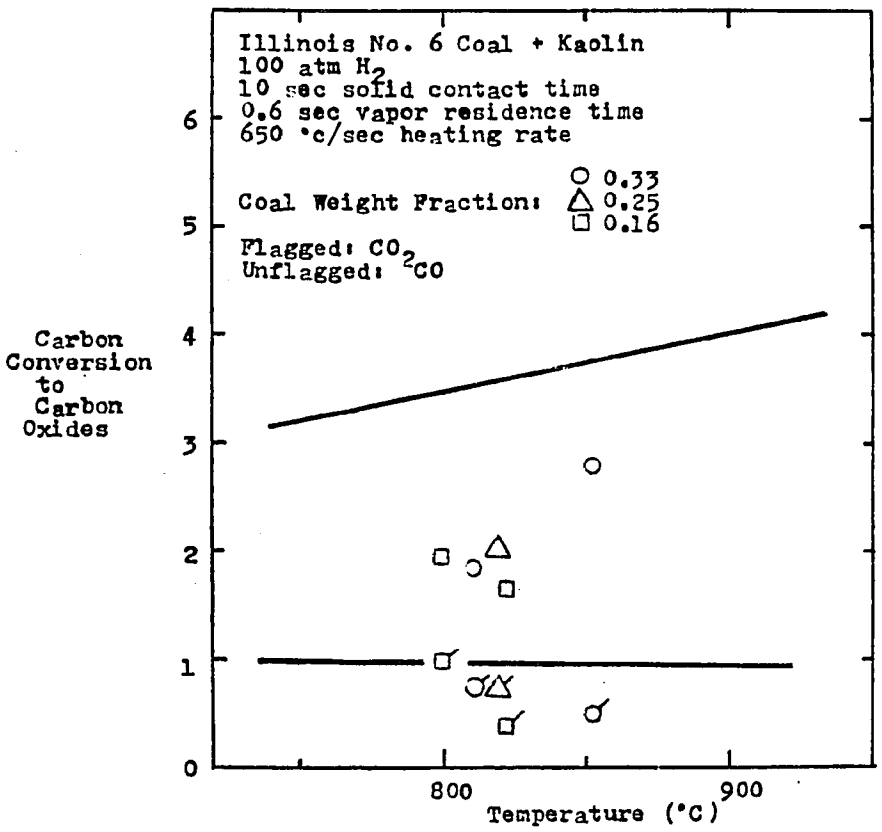


Figure 4.5.16. Yields of Carbon Oxides from Hydrogenation of Coal and Kaolin Mixtures.

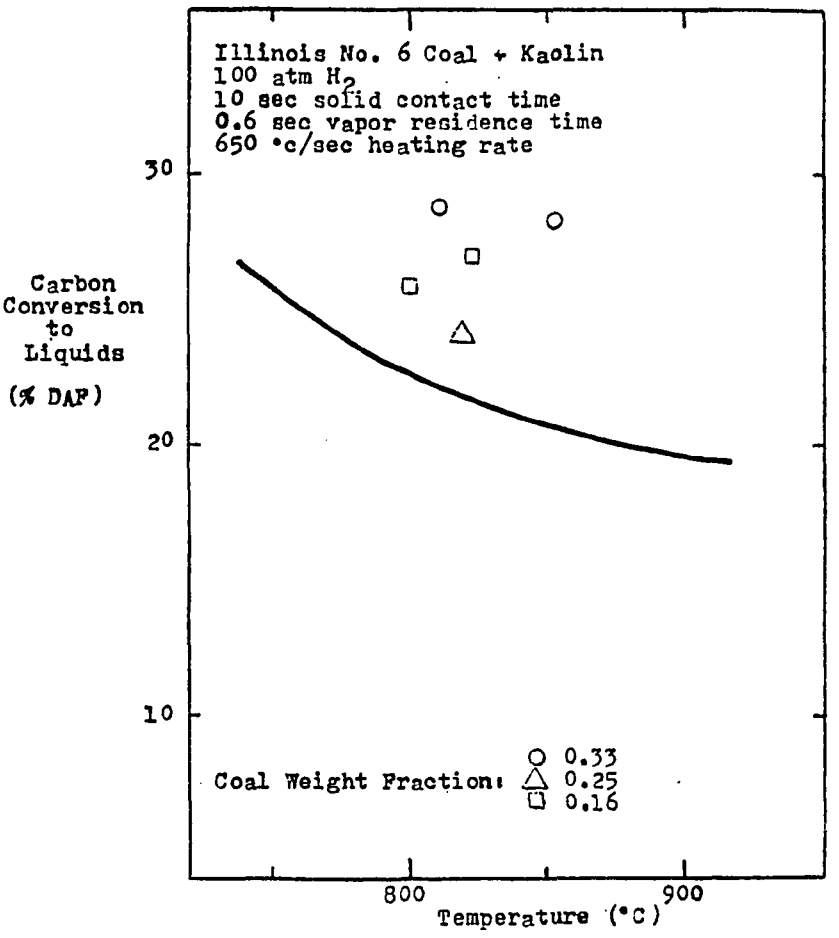


Figure 4.5.17. Liquid Yield from Hydrogenation of Coal and Kaolin Mixtures.

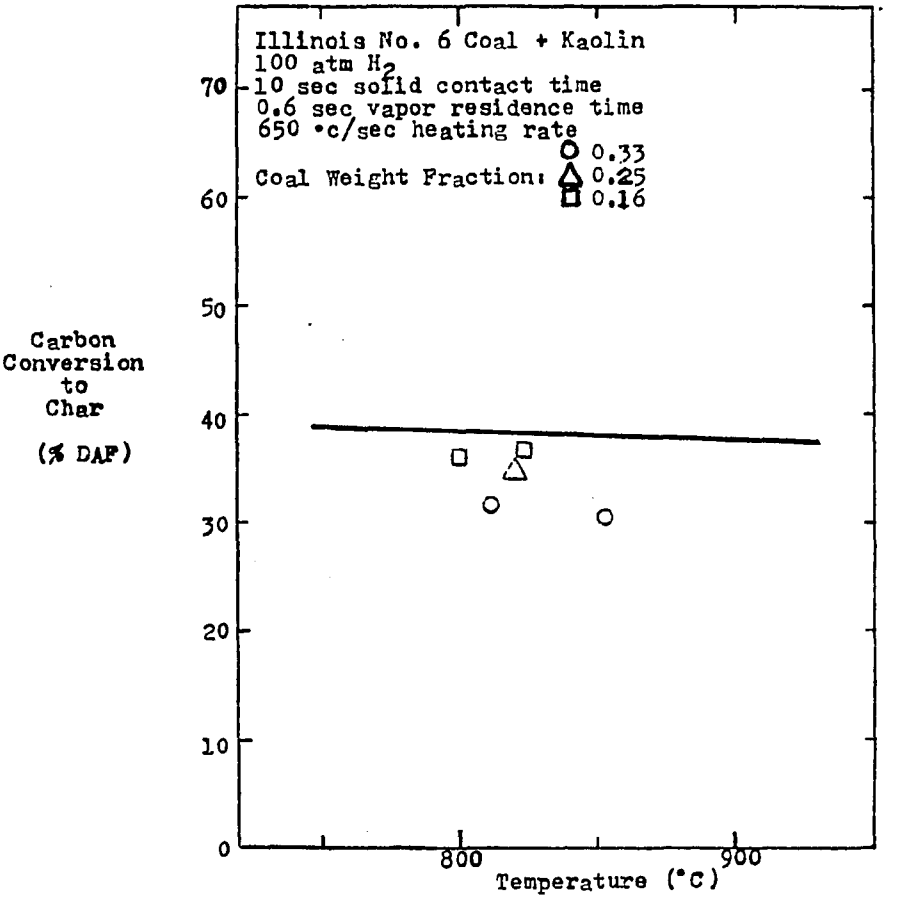
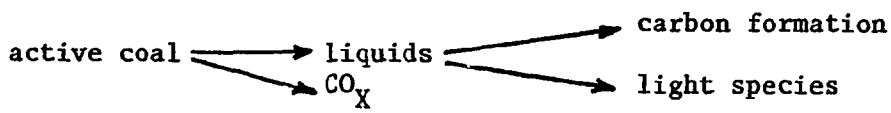


Figure 4.5.18. Char Yield from Hydrogenation of Coal and Kaolin Mixtures.

ratio equal to 2:1 while about 8% increase in total yield was found (Figure 4.5.6). An optimum yield can probably be reached at coal to kaolin ratio smaller the 2:1.

This result confirms an early study of Gray (1978) that coal agglomeration can be minimized by adding the inert mineral matter kaolin to various relative density fraction of a South African coal. Gray found a continued rise in total conversion with percentage kaolin in the fraction. Our data shows, however, a maximum yield occurs when the coal to kaolin ratio is smaller than 2:1. The difference may be due to the turbulance between particles in the rotating autoclave which Gray used for reactor. Our coal sample is a small fixed bed during the reaction which presumably has stronger tendency of agglomeration. The particle agglomeration prolongs the residence time of volatiles in the particle and, therefore, enhances the secondary reactions of the intermediates such as liquids:



The primary reaction of coal devolatilization to liquid is generally considered so fast that it is complete within 0.1 sec. Since the liquids residence time in the swelling particle is much longer than 0.1 sec at high pressure (section 4.3.4), the mass transfer limitation favors the competitive reactions of liquid to either carbon (char) or light species.

4.6 Effects of Coal Drying and Light Oxidation

4.6.1 Lignite Drying

In these experiments the objective was to determine whether or not yields from lignites are affected by drying. A sample of Texas lignite was obtained which had been taken from a freshly exposed mine face and transported under distilled water. The sample was ground and stored under humidified nitrogen. Four runs were made with undried lignite (containing about 20% moisture). A portion of the sample was dried in a vacuum oven overnight at 110°C and several runs made with the dried sample. The proximate and ultimate analysis of this Texas lignite sample is shown in Table 4.6.1. Both sets of hydrogenations were conducted at 100 atm, 650°C/sec heating rate, 10 sec solids contact time and covered the range from 700 to 800°C. No effect of drying was observed. The raw data are shown in Table 4.6.2.

4.6.2 Exposure of Coal to Ambient Air

Oxidation of coal occurs spontaneously at ambient conditions and results in changes in calorific value, cokeability and dilation. The sensitivity of coals to slight oxidation can be alarmingly high. Ignasiak, et al. (1976), for example, found that the exposure of -20 mesh (Tyler) high-volatile A coal for three days in a laboratory at room temperature caused a 5 to 10% decrease in dilation. An increase of only 1.3% in oxygen content (achieved by air oxidation for 72 hours at 100°C) caused the complete disappearance of both caking and dilation properties of this coal. Oxidative pretreatment of caking coals for feeding to fluid bed gasifiers causes reduced yields of

Table 4.6.1. Proximate and Ultimate Analysis of Texas Lignite

Proximate Analysis

	As Received	Dry Basis
moisture	2.05	
volatile	41.15	42.01
fixed carbon	38.35	39.15
ash	18.45	18.84
sulfur (total)	1.60	1.63
pyritic sulfur	0.23	0.23
organic sulfur	1.36	1.39
sulphate sulphur	0.01	0.01
B.T.U.	9,932	10,140

Ultimate Analysis

	As Received	Dry Basis
moisture	2.05	
carbon	57.50	58.70
hydrogen	4.53	4.63
oxygen	14.76	15.07
nitrogen	1.11	1.13
sulfur	1.60	1.63
ash	18.45	18.84

Table 4.6.2. Hydrogenation of Texas Lignite

Run I.D.	Temp (°C)	VRT (sec)	CH_4	C_2H_6	C_3H_8	Benzene	Toluene & Xylene	CO	CO_2	Char
TA1	754	0.6	19.6	9.2	0.9	7.4	2.4	1.5	1.7	22.1
TA2	773	0.6	18.1	8.6	0.8	8.1	1.3	11.5	1.5	29.0
TA3	790	0.6	19.0	9.1	0.4	8.8	0.8	3.8	1.5	27.8
TA4	752	0.6	15.2	8.6	1.4	6.5	2.2	12.9	1.8	34.2
TA5(D)*	770	3.6	29.1	5.3	0.5	10.4	0.0	5.3	1.9	26.0
TA6(D)	780	3.6	32.1	2.1	1.3	7.8	0.0	6.5	1.9	26.3
TA7(D)	769	1.8	23.3	6.9	0.2	10.3	0.0	5.3	1.9	30.3
TA8(D)	822	1.8	30.8	2.3	0.7	7.4	0.0	5.8	1.7	30.9
TB2(D)	765	0.6	16.1	9.1	0.2	7.8	1.2	3.5	1.1	31.0
TB3(D)	615	0.6	4.8	2.4	2.7	0.3	1.3	3.8	2.1	40.3
TB4(D)	760	0.6	15.1	8.9	0	6.6	1.9	1.8	1.1	0
TB8(D)	792	0.6	18.2	7.7	0	8.6	0.4	4.3	1.4	35.8
TB9	825	1.8	32.4	2.2	0.7	8.8	0.0	7.0	1.2	29.8
TB10	720	1.8	18.4	9.7	0.1	10.6	0.3	5.4	2.4	26.1
TB11	764	1.8	22.4	9.9	0.4	12.8	0.1	5.4	2.1	27.6
TC1(D)	804	7.2	33.8	3.3	0.6	7.7	0.0	4.8	1.2	34.5
TC2(D)	704	0.6	15.9	9.5	4.6	4.4	3.3	11.4	2.9	35.2
TC3(D)	736	0.6	20.9	13.0	1.1	8.8	2.0	16.8	1.6	34.1
TC4(D)	732	0.6	21.8	14.4	2.1	9.6	2.2	2.9	2.1	40.1
TD1(E)†	773	0.6	22.9	10.6	0.6	9.1	0.8	6.4	2.7	40.8
TD2(E)	792	0.6	21.9	10.8	0.2	9.6	1.0	4.1	2.5	44.1
TD3(E)	805	0.6	23.6	9.5	1.1	10.4	0.3	6.8	3.0	53.9
TD4(E)	790	0.6	18.5	10.9	2.6	8.7	1.0	6.7	1.2	41.8
TD6(E)	778	0.6	17.8	9.1	1.0	9.0	0.7	5.1	2.5	---
TD7(E)	720	0.6	15.4	8.6	3.4	4.9	6.8	7.1	3.3	---

* Dried Samples

† Exposed Samples

All runs were conducted at 100 atm H_2, 650°C/sec heating rate and 10 sec solid contact time.

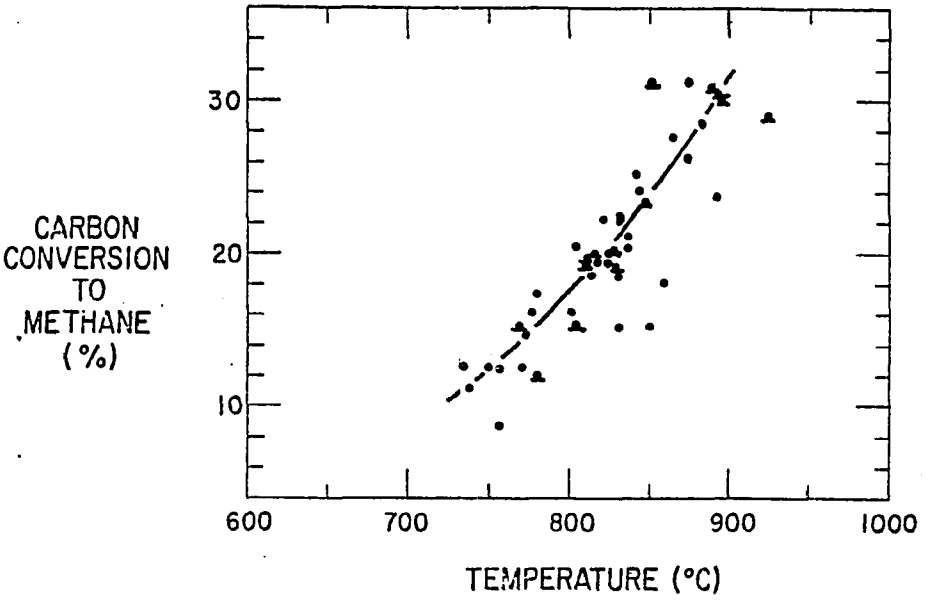


Figure 4.6.1. Carbon Conversion to Methane. Ireland Mine Coal, 100 atmospheres, hydrogen, 0.6 second vapor residence time, 10 seconds solids contact time, heating rate 650°C per second. **(Exposed samples are underlined).**

methane. These facts are cause for concern that oxidation of coal during storage and handling might affect yields in flash hydrogenation.

Two coals, one a Texas lignite and the other a bituminous coal ((hv Ab), Pittsburgh No. 8, Ireland Mine), were tested for their sensitivity to oxidation under ambient conditions. The lignite sample was taken from a freshly exposed mine face and transported under distilled water. The bituminous sample, of approximately 1 to 3-inch lumps, was taken from the mine bagged in plastic. Both coals were ground to -200 mesh and stored under humidified nitrogen. Their ultimate and proximate analyses have been shown in sections 4.2.1 and 4.6.1.

Samples of each coal were exposed to laboratory air at ambient conditions for 2½ months. Six runs were made with the exposed lignite and twenty-seven runs with the exposed Pittsburgh No. 8 coal. A temperature range from 720 to 900°C was covered at a heating rate of 650°C per second, a vapor residence time of 0.6 sec and a hydrogen pressure of 100 atm. For both coals no substantial difference in yield was observed between the exposed and unexposed samples. Raw data for Texas lignite is included in Table 4.6.2 and the results for Pittsburgh No. 6 coal is plotted in Figure 4.6.1 to 4.6.4.

It can be tentatively concluded that the processes which occur at low temperatures and which are inhibited by light oxidation have little to do with the processes occurring during the important stages of flash hydrogenation. The low temperature processes are associated with relatively weak bonds. At the higher temperatures of flash hydrogenation stronger bonds are ruptured. These must be rather different than those bonds involved in the low temperature processes.

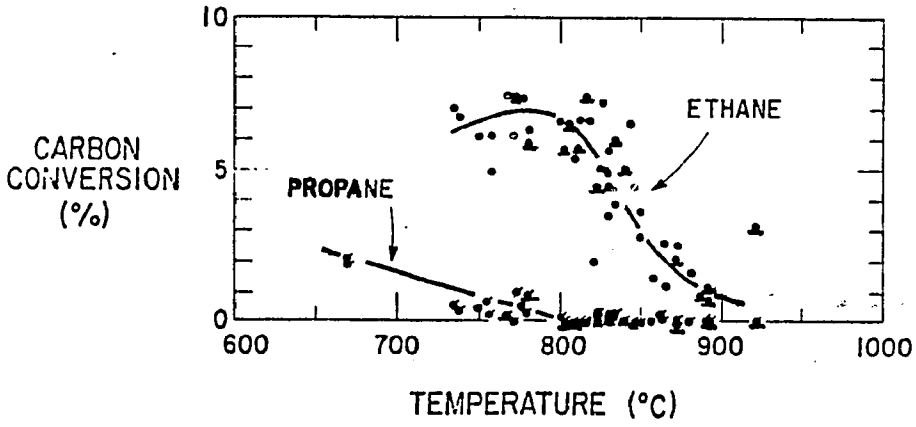


Figure 4.6.2. Carbon Conversion to Ethane and Propane. Ireland Mine Coal, 100 atmospheres, hydrogen, 0.6 second vapor residence time, 10 seconds solids contact time, heating rate 650°C per second. **(Exposed samples are underlined.)**

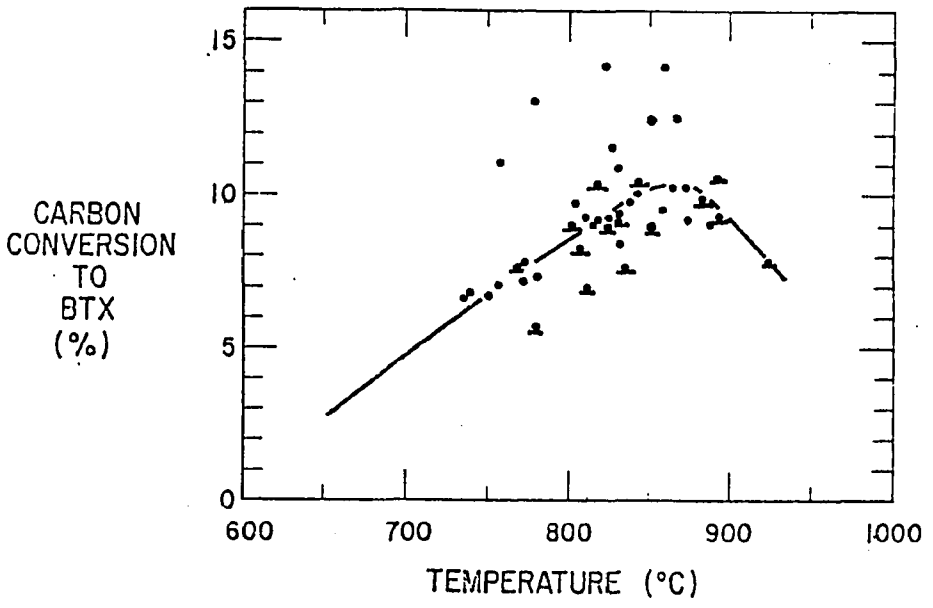


Figure 4.6.3. Carbon Conversion to BTX. Ireland Mine Coal, 100 atmospheres, hydrogen, 0.6 second vapor residence time, 10 seconds solids contact time, heating rate 650°C per second. **(Exposed samples are underlined.)**

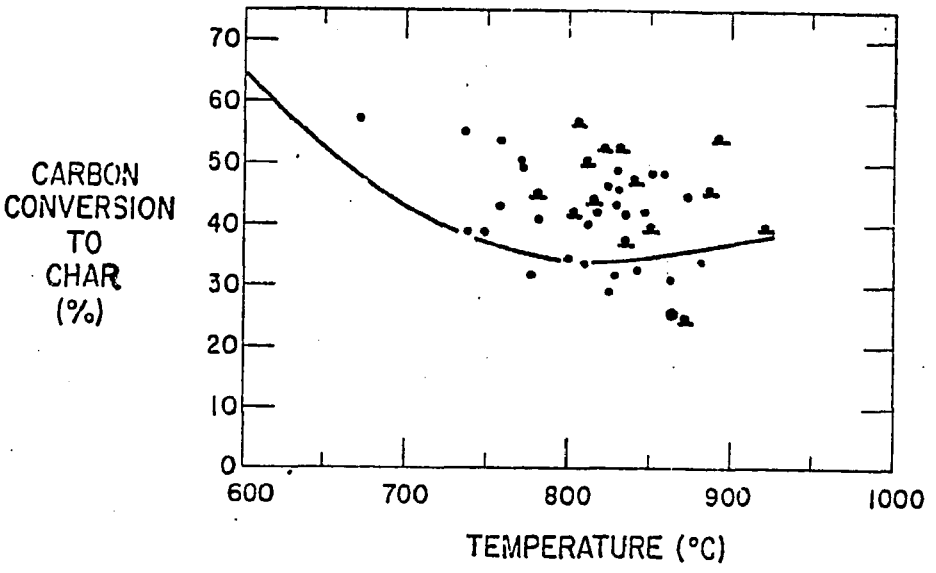


Figure 4.6.4. Carbon Conversion to Char. Data points are for the direct measurement of residual char by combustion. Solid line computed from Figures II-4 through 8 plus 2.4% carbon oxides. Ireland Mine Coal, 100 atmospheres hydrogen, 0.6 second vapor residence, 10 seconds solids contact time, heating rate 650°C per second.
(Exposed samples are underlined.)

4.7 Secondary Reactions of Volatiles in Vapor Zone

4.7.1 Tests for Wall Catalyzed Reactions

The hydrogenation experiments reported here were carried out in a flash-heated tubular reactor of 316 stainless steel. In such a reactor, the wall may ace as a catalyst surface altering the distribution of products. This possibility can be tested with reactor tubes having different internal surfaces.

The City College has previously carried out runs in reactor tubes sulfided by pretreatment with H_2S at elevated temperature, a technique well established in cracking technology and known to inhibit surface reactions. In those experiments no differences were observed. Since gold surfaces are generally regarded as being low in activity, we have now made tests with such surfaces.

A technique was successfully developed for the uniform electrodeposition of gold on the interior surface of our reactor tubes. Tubes were plated to a thickness of 75 thousandths mil and runs made in the usual way. These runs are plotted in Figures 4.7.1 to 4.7.6 (flagged points) for comparison with previously published data (Graff, et al., 1976). Six runs were made covering the temperature range 725 to 875°C at 100 atm hydrogen, 0.6 sec vapor residence time and 10 sec solids contact time using Illinois No. 6 coal. No substantial effect on yield is observed. This confirms previous results with sulfided tubes.

4.7.2 Secondary Reactions with Char

In all of the reactors proposed for commercialization of flash hydrogenation, char entrained in hydrogen is carried along with

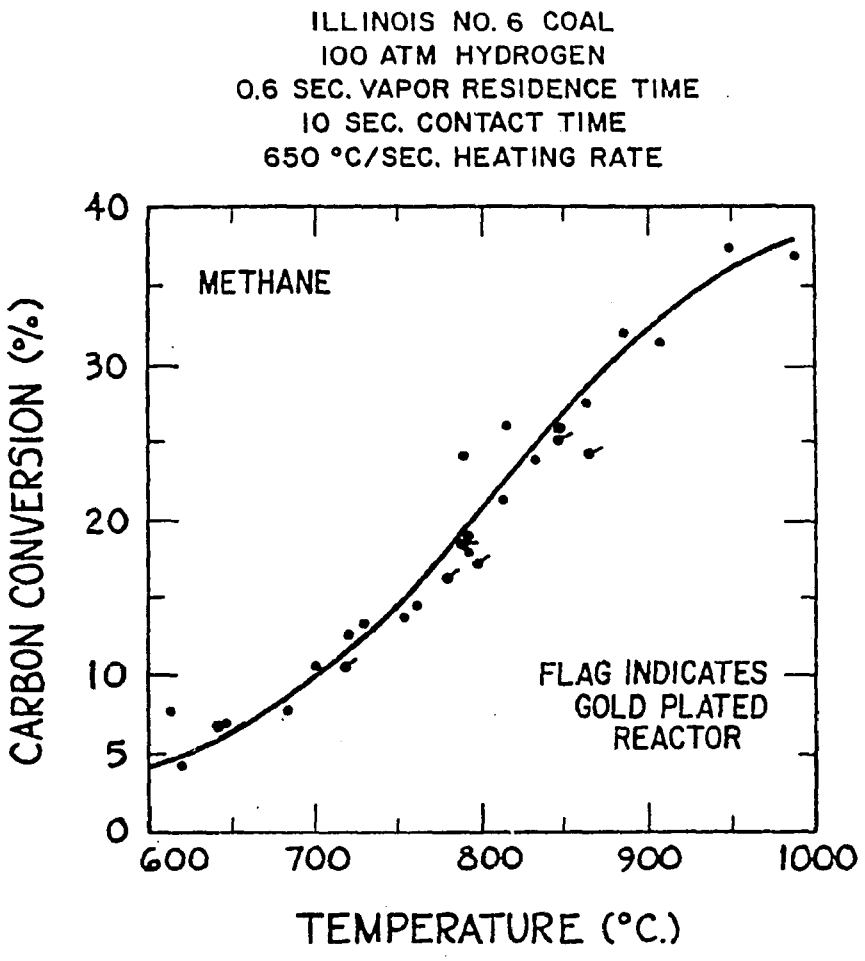


Figure 4.7.1. Comparison of methane yields in gold plated reactor with those obtained in the bare 316 stainless steel tube.

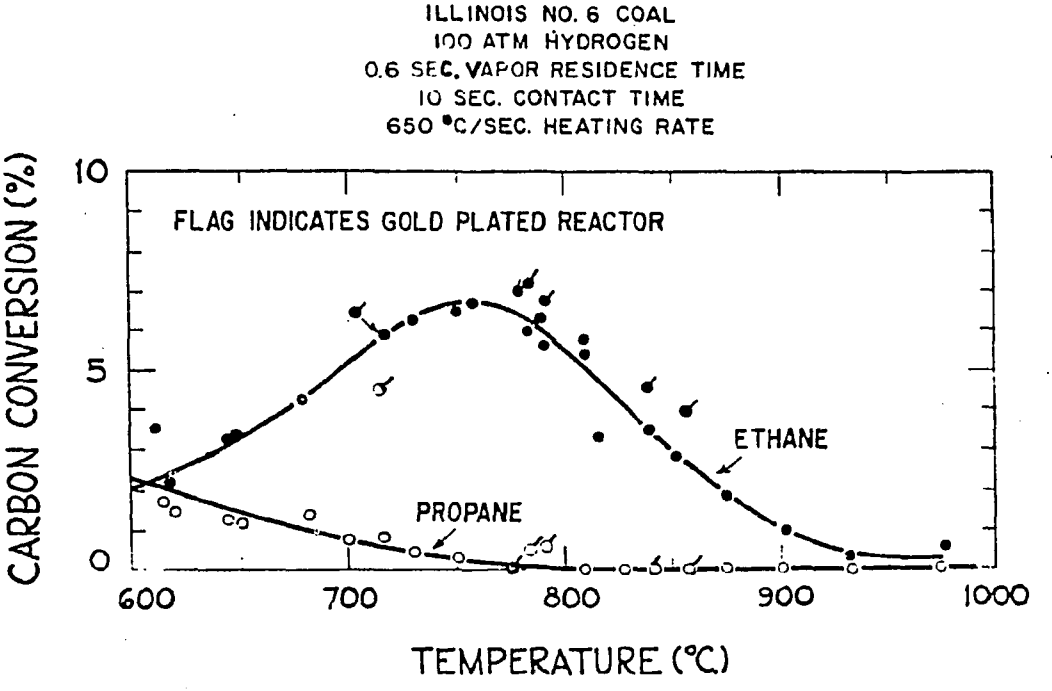


Figure 4.7.2. Comparison of ethane and propane yields in gold plated reactor with those obtained in the bare 316 stainless steel tube.

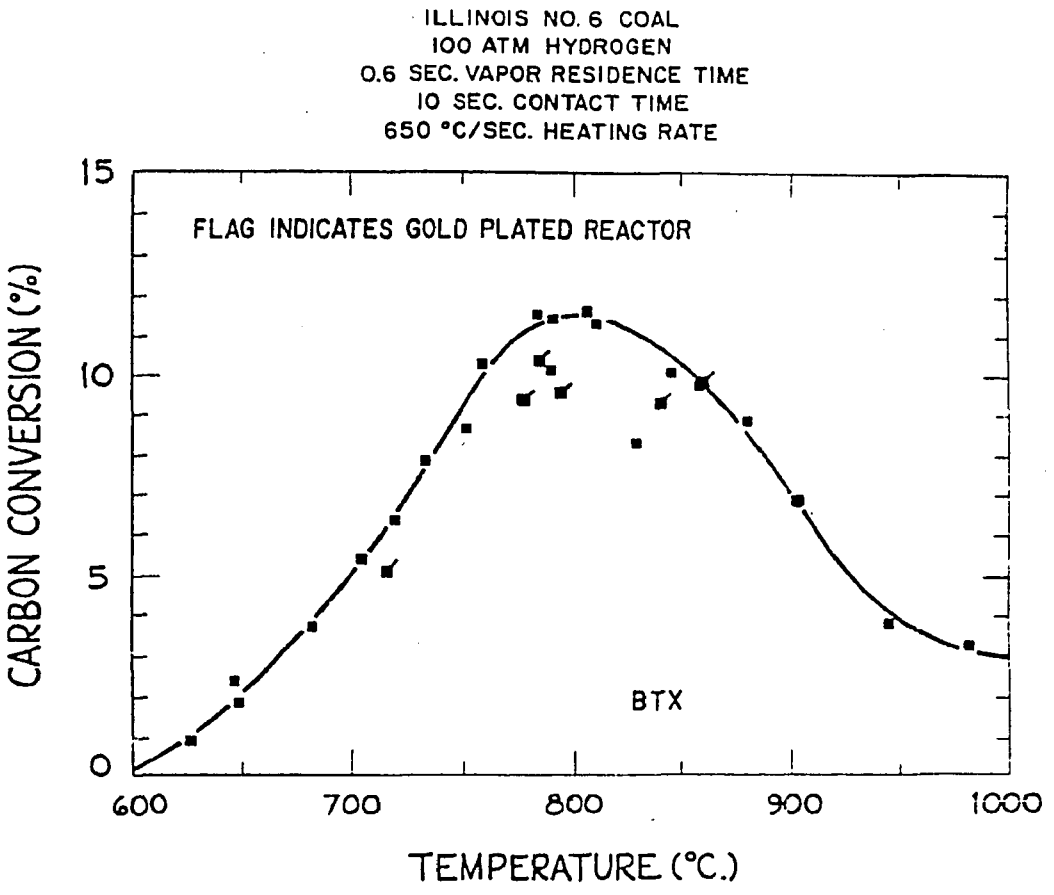


Figure 4.7.3. Comparison of BTX yields in gold plated reactor with those obtained in the bare 316 stainless steel tube.

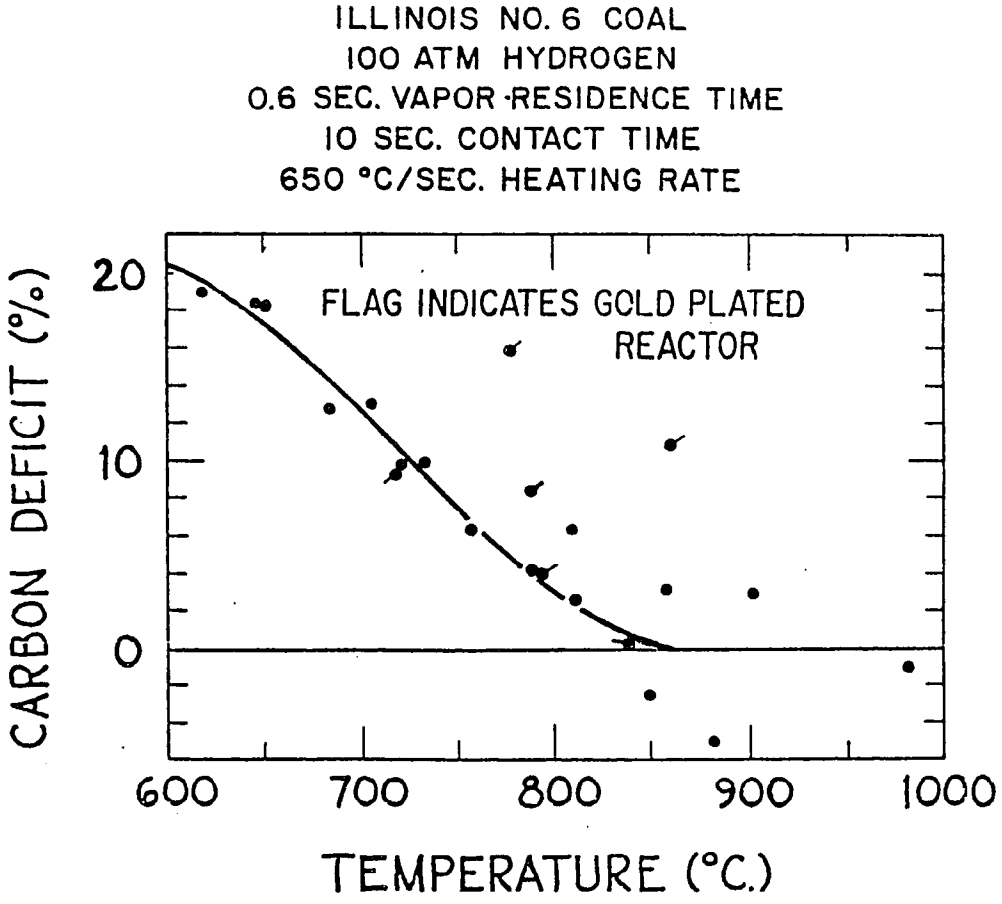


Figure 4.7.4. Comparison of carbon deficit yields in gold plated reactor with those obtained in the bare 316 stainless steel tube.

the volatilized product for their entire time of residence in the reactor. In our experimental reactor, on the other hand, the volatile products are promptly disengaged from the residual solid and swept away by the flowing hydrogen. There is the possibility that the continued contact of volatiles with char, as contemplated for the commercial system, will allow undesirable secondary reactions to substantially reduce product yield.

In order to test this possibility, runs were made in which a section of the reactor just downstream of the coal was packed with char. Pittsburgh No. 8 coal was used in these studies. The char had been obtained in 1973 from Illinois No. 6 coal at 1550°F in the stage 4 pyrolyzer of the COED process. Table 4.7.1 gives the char analyses as reported by the supplier.

In addition to runs with coal, char was run by itself to determine its contribution to the total yield. As expected, only methane is produced by the char in significant amounts. For the runs in which both coal and char were used, the contribution from char was subtracted from the total to obtain the yield attributable to coal.

The char was ground to -140 + 200 mesh, and bed depths of both 1 cm (122 mg) and 5 cm (630 mg) were used. In runs with char the coal sample was placed upstream of its usual position in order to maintain a vapor residence time of 0.6 sec. A temperature range from 600 to 1000°C was covered at a pressure of 100 atm of pure hydrogen.

The methane yields are a puzzle. Coal-plus-char yielded slightly less methane than was obtained from char alone. Because of the consistency of this result, we are reluctant to ascribe it to experimental error. Methane aside, the yields of all other species were

Table 4.7.1. Analysis of Illinois No. 6 Coal Char

Proximate Analysis, wt%	
Moisture	0.6
Volatile Matter	3.6
Fixed Carbon	73.0
Ash	22.8
Ultimate Analysis, wt%, dry	
Carbon	72.4
Hydrogen	0.8
Nitrogen	0.9
Sulfur	3.1
Oxygen (by difference)	0.0
Ash	22.8
Sieve Analysis, cum. wt%, Tyler	
14	3.1
28	27.9
48	58.9
100	78.6
200	88.6
325	93.0
Pan	100.0
Density, lb/cu. ft.	
Bulk	27.5
Pack	31.9

*Analysis provided by FMC Corporation, May 23, 1973.

indistinguishable from those obtained without char in the vapor residence zone.

We speculate that reduced yields of methane are a result of coke deposition on char, the source of this coke being the heavy species evolved from the coal. Because of the large quantities of char in these experiments, the amount left by the coal could not be determined. Consequently, we have no data on the net yield of heavy species. It should also be noted that the FMC char is likely to be less active than chars obtained in flash hydrogenation, and further experiments with chars more representative of the flash hydrogenation process are called for.

4.8 Short Contact Time Solvent Refined Coal

For their fundamental study of the early stages of coal liquefaction processes, Whitehurst, et al., (1976) have developed a batch autoclave system capable of rapid coal injection and rapid quenching. Reaction times as short as 15 sec are achieved. With this apparatus they have found that coal dissolution is very rapid in a hydrogen donor solvent, taking about 3 min for West Kentucky bituminous coal (both at 427°C). This early product more closely resembles the parent coal, in terms of aromaticity and number of fused aromatic rings, than does the product obtained at longer time. We wondered how this short contact time liquid would respond to flash hydrogenation.

Three samples of SRC were supplied by Mobil Research & Development

Corporation.* According to the type of coal and the conditions of preparation, these materials represent from 32 to 76% coal conversion by weight (Table 4.8.1).

Flash hydrogenation of these samples was conducted in 100 atm of pure hydrogen with 0.6 sec vapor residence time. The temperatures range from 750 to 850°C, where peak ethane and BTX yields are found . for whole coals, was covered. The observed yields were compared to those obtained with Illinois No. 6 coal (Dobner, et al., 1976) and a suite of eight other U.S. coals (section 4.1).

On the basis of percentage of the carbon in SRC converted to product, methane yields are the same as for the whole coal. Peak ethane yields are considerably higher than the 6 to 9% obtained for whole coals. BTX yields are also higher than any obtained for whole coal at the same conditions. Light oil yields (i.e., liquids heavier than xylene) are consistent with those obtained from whole coals at 800°C but the dependence on temperature is much stronger. SRC gives slightly lower char yields than untreated coal.

Short contact time SRC provides a somewhat enriched fraction for flash hydrogenation. However, the similarity in behavior of the coal and the SRC fraction is what is most striking. Evidently, the bonds which are broken to render the coal soluble at short liquefaction times have little to do with the high temperature processes flash hydrogenation.

*We thank the Electric Power Research Institute and Mobel Research and Development Corporation for providing these samples.

Table 4.8.1. Flash Hydrogenation of SRC

Coal	West Kentucky bituminous	Illinois No. 8 bituminous Monterey Mine	Wyodak sub-bituminous
Liquefaction conditions:			
Temperature (°C)	427	418	427
H_2 Temperature (psig)	1300	1500	inert gas
Run Time (min)	1.30	0.5	2.00
Coal Conversion (wt%)	76	32	38
Flash Hydrogenation Yields (% C in SRC):			
Methane (at 800°C)	18	21	20
Ethane (peak)	14.5	10.0	10.5
BTX (peak)	15	14.5	17
Light oils (at 800°C)	23	20	17
Char (at 800°C)	36	39	39

4.9 Char Composition

Four samples of char prepared from Ireland Mine coal were sent to an outside laboratory for analysis. These analyses allow us to calculate the conversion of each element to volatile species. Sulfur and nitrogen removal is of particular importance in determining the value of the char as a nonpolluting boiler fuel. A knowledge of the char hydrogen content permits an estimate of the hydrogen consumption of the process, an important economic factor.

These samples were prepared from 20 mg of coal. Our usual sample size of 10 mg provides too little char for accurate analyses. However, we have determined that conversions are not affect by increasing the size of the coal sample to 20 mg (With 50 mg reduced conversions of light species were obtained). In other respects, the hydrogenation follows the usual procedures. These samples were prepared in 100 atm of pure hydrogen, with a heating rate of 650°C/sec, a contact time of 10 sec, at temperatures from 777°C to 892°C; the vapor residence time is not material for these studies.

The char compositions are compared with that of the coal in Table 4.9.1. Oxygen is determined by difference. Element conversions are based on that of carbon as correlated from direct measurement in our reactor. The conversion of both nitrogen (69-85%) and sulfur (84-91%) are high, particularly when compared to previous results with Illinois No. 6 coal, 24-52% nitrogen removal, 74-84% sulfur removal (Graff, et al., 1976b). The higher sulfur removal from Pittsburgh No. 8 coal may be explained in part by the higher proportion of organic to pyritic sulfur (1.6:1) in this coal. We have speculated in past that all of the

Table 4.9.1. Analysis of Pittsburgh No. 8 Coal Char

Char analysis: Pittsburgh No. 8 Coal, 100 atm H_2, heating rate 650°C/sec, 10 seconds contact time, 20 mg. samples

	Coal	IR 140	IR 142	IR 144	IR 145
		Char Composition (wt%, MAF)			
C	79.8	94.1	92.6	90.0	91.3
H	5.6	2.1	2.3	2.7	2.9
N	1.4	0.6	0.8	1.1	1.1
S	6.6	1.8	1.6	2.0	2.6
O	6.6	1.4	2.7	4.2	2.2
Temperature (°C)		892	860	820	777
		Element Conversion to Volatile Species (%)			
C		59	58	56	54
H		87	85	81	80
N		85	81	70	69
S		91	91	88	84
O		93	86	76	87
Calorific Value BTU/lb (MAF)	14,700	14,885	14,693	14,500	14,910
Sulfur Content lbs S/MM BTU	4.6	1.2	1.1	1.37	1.73

organic and half of the pyritic sulfur is removed by flash hydrogenation.

The calorific values of these chars (also given in Table 4.9.1) have been calculated from the Mott-Spooner correlation (1940). They are equal to or higher than the calorific value of the starting coal, on an MAF basis. While the sulfur content on a BTU basis (Table 4.9.1) is greatly reduced compared to the raw coal, the EPA standard of 0.8 lbs per MM BTU is not met. A coal washing step preliminary to flash hydrogenation might reduce the pyritic sulfur content sufficiently so that the resulting char product meets EPA standards.

A hydrogen balance based on the char composition of Table 4.9.2 and Figures 4.6.1 to 4.6.4 at 860°C is given in Table 4.9.2. The hydrogen consumption is 4.74 lbs per 100 lbs of coal. This is more than twice the consumption of 2.1 lbs per 100 lbs of Illinois No. 6 coal at 700°C and 3 sec vapor residence time (where carbon conversion to benzene is also 10%, but no other liquids are obtained). The higher hydrogen consumption is almost entirely a result of the higher methane yield. A number of operating strategies for reducing the hydrogen consumption are possible.

Table 4.9.2. Hydrogen Balance for Pittsburgh No. 8 Coal at 860°C, 0.6 VRT, 10 sec contact time

	Coal Analysis (% MF)	% Converted	
C	69.6	58	26% CH_4
			2% C_2H_6
H	4.9	85	10% C_6H_6
			2% CO_x
N	1.2	80	18% oil
S	5.7	91	
O	5.8	86	
Ash	12.8	---	

Product	Lbs. Hydrogen per 100 lbs. Coal (MF)
CH_4	6.03
C_2H_6	0.35
C_6H_6	0.58
Oil ($CH_{0.8}$)	0.83
Char	0.74
H_2S	0.32
NH_3	0.20
H_2O	0.39
	9.64

Hydrogan consumed = 9.64 - 4.9 = 4.7 lbs/100 lbs coal

Appendix I. Heat Transfer to Hydrogen in the Flash Tube

Two approaches have been used to judge how well hydrogen follows the reactor wall temperature during flash heating. Both show that hydrogen reaches 98% of the wall temperature within 0.2 sec. Since this is much shorter than the time required for the gas to traverse the preheat region (1.6 sec), hydrogen is at wall temperature before the gas reaches the coal sample.

In the first approach, it is assumed that hydrogen in the tube is a stagnant cylinder and that conduction heat transfer dominates. The second approach is based on theoretical solutions for heat transfer in laminar flow with constant wall temperature.

(1) The solution of heat conduction in a cylinder with constant wall temperature was presented by Carslaw and Jaeger (1959). They also showed (Figure 24 in S 7.6 in the above reference) that the factor kt/a should be larger than 0.8 when the center temperature reaches 98 per cent of the wall temperature, i.e.,

$$\frac{kt}{a^2} > 0.8 \qquad \text{when} \quad \frac{T_c - T_o}{T_w - T_o} > 0.98 \tag{I-1}$$

where T_c is the center temperature, $k = K/pC_v$, K = heat conductivity, p = density, C_v = heat capacity and a is radius. From Reid and Sherwood (1958), heat conductivity can be calculated by

$$K = 2.2\ \mu C_v \tag{I-2}$$

where μ is viscosity. The values of viscosity and heat capacity at 800°C are taken from Perry's handbook (1963) and Daniels and Alberty's textbook (1966).

$$m = 0.00021 \text{ poise} \tag{I-3}$$

$$C_v = 5.0 \text{ cal/(°C)(g-mole)} \tag{I-4}$$

Therefore,

$$K = 2.2(0.00021 \frac{g}{cm \cdot sec}) \cdot (5.0 \frac{cal}{°C(g\text{-mole})}) \cdot (\frac{g\text{-mole}}{2\ g})$$

$$= 2.3 \times 10^{-3} \frac{cal}{cm \cdot sec \cdot °C}$$

At 100 atm, the correction factor for K, from Reid and Sherwood (1958), is about 1.06, therefore,

$$K_{100 \text{ atm}, 800°C} \cong (2.3 \times 10^{-3})(1.06)$$

$$= 2.4 \times 10^{-3} \frac{cal}{cm \cdot sec \cdot °C} \tag{I-6}$$

At 100 atm and 800°C,

$$P_{H_2} = 2 \times \frac{n}{v} = Z \frac{P}{RT} = 2.26 \times 10^{-3} \frac{g}{cm^3} \tag{I-7}$$

From (I-1)

$$t > \frac{0.8\ a^2}{k} = \frac{0.8\ a^2\ PC_v}{K}$$

$$\frac{0.8(0.23)2.(2.26 \times 10\text{-}3).5}{2.4 \times 10^{3}} = 0.2 \text{ sec}$$

This time is much shorter than the hydrogen residence time before it reaches the coal sample. The calculation also indicates the temperature measurement on the tube surface is satisfactory.

(2) The relation between the Nusselt number ($Nu_{\ell n}$) and flow conditions ($\pi KL/4wC_p$) is shown in Figure 13.2-5 in Bird, Stewart and Lightfoot's text (1960). Since

$$w = \text{flowrate} = (3000 \text{ standard c.c./min}) \cdot (2.26 \frac{g}{cm^3}) \cdot (\frac{\text{g-mole}}{2 \text{ g}})$$

$$(\frac{1073}{298})(\frac{1}{100})(\frac{1 \text{ min}}{60 \text{ sec}})$$

$$= 2 \times 10^{-3} \frac{\text{g-mole}}{\text{sec}},$$

$$\frac{\pi KL}{4wCp} = \frac{(3.14)(2.4 \times 10^{-3}}{(4)(2 \times 10^{3}3)(7)} \cdot L$$

$$= 0.13 \text{ L}$$

From the text of Bird, et al. (1960), the corresponding Nusselt Number equals to 4 when L is about 1 to 2 cm, i.e.,

$$Nu_{\ell n} = \frac{h_{1n}D}{K} = 4$$

$$\text{and} \quad h_{1n} = 4\frac{K}{D} = \frac{4(2.4 \times 10\text{-}3)}{0.5} = 0.019 \frac{\text{cal}}{\text{sec}(°C)(\text{cm2})} \qquad \text{(I-8)}$$

On the other hand, the definition of h_{ln} is

$$h_{ln} = \frac{wC_p}{\pi DL} \cdot \frac{(T_{b2} - T_{b1})}{(T_o - T_{b1})}$$

When the bulk hydrogen reaches 98% of the temperature difference on the entrance and the wall temperature is uniform at 800°C, T_{b1} = 25°C, $T_{o1} = T_{o2}$ = 800°C and T_{b2} = 784.5°C. Therefore,

$$(T_o - T_b)_{ln} = \frac{(T_{o1} - T_{b1}) - (T_{o1} - T_{b2})}{\ell n[(T_{o1} - T_{b1})/(T_{o2} - T_{b2})]}$$

$$= 194$$

and,

$$h_{ln} = \frac{(2 \times 10^{-3})(7)}{(3.14)(0.5)(L)} \cdot \frac{(759)}{194}$$

$$= \frac{0.035}{L} \frac{\text{cal}}{\text{sec}(°C)(\text{cm})^2} \qquad \text{(I-9)}$$

Comparing equations (I-8) with (I-9), the preheat region required is

$$L = 1.8 \text{ cm}$$

This distance corresponds to a residence time equal to

$$t = \frac{L}{v} = \frac{1.8}{(3000 \text{ SCCM})\left(\frac{1073°C}{298°C}\right)\left(\frac{1 \text{ atm}}{100 \text{ atm}}\right)\left(\frac{1 \text{ min}}{60 \text{ sec}}\right)\left(\frac{1}{\pi(0.23)^2}\right)} = 0.17 \text{ sec}$$

It is interesting to note that the two methods give very close results.

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