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MODIFICATION OF COAL BY SUBCRITICAL STEAM

*City University of New York*

Ph.D. 1986

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**MODIFICATION OF COAL BY SUBCRITICAL STEAM**

**by**

**Susan D. Brandes**

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

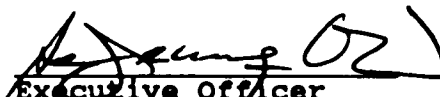
**1986**

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

19 September 1986  
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Chair of Examining  
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## Abstract

## MODIFICATION OF COAL BY SUBCRITICAL STEAM

by

Susan D. Brandes

Adviser: Professor R. A. Graff

It has been discovered at The City College of New York that exposure of coal to steam at temperatures and pressures below the critical point of water alters the coal so as to substantially increase yields obtained in subsequent processing. This hitherto unknown phenomenon has importance both for advancing basic coal science and for improving processes for converting coal to synthetic fuels. This dissertation is a report of an exploration of coal modification by treatment with subcritical steam.

In this work, the treatment of Illinois No.6 coal has been studied in 50 atm. steam. This treatment is effective at temperatures between 320 and 360°C. Liquid yields from the steam pyrolysis of treated coal is more than double the yield from raw coal. Extraction of pretreated coal with pyridine at room temperature yields 1.8 times as much extractable material as that obtained by extraction of raw coal.

Exploratory studies of the nature of treated coal and the products of its pyrolysis and extraction have been carried out. Solvent swelling studies of treated

coal show increased hydrogen bonding in comparison to raw coal.

It is concluded that during treatment coal is partially depolymerized, both thermally and by interaction with steam. Steam could play the physical role of acting to hold open the thermally ruptured structure. It may also react chemically with the coal. Aryl-ether groups may, for example, be hydrolyzed to form phenols. Although these phenols cross-link coal by hydrogen bonding, such bonds are easily disrupted explaining the increase in solvent swelling and the improved yields in pyrolysis and extraction.

### Acknowledgements

I would like to thank my mentor, Professor Robert A. Graff, for his advice and patience. His integrity and dedication to the work coupled with his enthusiasm made working for him a rewarding experience.

I would also like to thank the members of my thesis committee, Prof. H. Weinstein, Prof. L. Isaacs, Prof. K. McKeigue, and especially Dr. M. Farcasiu, all of whom have given me a great deal of advice and encouragement.

I would like to acknowledge the help afforded me by Mr. John Bodnaruk. Both his technical skills and his friendship are greatly appreciated.

Additional thanks is owed to the technical personnel of the Department of Chemical Engineering Mr. W. Hall, Mr. R. Smith, and Mr. I. Ortez, and the administrative personnel Mrs. N. Cohen, Mrs. E. Diamond, Mrs. V. Nikadetas, and Ms. L. Galman, all whose help made my job easier.

Those undergraduate research assistants who contributed significantly to this work were Mr. A. Rey, Ms. M. Monahan, Mr. Y. Langer, and Mr. C. Chan.

Coal samples were procured from Dr. R. Liotta and R. Neavel both of Exxon. Mr. E.W. Sheppard of Mobil CRL provided a great deal of assistance with the FTIR work. Elemental Analyses were performed by Galbraith Labs of

Knoxville, Tennessee. DSC work was done by Prof. L. Isaacs. Dr. P. Zhou and Mr. P. Stephenson produced the low pressure inert gas pyrolysis liquids for subsequent analysis. Dr. Zhou was responsible for refinements of the dry feeder design and implementation of the same.

This work was sponsored by the USDOE under Contract Numbers DE-AC21-80MC14875 and DE-AC21-84MC21315.

I would like especially to thank the members of my family for seeing me through. In particular, thanks goes to my husband, Lee, and my son, Derek for their love and understanding.

Dedication

This work is dedicated to my father, Dr. John Goldman. He explained to me what it is to get a doctorate!

Publication of This Work

The research presented here has also been in part reported in the following publications and presentations:

Graff, R.A. and S.D. Brandes (1984), "Coal Liquefaction by Steam Pyrolysis", ACS, Division of Fuel Chemistry Preprints, 29, (2), 104.

Graff, R.A. and S.D. Brandes (1984), "Coal Liquefaction by Steam Pyrolysis", Presented at the 186th National Meeting of The American Chemical Society, Division of Fuel Chemistry, St.Louis.

Graff, R.A. and S.D. Brandes (1986), "Rapid Devolatilization of Steam Treated Coal", Proceedings of New Fuel Forms Workshop, Office of Coal Utilization, Advanced Conversion, and Gasification, U.S. Department of Energy, CONF-860271/DE86006602,35.

Graff, R.A. and S.D. Brandes (1986), "Rapid Devolatilization of Steam Treated Coal", Presented at the New Fuel Forms Workshop, U.S. DOE, Office of Fossil Energy, Washington, D.C.

Graff, R.A. and S.D. Brandes (1986), "Modification of Coal by Subcritical Steam: Pyrolysis and Extraction Yields", submitted for publication to Energy and Fuels, July, 1986.

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## 1. SUMMARY

The ability of subcritical steam to modify coal has been discovered at The City College of New York. Modification of the coal results in a substantial increase in liquid yields in subsequent processing. The required conditions to bring about the beneficial change in coal are exposure to low temperature (320-360°C) steam at high pressure (50 atm.) for moderate amounts of time (5-30 min.). Liquid yields from flash pyrolysis in steam and room temperature extraction of this modified coal are both dramatically improved. This discovery has led to an investigation into the limits of the effect. Additionally, the altered nature of the coal, itself, has been examined.

The first part of this dissertation is a literature review covering the topics of low temperature activity of coal, steam reactivity with hydrocarbons, thermodynamics of water-hydrocarbon systems, methods of pretreatment of coal, and weathering of coal. Attention is also given to currently used methods of analysis of coal and coal liquids: Fourier transform infrared spectroscopy, liquid chromatography, size exclusion chromatography, gas chromatography, and extraction and swelling techniques.

The original work on coal modification by subcritical steam was conducted in a small flash tube

reactor (Graff, et al. 1980). Conversion to liquid product was 68% of the carbon in the sample charged to the reactor. This reactor, however, had a limited sample capacity (10mg) and a problem with heat transfer to the reacting atmosphere. In order to increase processing capacity, the investigation into the limits of the effect was undertaken in a bench scale reactor which could handle up to 25 times the amount of sample as the small flash tube reactor. Raw coal samples were pulsed into the reactor which was at a stable temperature with a flowing atmosphere of steam. In this reactor system only a ten percent increase over inert gas pyrolysis was obtained. Also, only one half the amount of conversion to liquids which was gotten in the small tubular reactor was achieved. Coal was then pretreated in situ with steam at 50 atm. at temperatures between 320 and 360°C prior to being pyrolyzed. This pretreatment produced the improved yield obtained in the flash tube reactor. The temperature range of the pretreatment is likely a function of the particular coal sample used, in this case an Illinois No.6 coal. Coal samples were also pretreated in helium and pyrolyzed in steam. These thermally treated materials show no improvement in liquid yield upon subsequent pyrolysis.

Steam pretreated samples were exposed to air when a test of the shelf life of the material was made. It was

found that exposure to air for even very short periods of time, two minutes or less, destroyed the effect of improved liquid yields.

Steam pretreatment has a number of physical effects on the coal. The coal loses 5-7% light volatile material during pretreatment. Some of this material is condensable liquid. Steam treatment causes the coal to agglomerate even at temperatures as low as 320°C. Treatment in helium does not have that effect even up to 375°C. The DSC curve of pretreated coal shows that there is no glass transition temperature in the region found for the raw coal's glass transition.

Elemental analysis of steam treated coal shows a reduction of the oxygen content at the temperature found to be optimum for liquid yields in pyrolysis and extraction studies. There is an increase in the C/H ratio for all steam treated samples. There appears to be no effect on the overall organic sulfur and nitrogen content.

Shelf life of the treated coal appears to be approximately 72 hours under a >98% oxygen free atmosphere. The <2% oxygen may be sufficient to cause changes in treated coal, as does exposure to atmospheric oxygen, as noted above, but at a slower rate. It, also, may be that there are other anaerobic processes at work changing the coal. This is not known at this time.

Extraction studies were performed with treated coal to begin to understand what has occurred in the pretreatment step. Extraction of treated coal under mild conditions, room temperature and atmospheric pressure, has produced a series of results which parallel the pyrolysis work. The solvent used for the extraction work was pyridine because of its ability to interact strongly with coal at room temperature. Additional heating, which might mask the alterations to the coal produced in treatment were thereby avoided. Coal treated at the optimum temperature for liquid production in pyrolysis also gives maximum yield of extractable material. Other traits of the treated coal, treatment temperature range, sensitivity to air, shelf life, and necessity of exposure to steam not just thermal conditions, are all manifested in extraction work as well as the pyrolysis studies.

This simple test, of extracting the sample at room temperature, has been adopted as a screening method for the integrity of all pretreated coal samples.

The solid coal sample was further analyzed by Fourier transform infrared spectroscopy (FTIR) using a diffuse reflectance technique. The treated samples (whether treated in steam or helium) all exhibit a shift in the two bands visible in the 3200-3700  $\text{cm}^{-1}$  region. This region is attributed to -OH species. The higher

energy peaks are considered to be less strongly hydrogen bond associated -OH having stronger primary bonds. There is seen a higher ratio of these less strongly hydrogen bonded species to the more hydrogen bonded -OH species in the pretreated samples. These spectra can be interpreted in two ways. If the total number of -OH species is kept at a constant then there is a shift in the kind of environment that the hydroxyl groups are found, more of them becoming less hydrogen bonded. This would lead to the conclusion that the coal is in a less hydrogen bonded state. If the total number of -OH species changed then by these spectra it can be speculated that there has been the formation of more strongly (primarily) bound -OH species. The presence of these new structures in the coal would bring about the likelihood for more hydrogen bonding. The evidence from the swelling work seems to support this second idea.

Some significant observations have been made regarding the formation of water slurries from treated coal. In order to make a pourable slurry with the treated coal more than twice the amount of water is necessary compared to what is needed with raw coal. Also, the slurries have a limited stability. It was found that with the addition of a polymeric thickening agent (Xanthum gum) to the water (in small amounts, <.1%) the slurry life is extended.

To increase the amount of coal processed, a dry feeder was designed for operation in an inert atmosphere. Pyrolysis work was continued in an inert gas at both atmospheric and elevated pressure with steam treated coal. Some improvement in yields was found in atmospheric pressure pyrolysis with steam treated coal, but not as dramatic an improvement as with high pressure steam pyrolysis (Graff, 1986).

Liquid material produced by the low pressure inert gas pyrolysis was analyzed using the following scheme:

- 1) Samples collected from different portions of the liquid collection apparatus were directly analyzed by gas chromatography.

- 2) These materials were then combined and the distribution of functional groups was determined by employing Sequential Elution by Solvent Chromatography, SESC, a liquid chromatographic technique.

- 3) Each SESC fraction was then further analyzed by gel permeation chromatography for molecular weight determination.

There is exhibited only some slight difference between raw coal liquids and those obtained from the pyrolysis of pretreated coals. The proportions of the functional groups as discerned by the SESC separation are very similar. Molecular weights of the fractions as determined by gel permeation chromatography indicate

that for the most part the steam treated coal SESC fractions fall intermediate in molecular weight between the helium treated and raw coal fractions. The most polar fractions of the SESC separation are lightest for the steam treated coal.

Liquid extracts obtained by room temperature extraction were also analyzed by the above procedure. There are some subtle differences between raw and pretreated coal. Discussion of these differences is found in Section 7.8.

Swelling studies were undertaken to evaluate the degree of cross-linking in the coal after treatment as compared to the degree of cross-linking in the native coal. The method employed was described by Liotta (1979) and expanded by Larsen (1985). Three solvents were used: pyridine, benzene, and water. Swelling of the solid coal samples followed an interesting pattern. Treated coal swells more than the raw coal in water and the water miscible solvent (pyridine), but not in the benzene. The amount of swelling has been used as an indicator of the degree of hydrogen bond cross-links in the solid structure. From these data it is evident that the steam treated coal is more H-bonded than the helium treated coal, or even the raw coal. The overtly large amount of swelling in water and water soluble solvents indicates that the steam treated coal is possibly bound by cross-

links which are water miscible and/or the modified coal produced by steam treatment contains a large amount of water or water penetrable species.

## 2. CONCLUSIONS

The conclusions derived from this work are given below.

### From the Literature:

The temperature range of 300-350°C, a hitherto unrecognized region for significant processes in coal technology was found to be a place where:

- a) thermal activity of coal begins
- b) steam is reactive with coal and other fossil fuels
- c) steam and hydrocarbons exhibit miscibility

### From the Pyrolysis Work:

The percent yield of condensable hydrocarbons from steam pyrolysis of an Illinois No.6 coal can be more than doubled if the coal is first exposed to steam at 50atm. and temperatures between 320 and 360°C.

The presence of steam in the pretreatment step for the improvement in pyrolysis yields is essential. Pretreatment in an inert atmosphere (helium) is not effective.

Samples pretreated in steam show an extreme sensitivity to air. Exposure to air for periods of time less than two minutes destroys all beneficial effect of pretreatment.

Samples can be stored for up to 72 hours in inert gas without significant deterioration of the treatment effect.

The presence of steam in the pyrolysis of treated coal seems to be almost as important as the presence of steam in the treatment step for improved yields. Pyrolysis of treated samples in an inert gas show only a modicum of improvement over raw coal samples.

Temperature boundaries for pretreatment are very sharp. The effect of improved pyrolysis yield manifests itself only after treatment of the Illinois No.6 coal sample studied was exposed to steam at temperatures between 320 and 360°C. These limits are believed to be peculiar for each particular coal considered.

There is a time/temperature dependence for the pretreatment procedure. As treatment times are shortened the temperature of treatment must be raised for the preservation of the good liquid yields.

#### From the Extraction Work

Results from the extraction of treated samples under mild conditions (room temperature, atmospheric pressure) with pyridine show a doubling of extraction yield if the samples are first treated in steam at temperatures between 320 and 360°C and 50 atm. pressure.

Extraction yields, with pretreated coal mimic

pyrolysis yields in all respects:

- a) loss of yield after exposure to air.
- b) maintenance of yields after storage of treated coal sample in inert gas atmosphere for up to 72 hours.
- c) temperature range boundaries are the same and just as severe.
- d) helium pretreatment is ineffective for the improvement of yield of extractable material.

#### From Swelling Experiments

Treated coal swells twice as much as raw coal in water. In water miscible organic solvents swelling is increased substantially. Swelling of treated coal is less in benzene than is that of raw coal. This information shows that there are hydrogen bonds intact in the steam treated coal (see Sec 7.9 for discussion). It is, therefore concluded that disruption of the original hydrogen bonds in the raw coal is not responsible for the improvement of yields in pyrolysis and extraction experiments. The decrease in swelling caused by exposure of steam treated coal to air indicates that there are sites in the coal easily attacked by oxygen. This is consistent with results of pyrolysis and extraction experiments with air-exposed samples.

### From Analysis of Liquid Products

Little difference is evident in the distribution of functional groups of liquids produced by atmospheric pressure inert gas pyrolysis whether the sample was pretreated or not. The liquid extract from room temperature pyridine extraction of the coal samples also shows only small changes in the distribution of functionality. The results of preliminary work conducted with coal liquids produced by steam pyrolysis under elevated pressure show the production of very different materials than from the inert gas pyrolysis. This leads to a conclusion that the presence of steam in the pyrolysis is as important as in the pretreatment.

Gel permeation chromatography was used for all SESC fractions. Preliminary evidence indicates that the process of steam treatment prior to pyrolysis has the effect of lowering the molecular weight of the most polar materials found in the pyrolysis liquids.

Materials which are produced in the inert gas pyrolysis of steam treated coals are very heavy. These materials do not, for the most part, elute from the gas chromatography columns, even at elevated temperatures (350°C). The portion of the material which does elute from the column shows no distinction between pyrolysis liquids from raw and pretreated coal.

### Generally

It is hypothesized from the information above that the steam pretreatment at 50 atm. has the effect of altering the coal structure in such a way as to make the material more accessible to water and water miscible materials. This can be envisioned as a two step process in which the existing bonds in the coal are thermally ruptured and the steam then forms bridges between the thermally ruptured sections of the coal. Alternately, steam may be instrumental in the formation of phenolic groups which are, themselves, hydrogen bonded in the coal structure. Thus producing an altered coal-like material which on further treatment (pyrolysis in steam, or extraction in a water miscible solvent, pyridine) produces improved yields over raw coal. The additional material may come from small occluded structures which can escape the coal matrix after the pretreatment weakens the structure, or it may be that the modified coal structure can simply rupture in more places after being thermally disrupted and stabilized by the steam interaction thus providing more liquid product.

The increased swelling in water and water miscible solvents, also, indicates sites of water solubility. The increased degree of hydrogen bonding in the steam treated coal substantiates the idea that water bridges

and/or hydrogen bonding species are formed in the treatment process.

The susceptibility to air of the treated samples implies that the modified coal exists with a large number of free radical sites. These sites, considering the behavior of the treated coal samples, should be found in addition to the ones modified by water. They are envisioned to be the result of an independent thermal mechanism.

### 3. INTRODUCTION

The inevitable dependence of the world energy market on coal as a source for a high proportion of fuel needs is not too far in the future. Recent fluctuations in crude petroleum supplies have alerted the general public to the idea that petroleum, and natural gas, are politically controlled commodities and as such are not always readily available. Adding to this knowledge is the realization that liquid and gaseous fuels are exhaustible resources. The recent glut of oil and its accompanying low price are false indicators of its availability in the future. Coal, however, available in huge supply in the United States, could conceivably become the mainstay of energy production needs for many years. At present greater than 90% of all coal mined in the United States is burned and used directly for the production of electricity. In the future the need for clean, high quality liquid products from coal will be inescapable.

The production of liquid fuels from coal has an extensive historical background. Most methods which produce sufficiently high quantities of liquid, however, entail the use of hydrogen and/or hydrogen donating substances, both of which add substantially to the cost of the process. Flash or rapid pyrolysis in an inert gas as a direct coal liquefaction method is less costly, but

produces relatively low yields of material which are of questionable quality. Commercial pyrolysis processes require that the system be at atmospheric pressure or below to achieve high yields. Most of these processes utilize catalysts and hydrogen in at least one stage of the process.

The use of a steam atmosphere for flash pyrolysis of coal has not held much interest for coal conversion. It has been shown, however, that flash pyrolysis in steam can improve the yield of material from an Illinois No.6 coal by about 10% over inert gas pyrolysis when experiments are conducted at elevated pressures (Graff,1980). More important, however, is the fact that yields of liquid product can be doubled if the coal is first exposed to low temperature (320-360°C) steam at elevated pressures (50 atm.) and then subjected to flash pyrolysis in steam. The system utilizes no additional hydrogen or catalyst.

This effect has stimulated an interest in the behavior of the steam treated coal and the nature of the structure of the coal after it has been exposed to the conditions which produce the improved yields.

Coal structure is a much debated topic. A number of points are, however, generally agreed upon. The first is that coal is made up of some kind of units connected by some kind of cross-links. It is also widely accepted

that by disrupting the cross-links lighter fuel products can be made. Another well known characteristic of coal is that heteroatoms are detrimental to the production of high quality liquids. A method which effectively breaks the cross-links and also removes the heteroatoms would provide an altered material. This material, on further processing, should produce high yields of good quality liquid. The treatment in steam, alluded to above and described in the following pages, has the effect of producing high liquid yields in flash pyrolysis and solvent extraction. There is also evidence in the literature that steam promotes the removal of heteroatoms from coal and/or coal liquid products in the process (Ross, 1983b, Tyler, 1981).

A study of the pretreated coal, itself, has been undertaken to determine what is occurring in steam treatment. Methods for examining the structure of whole, solid coal, with much success, are limited. Consequently, it is by inference, from examining the behavior of the treated coal in pyrolysis, extraction, and swelling tests and by examining the products of extraction and pyrolysis processes that two theories for the nature of the pretreated coal have been postulated. These postulated structures both account for all observed behavior.

#### 4. LITERATURE REVIEW

##### 4.1 Introduction

A literature survey has been conducted in support of this investigation of the modification of coal by subcritical steam as a pretreatment technique for improving liquid yields and quality in subsequent processing. Experiments so far show pretreatment to be effective from 320 to 360°C in 50 atm. steam. Information on thermal effects, steam reactivity, and phase equilibrium at temperatures and pressures which are relevant, but not restricted, to these conditions have been reviewed. This search embraces not only coal but other fossil fuels and model compounds.

Evidence for thermal activity below 350°C comes from observation of softening and/or melting, acidity, volatiles loss, solvent extraction, differential thermal analysis, differential scanning calorimetry, electron spin resonance, and mild oxidation reactions. Reaction of steam with shale oils at 425°C and with coal and model compounds in the neighborhood of the critical point have been reported. Phase equilibrium data show complete mutual solubility of water and aromatic hydrocarbons at conditions approaching those of pretreatment. A few pretreatments reported for other

processes are noted. A survey of studies of weathering is included for its possible relevance to the observed sensitivity of pretreated coal to ambient air exposure. These literature citations corroborate experimental findings and offer possible explanations for the pretreatment effect.

In this literature search information has also been sought which might shed light on physical or chemical changes occurring during pretreatment. In much of the literature coal is considered non-reactive below 350°C and has not been extensively studied at these temperatures. Furthermore, unless gasification or reforming conditions are reached, steam is usually considered to be an inert medium for treating fossil fuels. In spite of this, a surprising amount of pertinent information has turned up.

An analysis of the pretreated coal and the liquids produced in both pyrolysis and extraction experiments has been undertaken in this work. The means for analyzing solid coals that are included in the scope of this work, and also the methods of analysis used for the liquid products of both pyrolysis and extraction are documented here. These techniques for the solid coal include Fourier transform infrared spectroscopy, extraction, and swelling studies. The methods of analysis for the liquids are based on different

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separation schemes. This report is arranged in ten sections:

#### Section 4.2 Thermal Effects

This section is concerned with reports of changes induced in coal by heating to temperatures below 350°C. These changes may be physical and/or chemical but are not brought about by addition of reagent. Work on compounds used to model coal is also included.

#### Section 4.3 Low Temperature Reactions

Chemical reactions conducted at low temperatures are uncomplicated by thermal degradation. Studies of such reactions provide information on the structural features of coal which are susceptible to reaction under mild conditions as prevail during pretreatment.

#### Section 4.4 Steam Reactions

Though steam has traditionally been considered inert, recent studies of supercritical extraction of coal have refuted this notion. Other work with coal as well as shale oils, tar sands, petroleum asphaltene, residua, and model compounds show that steam, even subcritical, is reactive with fossil fuels.

#### Section 4.5 Thermodynamics of Water-Hydrocarbon Systems

Data on the phase behavior of water-hydrocarbon systems, though very limited, clearly show that an assumption of insolubility at pretreatment condition would be quite incorrect.

#### Section 4.6 Pretreatments

Pretreatments of coal or other fossil fuels that raise yields as a subsequent process step have been reported in the literature. Those pretreatments conducted at low temperature and/or with exposure to water are discussed in this section.

#### Section 4.7 Weathering

It has been reported that pretreated coal is very sensitive to exposure to air. The effect of air on pretreated coal is similar to, though much faster than weathering. Since the chemistries of the two may be similar, a survey of the weathering literature has been included here.

#### Section 4.8 FTIR

The use of Infra red spectroscopy to study coal samples is a fairly old one. It was not, however, until the advent of FTIR with integrated computerized data

handling systems that infrared spectroscopy has become an important method for the analysis of coal. Diffuse reflectance methods have been utilized in this research project with fairly good success. These methods and some historical background are discussed in this section.

#### Section 4.9 Extraction

Extractability can be directly expressed as the yield of material removable by solvent from the solid coal matrix. Methods of preparing the coal to optimize the amount of removable material are great in number. It is, for the purpose of this review, necessary to consider only mild treatment effects on extraction yields.

#### Section 4.10 Swelling

The application of polymeric swelling techniques to coal is based on regular solution theory for nonpolar solvents. Because coal is considered to contain a large amount of hydrogen bond cross-links the solvents which are hydrogen bond acceptors show enhanced ability to swell the coal structure.

#### Section 4.11 Analysis of Coal Liquids

Analysis of liquids produced from pyrolysis of the pretreated coal will hold the key to the success of the

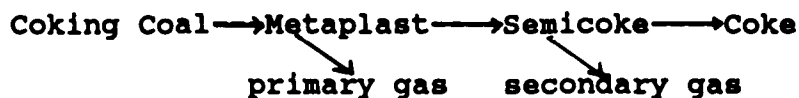
steam pretreatment/pyrolysis process. Methodology for analysis of coal derived liquids is extensive. The literature cited in this section provides the basis for experimental work performed. It is divided into three sections. The first deals with breaking the material into definable classes; the second is about the use of gel permeation chromatography for molecular weight determination and the third is a note on the use of gas chromatography, which is by no means intended to be all inclusive.

#### 4.2 Thermal Effects

It has been the general consensus of opinion among coal researchers that little or nothing occurs in coal below a temperature of 350°C. For example, Brown and Waters (1966) state that initial softening takes place between 350 and 400°C. Similarly, Neavel (1982) gives 350-450°C as the range in which plastic coals soften and become deformable when heated in an inert atmosphere. There is, however, a small but significant literature which points to important changes in the physical and chemical properties of coal occurring below 350°C. As early as 1898 Anderson and Roberts (1898) noted low temperature effects on coal. They observed that heating different Scottish coals for three hours in a current of dry carbon dioxide, excluding all air, at 300-305°C resulted in weight losses of the dry coal between 6.4 and 21.8%. They also report changes in the coking properties of these coals after this mild heat treatment.

The most often mentioned change is softening and/or melting of coal at temperatures of 300-350°C (Loison, 1963; Habermehl, 1981, and references therein; Anderson et al. 1898; Brown, and Waters 1966; Illingworth, 1922; Kirov and Stevens, 1967; Neavel, 1982). This effect is characterized by the loss of anisotropy and the rounding

and adhesion of coal grains. Various theories have been proposed to explain the softening of the coal at low temperatures. Neavel (1982) suggests that hydrogen bonds and Van der Waals forces begin to weaken and the mobility of the micellar structural units of the coal increases. Kirov (1967) also states that there is a breakdown of hydrogen bonding at 300°C and substantiates this by noting the work of Maher, et al. (1959) where the overall acidity of the coal had been found to decrease at this temperature. Brown and Waters (1966) state that the development of fluidity results from physical and physiochemical processes. They postulate a colloidal coal model based on the work of Hirst (1944) in which there are different molecular groupings. When a temperature of 200°C is achieved, one class of these compounds becomes mobile and solvated in the other materials. This in turn is postulated to weaken the micellar structure and produce a plastic state. The metaplast theory (Fitzgerald, 1956; Chermin and Van Krevelan, 1957) illustrated by the following equation:



suggests that plasticity is dependent on the production of the transient metaplast structure, the evolution and

transport of primary gases produced in the coal, and the rate at which the metaplast structure transforms to the semicoke structure.

A thermal/MS study conducted by Holden and Robb (1960) was carried out under conditions in which secondary reactions were minimized. The sample was pyrolyzed in vacuum at the entrance to a mass spectrometer. Volatile products were characterized as follows:

Pyrolysis Temperature Products

|           |                         |
|-----------|-------------------------|
| 90-150°C  | aliphatic materials     |
| 150-300°C | alkyl aromatics         |
| 300-350°C | methane<br>alkylphenols |

These workers suggest that alkyl aromatics released below 300°C are bound physically, rather than chemically, in coal. They believe that "true" decomposition begins at 320°C with the evolution of methane and that the alkylphenols result from methylene bridge rupture.

Juntgen and Van Heek (1968) observed that the thermal decomposition of coal was a function of the rate of heating. As the heating rate goes down, a component is volatilized at a lower temperature. Ethane, for

example, is evolved at about 400°C when the rate of heating in helium is  $2 \times 10^{-2}$  C/min. The temperature of evolution is 500°C when the heating rate is increased to 2°C/min. In the case of ethane, an additional peak which proved to be independent of heating rate was found at about 200°C. The size of this peak depended on particle size. Therefore diffusion controlled the release of this ethane.

Although heating rate affects emissions, pressure appears to have little or no effect at low temperature. Thermogravimetric analyses of three different coals under varying helium pressures from ambient to 5.6 MPa showed little if any effect on weight change during pyrolysis (Mahajan, 1976). Above 700°C, on the other hand, pressure does affect tar and methane yields (Howard, 1981).

Other low temperature effects include observable changes in the amount and kind of material extractable from the coal when it is heated in either an inert gas (Dryden and Parkhurst, 1955), or in solvents in their subcritical (Hargen, 1914 and Guin, et al. 1975) or supercritical state (Blessing and Ross, 1978, Bartle, 1980, Bartle, 1979). Radke (1982) states that the thermal effect in the temperature range 300-450°C is to dilate the pore structure of coal, due to molecular agitation, and allow the smaller aromatic molecules

which are occluded in the structure to be readily extracted.

Standing in contradiction to this interpretation of coal structure is the work of Chakrabartty and Kretschmer (1972). Their use of sodium hypohalite to attack methylene bridges in the coal, leaving the aromatic rings untouched, produced small, stable carboxylic acids in this low temperature reaction. Subbituminous coal, bituminous coal, and their respective chars and cokes all generate acetic and propionic acids. This evidence refutes the idea that there are small molecules occluded in the structure of the coal which escape on heating. Instead the coal structure contains stable (at least to 550°C) n-propyl and n-butyl groups. These groups remain in the structure (up to 550°C) and can react with the hypohalite.

Studies of free radical formation in coals show that, although there is a maximum number of free radicals formed at 600°C, there is an overall gradual trend of free radical formation in the 100-400°C range (Petrakis and Grandy, 1978). Hydrogen transfer reactions are associated with free radical existence. Studies by Heredy and Fugassi (1966) confirm the hydrogen shuttling ability of phenanthrene even at temperatures as low as 280°C. The increased extraction yields, with increasing temperature, indicate that the thermal effects promote

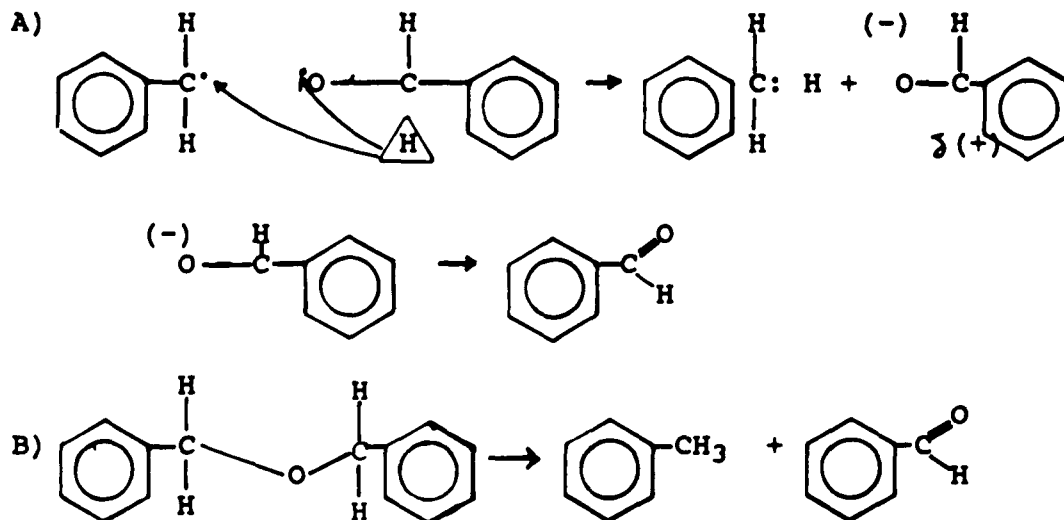
free radical formation. There appears to be an acceleration of this effect, or another superimposed effect, in the temperature range of 300-320°C where extractable yields jump from 40% to 85%.

In support of these low temperature free radical mechanisms is a study by Shibata and Arita (1985). In this work the electron spin resonance spectra of two subbituminous coals which had been dried and treated with pyrene were studied at temperatures between 150-450°C under N<sub>2</sub> at 1.1 MPa or about 0.1 atm. They show a temperature dependance of R (out of phase signal/in phase signal) which is proportional to T (spin lattice relaxation time). In the 150-300°C temperature range T increased, supposedly due to the loss of the paramagnetic oxygen molecules from the coal structure. At 380°C R showed a rapid decline due to pyrolysis which produced free radicals, and thus an increase in the number of paramagnetic species (and a decrease in T).

Additional evidence of low temperature activity below 350°C comes from DTA (Differential Thermal Analysis) and DSC (Differential Scanning Calorimetry) data. DTA and DSC studies of coal by different researchers yield conflicting information in this temperature region. Glass (1955) reports an endotherm in the 150-350°C region. Berkowitz (1957) reports an exotherm spread over the temperature range 200 to 340°C

(with a maximum at about 270°C). Later work by Mahajan et al. (1976) confirm the work of Glass and point out that studies which do not correct the DSC curves for weight losses are not accurate. These endothermic regions, between 250-330°C were also noted by Kirov (1967).

The most abundant element in coal, after carbon and hydrogen, is oxygen. Approximately 4% of the oxygen in a high volatile bituminous coal is present as diaryl or aryl-alkyl ether linkages (Lazalov and Angelova, 1968). Model compound studies using etheric reactants are used to predict the behavior of coal under different conditions. One such study at low temperature conditions (300-400°C) with a hydrogen donor solvent was reported by Cronauer, et al. (1979). Dibenzyl ether was pyrolyzed in the presence of tetralin (a hydrogen donor solvent) in low temperature regions 300-365°C and 365 - 400°C. In the lower temperature region tetralin was found to undergo only an insignificant amount of ring rearrangement. An interesting result was found at low temperatures. Dibenzyl ether reacted to form only benzaldehyde. At higher temperatures the benzaldehyde was formed, but only as a reaction intermediate to the formation of toluene. Two mechanisms were proposed:



The second mechanism (B) is favored at low temperatures. It is an intra-molecular hydrogen transfer reaction where the donor solvent does not participate.

Another study, also using dibenzyl ether as a model compound, shows a dependence of the products of pyrolysis on residence time (Schlosberg, 1981) and may be related to our observation that too long a pretreatment gives poorer liquid yields. Dibenzyl ether was pyrolyzed at 450°C in 4 MP of N<sub>2</sub> for 6 minutes and again for 90 minutes. The products of the short pyrolysis were exclusively toluene, benzaldehyde, and unreacted benzyl ether. The products of the 90 min. pyrolysis were toluene, benzaldehyde and numerous secondary reaction products including dimers, trimers and higher polymers of substituted benzenes.

Gethner (1985) has shown by use of FTIR that heating of thin sections of coal in vacuum to 100°C produces measurable changes in coal structure. He suggests that the chemistry involved concerns the cross-linking and/or hydrogen bonding in the coal structure. He speculates that the acidic C-O moieties in the coal are involved in thermally induced acid-base condensation reactions. The IR spectra also indicates that there is a formation of etheric links.

#### 4.3 Low Temperature Reactions

Low temperature reactions of coal with various reagents produce results which can be interpreted without the complications of thermal degradation of the coal.

One such study was reported by Chung, et al. (1983). In order to obtain structural information about coal they solubilized Wyoming No. 1, a subbituminous coal, in a NaOH/ethanol mixture at 210°C, 260°C, and 300°C. They obtained nearly complete dissolution of the coal at these low temperatures in the basic medium. This, according to the authors, indicates the presence of easily attacked oxygen functional groups in the coal structure.

Another reaction to which coal has been subjected at low temperatures is treatment with boron trifluoride

at 100°C to produce a "completely solubilized suspension resembling a thixotropic gel." This result is interpreted as support for the idea that the coal is depolymerized, even under these mild conditions (Heredy and Neuworth, 1962). Chow (1983) also showed that mild pretreatment of bituminous, subbituminous, and lignite coals in NaOH aqueous solutions (temperatures 100-300°C) is sufficient to cause an increase in the subsequent liquefaction product.

Evidence of low temperature bond disruption (depolymerization) can be found in experiments of coal swelling. Coals are known to swell at low temperatures with the addition of solvents (Mederios and Peterson, 1979; Neavel, 1982). Some researches note the incorporation of solvents at mild temperatures. Spencer (1984), for example, cites work done by SRI International in which low temperature (300°C) solubilization of coal in tetrahydroquinoline shows that even though the solvent loses hydrogen the coal does not accept the hydrogen. Instead, the coal forms a coal-solvent complex. This process is believed to occur with all solvents to some extent, it is, however, amplified in the work with basic nitrogen heterocyclic compounds. Additional information on coal swelling is given in Section 4.9.

In experiments done at Rockwell International, low

temperature base catalyzed reactions which involve the selective attack of oxygen functional groups were used to solubilize coal (Spencer 1984). Three classes of reactions of reactions were noted:

- 1)  $<215^{\circ}\text{C}$  - hydrolysis of ester groups
- 2)  $<260^{\circ}\text{C}$  - decarboxylation
- 3)  $<300^{\circ}\text{C}$  - hydrolysis of other-than-ester functionalities

In investigating pretreatment, the studies described above must be kept in mind. The same low temperature reactions may occur during exposure to steam.

#### 4.4 Steam Reactions

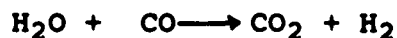
The steam-carbon and steam reforming reactions are well known but occur at higher temperatures than are of interest here. In thermal cracking of petroleum fractions, steam has been considered an inert medium. Some recent studies, however, show that steam can be more than a passive heat transfer agent even at lower temperatures.

The work of Tyler (1981), which is based on the work of Allred (1979) and Lewan, et al. (1979), deals not with coal but with shale oils. Shale oils are preponderantly heavy, highly nitrogenous, organic mixtures and fall between crude oil and coal in their complexity and difficulty in refining and handling.

Tyler demonstrated that cracking of shale oil liquids in supercritical steam at temperatures to 425°C and pressure up to 100 atm significantly reduces the average molecular weight of the greater than C-25 compounds and simultaneously hydrogenates the material. There is also a reduction in the sulfur and nitrogen content of the oil. The important point recognized by Allred, Lewan, and Tyler is that steam is not an inert medium for hydrocarbon thermal reactions, but instead is a highly reactive and participatory agent.

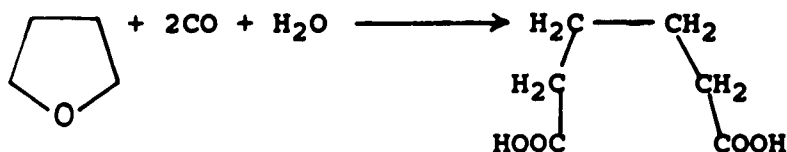
Model compound work by Ross, et al. (1982) shows that in deuterated steam at 400°C and 184 atm the ether bond in anisole reacts at a rate five times that calculated for thermal rupture. If anisole is considered to be a model for ether-aryl linkages in coal, these data imply that steam has the ability to bring about depolymerization of the coal structure by cleaving what are otherwise thermally stable bonds.

Experiments by Ross and co-workers (1983a) using supercritical water as a reaction medium produces more than 50% conversion of an Illinois No. 6 coal to benzene soluble products. This work, however, is an extension of the COSTEAM process which utilized synthesis gas (CO and H<sub>2</sub>) as the reducing agent in the liquefaction process. The hydrogen is produced from the water-gas shift reaction (WGSR):



Ross fairly conclusively showed that it is not the produced  $\text{H}_2$  which is the active agent in the system, but rather some, as of yet unidentified, intermediate in the WGSR which is formed only in the presence of  $\text{CO}$ .

When small amounts of water (12.5 - 17.5% by weight) are added to an oxidized coal and it is then autoclaved, under 1000-1500 psi  $\text{CO}$  pressure, for 0.3 - 60 minutes the combustion and carbonization properties of the coal are restored (Nandi, et al., 1981). The authors speculate that the hydrogen produced in the WGSR plays a direct role in improving the quality of the coal or the carbon monoxide in conjunction with the water plays a direct role in opening ether linkages in the coal as by the reaction:



Ross (1983b) has demonstrated that exposure of Illinois No.6 Coal to water at fairly low temperatures ( $400^\circ\text{C}$ ), but at high pressure (4000-5000psig) results in a loss of 38% of the coal's initial oxygen content. The oxygen may be lost from the coal in the form of  $\text{CO}$ ,  $\text{CO}_2$ ,

and H<sub>2</sub>O, but this has yet to be determined.

Studies with steam in its supercritical state give supporting data for the removal of heteroatoms from coal-model molecules (Tiffany, et al., 1984). At temperatures between 350-500°C isoquinoline was converted to non-nitrogenated species in the presence of supercritical steam 18-85%. Quinoline showed a stronger resistance to conversion at 7-62%. System pressure for these experiments was between 3640 and 5650 psi.

Steam can actively remove material from mineral matter which can be as high as 30% by weight of the coal. A study by Herod, et al. (1983) shows that on mild heating in helium coal releases HCl along with other volatile materials. The authors state that the release of HCl corresponds to a maximum for the emission of water from the coal. They conclude that the steam is carrying the HCl out of the coal. Holder, et al. (1983) report that supercritical steam leaches the inorganic sulfur from the ash content of the coal.

The effects of supercritical steam on glucose, cellulose, and sawdust were described by Modell, et al. (1980). All three organic materials were partially converted to gaseous products with no formation of char. The use of supercritical water for the conversion of coal to liquid and gaseous products was tested by Holder, et al. (1983), and Deshpande et al. (1984). Some

important results on the reactivity of coal in supercritical water has come from their work. First, the injection of coal, rapidly, into the supercritical conditions was found to yield 10 times less char than when the coal was allowed to heat slowly in water from subcritical to supercritical conditions. This is attributed to a rapid suspension and dilution of primary products in steam, retarding further reaction to heavier materials. Secondly, THF insolubles (char) were considerably decreased when higher supercritical densities were used. There was also observed a leveling off of product production with time of reaction. The percent of gases and liquids extractable from a bituminous coal was approximately constant at 50% after 30 minutes.

Tiffany (1984) reports the conversion of a number of aromatic hydrocarbons to other materials in the presence of supercritical steam, including 100% conversion of tetralin to benzene (1.5 mol %), toluene (7.0%) ethyl benzene (8.9%) and naphthalene (45%) as determined by gas chromatography. Indan and methyl indan have been tentatively assigned to the remaining chromatographic peaks. Dihydroanthracene was converted >50% and ethylbenzene 10%.

#### 4.5 Thermodynamics of Water-Hydrocarbon Systems

Attempts to understand the chemistry and physics of the pretreatment process will be severely hampered unless it is known what phases are present. Unfortunately, it is not presently possible to model the phase behavior of coal-steam systems reliably. From fragmentary information in the literature, the region appears to be complex.

Data for binary hydrocarbon water systems are summarized by Schneider (1970). Although these substances have little mutual solubility at ordinary conditions, even complete miscibility may be reached well below the critical point of water. This is especially true with aromatics. In the naphthalene-water system, for example, the critical solution temperature is as low as 310°C at 100 atm. More recent studies of the mutual solubility of hydrocarbons and water have been reported by Tsonopoulos and Wilson (1983) and Heidman, et al. (1985).

Studies designed to mimic the conditions of an oil basin were conducted using pressures to 2000 bar and temperatures up to 400°C to test the aqueous solubility of crude oils (Price, 1981). In the presence of light gases (CO, N<sub>2</sub>, CH<sub>4</sub>) the solubility of the high molecular weight hydrocarbons (larger than C-24) increased regardless of the temperature. The author also reports

an increase of the lower molecular weight material's solubility at the higher temperatures. There are a number of studies concerning the mutual solubilities of hydrocarbon water systems at elevated temperatures and pressures (Roof, 1970; Skripka, 1979; Skripka, 1976; Wormald, et.al., 1983). Measurements have been made of excess enthalpies and solubilities. Empirical correlations have been derived for determining the solubility of hydrocarbon mixtures in water based on the solubility of the pure compounds (Amirijafari and Campbell, 1972). Three phase critical points have also been determined (Pirela, 1968).

#### 4.6 Pretreatments

A number of interesting results have been obtained by researchers dealing with tar sands and heavy petroleum oils. Itoh (1983), and Suzuki (1982) have found that two stage thermal pyrolysis processes produce a better product. In both cases the organic material was subjected to a low temperature zone and then transported into a higher temperature zone. Fukuyama, et al. (1983) report that the low temperature thermal pretreatment of low rank coals (60 minutes in nitrogen at temperatures between 250 and 350°C) improve liquid yields in slurry liquefaction. Pretreatment of coal with water was studied by Mochida, et al. (1982). They find that

merely boiling coals in water produces significant increases in extractables.

Preheating bituminous coal at temperatures below 375°C in helium produced no significant weight losses or changes in elemental composition. However, when these coals were then subjected to sodium hypochlorite oxidation the yield of carboxylic acids varied with the temperature of the pretreatment (Chakrabartty, 1977). The authors postulate that this is caused by low temperature intra-molecular isomerization which alters the carbon-hydrogen configuration of the coal without the coal undergoing thermal cracking.

It has been noted (Palmer, 1984) that aromatic hydrocarbon molecules are approximately 200 times more water soluble than n-alkanes with the same carbon number. Studies done at temperatures below 250°C (Price, 1976) show sulfur containing compounds (thiophene and 2-ethylthiophene) to be approximately twice as soluble in water as aromatic hydrocarbons of similar molecular weight. The effects of these properties were demonstrated in work reported by Gould (1981). A comparison was made of the properties of asphaltenes (pentane insoluble, benzene soluble portion) of the crude oil from a steam stimulated well and a "cold boiled" (no steam) well. The asphaltenes from the steam produced oil showed a lower H/C ratio (i.e. a higher

aromatic content). Oil recovery has been likened to a giant chromatography column (Farcasiu and Brandes, 1980). The affinity of the more aromatic portions of the oil, in the steam (the carrier) than for the rock (the support) is evident in this work by Gould. The preponderance of these classes of material in the coal structure indicate the susceptibility of coal to alterations in its makeup in the presence of water (steam).

#### 4.7 Weathering

Weathering of raw coal spoils its coking properties and reduces yields in conversion processes. It has, consequently, been the subject of a fair degree of attention and detailed chemical studies. Thermogravimetric and differential thermogravimetric studies by Hill (1984) "support a weathering mechanism dominated by the formation of cross-links between coal molecules,..." for raw coal, where effects are noticeable after a number of days. The weathering process is known to reduce yields of coal derived liquids (Wachowska, 1977; Furminsky, 1983; Neavel, 1976; Davies, et al., 1976; Cronauer, et al. , 1984).

Other effects noted for "weathered" coal are a decrease in dilatation, an increase in reactive oxygen groups, and a small decrease in the aliphatic and

alicyclic carbon and hydrogen content (Ignasiak, 1972). The loss of activity of the exposed pretreated coal could be due to the formation of acidic hydroxyl groups (Ignasiak, 1974) or relatively stable ether links which Liotta (1983) claims are formed in freshly mined Illinois No. 6 coal at atmospheric conditions.

#### 4.8 FTIR

Infrared spectroscopy has been used to analyze coal for over thirty years. Brown (1955) using a pelleted sample obtained the relative proportions of -OH and -C-H groups in coal samples. He showed a rank dependence on the ratio of the intensity of the stretching mode of aromatic and aliphatic C-H bonds. Conventional ir, however, has inherent problems. Primarily, the signal to noise ratio for a solid sample such as coal is low. The sample must be dispersed in a non-adsorbing medium; traditionally alkali-halides (KBr, CsI, etc.) have been used. These materials, however, are hydrophilic and as such are difficult to use if the -OH region of the unknown material is to be investigated. Other sample preparation techniques are casting a film from solutions (this necessitates the sample to be soluble) and preparing a mineral oil mull. These techniques pose problems of reproducibility (Fuller, et al., 1982).

With the advent of computerized techniques to take

advantage of the increased sensitivity obtainable by using an interferometer rather than a conventional ir with diffraction gratings and narrow slits, there has been a resurgence in the use of ir for coal analysis.

Solomon (1982) outlined the advantages of FTIR for coal samples and they are listed here without further explanation:

1. speed
2. on-line analysis
3. high signal/noise (ability to co-add spectra and a high through-put)
4. digital storage of spectra which permits:
  - a. base line correction
  - b. smoothing
  - c. spectral comparison
  - d. spectral synthesis
  - e. factor analysis
  - f. correlation techniques
  - g. solvent subtraction
  - h. mineral subtraction
  - i. display and plotting flexibility
  - j. programmed control of experiments

Painter (1982) strongly warns of putting too much emphasis on spectral synthesis methods.

Diffuse reflectance techniques have been applied to coal since 1978 (Fuller and Griffiths, 1978). Other researchers have also utilized diffuse reflectance techniques for coal analysis (Krishnan, et al., 1980, Krishnan and Brown, 1980). In these works the powdered coal sample was diluted with powdered KBr or KCl. Vidrine (1980) and Fuller (1982) have shown that undiluted samples can be analyzed with a high degree of reproducibility. This is important for the use of FTIR

in following reaction processes where dilution of the coal would be undesirable. Gethner (1982) has shown that DRIS can be utilized with thin sections of native coal.

FTIR has been utilized in observing the hydroxyl hydrogen in coal (Gethner, 1982), the degree of oxidation of a coal (Fuller et al., 1980, Fuller and Smyrl, 1985) and low temperature drying effects on coal (Gethner, 1985). FTIR measurements have been made and correlations have been drawn between structures discernable in ir (namely the  $\text{CH}_2$  content) with the liquefaction behavior of a given coal (Senftle, 1984).

#### 4.9 Extraction

Extraction of coal and treated coal comprises a large section of the coal analysis literature. Here our concern is restricted to the effects that low temperature or steam treatment of coal has on the extraction yields.

An excellent review of coal solubility and extractability was given by Pullen (1981). Berkowitz (1985) offers a detailed, updated compilation of extraction literature. Both authors define distinct extraction regimes. These regimes are defined by extraction temperatures. This survey is concerned with the lowest temperatures, at or below the normal boiling point of common solvents.

Squires, et al. (1983), for example, found that heating Illinois No. 6 coal in vacuum caused a reduction in its pyridine solubility beginning at 200°C. A parallel effect was observed when samples heated in flowing methanol were subsequently extracted with pyridine.

Pyrolysis experiments with coal, or solvent-extracted portions of the coal, show increased amounts of aromatic extractables after treatment at about 350°C (Radke, 1982). The coals themselves, when subjected to temperatures of 250-340°C, show some rank dependent reactions. Low rank coals release quantities of chloroform soluble material; low and high rank coals release small quantities of alkyl aromatics (Kirov, 1967). Coking coals when preheated in the temperature range of 250-400°C in vacuum and then extracted with chloroform show a maximum in the amount of material extractable when the preheating temperature corresponds to the softening point of the coal (Chen, et al., 1985). This phenomenon is associated only with coking coals. The authors attribute the effect to the ability of small molecules in the coal structure to migrate to the surface of the coal where they are easily washed away with solvent; migration is most rapid at the softening point. If the plastic temperature region is exceeded, they believe larger molecules are broken from the

structure of the coal. These materials are not extractable. Given, et al. (1986) review other literature which supports the view that the coal is a matrix which contains small occluded structures which can be made accessible by a variety of means in extraction processes.

Brown and Waters (1966b) state that the yield of extractable material (via soxhlet extraction in pyridine for 66 hours) increases after heating in an inert atmosphere (250-450°C) followed by shock cooling the sample to ambient temperature. Their experiments mimic those done by Dryden and Pankhurst (1955) who clearly state that the effect is evident only with a coking coal.

Another low temperature extraction process is described by Iino and Matsuda (1983). They report that a mixed solvent of carbon disulphide and pyridine more than doubles the amount of extractable yield at room temperature than what is attainable in just pyridine alone.

#### 4.10 Swelling

The structure of coal contains numerous cross-links. Both covalent and hydrogen bonding are present. This structure will swell when exposed to suitable solvents. To measure the degree of swelling and hence be

able to determine the relative number of cross-links (and the nature of the cross-links), a distinction must be made between true swelling and the solvent uptake due to physical adsorption and pore filling by the solvent. (Nelson, et al., 1980). These two effects influence gravimetric swelling measurements. To get around this problem Dryden (1951) corrected for pore volume by making independent measurements of the pore volume in helium. There are problems associated with this approach in that different solvents interact with the pores differently.

Green, Kovac, and Larsen (1984) demonstrated that the bulk swelling, volumetric, technique developed by Liotta (1983) was superior to gravimetric methods. They state that the volumetric technique is one, more rapid and two, is insensitive to solvent that fills the pores, thus requiring no corrections to the data. The action of different solvents on the swelling behavior of the coal has been shown by Larsen, et al. (1985) to be a function of the solubility parameter of the solvent. It is also a function of the ability of the solvent to disrupt hydrogen bonds (Green and Larsen, 1984). For example coal swells more in pyridine-chlorobenzene than in chlorobenzene alone.

The use of this volumetric technique has been extended to determine the cross-link density of the

coal. Using an extension of regular solution theory, Larsen, Green, and Chiri (1983) have shown that using the Flory-Rehner equation, or a modification of it, the number average molecular weight between the cross-links ( $M_C$ ) can be calculated. An expansion of this work is presented in Larsen, et al. (1985).

Swelling measurements are useful for following the formation of cross-links as well as their disruption. Suudberg, et al. (1985) describe the decrease in swelling when bituminous and lignite coals are pyrolyzed. They also state that the presence of water in the lignite has the effect of causing cross-linking to occur more readily than in the dried sample. They suggest that the water may be involved in the pyrolysis process.

#### 4.11 Liquid Analysis

##### 4.11.1 Separation

There exist many methods for separation of coal derived liquids into defined classes. By analysis of each class a general understanding of the whole material can be approached.

Solvent solubility schemes have been widely used. Two of the most popular were proposed by Mima (1976) and Ruberto (1974). Whitehurst (1982) discusses the power of combining different separation techniques such as liquid

and gas chromatography and liquid chromatography coupled with field ionization mass spectroscopy. Herod, et al. (1986) point out that in most cases for coal liquids gas chromatography is not usable due to the low volatility of the samples. They instead make use of LC/MS techniques, but even here they have difficulty with some portion of the liquids not volatilizing into the ion source of the mass spec and, therefore, not being analyzed.

In this work the combination of liquid chromatography followed by GPC (Sec. 4.11.2) and gas chromatography (Sec 4.11.3) has been employed. The method used here for separation by liquid chromatography is that described by Farcasiu (1977).

#### 4.11.2 Molecular Weight Determination by GPC

The molecular weight distribution of product liquids from coal conversion studies is one of the biggest indicators of the effectiveness of the process. Lighter (smaller) condensible molecules are more easily upgradeable and present fewer problems in handling. Determining molecular weights of coal liquids, however, is still a difficult task.

Size exclusion chromatography (SEC) also known as gel permeation chromatography (GPC) is a technique in which the molecules are separated based on their ability

to permeate a porous support structure. They are, therefore, separated on a size basis. Larger molecules unable to penetrate the pores move through the column with the mobil phase. Smaller molecules are slowed by their excursions into the pores. The separation is therefore dependent on the size of the pores and the size of the molecules. It must be noted that whereas size is usually directly related to molecular weight this is not always the case. The determination of molecular weight from GPC data is made by calibration of retention volume (time) with a series of standards. Bartle, et al. (1984) have shown that for molecular weights up to 1000 polystyrene standards are acceptable. As is discussed in Sec. 4.11.2 this is not the opinion of this author. They suggest that above this weight alternative polymer standards such as polyacenaphthalene be used or a correction can be made to the polystyrene standard curve. Olson, et al. (1986) point out that by altering the method of detection in a GPC system the use of calibration curves can be eliminated. His group utilized low angle light scattering laser (LALLS) photometry. This method gives a direct determination of molecular weight as a number average, weight average and z-average value. The method has a number of drawbacks in that the sample must be colorless at 633nm (the laser wavelength) and there is only discernable an average

value of the molecular weight. The advantage GPC has over other methods for determining molecular weight (vapor phase osmometry, membrane osmometry, ultra centrifugation, and electron microscopy) is that a distribution of molecular weight not just an average value can be determined.

Another approach to the problem of calibration in GPC was made by Evans, et al. (1986). He shows clearly that on a calibration curve using THF as the eluting solvent not all the compounds considered (polynuclear aromatic hydrocarbons, PAH, polystyrene standards, and coal tar components) fall on a given line. If the solvent is switched to  $\text{CHCl}_3$  the discrepancies are eliminated. Hydrogen bonding to the THF of the phenolic groups in the species which fall farthest off the line when using THF is offered as an explanation for the shift.

GPC has also been used as a technique for preparative separation of coal liquids with some success (Bartle, et al., 1979, Deutcher, et al., 1983).

#### 4.11.3 Boiling point Distribution by GC

The use of gas chromatography to analyze volatile materials is a standard analytical technique. Commercially available equipment and columns are designed for the specific separation needs of the

researcher. Many reviews exist in the literature of the usefulness of the method and its application to fuel materials. McNeil (1981) gives a comprehensive review of the application of the method to coal tars.

The one limitation placed on the ability to separate materials in a GC is the volatility of the material. Even though stationary phases are made to withstand relatively high temperatures (320°C) there is considerable deposition of coal derived materials at the head of any column. Methods devised to get around this problem usually entail removal of the most polar materials from the high boiling liquids and then subjecting them to further separations prior to chromatographing them. A good example of such a procedure in the recent literature is the work of Poirier and Das (1984). There are many other examples of similar schemes (Wright, 1983).

#### 4.12 Conclusions

A number of important points can be noted from this literature survey:

The temperature range between 300 and 350°C is a very interesting one for coal. It is a threshold region where the softening of plastic coals is incipient. There is ample evidence (Section 4.3) that changes in chemical structure are induced merely by heating coal to

these temperatures or even below. Some of these changes result in increased yields of extractables. With the evidence cited in Section 4.4, it can no longer be assumed that steam is inert. The reports of steam reactivity toward oxygen functional groups in coal and a model compound are especially interesting. If this results in partial depolymerization of the raw coal, it offers an explanation of the increased yields of pyrolysis liquids. It also offers a link to another experimental observation: that pretreated coal is very sensitive to exposure to ambient air.

The complex phase behavior of steam-hydrocarbon systems opens several interesting possibilities for physical and chemical interaction. Even though pretreatment conditions are subcritical (the critical point of steam is 374°C, 218 atm.) we may expect a condensed aqueous phase and a high degree of mutual solubility. Water may dissolve in the coal (especially the partially softened material) greatly increasing chances of reaction. Internal hydrogen transfer may be improved. In water, at the densities of a condensed phase, ionic reactions are conceivable.

This literature search offers several avenues for explaining the empirical results. It does not, however, allow choice to be made among these or to provide a detailed description of the process.

The references cited in Sections 4.8-4.11 give a background on the techniques employed in this study to further understand the behavior of steam treated coal. They are not intended to be a complete survey, but offer significant justification for the usefulness of the methods.

## 5. EXPERIMENTAL EQUIPMENT

### 5.1 Steam Pyrolysis

#### 5.1.1 Reactor

The reactor developed for these studies, illustrated in Figure 5.1.1, is of the batch type. In order to obtain rapid heating, an externally held coal sample is injected into the hot reactor. The injected sample is captured on a trap, providing long solid reaction times, while the volatile products are swept away by a continuous flow of steam supplied to the reactor.

The reactor is constructed of 25 cm length of 316 stainless steel pipe, 2.5 cm i.d. and 3.8 cm o.d. A trap of -8+10 mesh quartz chips 2.5 cm deep, supported by a drilled steel plate is near the center of the reactor. The tip of the coal injection tube is located 15 cm or less from the trap. At this distance the angle of divergence of the jet (about 7°) is small enough to prevent impingement of coal particles on the reactor wall.

The reactor is provided with two outlets; one is used during pyrolysis and the other during oxidation of residual char. This avoids combustion of any volatile material which might deposit in the exit piping during pyrolysis. Outlet valves in these lines control the rate of flow of gases through the reactor. Across these

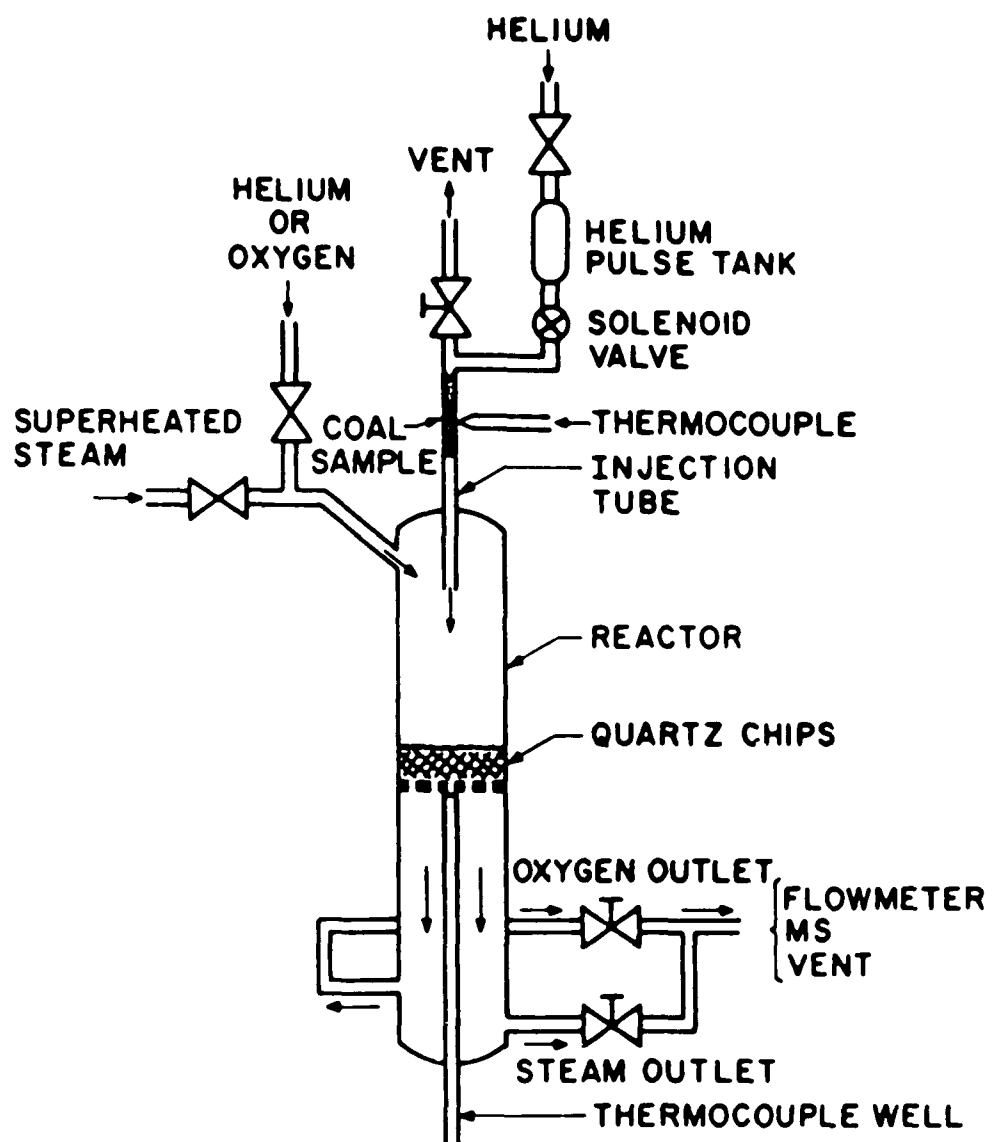


Fig.5.1.1.1 Steam Pyrolysis Reactor Using Batch Injection of Coal Sample

valves, which are located close to the reactor, the pressure drops to one atmosphere. The pressure and temperature drop across the steam outlet valve (downstream piping is at 150-200°C) serves to quench the reaction.

An inlet in the steam line just ahead of the reactor is used to terminate a run by rapidly flooding the reactor with helium. The same inlet is used to introduce oxygen for combustion of residual char.

Coal pretreatment, when desired, is carried out on the sample held in the injection tube. The tube is 5.1mm i.d., about 16cm long. The injection tube is fitted with an electric heating mantle and temperature is read from a thermocouple spot welded to the external surface of the tube. A vent valve above the sample is used to control the flow of gases through the injection tube.

#### 5.1.2 Reactor System

The system incorporating the steam pyrolysis reactor is diagrammed in Figure 5.1.2 (a key listing is provided in Table 5.1.1). Steam is raised at about 300°C and 50 atm in boiler 1. Air operated valve 2 controls steam pressure. While steam is vented, the remainder of the system is brought to temperature under a flow of helium. When the system is hot enough to avoid condensation, the helium supply is shut off and steam

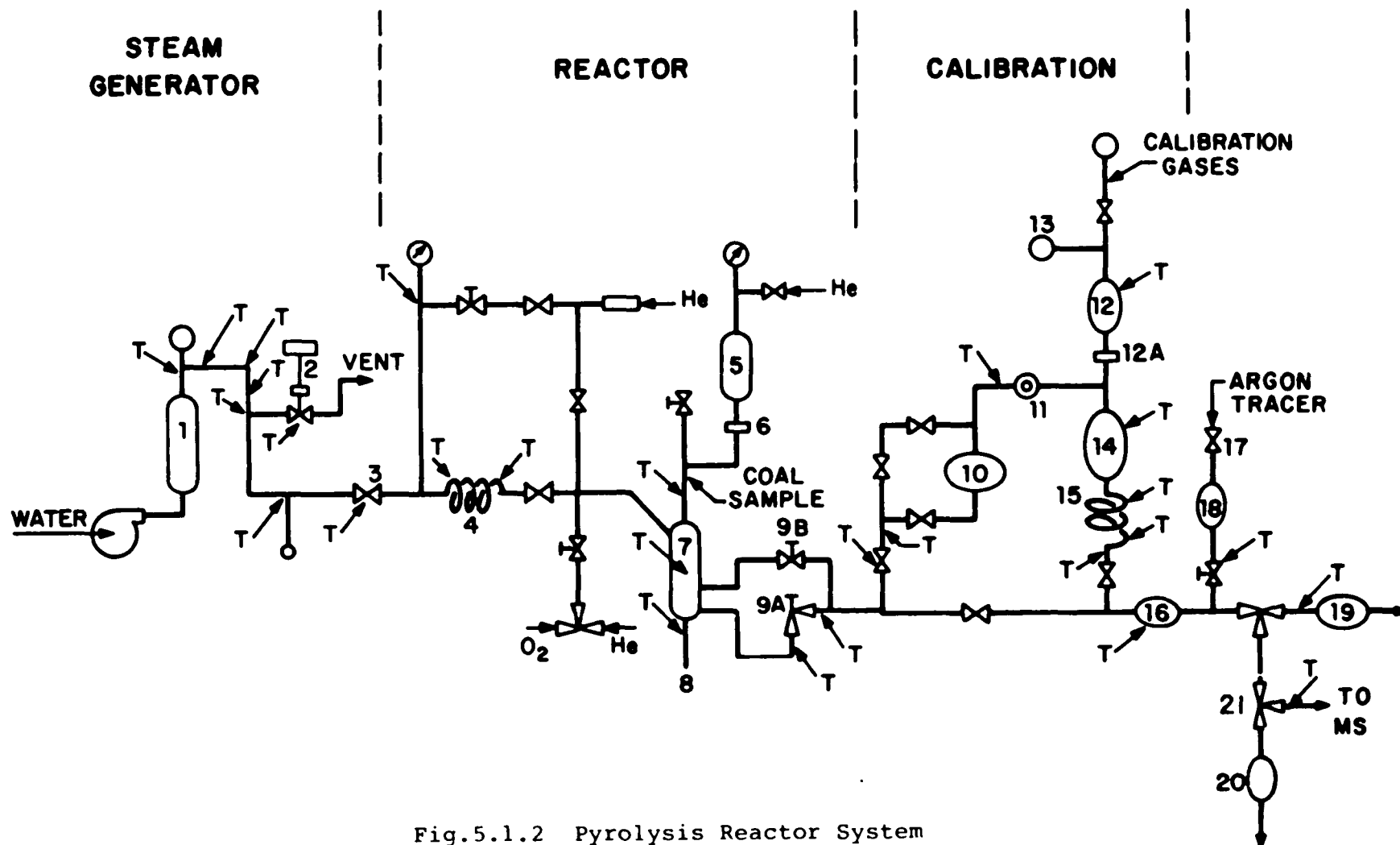


Fig.5.1.2 Pyrolysis Reactor System

Table 5.1.1

Key to Steam Pyrolysis System

| <u>Item</u> | <u>Description</u>          |
|-------------|-----------------------------|
| 1.          | boiler                      |
| 2.          | pressure control            |
| 3.          | steam supply valve          |
| 4.          | superheat coil              |
| 5.          | low pressure gas inlet      |
| 6.          | high pressure helium inlet  |
| 7.          | reactor                     |
| 8.          | reactor thermocouple        |
| 9.          | steam flow control valve    |
| 10.         | calibration loop            |
| 11.         | liquid injection port       |
| 12.         | calibration volume          |
| 12A.        | solenoid valve              |
| 13.         | differential pressure gauge |
| 14.         | surge volume                |
| 15.         | surge coil                  |
| 16.         | turbine flow meter          |
| 17.         | flow control valve          |
| 18.         | mass flow meter             |
| 19.         | condenser                   |
| 20.         | vacuum pump                 |
| 21.         | mass spec sampling point    |
| T.          | thermocouple                |

admitted through valve 3. Steam is superheated in coil 4 before entering reactor 7. Thirty thermocouples are located throughout the system at points indicated by the symbol T.

Steam flow rate is adjusted by means of manually operated valve 9A; downstream of this valve the pressure is one atmosphere. Turbine meter 16 is used to indicate steam flow rate. Calibrations for this meter are produced by direct measurement of the output from condenser 19.

Argon tracer, at a precisely controlled flow rate, is added to the steam flow after the turbine meter. A portion of the stream is drawn into a vacuum line from which it is sampled by the mass spectrometer. The use of tracer gas in this way makes the determination of yields independent of the steam flow rate and of the fraction diverted to the mass spectrometer.

During the time the system is being brought to a stable condition, the coal sample is held in an injection tube above reactor 7. Opening solenoid valve 6 allows a charge of helium stored in tank 5 to blow the coal sample into the reactor where it is trapped and rapidly heated. Data sampling by the mass spectrometer is triggered at about the same time so that the intensities of product and tracer species are automatically recorded when they are carried into the

instrument by the flowing steam.

To terminate the run, the steam flow is shut off and the system purged with helium. The pressure is reduced and oxygen is admitted to burn out the remaining char. Carbon oxide intensities are recorded during this step. A carbon balance is now calculated using the observed intensities and a series of calibrations determined separately.

Calibrations are performed using the piping circuit located between the reactor and the flow meter. Known amounts of components are injected into steam using calibrated volume 12 or loop 10 for gases or injection port 11 for liquids. Tank 14 and coil 15 provide the dispersion required to simulate the pulse which, during an experiment with coal, comes from the reactor. Calibrations for char combustion are determined by injecting a weighed amount of carbon black into the reactor and burning this material following the procedure used for char.

#### 5.1.3 Reactor Development

In the first version of the pyrolysis reactor (Fig.5.1.3A), the drilled steel plate supporting a trap of quartz chips was mounted on a sleeve sliding into the reactor. This was welded to a flange and bolted to the bottom of the reactor at a point below the reactor

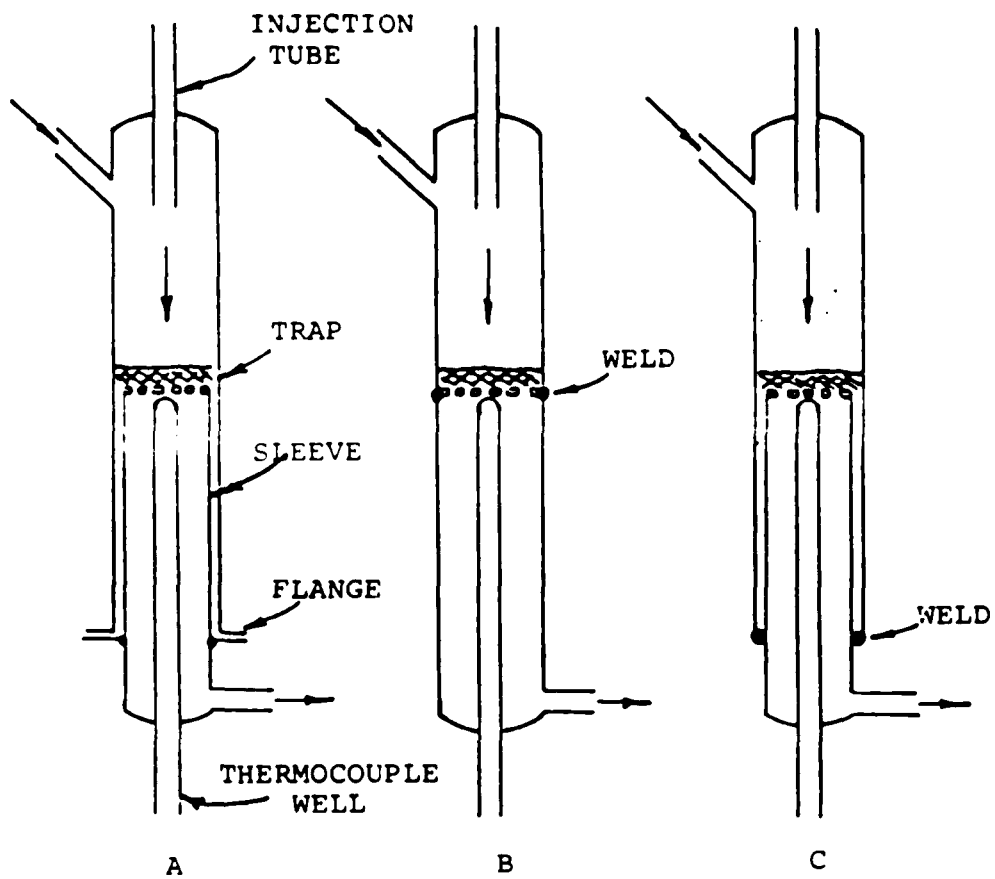


Fig.5.1.3 Steam Pyrolysis Reactor Modifications

furnace in order to allow the trap to be easily removed for char recovery and cleaning.

Initially the lower end of the reactor was maintained at about about 300°C. Excessive amounts of carbon monoxide were observed in the pyrolysis and oxidation steps. In some cases the total carbon recovered as CO and CO<sub>2</sub> in oxidation exceeded the amount of coal charged. Blank runs (without coal injection) showed CO in the oxidation step but not in pyrolysis. On the assumption that this was a result of condensation of heavy liquids in the bottom of the reactor, the temperature of this section was raised to 600°C. This reduced the CO to negligible levels in oxidation and to reasonable levels in pyrolysis.

At this higher operating temperature the seal at the flange could not be maintained. In the second version, the reactor was fabricated from two half-sections with the drilled plate welded in place (Fig. 5.1.3B). While this design made construction easier, it placed the weld at the hottest point in the reactor. After repeated failure of this weld over a period of a few months, the design was abandoned.

The third version (Fig. 5.1.3C) is similar to the first employed (Fig. 5.1.3A) except that the flange is replaced by a weld. Trap material is removed, when necessary, by aspiration through a tube inserted through

the top of the reactor. This design gives a reactor life of about six months.

After successive runs with this reactor design the reactor wall would bulge and eventually rupture. It was found that the inner and outer tube swelled apart from each other in the repeated heating and cooling cycles. This allowed deposits of char, quartz and scale from the upper part of the reactor to deposit between the two tubes. Eventually the accumulation was large enough to cause the outer reactor wall to crack. The design B was again employed. The welding was done by an outside contractor, no weld failures have occurred, however, the reactor system is no longer operating at temperatures above 900°C.

#### 5.1.4 System Modification

In the course of this study the system was modified a number of times. Each modification was made to check or improve the system performance. A major change was made for continuous coal feeding to increase the reactor capacity. Changes were also made in the liquid collection system (Sec 5.1.5).

#### 5.1.5 Liquid Collection

Two arrangements have been used for collecting liquids in the steam pyrolysis system. In the first

method, product was collected at reactor pressure. A trap, constructed of 40 feet of 1/4 inch stainless steel tubing wound into a coil, was inserted between the reactor and the main flow control valve (Fig. 5.1.4). This trap was maintained at 500°C and had a volume equivalent to 30 seconds of reactor output at 50 atm. In preparation for collection both air operated valves were open and the entire reactor effluent was allowed to flow continuously through the trap. Coal was injected into the reactor with a helium pulse and 30 seconds later the trap was sealed by simultaneously closing the air operated valves. The trap was then removed and its contents analyzed. For operation without collection the bypass line was used.

This arrangement had certain disadvantages. Since the collected liquids were held at 500°C for several minutes or more in a trap of high surface area, they were likely to react further (perhaps coking) before quenching. Also, the volume of the trap could not conveniently be increased to allow collection for longer times.

In the second arrangement product was collected in an evacuated tank at lower temperature. In this arrangement the sample tank is located after the main flow control valve (Fig. 5.1.5). During start-up, while the system is being brought to steady conditions, air

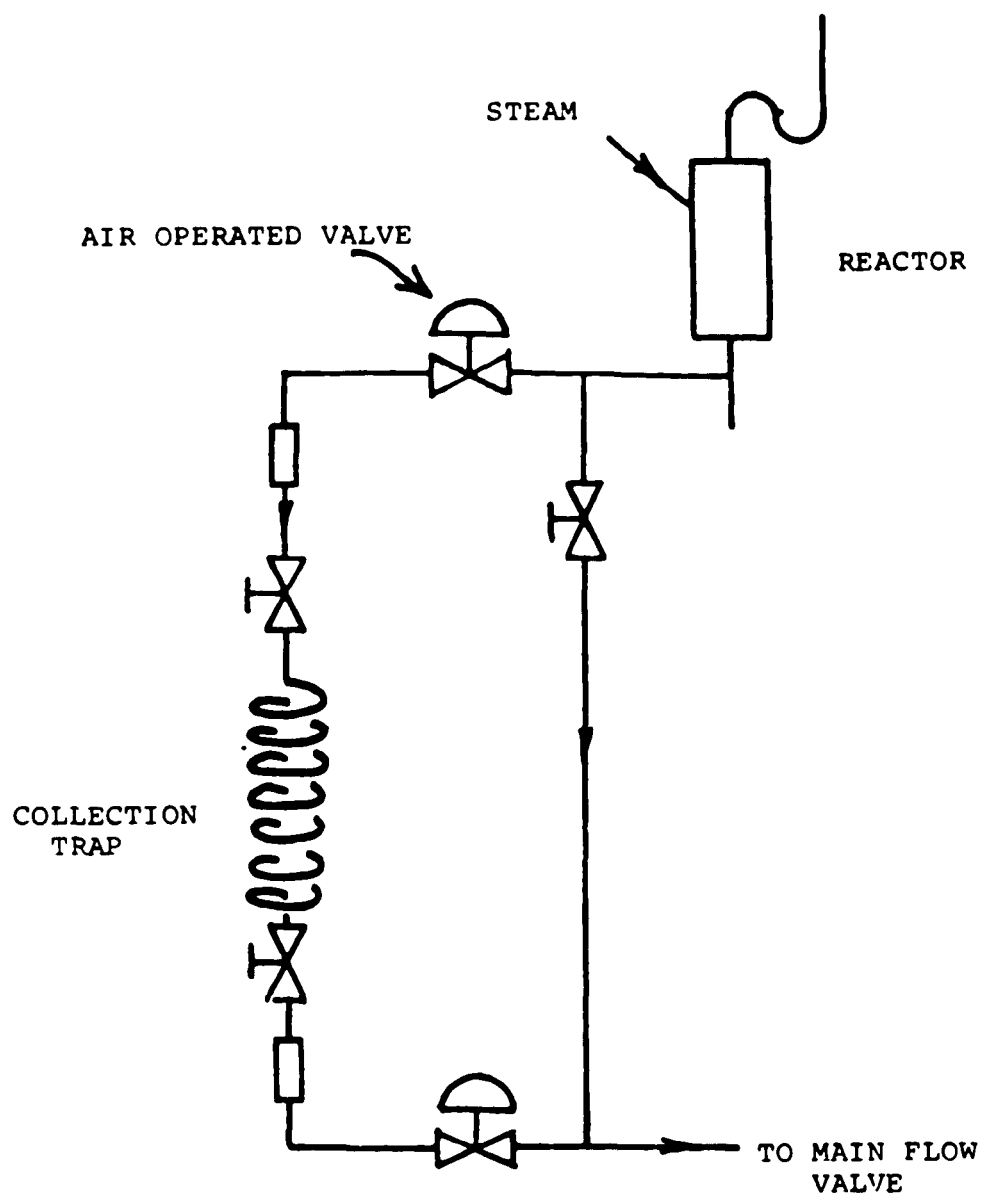


Fig.5.1.4 Steam Pyrolysis Liquids Collection System 1

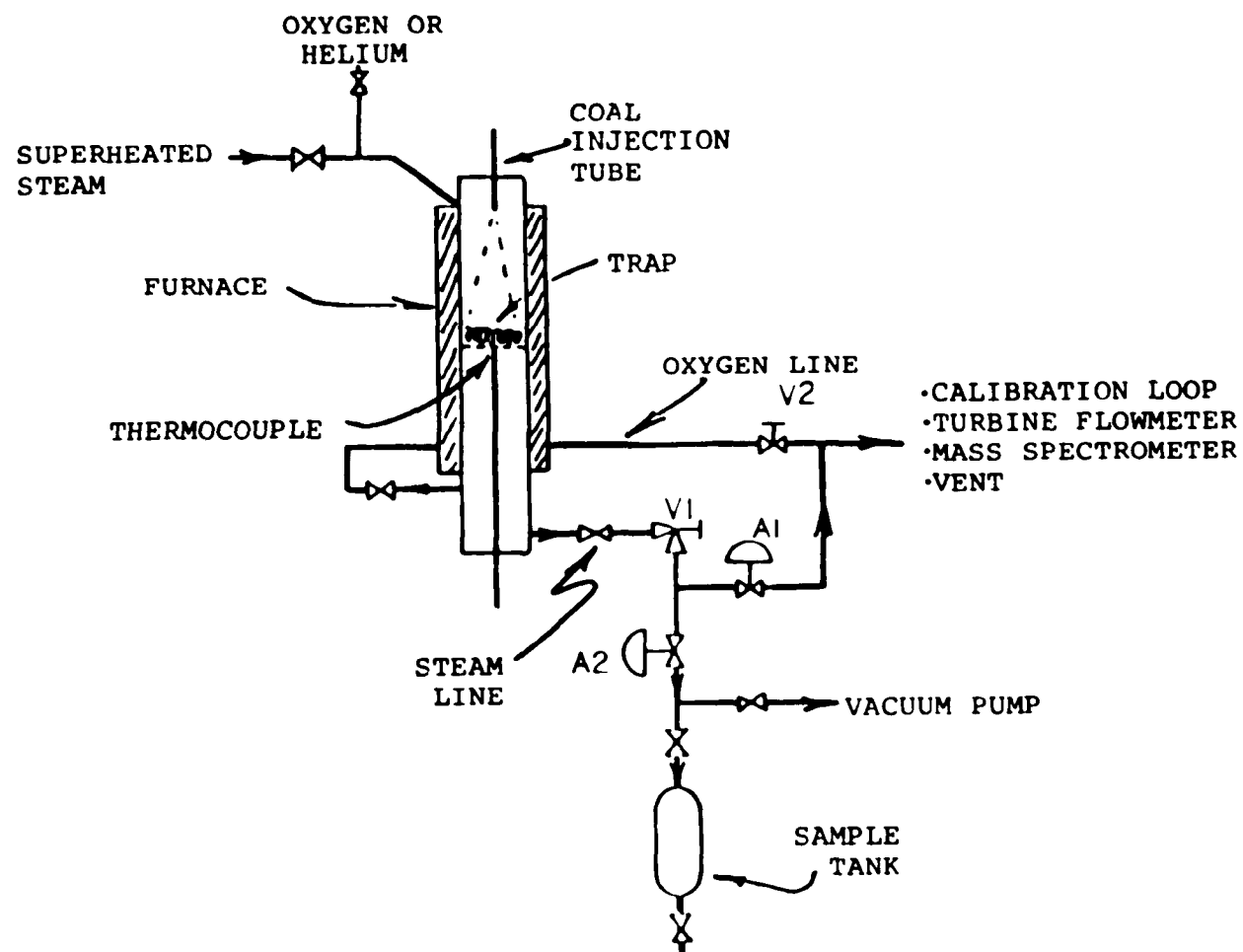


Fig.5.1.5 Steam Pyrolysis Liquids Collection System 2

operated valve A1 is open and valve A2 is closed. The sample tank is evacuated while steam is diverted to the vent. When the system is at temperature and steam is flowing at the desired rate, the coal is injected. Driver gas is switched from valve A1 to A2. A constriction has been placed in the driver gas line to ensure that A1 is closed before A2 opens (to avoid unnecessary collection of steam without product). To terminate collection valve action is reversed. Valve A2 is closed first to avoid loss of product. Helium is admitted directly to the reactor to stop further reaction with steam so that an accurate char determination can subsequently be made.

Cooling the sample tank in air, water or liquid nitrogen, will result in condensation of the steam and allow collection to proceed for many minutes in a volume less than one liter. Low temperature also avoids undesired reactions of the collected liquid. Placing the sample tank immediately after the flow control valve avoids changes in steam flow rate resulting from changes in back pressure during collection. In principle, since the valve is in critical flow, back pressures up to 375 psia (half the reactor pressure) will not affect flow rate. Simulated runs were carried out to test collection when the tank (300cc) was air cooled and when it was submerged in a water bath. With air cooling it was found

that the back pressure reached 350 psia in about 4 minutes and the tank becomes too hot to touch. In the same time with water cooling there is a negligible pressure rise.

### 5.2 Steam and Helium Treatment

Small samples of coal which were to be treated in place on the reactor were loaded into the same injection tubes used for raw coal samples (The procedure has been described in Sec. 5.1.1).

For treatment of large batches of coal (1.5-30 grams) a fixed bed reactor was designed (Fig. 5.2.1). The reactor is constructed of 316 stainless steel. End fittings are constructed from 1 inch stainless steel Swagelock plugs in which a 1/4 in. stainless steel Swagelock to weld fitting has been inserted. This provides for a minimum of dead space in reducing from 1 in. to 1/4 in. A high temperature shut off valve (Nupro SS-4MG) is fixed to the outlet side of the reactor. Central tubes of different diameters, 1/2 in.-1 in. o.d., and lengths from 5 to 20 inches, were used, depending on how much coal was to be treated in one batch.

The same treatment reactor as was described for steam treatment of coal was used for helium treatment of coal.

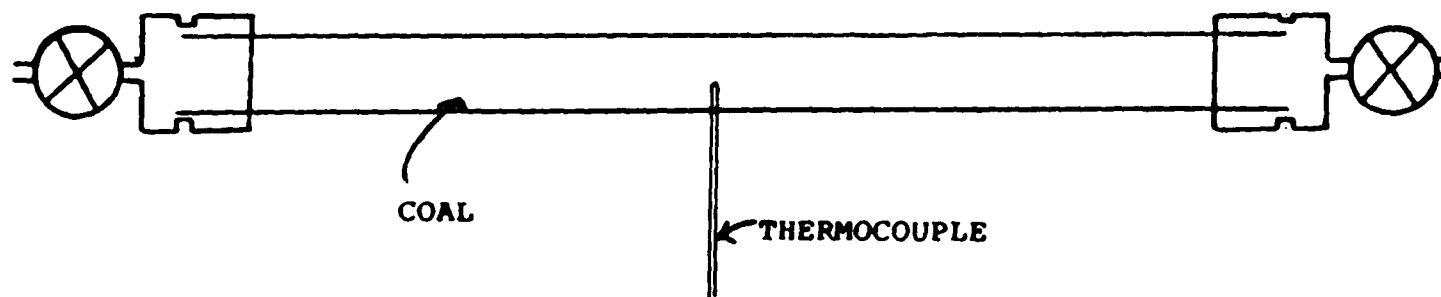


Fig.5.2.1 Pretreatment Reactor

### 5.3 Extraction

Extractions were carried out on about 1.5g of sample prepared as described above. Solvents used were pyridine, HPLC grade (Aldrich Chemical Co.), and Benzene/MeOH both HPLC grade (Fisher Scientific Co.). The high temperature extraction apparatus was a standard 250ml soxhlet extractor. Whatman No.2800 338 cellulose thimbles were used. Room temperature extractions were done using 250ml Erlenmeyer flasks, 1" teflon covered stirring bars, magnetic stirring plates, fluted filter paper (various manufacturers, all ashless medium filtering rate) supported in glass powder funnels. All extractions were carried out in a N<sub>2</sub> filled plastic glove bags (Aldrich Chemical Co.) which were installed in a laboratory fume hood.

### 5.4 Swelling

Swelling experiments were performed in 8mmX60mm pyrex test tubes. Sample heights were determined after centrifugation in a laboratory centrifuge by use of an external rule marked in millimeter divisions. Solvents used were HPLC grade pyridine (Aldrich Chemical Co.), HPLC grade benzene (Fisher Scientific), distilled, deionized water and distilled, deionized water with .1% by weight Xanthum Gum. Experiments were conducted in plastic N<sub>2</sub> filled glove bags (Aldrich Chemical Co.)

installed in a laboratory fume hood.

### 5.5 FTIR

Fourier transform infrared experiments were done on a Nicolet 7199 Instrument with a diffuse reflectance cell. Samples were handled in a N<sub>2</sub> filled glove bag which was attached directly to the sample chamber of the FTIR instrument.

### 5.6 Inert Gas Pyrolysis

#### 5.6.1 Dry Feeder

A feeder was designed (Zhou, 1986) for the input of approximately 1.0 grams/min. of dry powdered coal. The feeder (Fig. 5.6.1) consists of three main parts: a coal reservoir, a feed tube, and a motor drive. The feed tube is rigidly connected to the reactor and extends into the coal bed contained in the reservoir. As the entire reservoir is slowly and uniformly lifted by the motor drive (the feed tube remaining stationary but sliding through fitting) coal continually falls into the feed tube and into the reactor.

The feed tube extends into the reactor and is therefore heated to the temperature of the gas in the reactor. It is necessary to enclose the tube in a cooling jacket to prevent the coal which is slowly

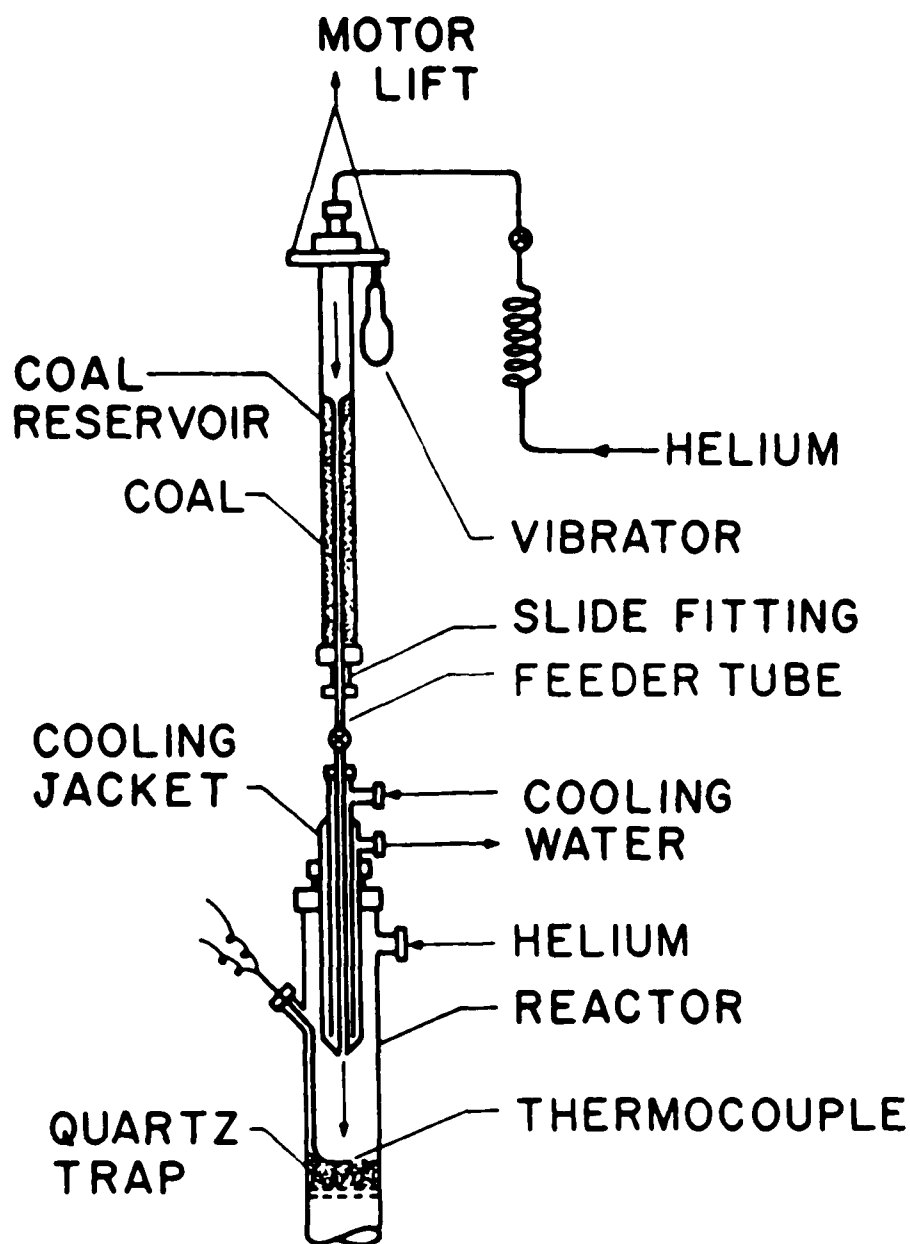


Fig 5.6.1 Continuous Dry Feeder for Inert Gas Pyrolysis

falling through the tube from softening and sticking in the tube or from pyrolyzing prematurely and clogging the tube with char. This was accomplished by encasing the tube in a water cooled jacket (Fig. 5.6.2). The disadvantage of this arrangement is that in a steam environment this cooling jacket acts as a cold finger and causes the steam to condense. This problem was solved by insulating the cooling jacket from the steam with another jacket of stagnant air.

In order to withstand the required pressure, the reservoir is made of a 50cm. length of 1/2" o.d. 316 stainless steel tubing, with an inner transport tube of 1/8" o.d. 316 stainless steel. For low pressure work a glass tube of the same o.d. was used. To seal the bottom of the reservoir and allow relative motion between it and the transport tube, a specially designed four-stage reducer fitting with Teflon seals was adopted (Fig. 5.6.3). Transport gas is required not only to carry coal particles down the feed tube but also to prevent steam from seeping up the feed tube from the reactor. This transport gas is supplied through a flexible line (15) to the top of the feeder. In order to shorten the coal path, thus decreasing chances of plugging and reducing the transport gas requirement, the feeder is placed directly above and close to the reactor. Devices are provided to pull the reservoir upward. This is a unique

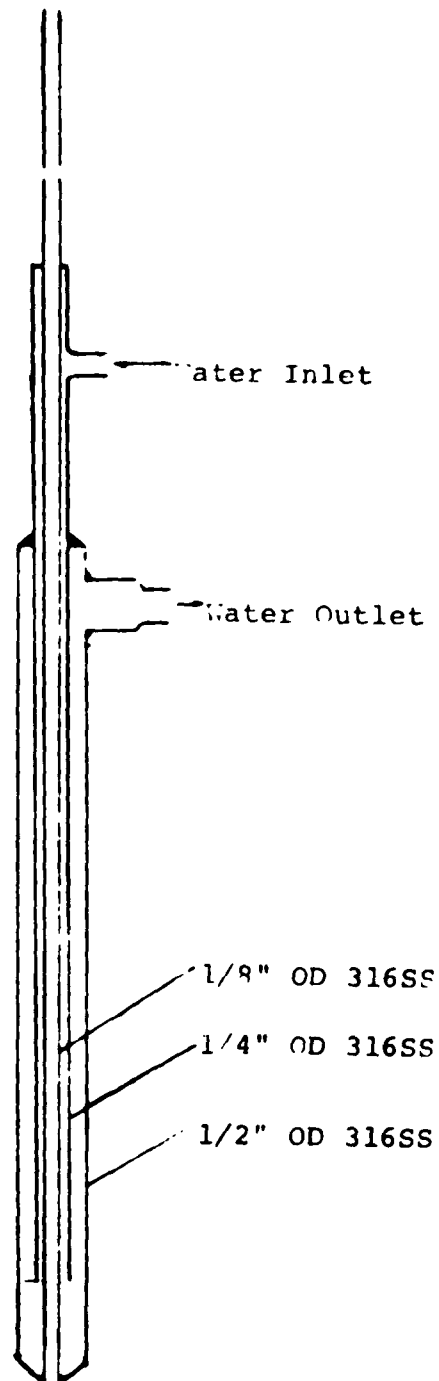


Fig.5.6.2 Water Cooled Feed Tube for Continuous Coal Feeding

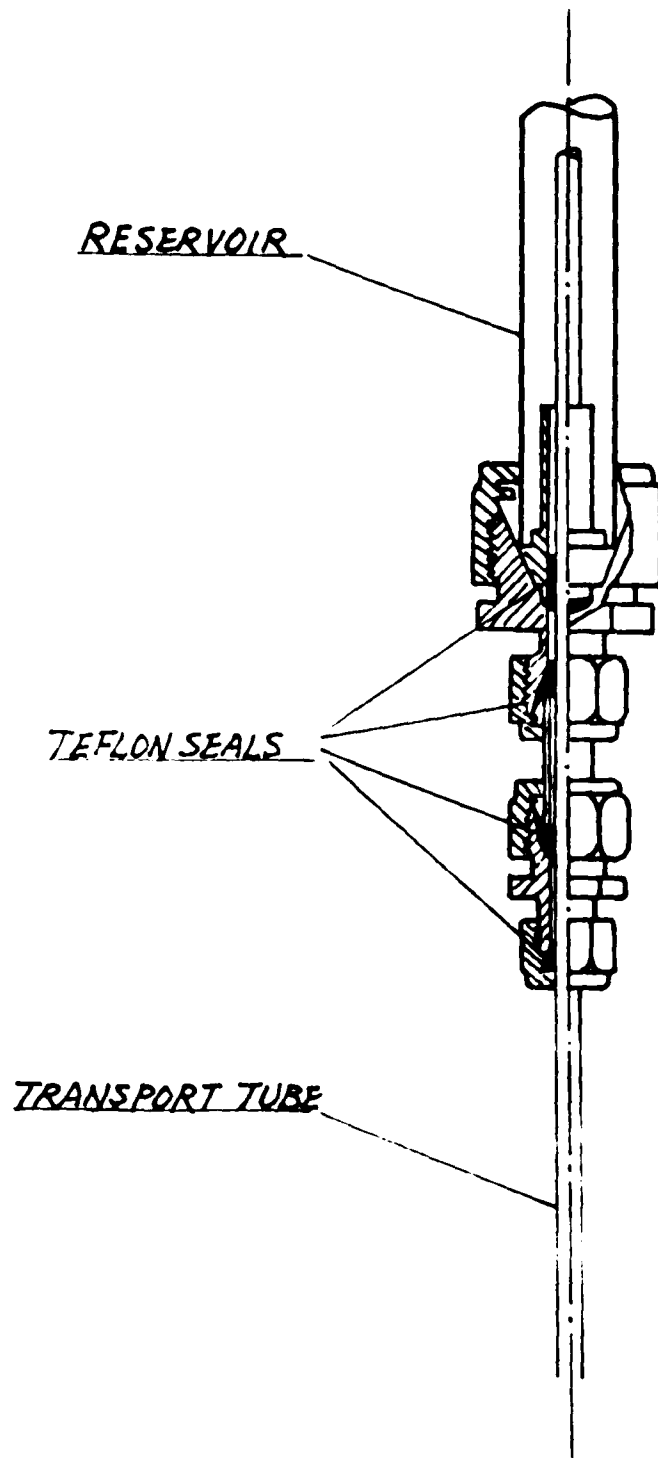


Fig.5.6.3 Four Stage Seal System for Dry Feeder

feature of the system.

The reservoir has a capacity of about 20 grams of coal. A variable speed motor with a reduction gear provides a feed rate ranging from 0.125 to 1.0 g/min. An engraving vibrator with a power of 0.2 watt is attached at the top of the reservoir to provide mechanical vibration. This was found to be essential for smooth coal delivery.

#### 5.6.2 Reactor and Collection System

The reactor is the same as described in section 5.1.1 except for the changes shown in Fig. 5.6.4. Pyrolysis gas enters the reactor through a side arm in the upper portion of the reaction zone. A thermocouple is inserted through the original steam entry port. The thermocouple well at the bottom of the reactor is replaced by an outlet to the collection system. The final collection system in use is diagrammed in Figure 5.6.5. The effluent leaves the reactor through the lower outlet where there is a drop out cap for the collection of particulates. This is followed by a 4 foot length of 1/2 inch o.d. ss tube shaped in a U. A large capacity filter, constructed by loosely packing a 6 inch length of 11/16 inch i.d. glass tubing with quartz wool captures the heavy tars. After the large capacity filter is a small filter designed specifically for the

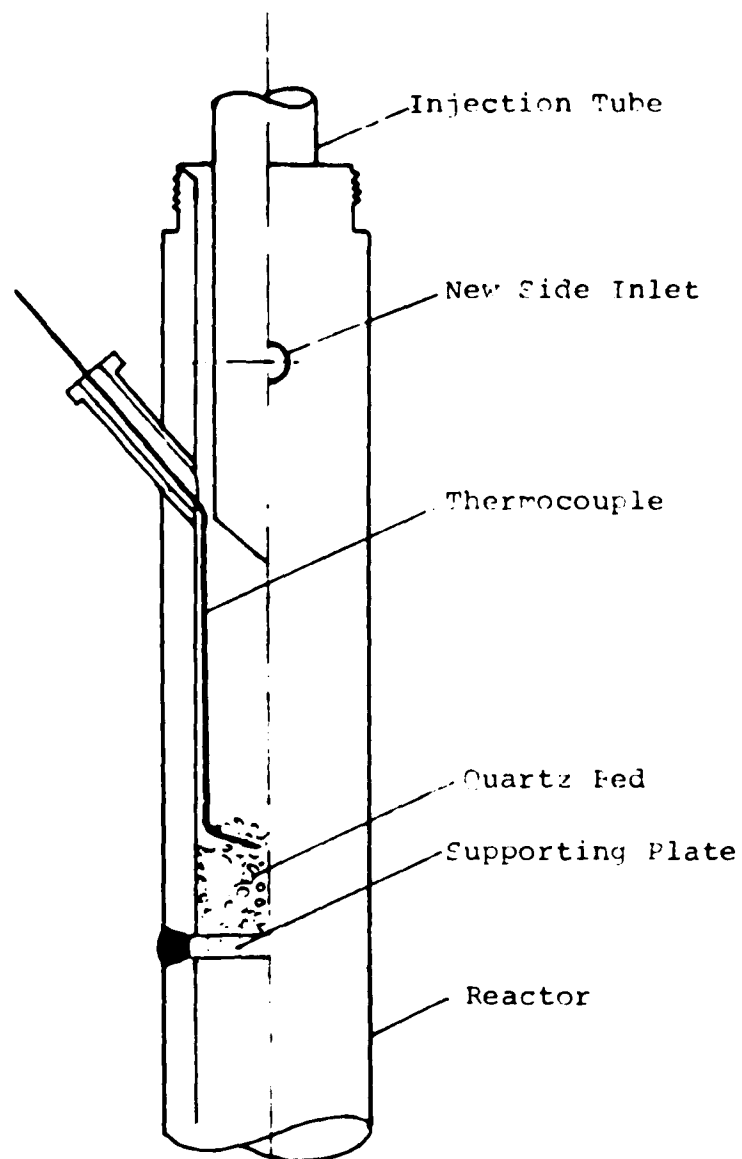


Fig.5.6.4 Altered Steam Pyrolysis Reactor

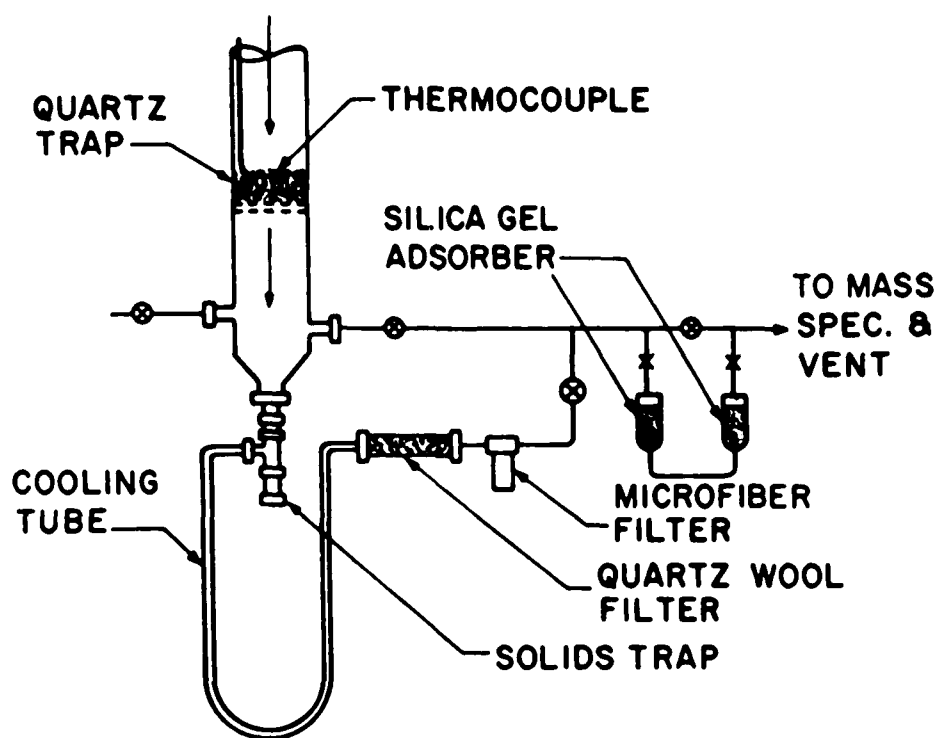


Fig.5.6.5 Four Stage Collection System for Inert Gas Pyrolysis

condensation of fine mists and aerosols. The last stage of the collection system is two adsorbant traps in series. They are glass vials filled with a weighed amount of silica gel.

### 5.7 Liquids Analysis

#### 5.7.1 Sequential Elution by Solvent

##### Chromatography (SESC)

SESC separations were done in 250 ml. pyrex chromatography columns to which a 200 ml. pyrex reservoir had been attached. Acid washed silica gel (Aldrich Chemical Co.) was used as the support. Solvents in the appropriate sequence are given in Table 7.7.1. Eluted samples were collected in 100 ml. graduated cylinders and transferred to 125 ml. tared round bottom flasks. They were dried of solvent on a Buchii Rotovaporizer, using a glycerol bath kept at approximately 110°C. Samples were further dried in a vacuum oven at 90°C.

#### 5.7.2 Gel Permeation Chromatography (GPC)

GPC work was done using a Dupont ZORBAX PSM60 column. The eluting solvent is HPLC grade tetrahydrofuran (THF) (Aldrich Chemical Co. or equivalent). Samples were solubilized in pyridine and further diluted in THF. Samples were then filtered

through .45 nylon membrane filter prior to injection on the column.

### 5.7.3 Gas Chromatography (GC)

Gas Chromatography was done using a Perkin Elmer Sigma 2000 instrument equipped with a PE 1000 integrator. Detection is by dual flame ionization detectors. Carrier gas is helium. The column is a SPB1 wide bore capillary (30m X .75mm) (Supelco).

## 6. EXPERIMENTAL PROCEDURES

### 6.1 Steam Pyrolysis

All samples (except where noted) are pyrolyzed in 50 atm of steam and pretreatments are conducted at the same pressure. During start up, the system is raised to near operating temperature under a flow of helium at 50 atm while steam generated in the boiler is vented.

From 120 to 250 mg. of coal are weighed into injection tubes. Several tubes are prepared in advance for conducting a series of runs. As many as six runs can be executed in a single day.

In preparation for tube attachment the system is first depressurized. The tube is attached to the pulse tank and to the reactor. Before fully tightening the fitting at the top of the reactor, the helium flow is resumed and the reactor partially repressurized. Gases are allowed to bleed from the top of the reactor removing air which would otherwise be trapped. The system is then sealed, fully pressurized and a flow of steam established. A steam flow of about 20 standard liters per minute is used giving a vapor residence time between trap and flow control valve of 6 to 8 seconds.

The run is initiated by triggering the solenoid valve allowing a pulse of helium to inject into the reactor. Data recording by the mass spectrometer is started at the same time. The run lasts 120 seconds. Ten

seconds before the end of the run the steam flow is replaced by helium allowing sufficient time for the inert gas to flood the reactor.

In preparation for oxidation of the residual char, helium pressures reduced to 14 atmospheres. The helium flow is replaced by oxygen at the same pressure flowing at 7 standard liters per minute for 60 seconds while carbon oxides are monitored on the mass spectrometer. At temperatures above 850°C the fraction of carbon appearing as CO is negligible. After sweeping the system with helium, it is depressurized and ready for loading with another coal sample. The ash content of the coal remains deposited in the bed.

Calibrations of mass spectrometer response are carried out daily. For pyrolysis, the response to methane, carbon monoxide and carbon dioxide in steam are routinely determined. No other light species have been observed in these experiments in yields exceeding one percent. While higher yields of BTX and naphthalene are found, these compounds are counted as part of the liquid yield. With steam flowing, sample tank 12 (Fig. 5.1.2) is charged with a calibration mixture containing about equal proportions of CH<sub>4</sub>, CO and CO<sub>2</sub>. A portion of the tank contents are discharged into the steam line by opening solenoid valve 12A for a fraction of a second. From the tank volume and drop in pressure (determined by

pressure transducer 13) the quantity of calibration mixture injected is calculated. This, together with the mass spectrometer response to each component establishes the required calibration factors. Replicate determinations are made as needed to assure reproducibility.

For char oxidation, carbon black is used as a standard. An injection tube is loaded with an amount of carbon black approximating the yield of char carbon anticipated. This sample is injected into the reactor under a flow of helium. Combustion of the injected sample is executed following the procedure used for char. The mass spectrometer response to carbon dioxide establishes the calibration for char carbon. These measurements are replicated for improved reliability.

Argon, at a rate of 20 standard cc per minute, is metered into the reactor effluent immediately after the turbine flowmeter where the pressure is atmospheric. A fraction of the stream is taken to a heated vacuum line kept at about 10 torr. The remainder is sent to a condenser and the noncondensibles vented. A fraction of this vacuum stream is allowed to enter the mass spectrometer source through a needle valve.

A computer is programmed to jump scan the mass spectrometer for up to twenty-six preselected masses in sequence, storing the intensity at each mass. About one

millisecond is required for each data point. For the duration of a run the mass spectrometer is repeatedly cycled through the selected mass sequence which, in addition to the components to be determined, includes argon and a baseline point.

Intensities recorded during the first ten seconds of the run, before the detection of reaction products, are averaged to establish background levels. Following a run the instantaneous intensities above background are normalized on the corresponding argon amplitudes above background. These corrected intensities are integrated over the duration of the run for each component. The integral responses, together with similarly determined calibrations, are used to calculate the yield of each species observed.

This use of argon as a reference compensates for a number of factors which would be otherwise difficult to control. A knowledge of the steam (or oxygen) flow rate, which may vary during the course of the run, is not required. The results are independent of the fraction of the total flow which, after two splits, enters the mass spectrometer. The method also compensates for variations in mass spectrometer source pressure and, to a large extent, fluctuations and drift of instrument components.

## 6.2 Steam and Helium Pretreatment

If a small coal sample is to be pretreated and pyrolyzed it is done in situ on the reactor after the injection tube is attached to the reactor as described in Section 6.1. Before steam is admitted to the reactor, a heating mantle is placed over the injection tube and the temperature brought to about 300°C while the sample is under helium. The reactor is then supplied with steam which is allowed to bleed through the sample and escape through the vent valve on top of the tube. Both the power input to the mantle and the steam rate are used to keep the sample at the desired temperature for the pretreatment. While the arrangement does not allow precise temperature control, it can usually be kept within 5°C of the desired value.

Pretreatment is terminated by allowing the temperature to drop while replacing the steam flow with helium until no condensate is observed to form on a cold metal surface inserted in the vent stream. The vent is then closed, steam flow through the reactor is resumed. The remainder of the run is then executed as described for raw coal (Sec 6.1).

Helium pretreatments are done in the same manner as the steam treatments. The temperature rise to the desired value is controlled by the power to the heating

mantle rather than by the admission of the hot steam.

Pretreatment of large coal samples for semi-continuous processes, extraction and swelling studies was carried out in a fixed bed reactor designed for that purpose (Sec. 5.2). This reactor has the capacity to pretreat 1.5 to 30 grams of coal at one time.

The coal is loaded into the reactor and the reactor is then placed horizontally so that there is a space above the coal for the flow of steam and the gases evolved from the pretreatment of the coal. The reactor is attached to a source of helium and/or steam. A thermocouple is wired on to the midpoint of the tube and a 1/4in OD stainless steel tube is attached to the outlet end of the reactor to deflect the steam and expelled gases into a waste bucket. This point of attachment could be used for directing the off gas flow into the mass spectrometer for analysis. These gases have been determined, in separate experiments, to be approximately 7% of the total weight of the coal sample. The reactor, including the valves, is wrapped in eight feet of flexible heating tape. A flow of helium at 50 atm is established through the reactor. With helium flowing at a minimal rate, controlled by the needle valve, the reactor is heated to a temperature of 300°C. This is above the condensation point of the superheated steam (265°C). The helium is then switched

off and steam at 50 atm. is admitted. The flow of steam is adjusted so that there is a steady discharge of steam vapor from the exit tube. The reactor is further heated to the desired pretreatment temperature in the first 2-3 minutes of steam flow. The pretreatment temperatures are in the range of 300-360°C. The temperature is maintained for the desired length of time (typically 15 minutes) by adjusting the voltage to the heating tape. To stop the pretreatment the heating tape is turned off, as is the steam flow, and the flow of helium is reestablished. The reactor is allowed to cool to room temperature. The flow of helium is maintained until there is no detectable moisture in the flow exiting the reactor. This is determined by placing a cold metal object in the flow of helium and observing any condensation which forms. Both inlet and outlet valves are then shut, and the tube is removed from the source of the gas. The pretreated coal is thus still under a 50 atmosphere helium blanket.

### 6.3 Extraction

All extractions unless otherwise indicated were carried out in a nitrogen filled glove bag at room temperature. The pretreated coal was removed from the pretreatment tube, crushed in a mortar and weighed under N<sub>2</sub> in the glove bag. Samples of approximately 1.5g were transferred to 250 ml Erlenmeyer flasks and 100 ml of

pyridine were added. If the coal sample was to be exposed to the air, the flask was removed from the glove bag, the contents stirred, and then the pyridine was added. The contents of the flask were stirred with a teflon covered stirring bar for fifteen minutes. The stirring was halted and the particles were allowed to settle to the bottom of the flasks. The solution was decanted into a weighted, fluted filter paper. An additional 100ml of fresh pyridine was added to the residue in the flask and the solution was stirred another 15 minutes. The procedure for decanting was repeated using the same filter paper. A final volume of fresh pyridine, 150ml, was added and the solution was stirred another 15 minutes. The stirring plate was turned off and the sample was loosely covered and was left 16 hours immersed in pyridine. The solution then quickly agitated and then filtered through the weighed filter paper. The filter paper was left to dry for approximately 2 hours. Any remaining pyridine was removed in a vacuum oven at 90°C for 2 hours. The residue left in the filter was weighed, and percent extractable was determined, based on the initial weight of the coal charged to the pretreater. The percent extractable, therefore, includes the loss of light volatile material evolved during the pretreatment.

Mass balances were checked in a few runs by driving

off the pyridine from the extract using a rotovaporizer and a glycerol bath at 110°C and then drying the sample in a vacuum oven at 90°C for 4 to 6 hours.

#### 6.4 Swelling

Swelling experiments were carried out as described in Green, et al. (1984). Samples of approximately 1g of coal measured into a 10mm X 80mm centrifuge tube and covered with neoprene stoppers. The samples were centrifuged at 1700 rpm for approximately 10 minutes to settle the dry coal. The height of the sample ( $h_1$ ) was then measured by use of an external rule. Solvents were added to the tube and the tubes were capped and shaken until there was complete homogeneity. The tubes were left to stand 18 hours and then were centrifuged again until a constant height of the solid material was attained. In the case of pyridine, because of the dark color of the solution, the tube was turned upside down in order to read the height of the solids. Experiments were done under N<sub>2</sub> in a glove bag unless the sample was to be deliberately exposed to air, then no precautions were taken in handling the sample in any step of the above procedure.

#### 6.5 FTIR

Diffuse reflectance infrared spectroscopy (DRIS)

was used to analyze both raw and pretreated coal samples. DRIS is a technique ideally suited to solid samples which are ground to uniform, although not necessarily very small, size. In this study the coal was ground to pass 200 mesh, prior to pretreating. Samples after pretreatment were ground and resieved, under a  $N_2$  atmosphere, to pass 200 mesh. The DRIS spectra were obtained using a Nicolet 7199 instrument. The samples were handled under a  $N_2$  blanket in a glove bag directly attached to the sample chamber of the machine. A constant purge of  $N_2$  was maintained through the instrument. Data was acquired over approximately 13 minutes. The number of data points was 8192 over 1000 scans.

#### 6.6 Inert Gas Pyrolysis

Operating procedures for the inert gas pyrolysis system necessitate careful balancing of the system and feeder pressures as the coal reservoir is susceptible to wild fluctuations in height with very small pressure changes. This causes premature or uneven deposition of coal into the reactor. Feeder pressure is maintained just above the system pressure to cause the coal to feed.

A cooling water flow is established in the feed tube prior to reactor heat up to ensure that the coal

does not stick in the tube and prematurely pyrolyze. The coal is fed, by raising the coal reservoir around the stationary feed tube, at a rate of  $\sim 2\text{g}/10\text{ min}$ . It is carried into the reactor by a carrier flow of helium. This helium flow serves the purpose of carrying the coal particles down and also prevents steam from seeping back into the feed reservoir. Inert gas is fed through the superheater and into the upper side arm of the reactor at a rate of 6-12 l/min. The reaction is initiated when the coal begins feeding. Light gases are monitored on the mass spectrometer. Condensibles are caught in the four stage trapping system (Sec. 5.6.2). The reaction is quenched by stopping the coal flow, blowing clear the feed tube and lowering the reaction temperature.

## 6.7 Liquid Analysis

### 6.7.1 Sequential Elution by Solvent Chromatography (SESC)

The chromatographic support is silica gel. It is washed in dilute HCl and then repeatedly rinsed with MeOH. The wet silica is dried of MeOH on a rotovaporizer and then rehumidified to 4% by weight moisture. Chromatography columns are packed with  $\sim 250\text{ ml}$  of prepared silica gel slurried in the first solvent of the separation scheme, hexane.

Samples are prepared by dissolving in  $\text{CH}_2\text{Cl}_2$  and

mixing with clean, ignited sand. The solvent is then evaporated off and the sample coated on the sand is applied to the top of the column.

Samples are eluted slowly (dripping rate of 1cc/min). Each aliquot of 100ml is dried and a constant tally of the fraction weight is recorded. Solvents are changed, as noted in the sequence given in Table 7.6.1, when there is no appreciable change in fraction weight. Color is also a useful indicator of the sample end as many of the fractions contain chromophores.

#### 6.7.2 Gel Permeation Chromatography (GPC)

Gel permeation experiments are run on dilute (<1% by weight) samples. The pumping rate of the eluting solvent, THF, is 1cc/min. The sample is injected via a 20cc sampling loop. Measurements of retention volume are made for both the range of molecular weights and for the center of the most prominent peaks indicated by a UV detector.

#### 6.7.3 Gas Chromatography (GC)

Gas chromatography is done with a temperature gradient program of 10°C/min. Samples are diluted in pyridine or THF. Approximately 0.1ul of sample was injected on column (no split).

## 7. RESULTS AND DISCUSSION

### 7.1 Background

Studies were undertaken at The City College of New York on flash pyrolysis of coal in steam. These studies employed the use of a small tubular reactor packed with approximately 10mg. of coal (Fig. 7.1.1) (for further details see Graff, et al., 1980). In order to prevent condensation of steam in the tube, the tube was first heated in a flowing stream of inert gas. The condensation point for steam at 50 atm. is 265°C. A safety factor of 20° was allowed for and the tube was heated to about 285°C (and as high as 320°C) before the steam flow was started. At the time, these low temperature conditions were thought to have no effect on coal. After admitting steam and maintaining the flow at these low temperatures for periods of time up to 30 minutes, the sample was pyrolyzed by passing a high current through the tube walls to reach final temperatures between 650 and 1100°C. The effluent of the reaction was carried downstream to an on-line mass spectrometer in the steam flow. The liquid yields obtained in this apparatus accounted for over 65% of the carbon in the sample originally charged to the reactor tube. This work showed that pyrolysis in steam could

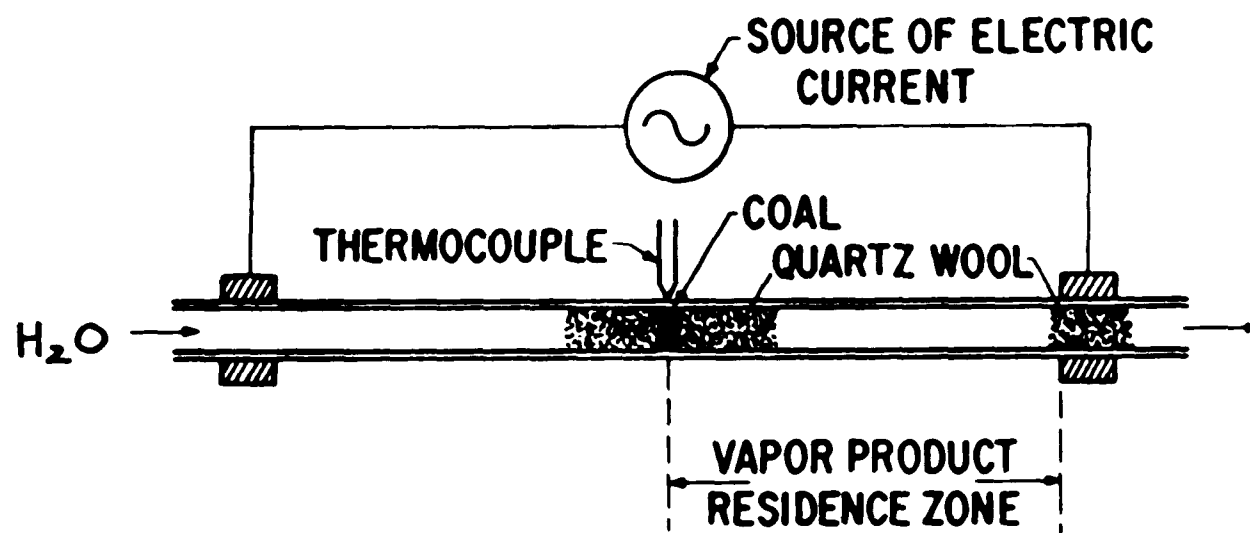


Fig.7.1.1 Small Flash Tube Reactor

produce almost three times the amount of liquid product obtained from inert gas pyrolysis at the same conditions (Fig. 7.1.2).

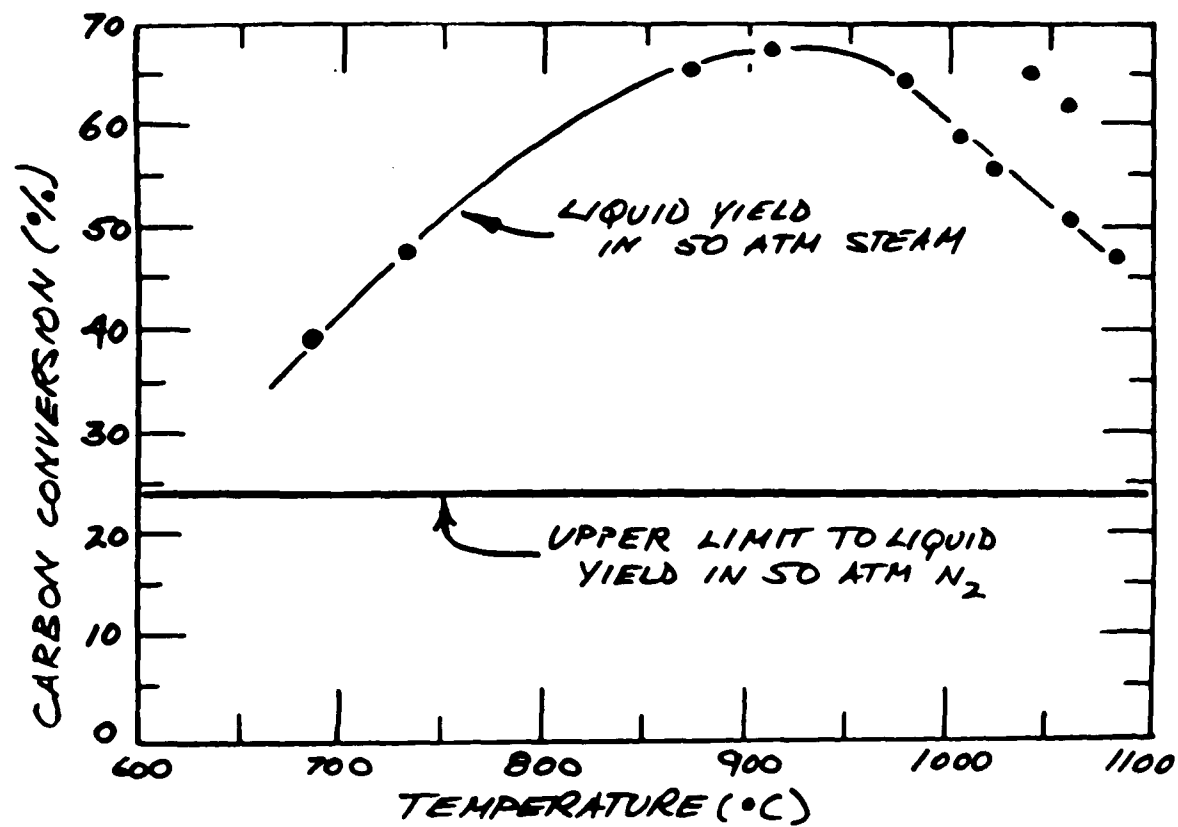


Fig.7.1.2 Liquid Yields in the Pyrolysis of Illinois No. 6 Coal in Steam and Nitrogen at 50 Atmospheres (from Graff, et al. 1980)

## 7.2 Flash Pyrolysis in Steam

An expansion of the work performed in the small flash tube reactor was started with the main goal of processing larger samples of coal to produce greater quantities of liquid product. A new reactor system was developed which could handle up to 250mg. or 25 times more coal than the flash tube reactor (Sec.5.1.1).

A series of runs was made with coal sample CFI#16 (Table 7.2.1). The coal was pyrolyzed in 50atm. of pure steam at temperatures from 690-780°C.

The liquid yields obtained from this apparatus were very low (Table 7.2.1). The total volatiles yields are determined by the difference in the amount of carbon measured as CO<sub>2</sub> in the combustion of the char and the amount of carbon charged to the reactor. A typical combustion curve is given in Figure 7.2.1. As can be seen in this figure the carbon oxide produced in the combustion of the char is predominately carbon dioxide; very little carbon monoxide is formed. This and the reduction of carbon oxide species to zero toward the end of the burn time indicates that there is complete combustion of the material in the reactor. The integral for the area under the curve is normalized against the argon value as was discussed in Sec.6.1. The liquid yield is determined by the difference of the total volatiles yield and the carbon content of the light

Table 7.2.1

Steam Pyrolysis Yields Illinois No.6 Coal, Lot No. 16

| Run<br>No. <sup>†</sup> | Reactor<br>Temp(°C) | Carbon Conversion (%) |          |      |
|-------------------------|---------------------|-----------------------|----------|------|
|                         |                     | Total Gas             | Liquids* | Char |
| P29                     | 551                 |                       | 10.0     |      |
| P30                     | 513                 |                       | 7.6      |      |
| P33                     | 627                 |                       | 6.3      |      |
| P34                     | 696                 |                       | 9.5      |      |
| P35                     | 700                 |                       | 7.34     |      |
| P36                     | 750                 |                       | 6.28     |      |
| E41                     | 697                 | 31.0                  | 20.5     | 48.5 |
| E44                     | 738                 | 37.4                  | 19.7     | 42.9 |
| E47                     | 690                 | 29.6                  | 24.3     | 46.1 |

<sup>†</sup>Runs designated P reported in Graff and LaCava (1983)

\*Determined by difference

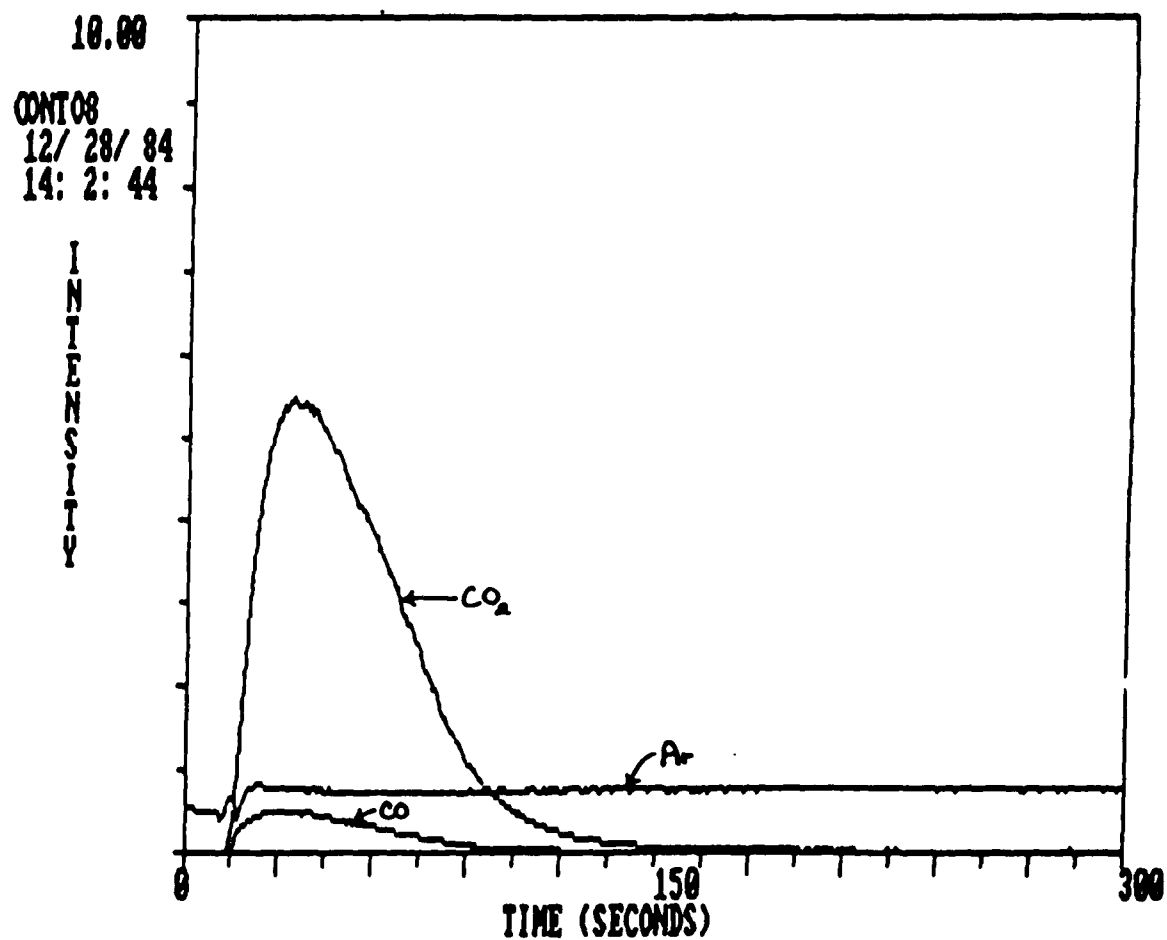


Fig.7.2.1 Typical Mass Spectrum of Char Oxidation;  
Intensity vs Time

gases evolved during the pyrolysis.

The liquid yields determined in runs E41 and E44 are just a little higher than what is expected for pyrolysis in an inert gas (Howard, 1981). These results were so far out of agreement with the flash tube studies that questions were raised about the possible cause. The first possibility considered was the method of sample injection into the reactor. Since the coal is injected using a pulse of helium, it was found necessary to eliminate the helium atmosphere surrounding the coal particle to test if it was an envelope of inert gas around the particle which was inhibiting liquid formation.

The idea was tested in the following way. The injection tube containing coal was filled with water (about one milliliter) and the mixture injected with helium in the usual way. This overloaded the reactor causing a severe temperature drop, pressure reduction and ejection of condensate through the main flow valve. In the next two trials, the injection tube was drained after flooding with water. These wet samples (E50 and E51) were successfully injected without overloading the reactor. The results are given in Table 7.2.2. The high liquid yield obtained in run E50 could not be accounted for at the time of these experiments and was considered anomalous. It is possible that what was observed here

Table 7.2.2

Comparison of Wet and Dry Injection Technique  
on Product Yields

| Run No.                  | <u>E47</u> | <u>E50</u> | <u>E51</u> | <u>E52</u> |
|--------------------------|------------|------------|------------|------------|
| Injection Method         | dry        | wet        | wet        | wet        |
| Reactor Temperature (°C) | 690        | 730        | 780        | 705        |
| Carbon Conversion (%)    |            |            |            |            |
| CH <sub>4</sub>          | 13.7       | 5.7        | 10.5       | 7.6        |
| CO                       | 6.9        | 8.0        | 13.9       | 10.7       |
| CO <sub>2</sub>          | 9.0        | 12.3       | 31.1       | 13.5       |
| Liquid                   | 24.3       | 34.8       | 14.4       | 18.8       |
| Char                     | 46.1       | 39.2       | 30.1       | 49.4       |

was a steam pretreatment effect which was later found to be so beneficial. The values for E51 and another run E52 are no better than for injection of dry samples. It was, therefore, concluded that helium used for injection is not a factor in obtaining low liquid yields from these experiments.

A number of injection runs (values are given in Table 7.2.3) are plotted in Fig. 7.2.2. At a temperature of 750°C and below, the liquid yield is about 23%. This is approximately 10% higher than liquid yields reported in the literature for inert gas pyrolysis conducted under similar conditions (69atm., in the same temperature region, for a Pittsburgh No.8 bituminous coal, Howard, 1981). Total weight loss in the inert gas experiments was reported to be approximately 38%. The higher yields of both liquids and total volatiles reported here are considered to be a result of reaction with steam.

In the previous steam pyrolysis work using the flash tube reactor, however, liquid yields were much higher, reaching 68% carbon conversion at about 730°C (Graff, et al., 1980). In those experiments inert gas flowed continuously through the reactor containing the coal sample as it was heated above the condensation point of the steam. Steam was admitted and adjustments made to the system before pyrolysis was initiated.

Table 7.2.3

Raw Illinois No.6 Coal Steam Pyrolysis Yields,  
Batch Injection

| Run<br>No. | Reaction<br>Temperature | Carbon Yields (%) |      |                 |           |         |      |           |
|------------|-------------------------|-------------------|------|-----------------|-----------|---------|------|-----------|
|            |                         | CH <sub>4</sub>   | CO   | CO <sub>2</sub> | Total Gas | Liquids | Char | Volatiles |
| E41        | 697                     | 4.4               | 13.5 | 13.1            | 31.0      | 20.5    | 48.5 | 51.5      |
| E44        | 738                     | 7.6               | 12.3 | 17.5            | 37.4      | 19.7    | 42.9 | 57.1      |
| E47        | 690                     | 13.7              | 6.9  | 9.0             | 29.6      | 24.3    | 46.1 | 53.9      |
| E51        | 781                     | 10.5              | 13.9 | 31.1            | 55.5      | 14.4    | 30.1 | 69.9      |
| E52        | 705                     | 7.6               | 10.7 | 13.5            | 31.8      | 18.8    | 49.4 | 50.6      |
| E74        | 742                     | 10.0              | 6.1  | 17.5            | 33.6      | 27.8    | 38.6 | 61.4      |
| E85        | 727                     | 5.8               | 7.5  | 20.9            | 34.2      | 26.8    | 39.0 | 61.0      |

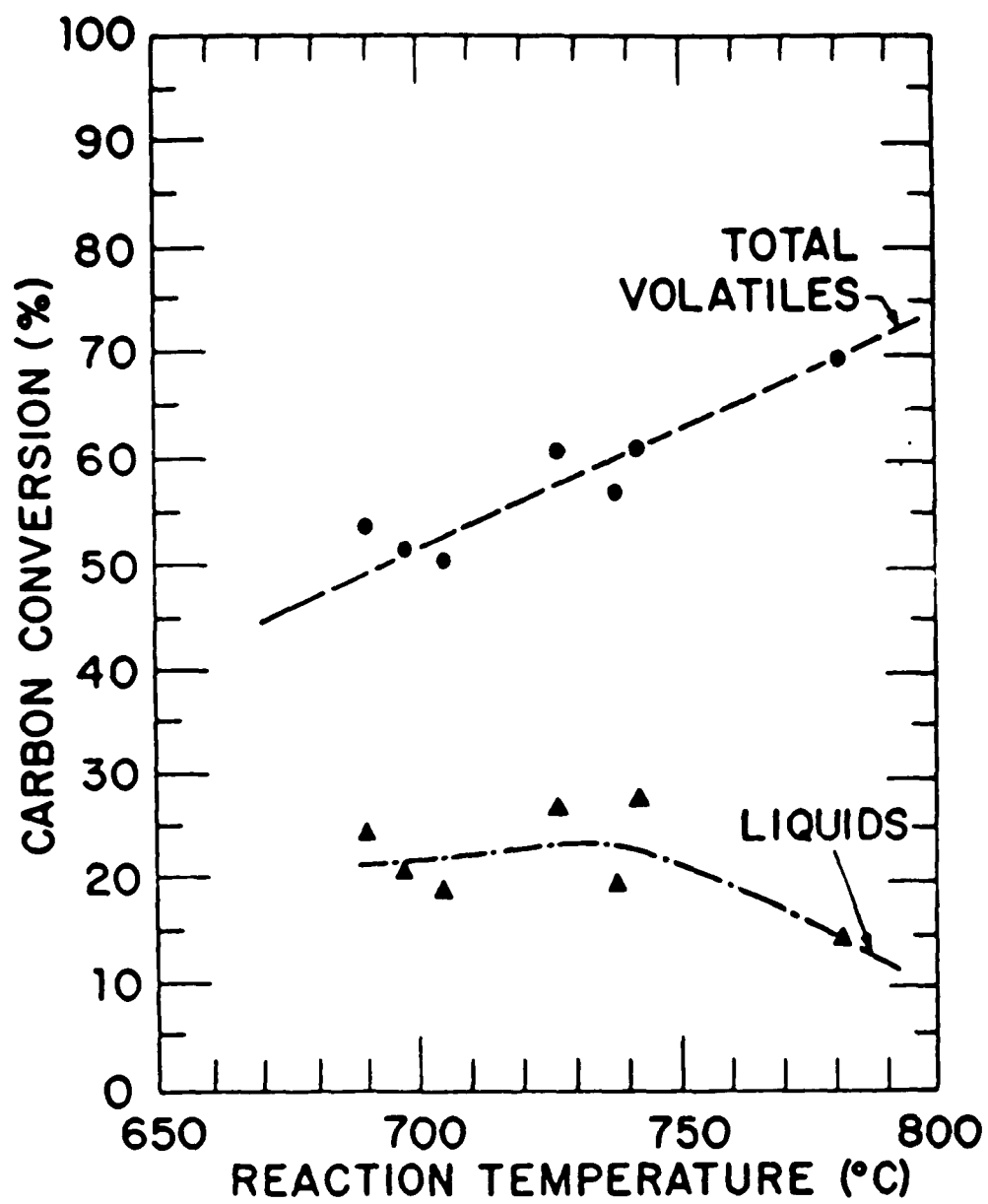


Fig.7.2.2 Steam Pyrolysis of Raw Illinois No. 6 Coal

During this time the coal sample was exposed to high pressure gas for perhaps as long as 30 minutes. This aspect of the flash tube technique was absent from experiments with the injection reactor.

In order to test the idea that exposure to gas at high pressure, but low temperatures (300-370°C) is a necessary preliminary step in flash steam pyrolysis for the achievement of high liquid yields the reactor was modified (Sec 5.1.4). A procedure was developed to expose the coal to 50 atm. of steam or helium at temperatures between 300 and 370°C (Sec 6.2) prior to pyrolysis.

Yields obtained for pretreated coal are given in Table 7.2.4 and shown in Figure 7.2.3 (data and solid lines) together with the curves for raw coal from Figure 7.2.2 (dashed lines). Above a temperature of 670°C liquid yields are increased. A maximum of over 50% carbon conversion to liquids is reached at about 740°C, more than twice the yield for raw coal. Total volatiles yield is also increased; at 740°C this increase is 20%. At this temperature, however, the gas yield is substantially reduced (from 37% to 26% carbon conversion).

Yields shown in Figure 7.2.3 were obtained from coals pretreated by exposure to 50 atm. steam for 5 to 30 minutes at temperatures from 300 to 360°C. One sample

Table 7.2.4

Steam Treated<sup>1</sup>\* Illinois No.6 Coal Steam Pyrolysis  
Yields, Batch Injection

| Run<br>No. | Pretreat<br>Temp(°C) | Reaction<br>Temp(°C) | Carbon Yields (%) |      |                 |           |         |      |           |
|------------|----------------------|----------------------|-------------------|------|-----------------|-----------|---------|------|-----------|
|            |                      |                      | CH <sub>4</sub>   | CO   | CO <sub>2</sub> | Total Gas | Liquids | Char | Volatiles |
| E73        | 330-340              | 745                  | 5.2               | 2.6  | 15.7            | 23.5      | 51.6    | 17.9 | 82.1      |
| E75        | 321-346              | 765                  | 16.0              | 8.9  | 18.7            | 43.6      | 38.7    | 10.7 | 89.3      |
| E83        | 309-360              | 722                  | 7.6               | 11.8 | 15.0            | 34.4      | 48.3    | 13.3 | 86.7      |
| E84        | 284-342              | 675                  | 5.7               | 16.9 | 11.6            | 34.1      | 21.2    | 37.7 | 62.3      |
| E86        | 312-314              | 703                  | 3.1               | 5.5  | 12.8            | 21.4      | 35.9    | 23.3 | 76.7      |
| E93        | 265-339              | 720                  | 2.9               | 5.4  | 13.7            | 22.0      | 25.7    | 44.5 | 55.5      |
| E97        | 266-349              | 731                  | 3.5               | 5.2  | 16.0            | 24.7      | 52.4    | 15.9 | 84.1      |

\*Treatment times between 10 sec. and 30 min.

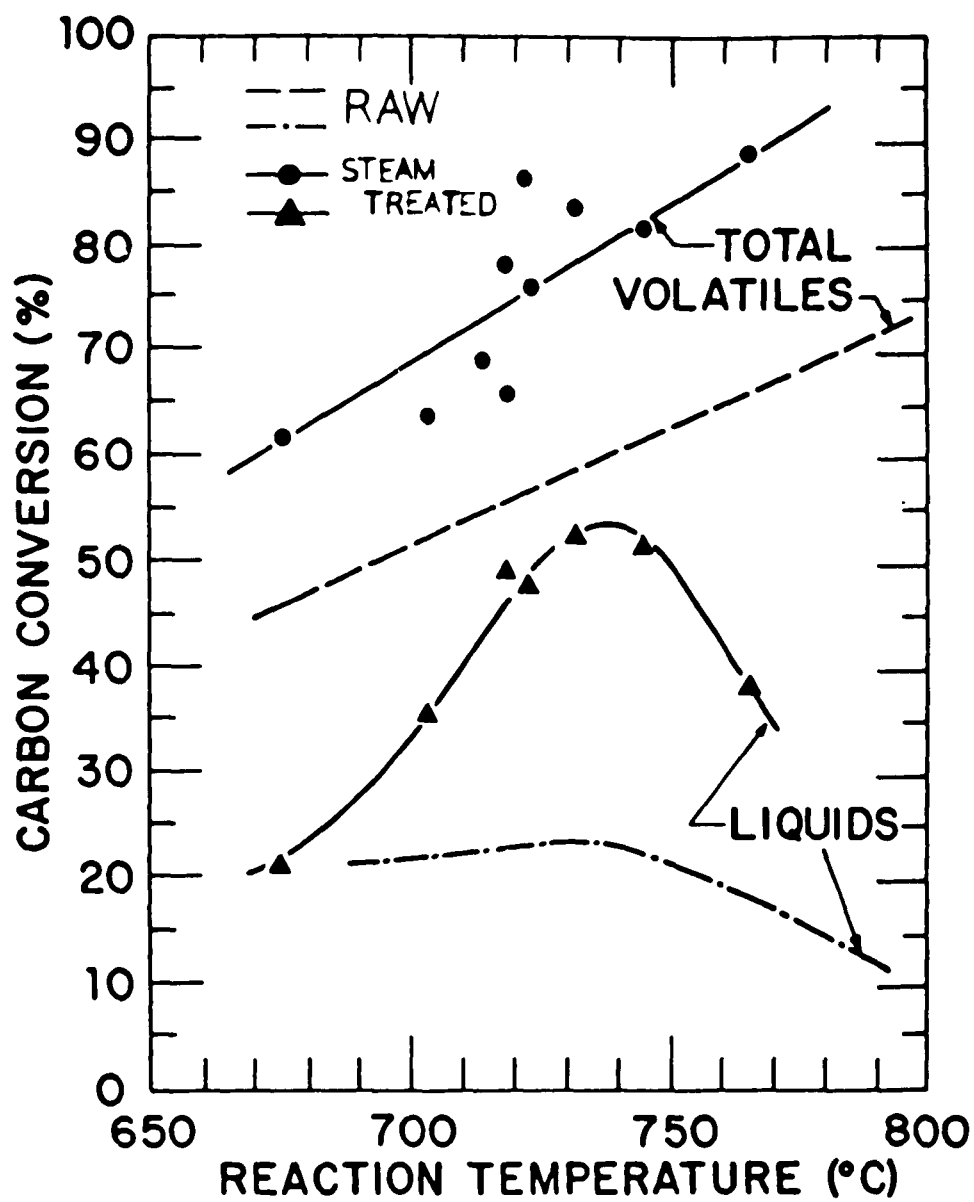


Fig.7.2.3 Steam Pyrolysis of Steam Pretreated Illinois No. 6 Coal

was pretreated for a very short time estimated to be 10s (shown in Figure 7.2.3 at reaction temperature of 703°C).

As pretreatment times are decreased, (Table 7.2.5), higher temperatures are required for good liquid yields. Successful 15 minute pretreatments were conducted in the 330-340°C range. In run E113, the sample was pretreated for 15 min. at temperatures mostly around 320°C. Both total volatiles and liquid yields were considerably lower than for 30 minute pretreatments. Yields were brought into agreement with the 30 minute pretreatments in run E114 by keeping the pretreatment temperature mostly around 330-340°C. A 5 minute pretreatment, mostly about 340°C, gave low volatiles yield, but good liquid yields (run E115). When a sample of coal was held at around 350°C for the 5 minute pretreatment, the volatiles yield was raised to the value obtained for 30 minute pretreatments.

The equipment used in these studies is not suitable for reproducible steam treatments less than 5 minutes in duration. The successful 10 second pretreatment, noted above, shows, however, that good liquid yields can be maintained at quite short treatment times. This will be an important consideration if the process is to be commercialized.

In order to see if the presence of steam is

Table 7.2.5

Time-Temperature Dependence in Steam Pretreatment  
on Illinois No.6 Coal

| <u>Pretreatment</u> |                   |                    | <u>Carbon Conversion(%)</u> |                |                    |
|---------------------|-------------------|--------------------|-----------------------------|----------------|--------------------|
| <u>Run No.</u>      | <u>Time (min)</u> | <u>Temp. Range</u> | <u>Pyrolysis Temp. (°C)</u> | <u>Liquids</u> | <u>Total Vol's</u> |
| E113                | 15                | 301-348            | 733                         | 35.9           | 71.7               |
| E114                | 15                | 260-353            | 723                         | 54.9           | 78.1               |
| E115                | 5                 | 286-340            | 718                         | 49.4           | 65.4               |
| E117                | 5                 | 313-370            | 746                         |                | 82.5               |

necessary in the pretreatment step as well as the pyrolysis, coal samples were pretreated in helium under the same conditions as the steam treated samples. The results are shown in Figure 7.2.4. It appears that helium treatment may effect the total volatile yields as does the steam treatment, but there is a shift in the composition of the volatiles toward less condensable material if the sample is only thermally treated in helium.

The temperature boundaries on the steam treatment appear to be very sharp. If the temperature does not reach 320°C little, if any, yield improvement results. If a temperature above 360°C is reached there are no benefits from the pretreatment. These limits are likely to be peculiar to each particular coal sample. The sharpness of the boundaries however, will, it is believed, be a persistent trait.

While performing a series of runs to test the effects of sample storage between treatment in steam and flash steam pyrolysis it was found that the treated coal exhibits an extreme sensitivity to air. (Table 7.2.6 and Fig. 7.2.5).

In runs E93, 95, and 98 batch samples of about one gram were pretreated. After cooling in helium, the light agglomerate which had formed was easily broken up and stored in small vials. During handling and storage, no

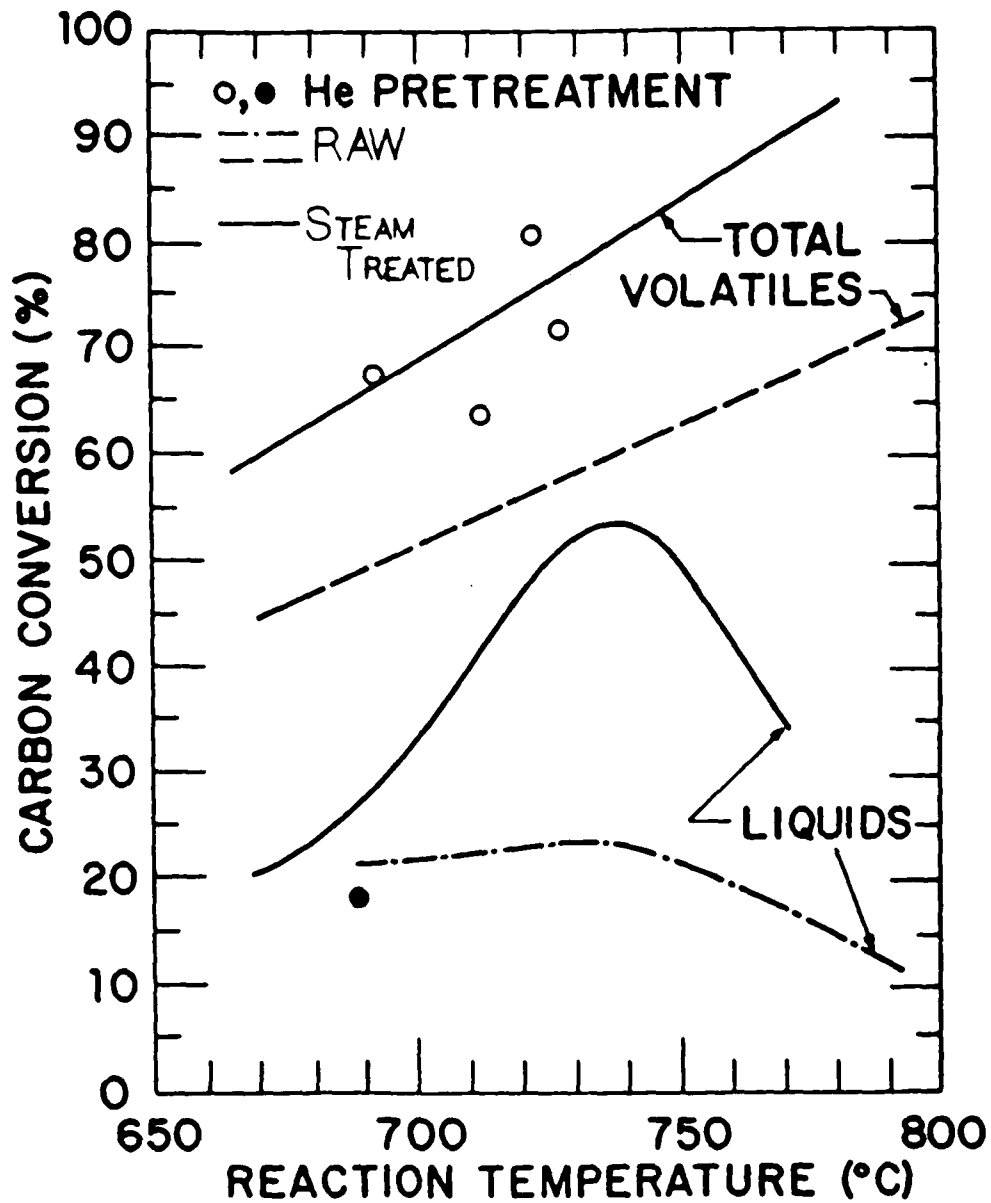


Fig.7.2.4 Steam Pyrolysis of Helium Pretreated Illinois No. 6 Coal

Table 7.2.6

Effect of Storage in Air and Helium on Steam  
Pyrolysis Yields of Steam Treated Illinois No.6 Coal

| Run  | <u>Steam Treatment</u> |                    | <u>Storage</u> |               | <u>Carbon Conversion</u> | <u>Total No. Vol's</u> |
|------|------------------------|--------------------|----------------|---------------|--------------------------|------------------------|
|      | <u>Time (min)</u>      | <u>Temp. Range</u> | <u>Time</u>    | <u>Medium</u> | <u>(wt%) Liquids</u>     |                        |
| E93  | 30                     | 265-339            | 12d            | Air           | 25.7                     | 55.5                   |
| E95  | 30                     | 289-335            | 4d             | Air           | 14.8                     | 53.4                   |
| E98  | 30                     | 289-335            | 25d            | Air           |                          | 44.5                   |
| E118 | 15                     | 274-358            | 4h             | He            |                          | 94.0                   |
| E120 | 15                     | 288-377            | 4h             | He            |                          | 74.9                   |
| E126 | 15                     | 311-358            | 2m             | Air           | 25.5                     | 64.0                   |
| E127 | 15                     | 299-362            | 18h            | He            | 61.3                     | 86.5                   |

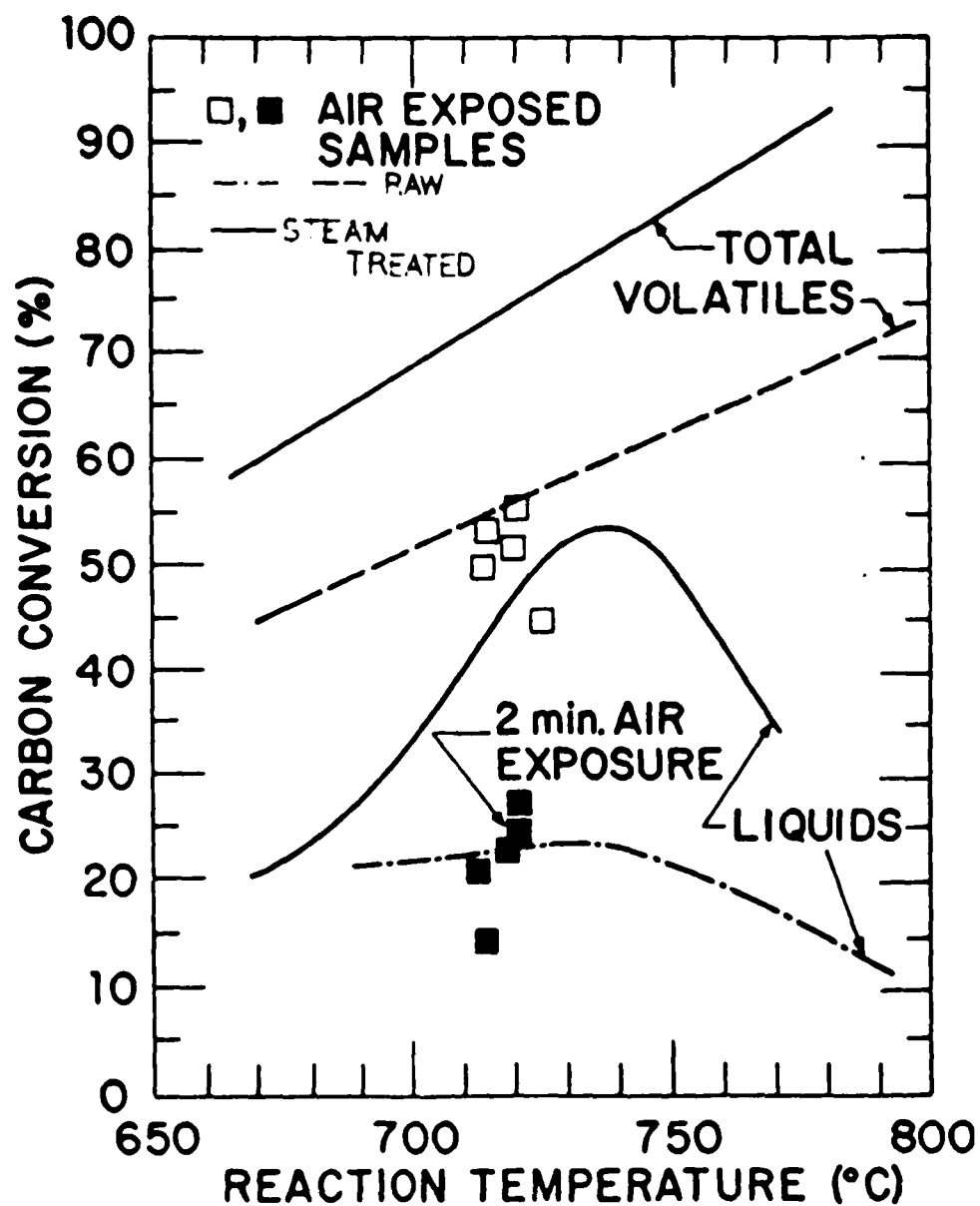


Fig.7.2.5 The Effect of Exposure to Air on Steam Pyrolysis of Steam Pretreated Illinois No.6 Coal

precautions were taken to exclude air. After the time period noted, the sample was reacted in the usual way. In E119 and 125 pretreatment and storage was carried out in the coal injection tube. These samples were left under helium which leaked out during the storage period; consequently they are classified with those samples stored in air. All samples show volatiles yields less than that for untreated coal and liquid yields about the same as for untreated coal. One sample (E126) was flushed with air for 2 minutes after cooling in helium. Volatiles yield was slightly higher and liquids yield the same as for untreated coal.

Storage for four hours in helium gave the same volatiles yield as pretreated and promptly injected coal (E120, no liquids yield available). A sample stored for eighteen hours in helium gave higher yields of both volatiles and liquids than promptly injected coal (E127). This sample may have received further exposure to steam in the minutes before injection.

From this series of runs, it is concluded, that even brief exposure of coal to air negates the improvement in yields derived from pretreatment.

These results suggest to this author that the same effect which is known as weathering may be occurring here.

In weathering of coal the freshly exposed face of

the coal adsorbs oxygen. It is known that at least some of the oxygen enters the coal structure and forms acidic groups (Ignasiak, 1974) and etheric linkages (Liotta, 1983).

The weathering process has been shown to reduce yields in liquefaction and hydrogenation processes. The time scale for this to occur at ambient conditions is over a period of days, weeks, and even months. It may be that the same effect is occurring with the treated samples, but on an accelerated time scale because of alterations in the coal structure caused by the steam treatment.

### 7.3 Effects of Steam and Helium Treatment

Several observations in addition to yield increases have been made when Illinois No.6 coal is exposed to 50 atm. of steam at temperatures between 320 and 360°C and times up to 30 minutes.

The first observation made is that the coal has become lightly agglomerated even at the lower end of the temperature range. It has been noted that in the temperature range of 300-370°C plastic coals begin to soften and melt. It would be expected that treatment in 50 atm. of helium would produce the same effect. This is not the case. Pretreatments in helium conducted in the same way as pretreatments in steam produced a completely non-agglomerated material, even up to 375°C.

The second observation made about the steam pretreatment is that the coal loses 5-7% volatile material in the process. This material is accounted for in the total volatiles curve, Figure 7.2.3, but not in the liquid curve. This has been done even though these off gases contain a significant amount of condensable material. This volatile material has been trapped in a few experiments and the gases analyzed. Preliminary results indicate that of the 5-7% total loss approximately 20% of this material is carbon containing gas (detectable in the mass spectrometer as CH<sub>4</sub>, CO, and CO<sub>2</sub>). The remainder of the material is presumed heavier

than benzene, the highest mass scanned in the mass spectrometer.

Treated coal samples have been analyzed for their elemental composition. Table 7.3.1 shows these analyses on an ash free basis. The oxygen values are given as measured directly. There is a reduction in the oxygen content for all the steam pretreated samples. Sample PY9 which was pretreated at the temperature which produces the optimum yield in steam pyrolysis (Fig. 7.3.1) shows the greatest reduction. The problem with using these analyses is that the oxygen values are obtained by combusting the coal. The value, therefore, also contains some portion of the inorganic oxygen. The inorganic portion of the coal is measured by the ash content, thus some of the oxygen is actually counted twice. If instead of direct determination the value of the oxygen is determined by the difference of 100% minus the value of the other elements and the ash (Table 7.3.2) there is no decrease in the oxygen content. There is an inherent problem associated with using oxygen by difference values and that is that the error associated with the determination of each element is compounded into the value for the oxygen. In either case the determination of the oxygen value is questionable.

The nitrogen and sulfur contents appear to be relatively stable from sample to sample. The C/H ratio

Table 7.3.1

Elemental Composition\* of Steam Treated Illinois No.6 Coal  
at Differing Treatment Conditions  
Oxygen by Direct Measurement\*\*

| <u>Treatment</u><br><u>Conditions</u> | <u>Raw Coal</u> | <u>PY4</u> | <u>PY5</u> | <u>PY7</u> | <u>PY9</u> | <u>PY10</u> | <u>PY11</u> |
|---------------------------------------|-----------------|------------|------------|------------|------------|-------------|-------------|
| Temp. (°C)                            | -               | 320        | 320        | 322        | 330        | 344         | 360         |
| Time (min)                            | -               | 15         | 15         | 15         | 15         | 15          | 15          |
| C                                     | 73.98           | 75.59      | 75.00      | 75.12      | 77.29      | 74.55       | 75.50       |
| H                                     | 5.56            | 5.06       | 4.80       | 5.42       | 5.36       | 5.30        | 5.32        |
| O                                     | 14.14           | 12.53      | 13.47      | 13.10      | 10.80      | 12.74       | 12.75       |
| N                                     | 1.26            | 1.71       | 1.69       | 1.20       | 1.45       | 1.39        | 1.48        |
| S(total)                              | 5.08            | 5.11       | 5.04       | 5.16       | 5.10       | 4.93        | 4.95        |
| C/H                                   | 13.30           | 14.94      | 15.63      | 13.86      | 14.42      | 14.10       | 14.19       |
| C/O                                   | 5.23            | 6.03       | 5.56       | 5.73       | 7.15       | 5.85        | 5.92        |

\* Ash free basis

\*\*May contain inorganic oxygen

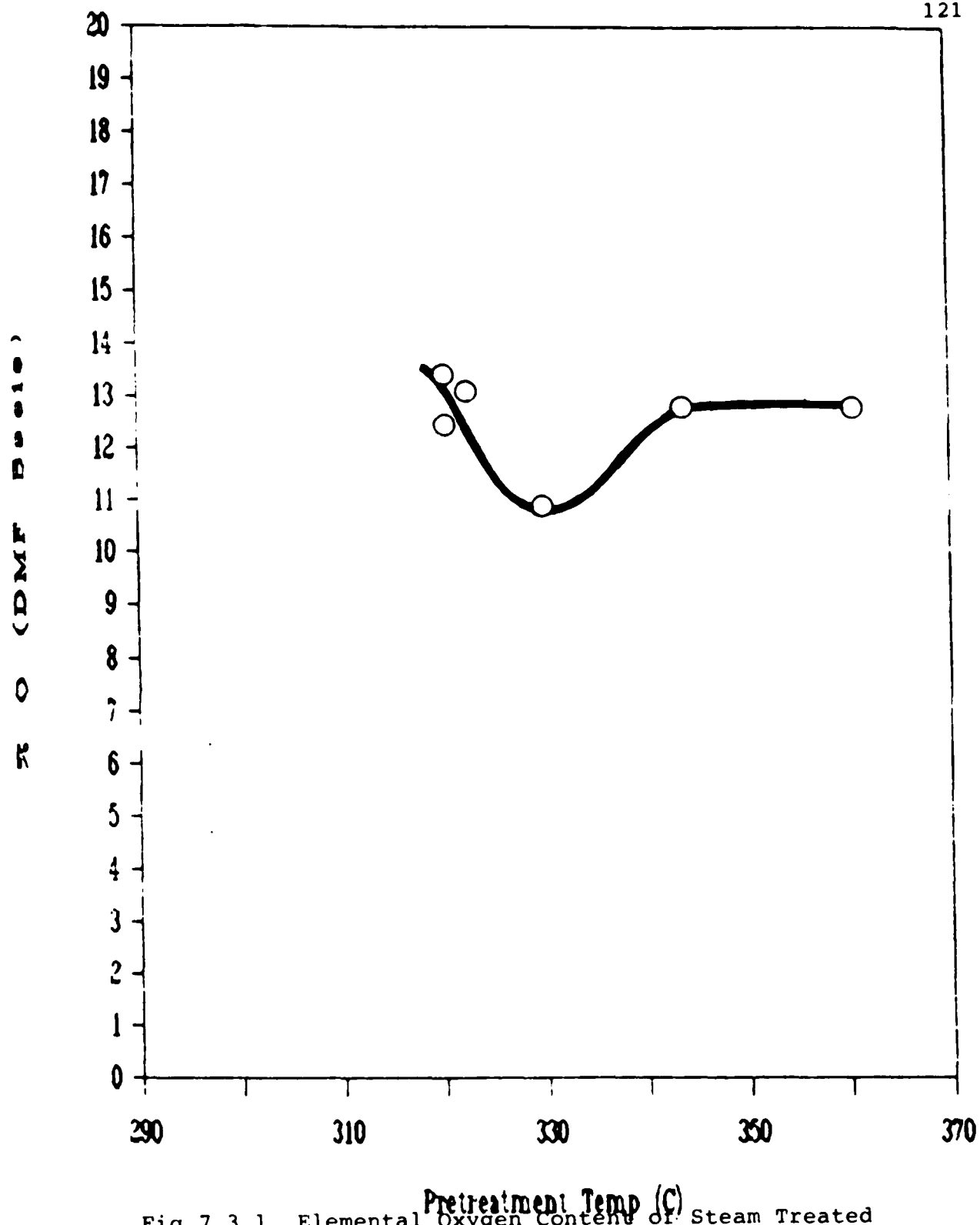


Fig.7.3.1 Elemental Oxygen Content of Steam Treated Illinois No.6 Coal vs Treatment Temperature

Table 7.3.2

Elemental Composition\* of Steam Treated Illinois No.6 Coal  
at Differing Treatment Conditions  
Oxygen by Difference\*\*

| <u>Treatment</u><br><u>Conditions</u> | <u>Raw Coal</u> | <u>PY4</u> | <u>PY5</u> | <u>PY7</u> | <u>PY9</u> | <u>PY10</u> | <u>PY11</u> |
|---------------------------------------|-----------------|------------|------------|------------|------------|-------------|-------------|
| Temp. (°C)                            | -               | 320        | 320        | 322        | 330        | 344         | 360         |
| Time (min)                            | -               | 15         | 15         | 15         | 15         | 15          | 15          |
| C                                     | 75.09           | 76.08      | 76.44      | 77.40      | 75.09      | 76.98       | 75.61       |
| H                                     | 5.68            | 5.09       | 4.89       | 5.58       | 5.68       | 5.47        | 5.33        |
| O                                     | 12.90           | 11.96      | 11.81      | 10.46      | 12.90      | 10.92       | 12.66       |
| N                                     | 1.29            | 1.72       | 1.72       | 1.23       | 1.29       | 1.43        | 1.48        |
| S(total)                              | 5.16            | 5.15       | 5.14       | 5.31       | 5.16       | 5.20        | 4.96        |
| C/H                                   | 13.22           | 14.94      | 15.63      | 13.87      | 13.22      | 14.07       | 14.18       |
| C/O                                   | 5.82            | 6.35       | 6.47       | 7.40       | 5.82       | 7.04        | 5.97        |

\* Ash free basis

\*\* Compounded error  $\pm 10\%$

is altered slightly; for treated coals it is higher. The values given in Table 7.3.1 are not corrected for treatment losses. This could be accomplished when the condensible materials from the pretreatment are also analyzed.

In order to provide information on the pretreatment process, measurements of the glass transition temperature were made on raw coal, steam pretreated coal, and steam pretreated coal exposed to air using a differential scanning calorimeter (DSC) (Isaacs, 1986). Raw coal shows a glass transition in the temperature range 310-350°C. No glass transition is observed for pretreated coal down to 270°C. A pretreated sample exposed to air has the same glass transition as raw coal.

The glass transition temperature range is almost identical to that found effective for pretreatment (320 to 360°C). The increase in mobility which occurs during this transition may play a role in pretreatment (e.g. enhancing diffusion of steam into coal). The disappearance of the glass transition upon pretreatment is consistent with partial depolymerization. The glass transition is observed upon cooling a sample which has first been heated to 360°C in an inert gas. Since this is higher than the pretreatment temperature, the disappearance of the transition is not a purely thermal

effect. The return of the glass transition upon exposure to air parallels the previous observations that the effects of pretreatment on pyrolytic yields are erased by exposure to air. It may be that pretreatment depolymerizes coal by disrupting linkages, and that these are rapidly restored by air at room temperature.

Receipt of a number of different Illinois No.6 coal samples was made by this laboratory. Each sample was divided into small batches of three to five hundred grams, sealed under nitrogen and stored in a freezer. The history of each sample prior to its arrival was not known. Samples numbered 16, 17, and 18 were found to have different amounts of oxygen (Table 7.3.3) and S as sulfate indicating different degrees of oxidation.

Different coal batches, even if originally from the same large sample of coal respond differently to pretreatment. It is believed that samples of coal which have not been adequately protected from air, heat, and light are less likely to respond to steam treatment. In a number of runs using sample CFI#18 (Table 7.3.4) there was no improvement of yield following pretreatment. The history of this sample, as was noted above, was not well documented. There is a possibility that the sample was partially oxidized during storage. Uneven oxidation may explain the poor reproducibility of the data. Batch CFI#17CD (Table 7.3.5) also gave highly irreproducible

Table 7.3.3

Coal Analyses, Illinois No.6 Coal  
Lot No.'s 16, 17, 18 (Wt %)

| <u>Lot Number</u> | <u>16</u> | <u>17</u> | <u>18</u> |
|-------------------|-----------|-----------|-----------|
| Moisture          |           | 0.7       | 10.7      |
| Volatile Matter   |           | 41.1      | 34.5      |
| Fixed Carbon      |           | 47.8      | 45.3      |
| Ash               | 12.3      | 10.0      | 9.9       |
| H (MAF)           | 5.9       | 5.3       | 7.1       |
| C (MAF)           | 78.8      | 76.5      | 76.0      |
| N (MAF)           | 1.4       | 1.3       | 1.2       |
| O (MAF)           | 10.5      | 11.8      | 10.1      |
| S (MAF)           | 3.4       | 5.1       | 5.6       |
| Sulfate S (MAF)   |           | 0.025     | 0.52      |

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**Notes:**

Lot 16: Analysis supplied by Exxon R&E Co. Ash is % mineral matter on a dry basis, elemental composition on dmmf basis, S and O are organic S and O for this column only.

Lot 17 & 18: Analysis by Galbraith Laboratories; Volatile matter and fixed carbon from analyses by Smith, Rudy and Co.

Table 7.3.4

Steam Pyrolysis of Illinois No.6 Coal, Lot No. 18

| Run No. | Time (min) | Pretreatment |       | Pyro T(°C) | Carbon Yields (%) |      |                 |      |      |
|---------|------------|--------------|-------|------------|-------------------|------|-----------------|------|------|
|         |            | Max          | T(°C) |            | CH <sub>4</sub>   | CO   | CO <sub>2</sub> | Liq  | Vol  |
| CL6     | -          | -            |       | 773        | 9.0               | 15.0 | 38.0            | 1.0  | 38.0 |
| SPCL19  | 15         | 350          |       | 743        | 6.1               | 12.0 | 27.1            | 16.6 | 61.8 |
| SPCL20  | 15         | 345          |       | 771        | 5.7               | 11.0 | 43.5            | 16.0 | 76.0 |
| SPCL21  | 15         | 335          |       | 766        | 6.0               | 11.1 | 43.6            | 14.5 | 75.2 |
| CL8     | -          | -            |       | 725        | 3.8               | 9.4  | 29.0            | 12.8 | 55.0 |
| CL9     | -          | -            |       | 742        | 5.3               | 11.5 | 29.9            | 14.3 | 61.0 |
| CL11    | -          | -            |       | 761        | 8.4               | 10.8 | 27.1            | 2.7  | 49.0 |
| CL12    | -          | -            |       | 759        | 7.2               | 8.7  | 20.5            | 4.6  | 41.0 |
| CL13    | -          | -            |       | 753        | 4.7               | 9.3  | 20.5            | 6.9  | 41.4 |
| SPCL22  | 15         | 326          |       | 735        | 3.5               | 6.6  | 16.9            | 23.3 | 50.3 |
| SPCL23  | 15         | 330          |       | 746        | 3.8               | 8.3  | 22.9            | 29.5 | 64.5 |
| SPCL24  | 15         | 326          |       | 740        | 2.5               | 7.6  | 18.8            | 27.2 | 56.1 |
| CL14    | -          | -            |       | 745        | 4.7               | 9.4  | 26.5            | 7.4  | 48.0 |
| CL15    | -          | -            |       | 760        | 4.9               | 2.9  | 36.0            | 0.0  | 40.7 |
| CL17    | -          | -            |       | 738        | 5.8               | 18.9 | 33.8            | 12.8 | 71.3 |
| CL18    | -          | -            |       | 746        | 6.1               | 20.7 | 33.1            | -1.0 | 58.9 |
| SPCL28  | 15         | 326          |       | 753        | 5.6               | 10.7 | 31.0            | 0.0  | 47.0 |
| CL19    | -          | -            |       | 762        | 7.1               | 15.8 | 40.6            | 10.5 | 74.0 |
| CL22    | -          | -            |       | 759        | 6.7               | 19.9 | 41.7            | 2.5  | 70.8 |
| CL23    | -          | -            |       | 704        | 5.4               | 14.8 | 20.8            | 5.3  | 46.3 |
| CL24    | -          | -            |       | 732        | 6.3               | 15.2 | 24.0            | 17.0 | 62.5 |
| SPCL33  | 15         | 339          |       | 755        | 5.2               | 7.1  | 15.5            | 24.5 | 52.3 |
| CL25    | -          | -            |       | 733        | 5.5               | 11.6 | 24.5            | 3.9  | 45.5 |
| CL26    | -          | -            |       | 734        | 5.2               | 13.4 | 23.5            | 11.1 | 53.2 |
| CL27    | -          | -            |       | 742        | 4.2               | 10.6 | 19.5            | 25.9 | 60.2 |
| SPCL35  | 15         | 350          |       | 754        | 5.0               | 10.9 | 20.9            | 22.2 | 59.0 |
| SPCL36  | 15         | 331          |       | 755        | 6.7               | 9.8  | 19.0            | 5.6  | 41.1 |
| SPCL37  | 15         | 340          |       | 746        | 5.9               | 14.0 | 23.4            | 16.6 | 59.9 |
| SPCL38  | 5          | 340          |       | 744        | 5.6               | 6.0  | 22.3            | 8.7  | 42.6 |

Table 7.3.4 (cont.)

Steam Pyrolysis of Illinois No.6 Coal, Lot No. 18

| <u>Run No.</u> | <u>Time (min)</u> | <u>Pretreatment</u> |              | <u>Pyro T(°C)</u> | <u>Carbon Yields (%)</u> |           |                       |            |            |
|----------------|-------------------|---------------------|--------------|-------------------|--------------------------|-----------|-----------------------|------------|------------|
|                |                   | <u>Max</u>          | <u>T(°C)</u> |                   | <u>CH<sub>4</sub></u>    | <u>CO</u> | <u>CO<sub>2</sub></u> | <u>Liq</u> | <u>Vol</u> |
| SPCL39         | 5                 | 348                 |              | 740               | 5.8                      | 7.5       | 24.1                  | 10.8       | 48.2       |
| CL30           | -                 | -                   |              | 739               | 4.8                      | 8.7       | 28.9                  | 10.3       | 52.7       |
| SPCL41         | 7                 | 351                 |              | 751               | 4.9                      | 6.0       | 20.9                  | 16.8       | 48.6       |
| SPCL42         | 15                | 339                 |              | 743               | 3.6                      | 7.7       | 17.1                  | 40.2       | 68.6       |
| SPCL43         | 7                 | 342                 |              | 743               | 6.6                      | 11.4      | 17.9                  | 8.2        | 44.1       |
| SPCL44         | 30                | 320                 |              | 710               | 5.5                      | 18.7      | 21.6                  | 14.4       | 60.2       |
| SPCL46         | 30                | 322                 |              | 717               | 5.9                      | 14.1      | 19.8                  | 6.3        | 46.1       |
| CL32           | -                 | -                   |              | 707               | 5.6                      | 10.1      | 11.5                  | 22.1       | 49.3       |
| SPCL47         | 30                | 306                 |              | 756               | 6.1                      | 13.7      | 28.4                  | 18.8       | 67.0       |
| CL35           | -                 | -                   |              | 711               | 5.1                      | 14.0      | 11.6                  | 9.3        | 40.0       |
| CL36           | -                 | -                   |              | 737               | 5.7                      | 13.0      | 22.1                  | 1.6        | 42.4       |
| CL37           | -                 | -                   |              | 708               | 5.0                      | 15.9      | 15.1                  | 4.8        | 40.8       |
| CL39           | -                 | -                   |              | 726               | 5.0                      | 13.2      | 16.7                  | 1.6        | 36.5       |
| CL40           | -                 | -                   |              | 739               | 4.5                      | 13.3      | 13.6                  | 17.1       | 48.5       |
| CL41           | -                 | -                   |              | 743               | 5.2                      | 13.1      | 18.1                  | 9.7        | 46.1       |
| SPCL48         | 15                | 335                 |              | 740               | 3.9                      | 10.5      | 15.7                  | 9.3        | 39.4       |
| CL42           | -                 | -                   |              | 732               | 5.3                      | 9.5       | 14.8                  | 7.9        | 37.5       |
| CL43           | -                 | -                   |              | 736               | 5.1                      | 11.8      | 15.4                  | 12.3       | 44.6       |
| CL46           | -                 | -                   |              | 732               | 5.3                      | 13.1      | 16.9                  | 11.1       | 46.4       |

Table 7.3.5

Steam Pyrolysis of Illinois No.6 Coal, Lot 17CD

| Run No. | Time (min) | Pretreatment |       | Pyro T(°C) | Carbon Yields (%) |      |                 |      |      |
|---------|------------|--------------|-------|------------|-------------------|------|-----------------|------|------|
|         |            | Max          | T(°C) |            | CH <sub>4</sub>   | CO   | CO <sub>2</sub> | Liq  | Vol  |
| CL51    | -          | -            | -     | 708        | 4.6               | 8.0  | 12.8            | 28.1 | 53.5 |
| CL52    | -          | -            | -     | 773        | 5.5               | 9.9  | 23.9            | 24.4 | 63.7 |
| CL53    | -          | -            | -     | 725        | 4.7               | 8.6  | 16.6            | 27.3 | 57.2 |
| CL54    | -          | -            | -     | 689        | 4.3               | 7.9  | 13.1            | 21.1 | 46.4 |
| CL55    | -          | -            | -     | 746        | 5.4               | 14.3 | 18.4            | 9.9  | 48.0 |
| CL57    | -          | -            | -     | 760        | 4.4               | 9.2  | 13.9            | 8.3  | 35.8 |
| CL58    | -          | -            | -     | 736        | 4.6               | 10.1 | 16.6            | 10.8 | 42.1 |
| CL59    | -          | -            | -     | 730        | 5.0               | 8.1  | 14.4            | 12.2 | 39.7 |
| CL60    | -          | -            | -     | 713        | 4.6               | 8.3  | 18.4            | 11.3 | 42.6 |
| CL61    | -          | -            | -     | 675        | 4.2               | 10.1 | 16.7            | 4.4  | 35.4 |
| CL62    | -          | -            | -     | 705        | 4.3               | 8.2  | 9.9             | 12.8 | 35.2 |
| CL63    | -          | -            | -     | 681        | 4.1               | 8.9  | 10.9            | 15.0 | 38.9 |
| CL64    | -          | -            | -     | 649        | 3.8               | 6.9  | 8.0             | 16.7 | 35.4 |
| CL65    | -          | -            | -     | 623        | 3.3               | 6.2  | 8.6             | 21.3 | 39.4 |
| CL66    | -          | -            | -     | 789        | 2.9               | 8.2  | 10.3            | 8.0  | 29.4 |
| CL67    | -          | -            | -     | 607        | 3.0               | 7.4  | 9.0             | 12.1 | 31.5 |
| SPCL53  | 15         | -            | 331   | 647        | 3.0               | 8.7  | 8.4             | 23.8 | 43.9 |
| SPCL54  | 15         | -            | 327   | 625        | 3.4               | 8.7  | 4.3             | 13.2 | 29.6 |
| SPCL55  | 15         | -            | 331   | 686        | 3.6               | 7.9  | 7.8             | 11.8 | 31.1 |
| SPCL56  | 15         | -            | 330   | 671        | 3.1               | 6.7  | 5.8             | 17.7 | 33.3 |
| CL68    | -          | -            | -     | 647        | 3.4               | 9.9  | 10.5            | 10.8 | 34.6 |
| CL69    | -          | -            | -     | 652        | 3.8               | 9.2  | 9.7             | 12.8 | 35.5 |
| CL70    | -          | -            | -     | 655        | 3.6               | 8.6  | 9.6             | 14.9 | 36.7 |
| CL71    | -          | -            | -     | 646        | 3.5               | 7.6  | 10.8            | 11.3 | 33.2 |
| SPCL57  | 15         | -            | 330   | 633        | 2.3               | 7.9  | 3.9             | 23.1 | 37.2 |
| CL72    | -          | -            | -     | 655        | 3.3               | 7.8  | 8.6             | 23.6 | 43.3 |
| CL73    | -          | -            | -     | 655        | 3.6               | 6.3  | 6.4             | 19.6 | 35.9 |
| CL74    | -          | -            | -     | 655        | 7.3               | 9.2  | 13.4            | 10.0 | 39.9 |

Table 7.3.5 (cont.)

Steam Pyrolysis of Illinois No.6 Coal, Lot 17CD

| Run No. | Time (min) | Pretreatment |       | Pyro T(°C) | Carbon Yields (%) |     |                 |      |      |
|---------|------------|--------------|-------|------------|-------------------|-----|-----------------|------|------|
|         |            | Max          | T(°C) |            | CH <sub>4</sub>   | CO  | CO <sub>2</sub> | Liq  | Vol  |
| CL75    | -          | -            | -     | 653        | 3.3               | 7.3 | 5.2             | 20.5 | 36.3 |
| CL76    | -          | -            | -     | 690        | 3.9               | 8.7 | 8.9             | 20.3 | 41.8 |
| CL77    | -          | -            | -     | 668        | 3.3               | 6.8 | 9.3             | 25.8 | 45.2 |
| CL78    | -          | -            | -     | 623        | 2.7               | 7.4 | 7.5             | 18.1 | 35.7 |
| CL79    | -          | -            | -     | 719        | 3.8               | 8.6 | 13.7            | 14.5 | 40.6 |
| CL80    | -          | -            | -     | 608        | 2.4               | 7.5 | 7.3             | 15.7 | 32.9 |
| SPCL58  | 15         | 322          | -     | 650        | 3.3               | 7.6 | 4.6             | 23.2 | 38.7 |
| SPCL59  | 15         | 345          | -     | 653        | 2.4               | 7.5 | 5.0             | 34.1 | 49.0 |
| SPCL60  | 15         | 344          | -     | 653        | 3.2               | 7.9 | 6.2             | 20.6 | 37.9 |
| SPCL61  | 15         | 351          | -     | 648        | 2.5               | 5.6 | 4.9             | 31.2 | 44.2 |
| SPCL62  | 15         | 399          | -     | 650        | 3.0               | 6.8 | 4.7             | 16.5 | 31.0 |
| SPCL63  | 15         | 335          | -     | 652        | 3.3               | 6.4 | 4.3             | 17.0 | 31.0 |
| CL81    | -          | -            | -     | 662        | 3.9               | 8.1 | 5.8             | 20.9 | 38.7 |
| SPCL64  | 15         | 344          | -     | 661        | 3.9               | 7.6 | 7.6             | 19.3 | 38.4 |
| SPCL65  | 15         | 330          | -     | 652        | 3.4               | 8.2 | 9.0             | 19.3 | 39.9 |

results. The total amount of conversion with the #17 coal was, however, higher overall than for the #18 coal. Samples of #17 and #18 coal were analyzed for their free swelling index (FSI) (Table 7.3.6). It was found that the coal which produced the lower liquid yields (CFI#18) also showed the smallest FSI. This test is a strong indicator of sample oxidation. These test results seem to substantiate the observation detailed above. The high S as Sulfate content of the #18 coal is another indication of its oxidized state (Table 7.3.3).

Combined batches of coal which were ground at different times also show different qualities. Six combined batches of CFI#17 coal were ground to pass 200 mesh (CD,EF,BGH,IJK,LMN,OPQ). Of these six only BGH and OPQ exhibited consistent improvement in liquid yield after steam treatment. Batch CD gave inconsistent results and batches IJK and LMN showed no improvement in either pyrolysis or extraction (Tables 7.3.7 and 7.3.8). It is believed that excessive handling, overheating on the shaker while sieving, and possibly exposure to air during grinding destroyed, in the same way, the IJK and LMN batches. The BGH and OPQ batches were sieved by hand and had no exposure to air until use in extraction, swelling, or pyrolysis experiments.

Table 7.3.6

Free Swelling Index  
Illinois No.6 Coal, Samples 17 and 18\*

| <u>Sample</u>               | <u>FSI</u> |
|-----------------------------|------------|
| CFI#17 as received, 60 mesh | 3.5        |
| CFI#17 CD, 200 mesh         | 4.5        |
| CFI#18 C, large pieces      | 1.5        |
| CFI#18, 200 mesh            | 0.5        |

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\*Measurements were made courtesy of Dr. C.W. Kruse,  
Illinois Dept. of Energy and Natural Resources,  
State Geological Survey Division

Table 7.3.7

Inert Gas Pyrolysis of Illinois No.6 Coal  
Samples CFI#17 IJK and LMN

| <u>Run No.</u> | <u>Coal Batch</u> | <u>Pretreat T (°C)</u> | <u>Pyro T (°C)</u> | <u>Conversion (wt%)</u> |                  |
|----------------|-------------------|------------------------|--------------------|-------------------------|------------------|
|                |                   |                        |                    | <u>Liquid</u>           | <u>Volatiles</u> |
| 19             | IJK               | 340                    | 802                | 12.1                    | -                |
| 20             | IJK               | 335                    | 849                | 11.0                    | -                |
| 21             | IJK               | 330                    | 843                | 12.4                    | -                |
| 22             | IJK               | 325                    | 790                | 13.7                    | -                |
| 47             | LMN               | RAW                    | 570                | 28.5                    | 52.5             |
| 48             | LMN               | RAW                    | 596                | 34.3                    | 51.6             |
| 49             | LMN               | RAW                    | 567                | 29.2                    | 52.3             |
| 50             | LMN               | 337                    | 556                | 31.2                    | 47.0             |
| 51             | LMN               | 335                    | 587                | 46.4                    | 54.9             |
| 52             | LMN               | 331                    | 590                | 29.1                    | 42.1             |
| 53             | LMN               | 335                    | 667                | 25.1                    | 47.0             |
| 54             | LMN               | 325                    | 685                | 32.3                    | 47.6             |
| 55             | LMN               | RAW                    | 672                | 33.4                    | 60.7             |
| 56             | LMN               | 325                    | 679                | 26.9                    | 53.4             |
| 57             | LMN               | RAW                    | 740                | 28.0                    | 63.7             |
| 58             | LMN               | RAW                    | 674                | 35.5                    | 60.2             |
| 59             | LMN               | RAW                    | 679                | 35.1                    | 56.4             |
| 60             | LMN               | RAW                    | 696                | 32.1                    | 62.4             |

Table 7.3.8

Room Temperature Extraction of Illinois No.6 Coal  
Samples CFI#17 IJK and LMN

| <u>Coal Batch</u> | <u>Pretreatment Temperature (°C)</u> | <u>Extract Yield (%) *</u> |
|-------------------|--------------------------------------|----------------------------|
| IJK               | RAW                                  | 15.88                      |
| IJK               | RAW                                  | 16.85                      |
| IJK               | RAW                                  | 16.93                      |
| IJK               | 310                                  | 9.85                       |
| IJK               | 317                                  | 10.75                      |
| IJK               | 324                                  | 20.64                      |
| IJK               | 330                                  | 9.46                       |
| IJK               | 333                                  | 16.79                      |
| IJK               | 334                                  | 18.64                      |
| IJK               | 340                                  | 18.23                      |
| LMN               | RAW                                  | 14.57                      |
| LMN               | RAW                                  | 13.41                      |
| LMN               | RAW                                  | 13.77                      |
| LMN               | RAW                                  | 19.60                      |
| LMN               | RAW                                  | 19.90                      |
| LMN               | 290                                  | 20.43                      |
| LMN               | 315                                  | 25.89                      |
| LMN               | 320                                  | 22.06                      |
| LMN               | 325                                  | 27.51                      |
| LMN               | 325                                  | 18.54                      |
| LMN               | 326                                  | 27.69                      |
| LMN               | 340                                  | 21.59                      |
| LMN               | 350                                  | 24.25                      |
| LMN               | 360                                  | 28.43                      |

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\* Includes losses due to pretreatment

#### 7.4 Inert Gas Pyrolysis

In order to produce larger quantities of liquid product for analysis, a semi-continuous dry feeding system was developed and installed.

The first pyrolysis experiments with this modification were conducted with an inert gas using both steam treated and raw coal (Graff, 1986) at 20psi (Sec 6.6).

The pyrolytic yields obtained from Illinois No.6 raw coal in these conditions are consistent with those reported in the literature for other bituminous coals (Tyler, 1980).

Twenty-two runs were made with pretreated coal and eight with raw coal (Table 7.4.1). Based on these yields it was determined that the lightest condensible components of the product were being lost. Alterations to the collection system were made and total carbon balances approached 95%. The final configuration for the collection of liquids in the low pressure inert gas system is shown in Figure 5.6.4.

Yield of liquid product, using coal sample BGH pretreated for 15 minutes at 340°C showed an approximate 7% increase over raw BGH coal samples at a reactor temperature of about 640°C (Fig. 7.4.1). Increasing the pressure of the system to 200 psi diminished the effect, there was no difference in the yields.

Table 7.4.1

Inert Gas Pyrolysis Yields

| <u>Run No.</u>  | <u>Reactor T (°C)</u> | <u>Pretreat T (°C)</u> | <u>Total Liquid (%)</u> |
|-----------------|-----------------------|------------------------|-------------------------|
| 18              | 814                   | 340                    | 22.1                    |
| 19              | 802                   | 340                    | 12.1                    |
| 20              | 849                   | 335                    | 11.0                    |
| 21              | 843                   | 330                    | 12.4                    |
| 22              | 790                   | 325                    | 13.7                    |
| 23              | 821                   | 340                    | 13.2                    |
| 24              | 837                   | 340                    | 12.8                    |
| 25              | 763                   | 335                    | 11.0                    |
| 26              | 811                   | 335                    | ----                    |
| 27              | 815                   | 335                    | 18.5                    |
| 28              | 845                   | ---                    | 16.5                    |
| 29              | 865                   | 340                    | 12.2                    |
| 30              | 905                   | 334                    | 14.1                    |
| 31              | 896                   | 335                    | 9.2                     |
| 32 <sup>+</sup> |                       |                        |                         |
| 33              | 924                   | 333                    | 9.8                     |
| 34              | 926                   | 333                    | 9.7                     |
| 35              | 914                   | 333                    | 13.6                    |
| 36              | 924                   | 335                    | 13.7                    |
| 37              | 906                   | ---                    | 10.8                    |
| 38              | 795                   | 333                    | 24.3                    |
| 39              | 783                   | ---                    | 16.5                    |
| 40              | 769                   | 335                    | 27.0                    |
| 41              | 742                   | 335                    | 28.4                    |
| 42              | 695                   | 333                    | 27.7                    |
| 43 <sup>#</sup> | 714                   | ---                    | 37.6                    |
| 44 <sup>*</sup> | 610                   | 335                    | 35.6                    |
| 45              | 614                   | ---                    | 30.2                    |
| 46 <sup>+</sup> |                       |                        |                         |
| 47              | 570                   | ---                    | 28.5                    |
| 48              | 596                   | ---                    | 34.3                    |
| 49              | 567                   | ---                    | 29.2                    |

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<sup>+</sup>Run Aborted

<sup>#</sup>Abnormally high yield, possible incomplete removal of wash solvent

<sup>\*</sup>Abnormally high yield, possibly due to moisture absorption by silica gel traps

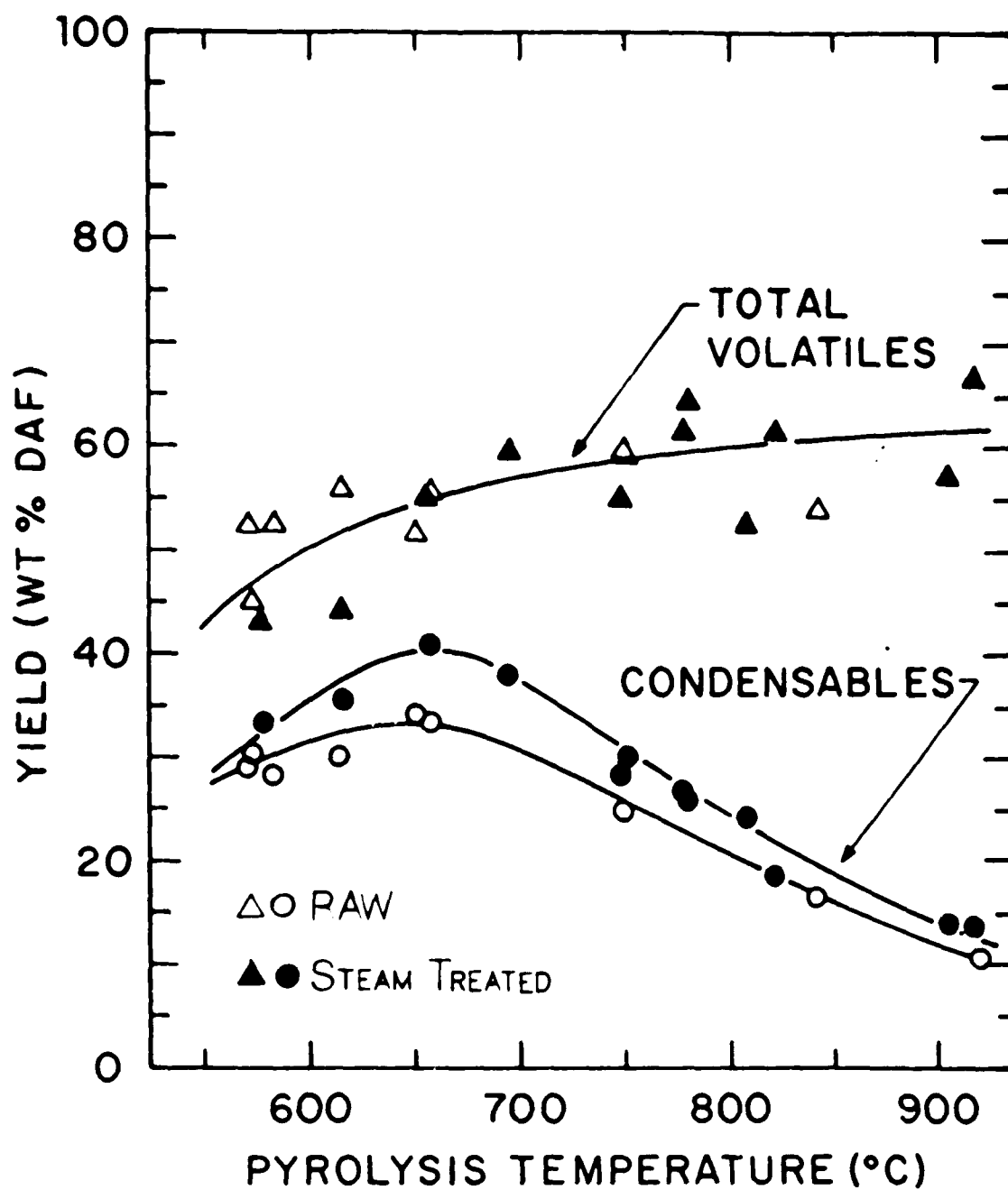


Fig.7.4.1 Low Pressure Inert Gas Pyrolysis yields of Illinois No. 6 Coal, Lot# 17 BGH and OPQ (from Graff, 1986)

In parallel with what was found in the extraction work (Sec. 7.5) the use of coal samples IJK and LMN showed no response to steam pretreatment in the pyrolysis experiments (Table 7.3.6). Coal sample OPQ responded in the same way in the pyrolysis (after pretreatment) as did the BGH sample.

Liquids were obtained from the collection system after it was cooled by washing the different sections with HPLC grade pyridine. Liquids were removed from the adsorbers by soxhlet extraction in pyridine. This material was then analyzed as discussed in Sec 7.6.

### 7.5 Extraction

The effect of steam pretreatment on Illinois No.6 coal has been shown to produce, upon subsequent pyrolysis in steam, an increased liquid yield over unpretreated coal (Sec 7.2). This increased yield has been attributed to some disruption of the coal's natural cross-linked structure.

Extraction of coal solids with various solvents has yielded information on the degree of cross-linking (Peppas, 1981; Hombach, 1981). Consequently, a study of an Illinois No.6 coal pretreated under various conditions and subsequently extracted was carried out in order to learn something of the altered nature of the coal after pretreatment.

The severity of the extraction can alter the amount and kind of material extracted (Friedel, 1963, Ruberto, 1979). So as not to mask any small changes which may have occurred by using too harsh a system it was decided to use a strong solvent, at room temperature, for a short amount of time. The solvent chosen for this study was pyridine because of its strong dispersion forces and large dipole interaction. The procedure was carried out at room temperature so that the samples would not be exposed after pretreatment to any chance for additional thermal alteration (Sec 6.3).

A number of samples of Illinois No.6 coal were used

for the extraction experiments. Sample BGH was used first. The extraction yields are given in Table 7.5.1. Raw coal (Runs I,K,M,V,AD) when extracted in a nitrogen atmosphere (as described in Sec 6.6) gives values averaging about 17%. Extractions of raw coal under slightly different conditions (shorter and longer times, larger and smaller pyridine to coal ratios), the data, which is not found on Table 7.5.1, yield values averaging approximately 18%, with no single value exceeding 21.8%.

Samples of BGH were then pretreated in steam (conditions are given in Table 7.5.2). If those samples pretreated in steam and extracted under a nitrogen blanket are considered, a curve can be drawn which puts a maximum of extractability at a pretreatment temperature of 340-350°C. (Fig. 7.5.1). The bracketed point (P) is questionable. Sample P may have been exposed to air prior to or during extraction. Sample X (Table 7.5.1) is at this time an unexplained anomaly.

Liquefaction yields of pretreated coal were found to be dependent on how the coal was handled after pretreatment. Pretreated coal when exposed to air prior to pyrolysis lost all the beneficial effects of the pretreatment. Liquid yields fell to the level of raw coal. To test whether this effect would carry over to the extraction experiments several batches

Table 7.5.1

Room Temperature Extraction of Illinois No.6 Coal  
Sample CFI#17 BGH

| <u>Run Number</u> | <u>Pretreatment Temp. (°C)</u> | <u>Extraction Atmosphere</u> | <u>Extraction Yield (%)</u> * |
|-------------------|--------------------------------|------------------------------|-------------------------------|
| I                 | raw                            | N <sub>2</sub>               | 16.00                         |
| J                 | 335                            | "                            | 30.00                         |
| K                 | raw                            | "                            | 15.6                          |
| L                 | 338                            | "                            | 13.31                         |
| M                 | raw                            | "                            | 21.49                         |
| N                 | 335                            | "                            | 13.57                         |
| O                 | 338                            | Air                          | 20.48                         |
| P                 | 338                            | N <sub>2</sub>               | 18.51                         |
| Q                 | 335                            | "                            | 23.36                         |
| R                 | "                              | "                            | 9.59                          |
| S                 | "                              | Air                          | 12.96                         |
| T                 | "                              | "                            | 9.31                          |
| U                 | 335                            | N <sub>2</sub>               | 16.50                         |
| V                 | raw                            | "                            | 14.21                         |
| W                 | 353                            | "                            | 28.82                         |
| X                 | 339                            | "                            | 60.27                         |
| Z                 | "                              | Air                          | 30.27                         |
| AA                | "                              | "                            | 20.59                         |
| AB                | 365                            | N <sub>2</sub>               | 15.72                         |
| AC                | 375                            | "                            | 15.15                         |
| AD                | raw                            | "                            | 16.38                         |
| AE                | 365                            | "                            | 19.47                         |
| AF                | "                              | "                            | 26.06                         |
| AG                | 300                            | "                            | 6.49                          |
| AH                | "                              | "                            | 15.93                         |
| AI                | 320                            | "                            | 23.93                         |
| AJ                | "                              | "                            | 7.16                          |

---

\* Includes losses due to pretreatment

Table 7.5.2

Pretreatment Conditions<sup>1</sup> Illinois No.6 Coal  
Sample CFI#17 BGH

| <u>Sample<br/>ID</u> | <u>Atmosphere</u> | <u>Temperature<br/>(°C)</u> | <u>Sample<br/>Weight <sup>2</sup></u> |
|----------------------|-------------------|-----------------------------|---------------------------------------|
| J                    | Steam             | 335                         | 1.5                                   |
| L                    | Helium            | 338                         | 1.5                                   |
| N                    | Helium            | 335                         | 1.5                                   |
| O                    | Steam             | 338                         | 3.0                                   |
| P                    |                   |                             |                                       |
| Q                    | Steam             | 335                         | 6.0                                   |
| R                    |                   |                             |                                       |
| S                    |                   |                             |                                       |
| T                    |                   |                             |                                       |
| U                    | Helium            | 335                         | 1.5                                   |
| W                    | Steam             | 353                         | 1.5                                   |
| X                    | Steam             | 339                         | 6.0                                   |
| Y                    |                   |                             |                                       |
| Z                    |                   |                             |                                       |
| AA                   |                   |                             |                                       |
| AB                   | Helium            | 365                         | 1.5                                   |
| AC                   | Helium            | 375                         | 1.5                                   |
| AE                   | Steam             | 365                         | 3.0                                   |
| AF                   |                   |                             |                                       |
| AG                   | Steam             | 300                         | 3.0                                   |
| AH                   |                   |                             |                                       |
| AI                   | Steam             | 320                         | 3.0                                   |
| AJ                   |                   |                             |                                       |

1 All pretreatments carried out for 15 minutes at 50 atmospheres

2 Grams per batch of coal

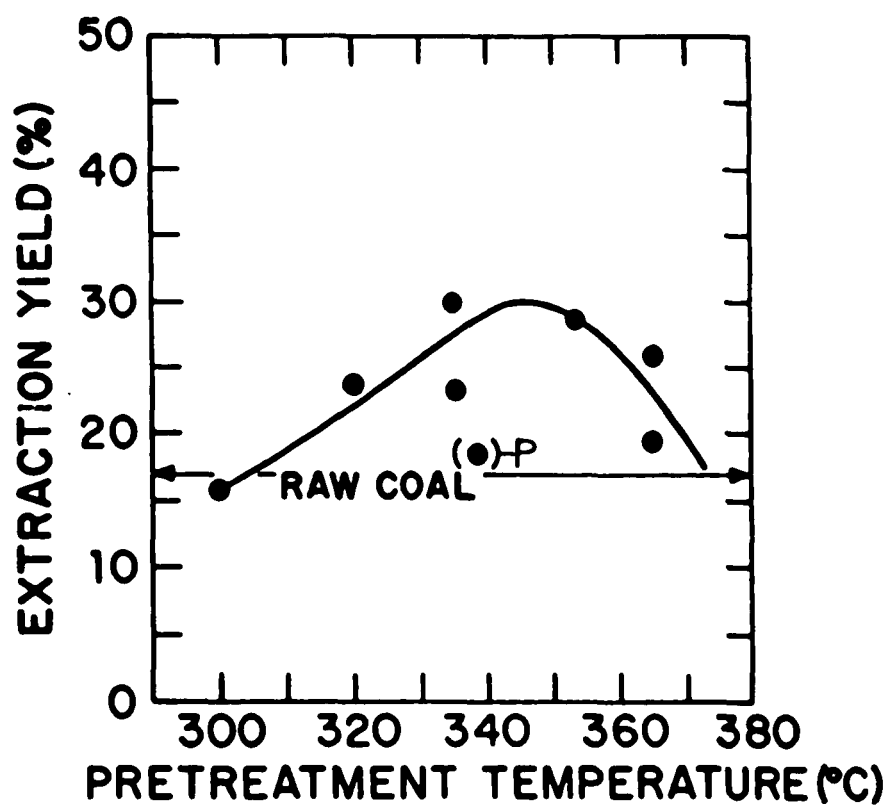


Fig.7.5.1 Room Temperature Extraction Yields of  
Steam Treated Illinois No. 6 Coal,  
Lot#17 BGH

of coal were pretreated and then divided under a  $N_2$  atmosphere. Part of the sample was removed from the glove bag and extracted in air (runs O,P; Q,R,S,T; and X,Z,AA). It is believed that the very close values of O and P resulted from inadvertent exposure of sample P to air at some point. The same explanation must be relied on for sample R. The very high values for X,Z and AA are not understood, but it is interesting to note that the relative ratio of extractables of the protected sample to the air exposed sample is still 2:1.

Other samples of Illinois No.6 coal were also extracted. Samples IJK and LMN also had average raw coal extractable yields of approximately 17%. The steam pretreated coal, however, showed no improvement at all. (see Table 7.3.8 for conditions and yields). As it was discussed in Sec 7.3 these two samples were believed to have undergone a great deal of oxidation while being ground. Sample OPQ, on the other hand, gives reproducibly improved extraction yields after steam treatment and behaves very much like sample BGH (Fig. 7.5.2).

Storage of pretreated coal in an inert atmosphere was shown to be possible in the pyrolysis studies. The high yield of extractable material is also retained if the sample is carefully stored in the absence of air (Table 7.5.3).

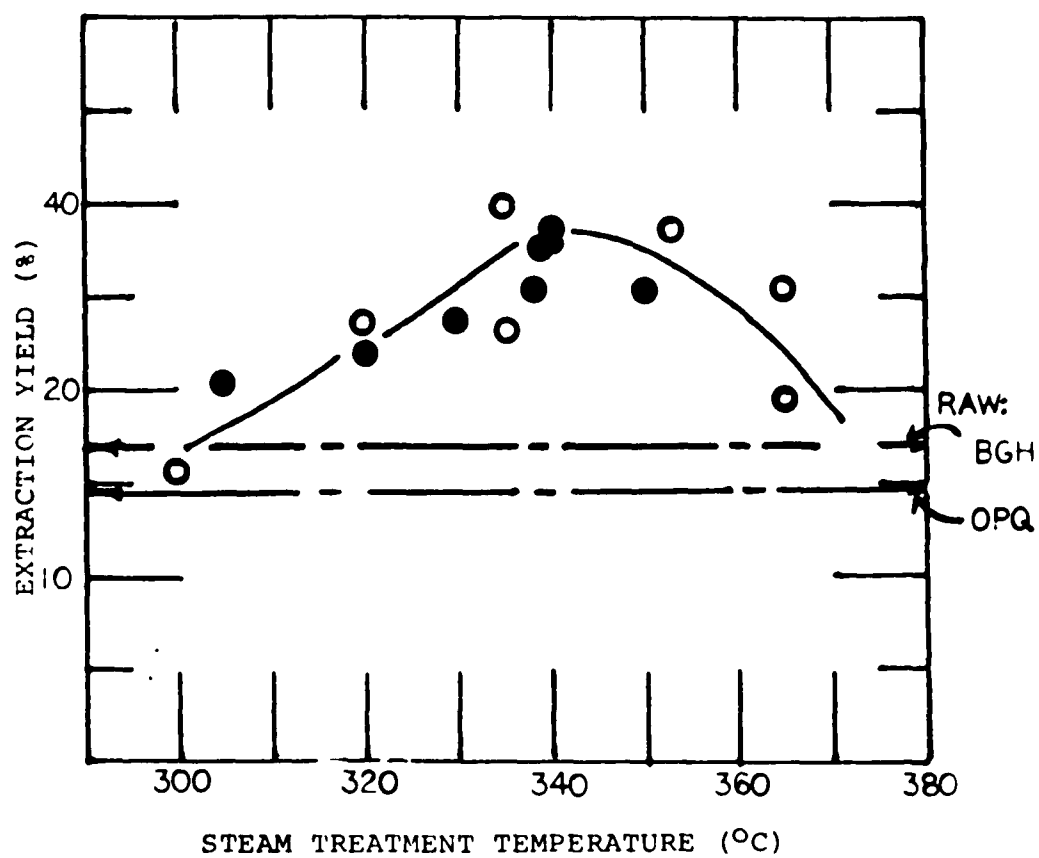


Fig.7.5.2 Room Temperature Extraction Yields of Steam Treated Illinois No. 6 Coal, Lot#17 BGH and OPQ

Table 7.5.3  
Effect of Inert Gas Storage on Steam Treated  
Illinois No.6 Coal\*

| <u>Day</u> | <u>Extraction Yield</u> |
|------------|-------------------------|
| 1          | 24.93<br>24.81          |
| 4          | 25.53                   |
| 8          | 23.23<br>23.51          |

---

\*25 grams CFI#17 OPQ Steam Treated at an average temperature of 339°C

The final piece of information which comes from these room temperature experiments is that pretreatment in steam produces upon subsequent extraction a greater yield of soluble material than coal pretreated in helium (Fig. 7.5.3). Although this data appears to be contradictory with other inert gas preheating experiments (Illingworth 1922, Dryden and Pankhurst 1955, and Brown and Waters 1966) it is not directly comparable due to the different experimental techniques used. Those experiments, which show improved yields after heating in inert gas, differ in two important ways from the experiments reported here; 1) The experiments reported in the literature involved a shock cooling of the sample after achievement of the desired temperature, and 2) All experiments were conducted under atmospheric pressure. The slow cooling of the samples in this work may give the material time to reform thermally disrupted bonds. Also the elevated pressure would promote mobility of the structures making the achievement of more stable conformations possible.

Limited pyrolysis data for helium pretreated samples makes direct comparison between these results and steam pyrolysis yields difficult, however, it does strongly suggest that pyrolysis yields would follow a similar trend. This evidence indicates that the steam pretreatment process produces more than just a thermal

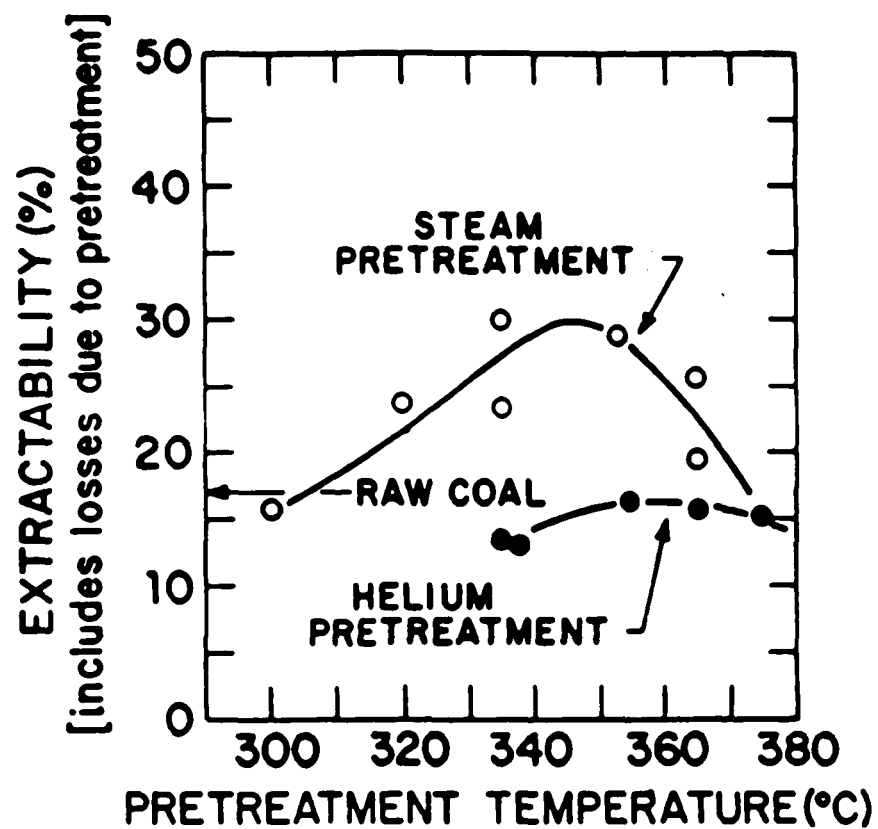


Fig.7.5.3 Room Temperature Extraction Yields of Helium Treated Illinois No. 6 Coal, Lot #17 BGH

alteration of the coal. The steam, at 50 atm., is in some way interacting with the coal to alter the degree of cross-linking.

It is apparent from the above discussion that the behavior of the treated coal in extraction experiments mimics the behavior found in the steam pyrolysis experiments (Sec 7.2). It is because of this and because of the ease of this experiment, and the reproducibility of the data, room temperature extraction has been adopted as a screening test for coal samples and treatment conditions.

Coal samples were also subjected to soxhlet extraction. The experiments were undertaken to see if the ultimate yields from raw and pretreated coal would vary significantly if the steam treated coal was again exposed to a thermal treatment subsequent to the low temperature exposure to steam. It was also considered important to see if the remaining material, after the room temperature extraction, (the 'backbone' structure of the coal) differed in the steam treated and raw coal. The experiments were done in two parts. In the first part the raw and steam pretreated coal were directly extracted in a soxhlet apparatus with pyridine (under atmospheric pressure nitrogen). In the second part, the residue from a room temperature extraction under  $N_2$  was directly transferred to a soxhlet and the extraction

continued to exhaustion.

The results of this experiment are given in Table 7.5.4. The direct soxhlet extraction yields are, on an average, 5% greater for steam pretreated coal than raw coal. When it is considered that the experimental limits of accuracy are about  $\pm 2\%$  the extra amount of material extractable by soxhlet ( $\Delta$ ) in the two step process is the same for either raw or pretreated coal, 5-7%. These values are determined by the difference of the amount of residue left after the soxhlet extraction and the amount of extract obtained from the room temperature step. In Ex.4 the additional amount of material obtained from the soxhlet extraction is only 1.6%. This low value was checked in the subsequent two experiments (Ex.5 and Ex.6) by drying the extract from the soxhlet step of the two step process and weighing the material. The results fit the data of Ex.1,2, and 3. The value for  $\Delta$  in Ex.4 is consequently considered anomalous.

Room temperature extracts of steam treated and raw Illinois No.6 coal are different by about 10% (not including the losses due to pretreatment) (see Fig. 7.5.1 as well as data on Table 7.5.4). This 10% increase in room temperature extraction yield of steam treated coal at the optimum pretreatment temperature is not maintained in the direct soxhlet experiment. The raw coal yields an additional 5% as does the steam treated

Table 7.5.4

Extraction Yields from Room Temperature,  
Two Step and Direct Soxhlet Extraction of  
Illinois No. 6 Coal

| Exp. No.       | Sample        | Yields (%) |          |               |                |
|----------------|---------------|------------|----------|---------------|----------------|
|                |               | Room T     | Two Step | $\triangle^*$ | Direct Soxhlet |
| 1              | Raw           | 15.62      | 21.59    | 5.97          | 32.7           |
| 2              | Raw           | 26.0       | 32.0     | 6.0           | 29.01          |
| 3 <sup>+</sup> | Steam Treated | 26.98      | 34.86    | 7.88          | 36.88          |
| 4 <sup>+</sup> | Steam Treated | 22.6       | 24.29    | 2.0           | 34.7           |
| 5 <sup>+</sup> | Steam Treated |            |          | 4.94          |                |
| 6              | Raw           |            |          | 4.92          |                |

\* Amount of material additionally extracted in the Soxhlet in a two step extraction.

<sup>+</sup> Yields do not include pretreatment losses

coal giving a difference between raw and pretreated coal of only 5%.

These results indicate that the effect of the pretreatment is to not change the backbone structure of the coal, no more additional material can be extracted in elevated temperatures from the steam treated coal than what can be gotten from the raw coal. It also shows that the exposure to an elevated temperature in solvent, under nitrogen does not seem to adversely effect the steam treated coal, yields of extractable material from the direct soxhlet experiment are the same as for the two step process.

## 7.6 Analysis of Pyrolysis Liquids

### 7.6.1 Chromatographic Separation

Coal is a complex heterogeneous substance. It is essentially an organic rock that varies in composition from sample to sample. The liquid materials produced from this material, by breaking down the coal structure into smaller molecular weight units, are just as complex. By looking at a simulated structure of an average coal molecule (Fig. 7.6.1) it is possible to envision the types of materials which will be produced by bond breakage and rearrangement reactions.

Many methods have been devised for the analysis of these coal derived organic products (Crynes, 1983 and Wright, 1983). It is the aim of this research to extract from a few simple analytical schemes enough information to make a comparative evaluation of the effect of the pretreatment vs. non-pretreatment on the quality of the liquids produced in flash pyrolysis and also by extraction. It is also part of this work to discern the effects of altering pretreatment conditions on the liquid quality. The majority of methods for analysis of coal liquids are limited by restricting the analysis to portions of the mixture which are soluble in pentane or benzene (respectively called oils and asphaltenes). This preliminary separation of the coal liquid leads to faulty information because the solubility of the

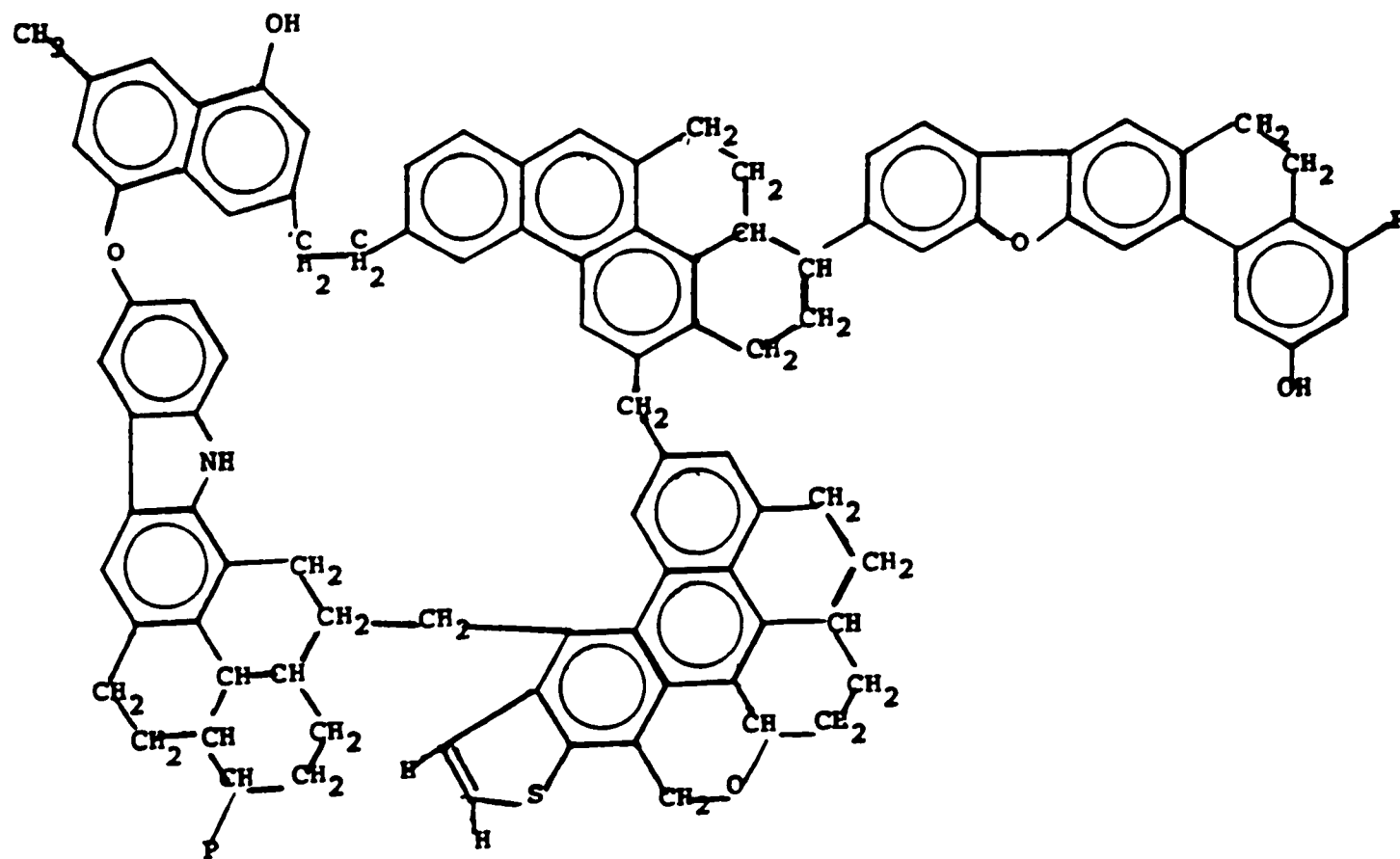


Fig.7.6.1 Proposed Structure of the Coal Model Molecule  
(Heredy and Wender, 1980)

hydrocarbon material is not solely a function of its carbon-hydrogen skeleton. It is dependent on the interaction of that substance with the other materials in the mixture. Thus there are co-solvent effects which cause the hydrocarbon in question to appear as an "oil" or "asphaltene" due only to the presence or absence of another material in the coal liquid. To avoid this problem, separation of the whole coal liquid, by liquid chromatography has been chosen to establish broad classifications of the material present in the mixture. One such scheme is SESC, Sequential Elution by Solvent Chromatography, as described by Farcasiu (1977). This is a separation scheme based on the functionality of different components of the coal liquid mixture. The procedure was designed to ensure separation of the polar constituents of the mixture which Farcasiu estimates to be ca. 85% of the solvent refined coal liquids (Kentucky SRC) used in their study. The solvent sequence was chosen based on the Hildebrand parameter ( $\delta$ ) and the specific solubility parameters ( $\delta_a, \delta_o, \delta_d, \delta_h$ ) (Karger, Snyder, and Horvath, 1973). Solvents used for the separation of the polar material change from chloroform (which has a dipole moment, but not proton acceptor properties) to pyridine (which is highly polar with good acceptor properties) (see Table 7.6.1). Based on analyses of the fractions obtained from the

Table 7.6.1

Solvent Sequence for SESC Analysis

1. Hexane
2. Hexane/15% Benzene
3. Chloroform
4. Chloroform/10% Ethyl Ether
5. Ethyl Ether/3% Ethanol
6. Methanol
7. Chloroform/3% Ethanol
8. Tetrahydrofuran/3% Ethanol
9. Pyridine/3% Ethanol

chromatography of the SRC liquids, and model compound studies, broad classes of compounds were assigned to each fraction (Table 7.6.2). This method, or variations of it, can provide a set of comparable data between raw and pretreated coal, directly, by indicating the quantity of each group of compounds obtained from the separation.

Liquids from the low pressure inert gas pyrolysis of raw coal, steam treated coal and helium treated coal were separated using the SESC scheme. One sample of each material was split into two portions and separated on a gravity fed open chromatography column (Sec 5.7.1 and 6.7.1).

The resulting average value of weight percent of sample is given in Table 7.6.3 and plotted in Figure 7.6.2. Fraction 9 and the non-elutable material have been combined in this figure. This is justifiable considering the chemical nature of the two fractions is expected to be the same and the fractions differ only in molecular weight (Whitehurst, et al., 1980).

There appears to be little, if any, difference among the fractions of the three different materials. Fraction 5 and 9+ne show that the thermal treatment (in helium) has produced a preponderance of small basic nitrogen heterocycles at the expense of large multifunctional materials. The same trend is observed

Table 7.6.2

Fractions Obtained from SESC Analysis

| <u>Fraction</u> | <u>Major Components</u>                             |
|-----------------|-----------------------------------------------------|
| 1.              | Saturates                                           |
| 2.              | Aromatics                                           |
| 3.              | Polar Aromatics, Non-Basic N,O,S heterocycles       |
| 4.              | Monophenols                                         |
| 5.              | Basic Nitrogen Heterocycles                         |
| 6.              | Highly Functional Heterocycles (>10wt% Heteroatoms) |
| 7.              | Polyphenols                                         |
| 8.              | Increasing O Content and Basicity of Nitrogen       |
| 9.              |                                                     |
| 10.             | Non-eluted, unidentified material                   |

Table 7.6.3

SESC Yields of Inert Gas Pyrolysis Products

|          | <u>Raw Coal</u> | <u>Steam Treated</u> | <u>Helium Treated</u> |
|----------|-----------------|----------------------|-----------------------|
| Run No.  | S6 and S7       | S8 and S9            | S10 and S11           |
| FRACTION |                 |                      |                       |
| 1        | 2.5             | 1.75                 | 0.8                   |
| 2        | 4.0             | 1.2                  | 1.8                   |
| 3        | 12.0            | 9.9                  | 10.0                  |
| 4        | 8.6             | 11.5                 | 9.8                   |
| 5        | 12.0            | 20.2                 | 21.2                  |
| 6*       | 26.6            | 28.4                 | 31.2                  |
| 7        | 8.9             | 7.8                  | 5.8                   |
| 8        | 6.1             | 6.7                  | 8.9                   |
| 9+ne     | 19.5            | 13.75                | 11.8                  |

---

\*f6 value corrected for colloidal silica present in sample

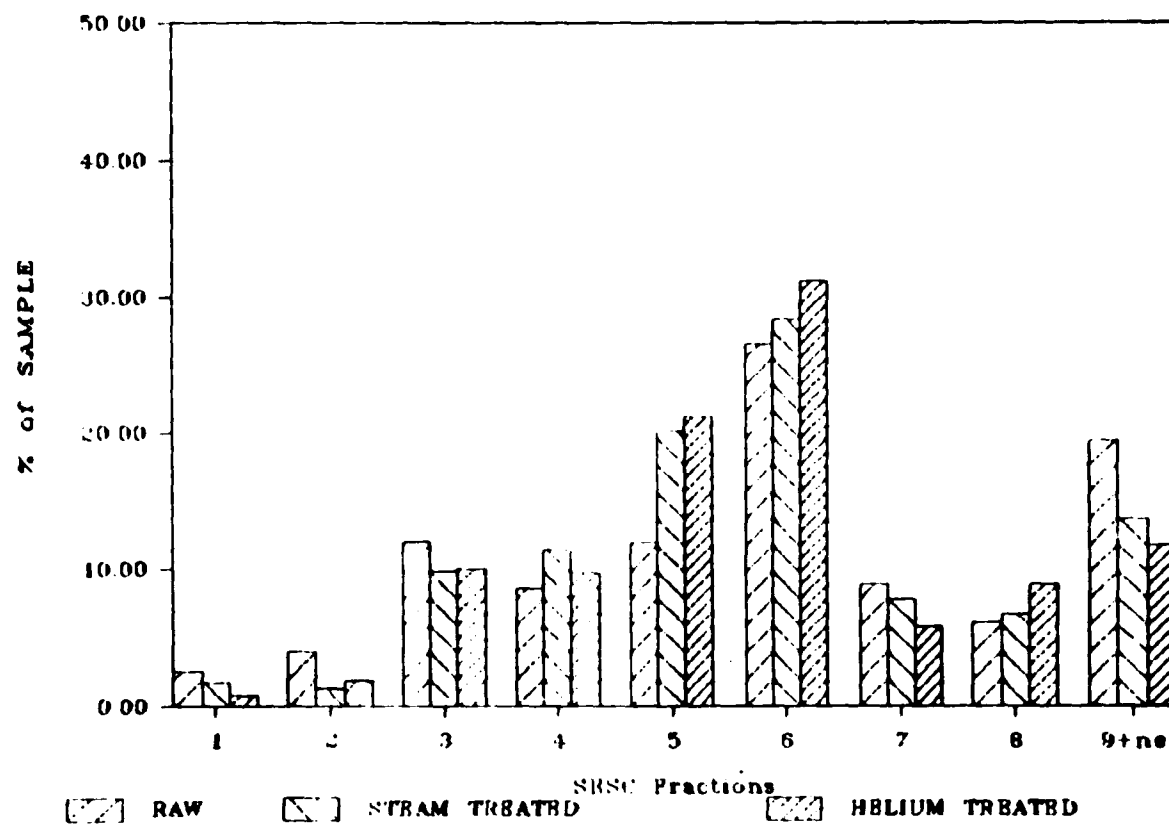


Fig.7.6.2 SESC Fractionation of Low Pressure Inert Gas Pyrolysis Liquids

for steam treated samples, but not to as great an extent. The reproducibility of fraction 6 was poor for all samples studied (see Table 7.6.3). The MeOH fraction may carry with it some small colloidal portion of the column itself causing the irreproducibilities; Consequently the samples collected in fraction 6 were ashed and the values corrected for the ash content of the sample.

There is some concern that because all the coal liquids were handled in air and dried on a rotovaporizer before and after fractionating (Sec 6.7.1) they were oxidized. It has been noted above that exposure to air of the pretreated coal samples produced a change which manifested itself as a depression of the liquid yields in pyrolysis and extraction experiments. It is conceivable that the same sensitivity could be exhibited by the liquids. In order to test this an extensive revision of the collection apparatus would have to be made. This is not feasible at the time of writing.

Some preliminary work done on a liquid sample produced in steam pyrolysis of a raw coal shows a very different distribution of the functional groups than what is obtained from the separation of a coal pyrolyzed in inert gas (Table 7.6.4). This sample was collected in the first collection system described in Sec. 5.1.5. It was washed from the collection system with THF,

Table 7.6.4

SESC Analysis of Steam Pyrolysis Liquids  
Untreated Illinois No.6 Coal

| <u>Fraction</u> | <u>Weight Percent*</u> |
|-----------------|------------------------|
| 1.              | 28.51                  |
| 2.              | 0.94                   |
| 3.              | 27.46                  |
| 4.              | 15.61                  |
| 5.              | 23.84                  |
| 6.              | 2.07                   |
| 7.              | 0.60                   |
| 8.              | 0.46                   |
| 9.              | 0.50                   |

---

\* Normalized

however precautions were taken to prevent the sample from becoming excessively oxidized. If this difference is indicative of the effect of steam in pyrolysis on the resulting liquid product it is speculated that the effects of steam pretreatment followed by steam pyrolysis will produce a liquid of exceptional quality.

#### 7.6.2 Molecular Weight Determination

Each of the fractions obtained in the SESC separation were further analyzed for their molecular weight distribution. The samples were subjected to size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC) (Sec 5.7.2 and 6.7.2). The technique is one that is not that reliable for coal liquids. Separation is based on the size of the molecule or aggregates and is related to molecular weight by a calibration curve. This is ineffective if the materials used for calibration are not the same shape as the unknown materials. It is unfortunate that the higher molecular weight materials which are available to calibrate the equipment are long chain polymers, materials very unlike coal liquids.

With these shortcomings in mind the data for the SEC work is presented in Figure 7.6.3. This data has been normalized to a constant value for the area under the curve so that the effects of sample dilution can be

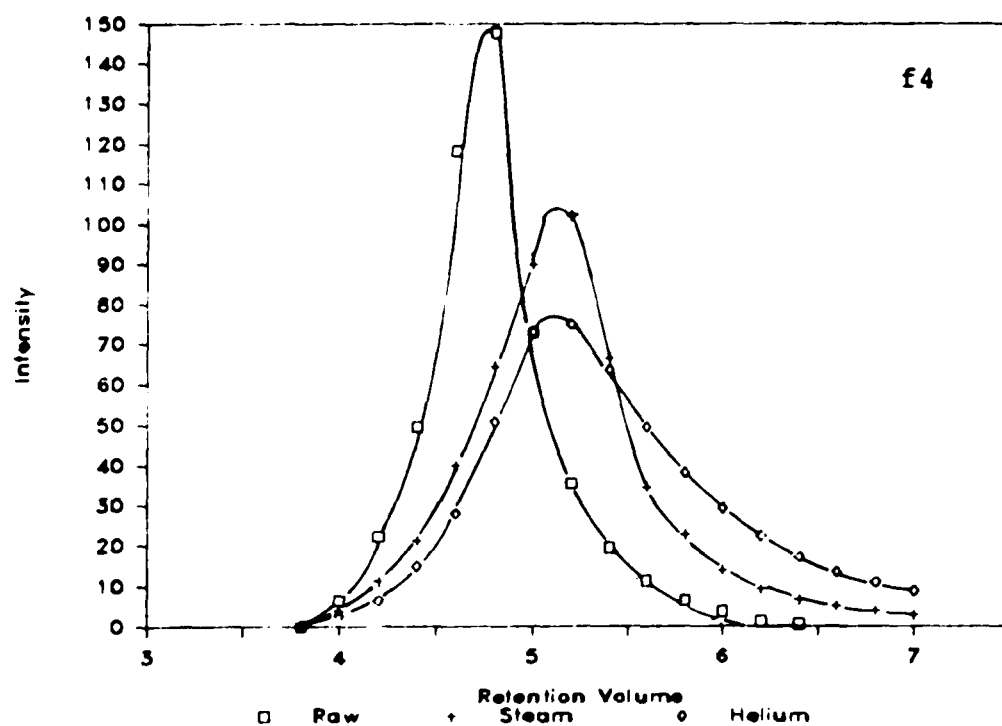
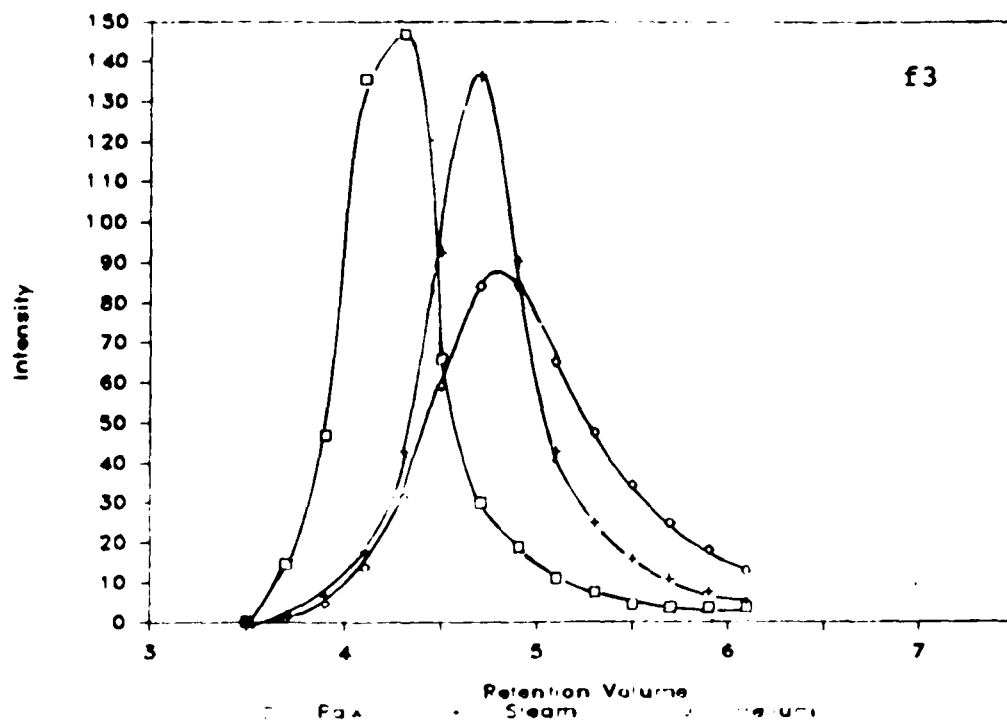


Fig.7.6.3 Molecular Weight Range of SESC Fractions  
Illinois No.6 Coal Low Pressure Inert Gas  
Pyrolysis Liquids; Raw, Steam Treated and  
Helium Treated Samples

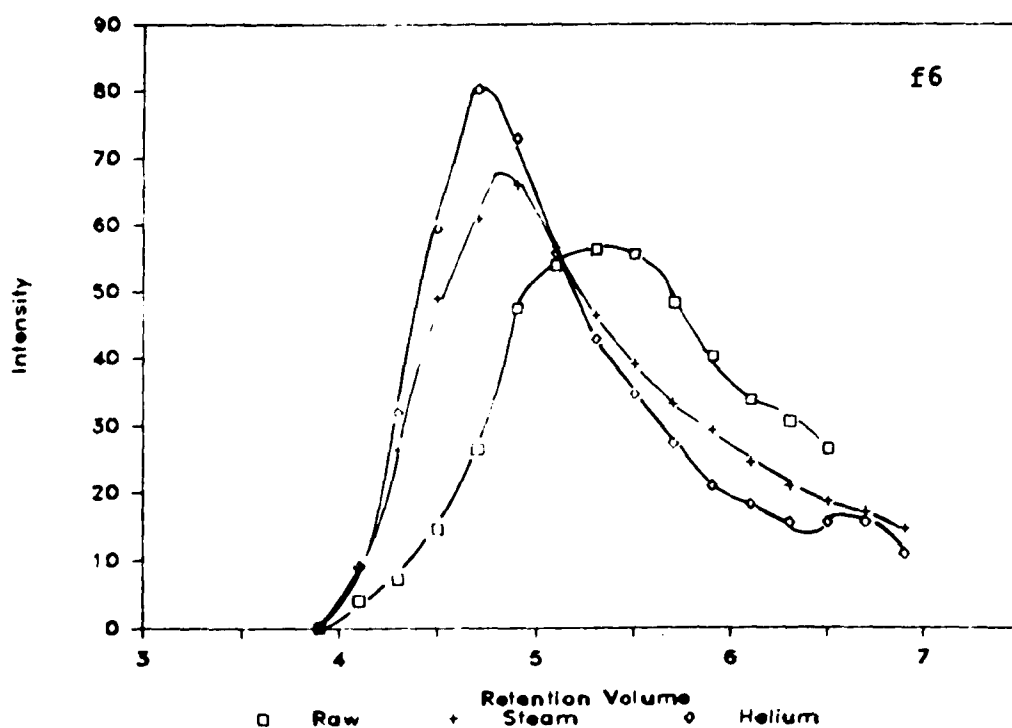
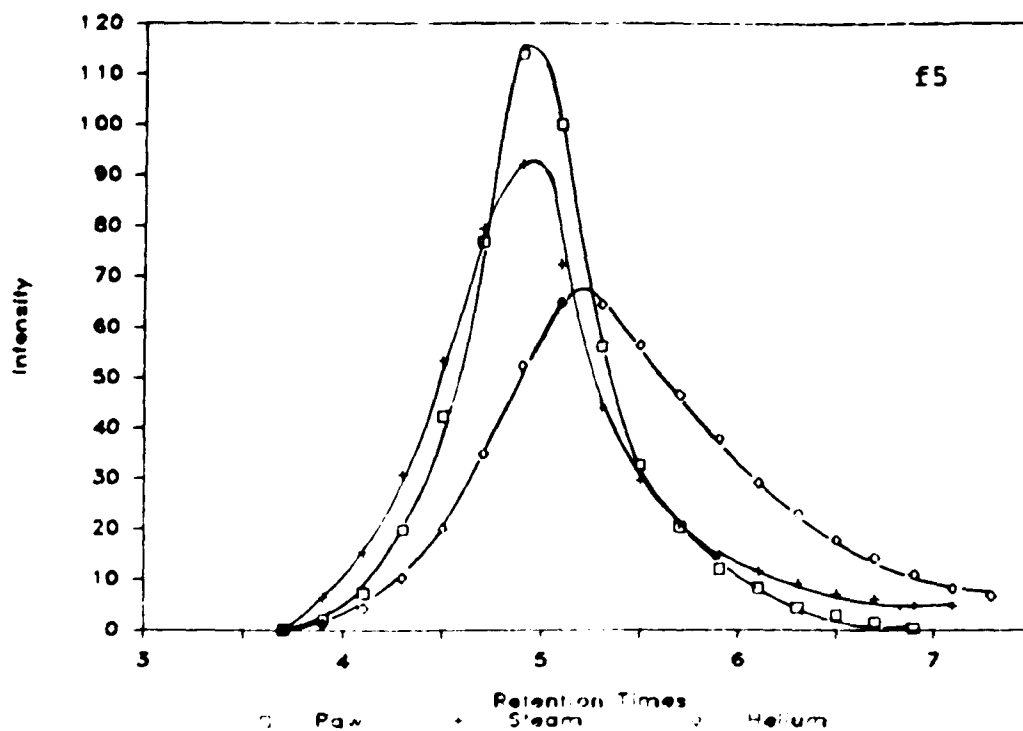


Fig.7.6.3  
(cont.)

Molecular Weight Range of SESC Fractions  
Illinois No.6 Coal Low Pressure Inert Gas  
Pyrolysis Liquids; Raw, Steam Treated and  
Helium Treated Samples

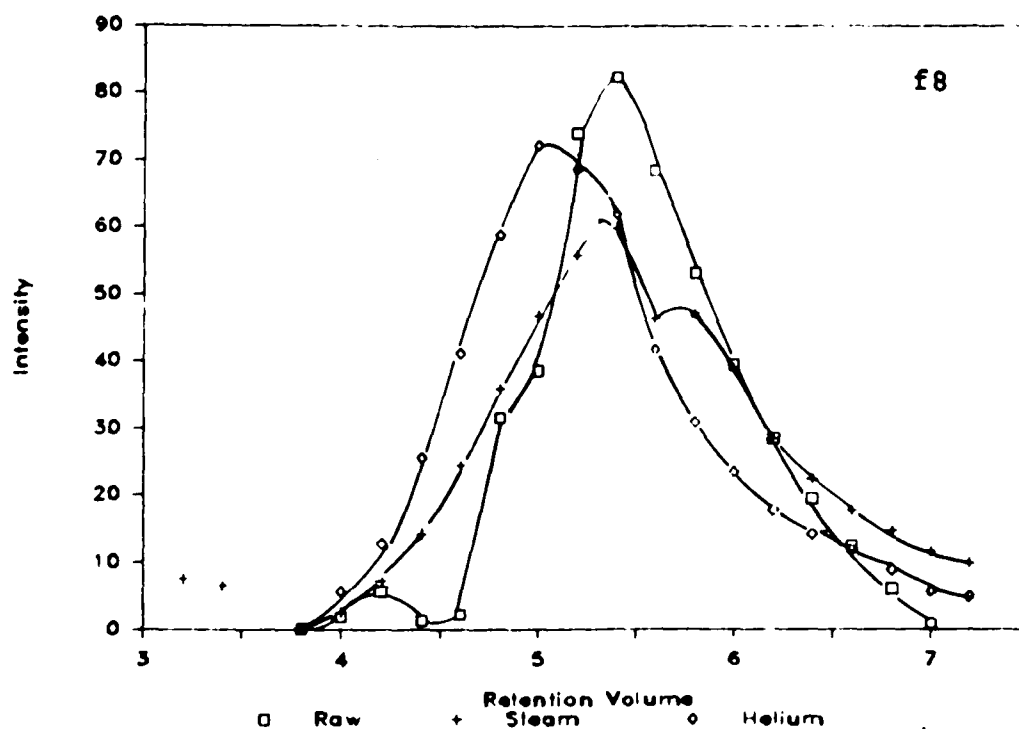
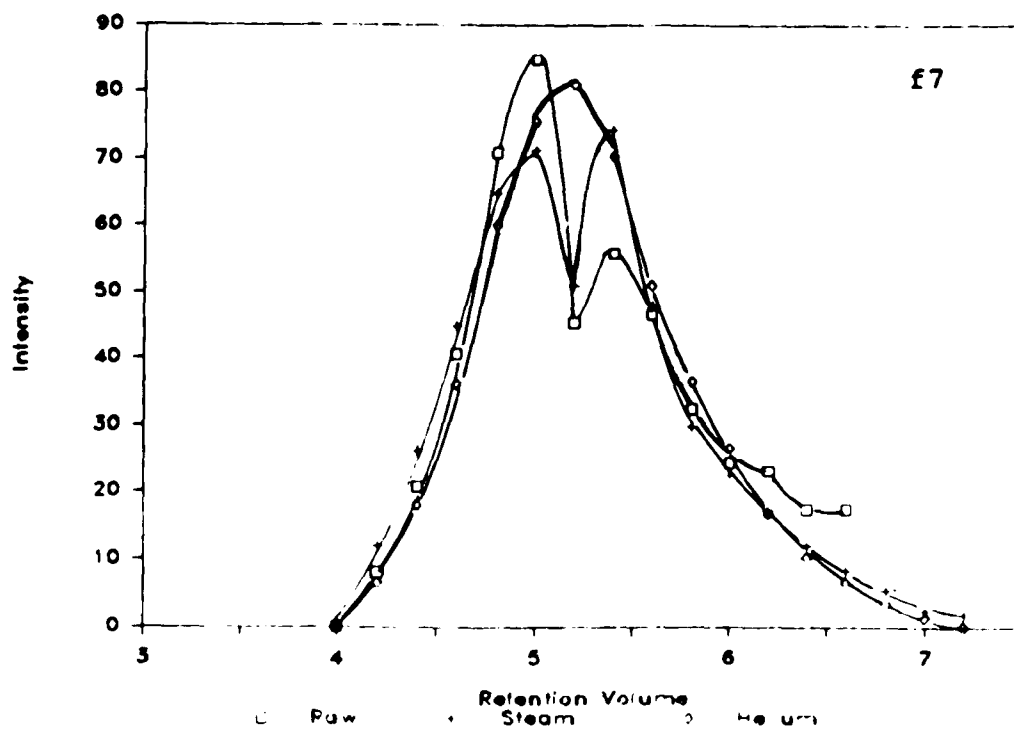


Fig.7.6.3  
(cont.)

□ Raw + Steam ○ Helium  
Retention Volume  
Molecular Weight Range of SESC Fractions  
Illinois No.6 Coal Low Pressure Inert Gas  
Pyrolysis Liquids; Raw, Steam Treated and  
Helium Treated Samples

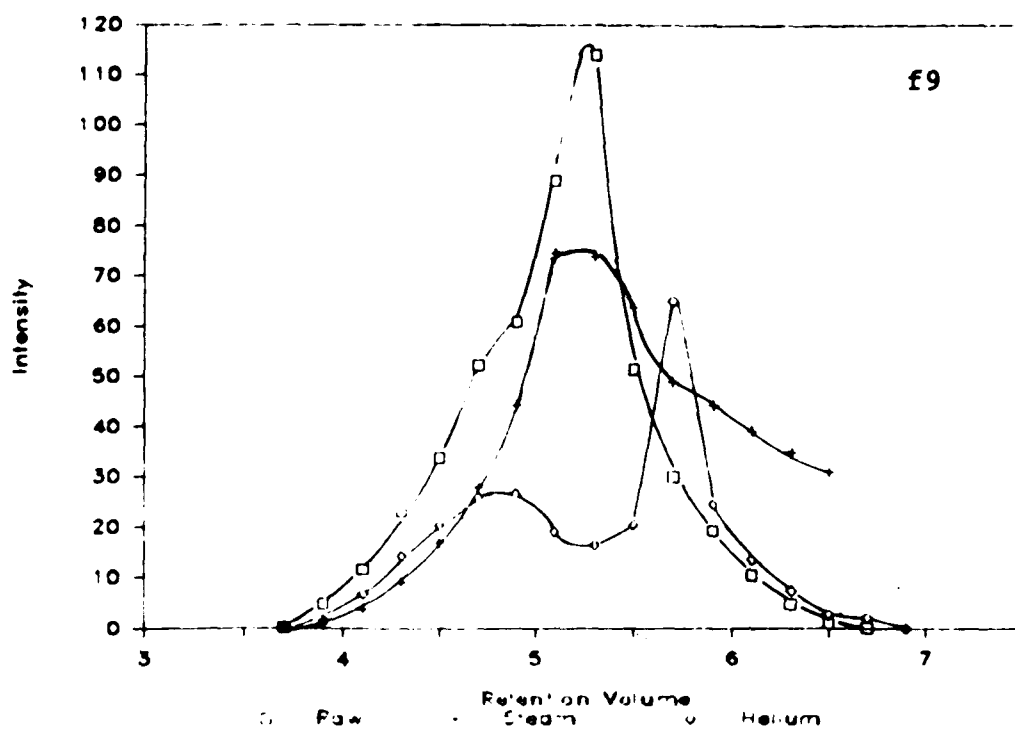


Fig.7.6.3 Molecular Weight Range of SESC Fractions  
(cont.) Illinois No.6 Coal Low Pressure Inert Gas  
Pyrolysis Liquids; Raw, Steam Treated and  
Helium Treated Samples

ignored. The calibration curve used to determine the molecular weights is also given (Fig. 7.6.4). In gel permeation chromatography the heaviest (largest) material elutes from the column first. It is, therefore, obvious from the first two fractions presented in Figure 7.6.3 that the effect of pretreating the coal in either steam or helium is to lower the molecular weight of each successive SESC fraction, the raw coal curve leads the other two. In fraction 5 the raw coal curve is superimposed on the steam treated coal curve. and the lightest material appears to be the helium treated sample. It should be noted, however, that the SESC fractionation produced much more material in the 5th fraction of helium treated coal pyrolysis liquids than of the raw or steam treated materials. It is conceivable then that the rupture of highly functional materials, those materials which would be found in the last fraction of the separation scheme for raw coal, end up in the 5th fraction after a helium treatment. These materials would contain basic nitrogen heterocycles. In fraction 6 the lowest molecular weight material is that produced from the raw coal. The curves of fractions 7, 8, and 9 are harder to interpret. In fraction 7 both raw and steam treated coal show a bimodal distribution whereas the helium curve is a single continuum. Fraction 8 shows that the raw coal is preponderantly the lightest

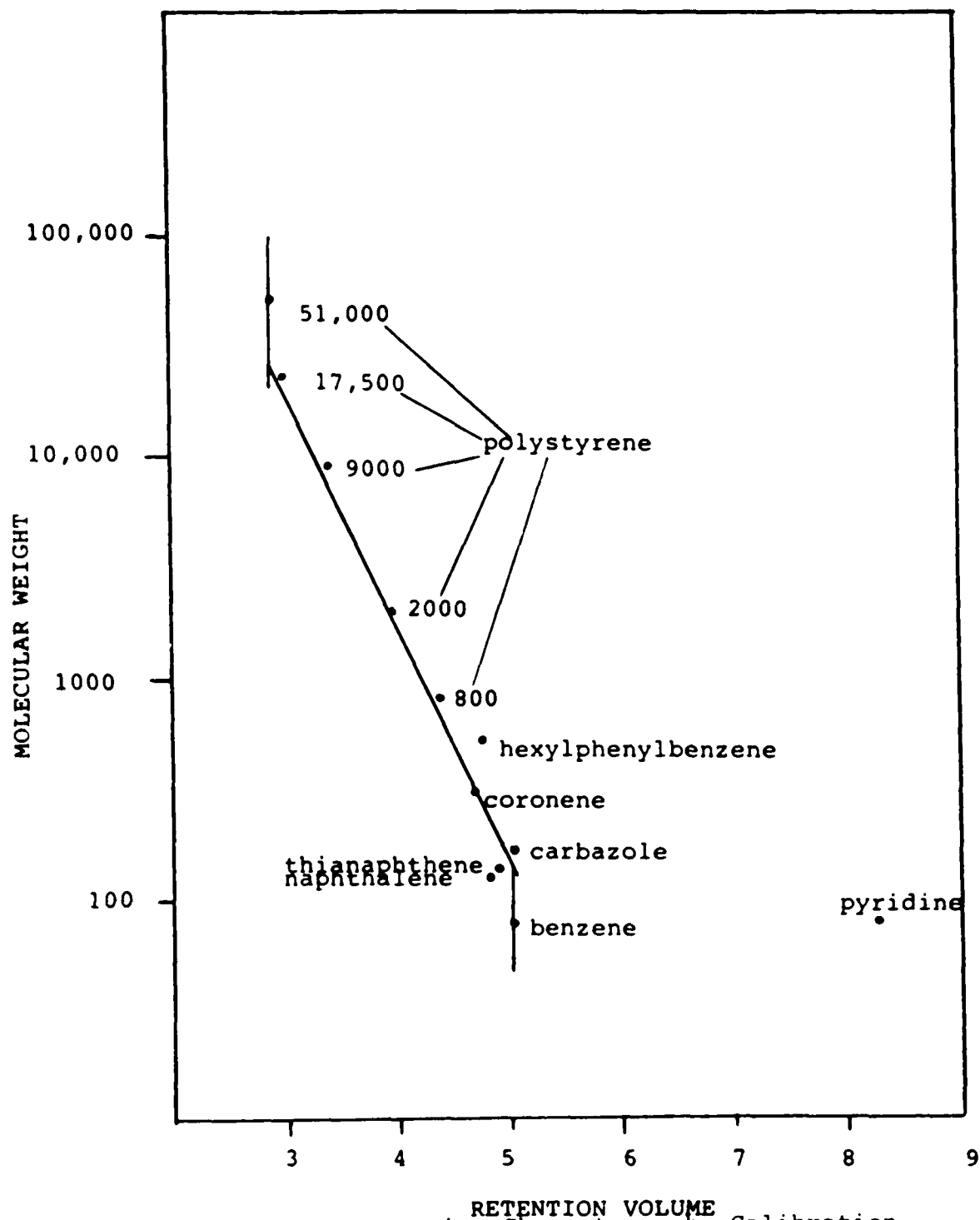


Fig.7.6.4 Gel Permeation Chromatography Calibration Curve

of the three although the steam and helium treated pyrolysis liquid curves do not return to baseline. This may indicate that there is additional light material not accounted for. This is very much the case in fraction 9. The steam treated coal curve is far above baseline at the lower molecular weight end of the scale. This would seem to indicate that the steam pyrolysis produces a reduced molecular weight, albeit highly functional material.

#### 7.6.3 Gas Chromatography

Gas chromatographs of inert gas low pressure pyrolysis liquids artificially separated by the different stages of the liquid collection system (Sec. 5.6.2) show a very slight shift to a broader, higher, boiling point range for the steam treated coal in the second stage of the collection apparatus (Figs. 7.6.5-7.6.7). It is difficult at this time, with limited data, to determine the reality of this shift. It is possible that lighter material caught in the filter for extended time reacted and formed higher molecular weight species and/or more functional (oxidized) species.

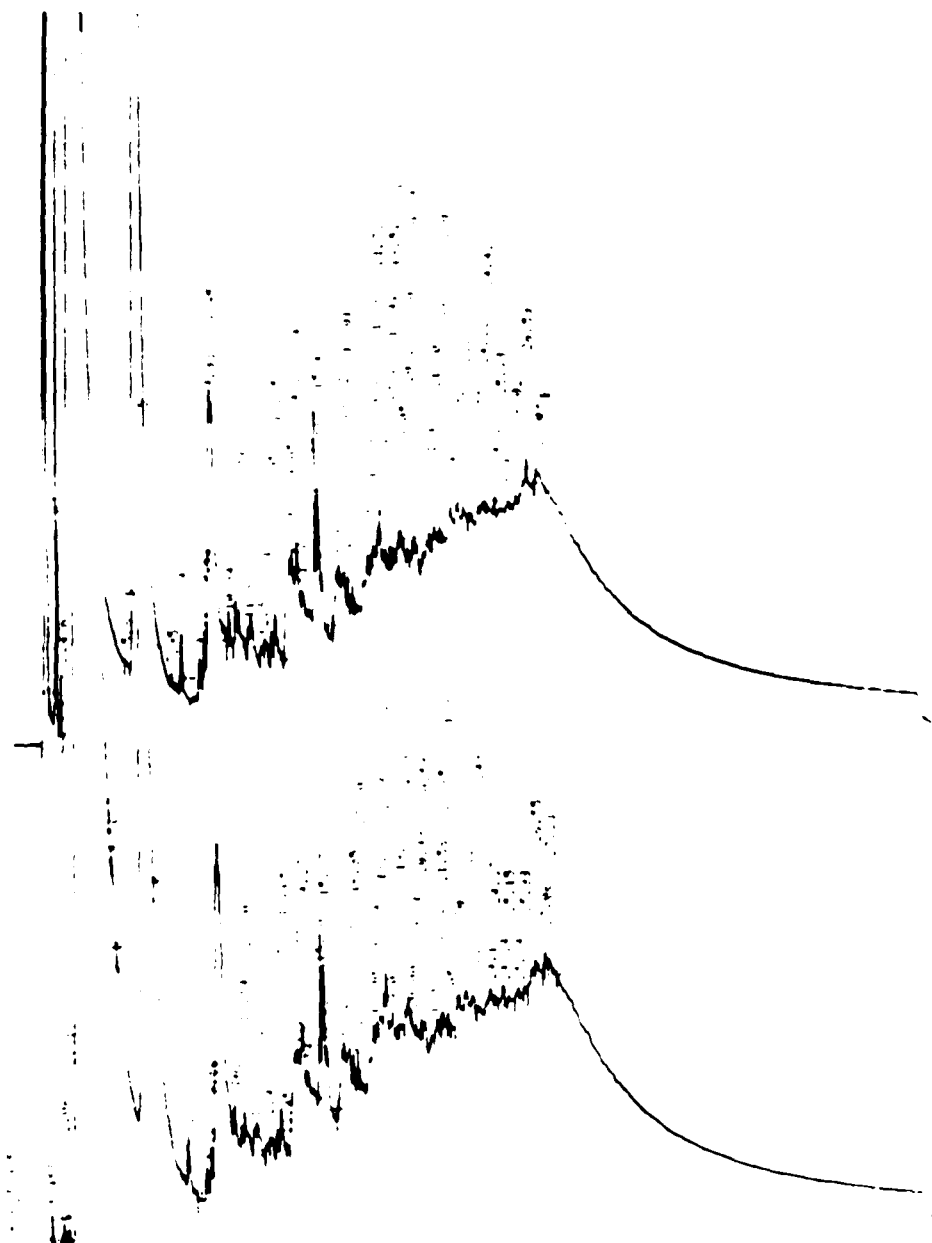


Fig.7.6.5 Gas Chromatograph of LPIG Pyrolysis Liquids from Stage 1 of Collection System, Comparison of Raw and Steam Treated Illinois No. 6 Coal Pyrolysis Liquids

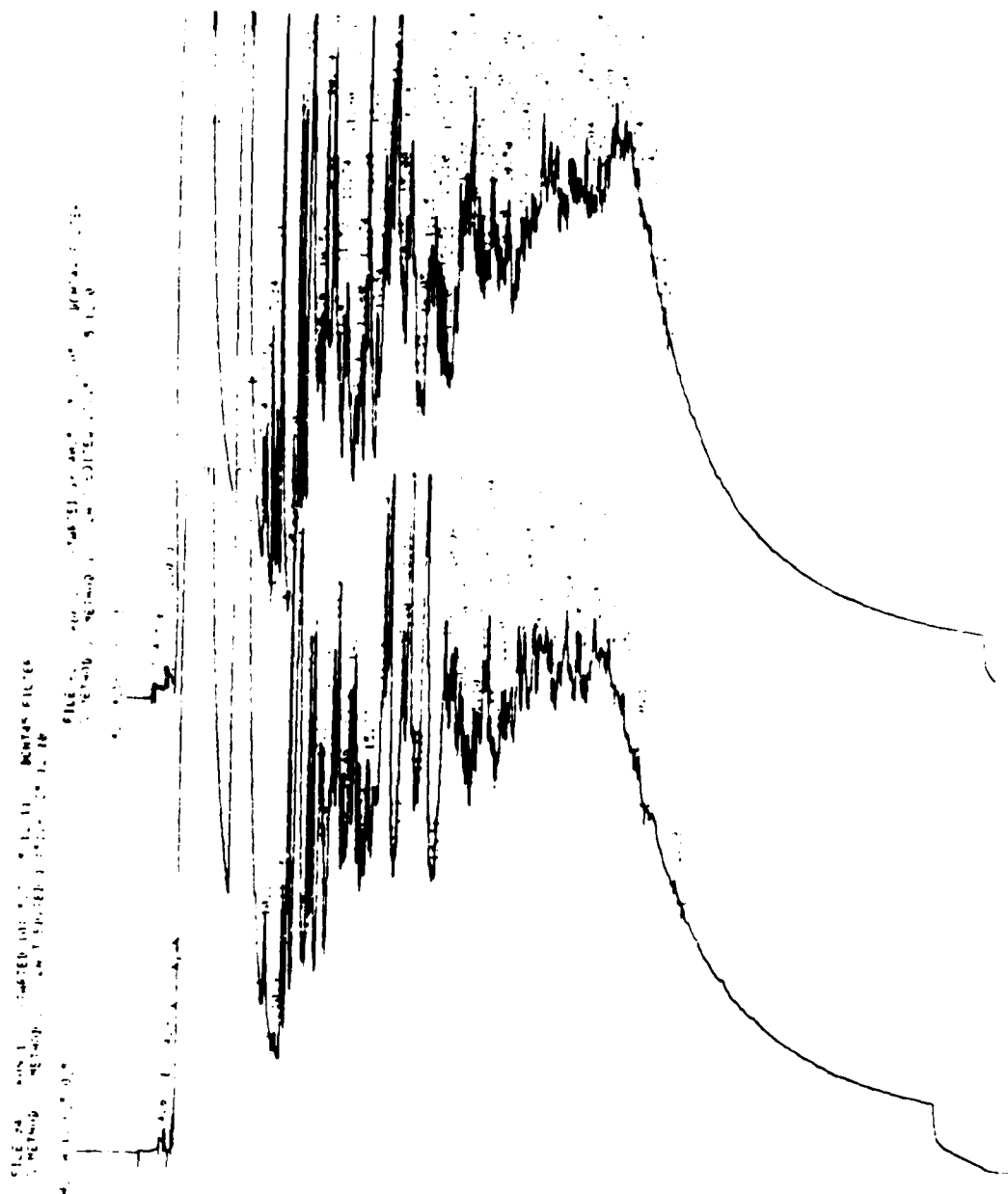


Fig.7.6.6 Gas Chromatograph of LPIG Pyrolysis Liquids from Stage 2 of Collection System, Comparison of Raw and Steam Treated Illinois No. 6 Coal Pyrolysis Liquids

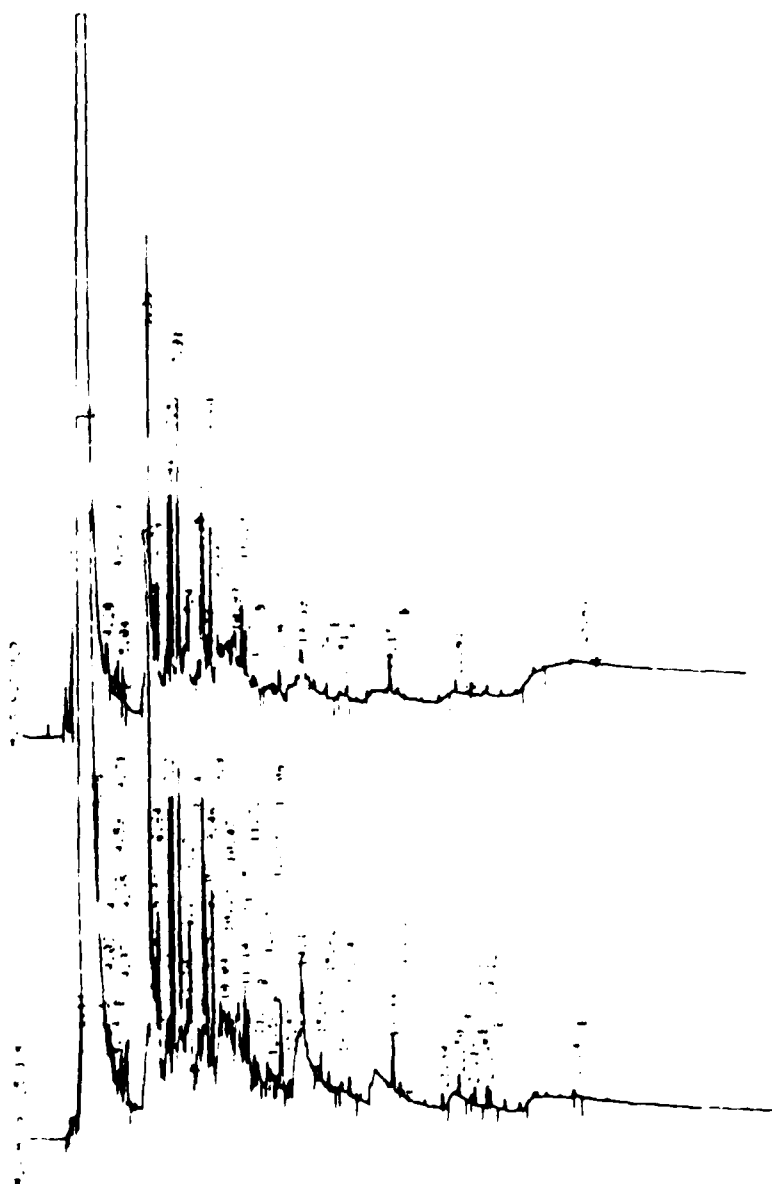


Fig.7.6.7 Gas Chromatograph of LPG Pyrolysis Liquids from Stage 4 of Collection System, Comparison of Raw and Steam Treated Illinois No. 6 Coal Pyrolysis Liquids

## 7.7 Analysis of Extraction Liquids

### 7.7.1 SESC

The ability to extract more material from a steam treated coal over a raw coal was clearly demonstrated (Sec. 7.5). The question which remains is whether or not the additional material is different than the material extracted from raw coal. In order to determine this, the SESC separation (described in Sec 6.7) was also applied to these samples. The results of this separation are given in Figure 7.7.1.

There is an increase over raw coal in the lighter, less polar fractions for both steam and helium treated coal (f1-f5). Only in fraction 6 and 9+ne does the steam treated coal extract differ significantly (more than one or two percent) from the helium treated coal extract. As with the pyrolysis liquids the steam treated coal extract fraction 9 shows the largest drop from the value for the untreated coal. Unlike the pyrolysis liquids the steam treated material is a smaller percentage than the helium treated material in fraction 9. This appears to indicate that the severity of the pyrolysis was necessary to rupture the heavy material which elutes from the chromatography column in fraction 9 when the coal is only helium treated. Conversely steam treatment produces a more ruptured material without the need for

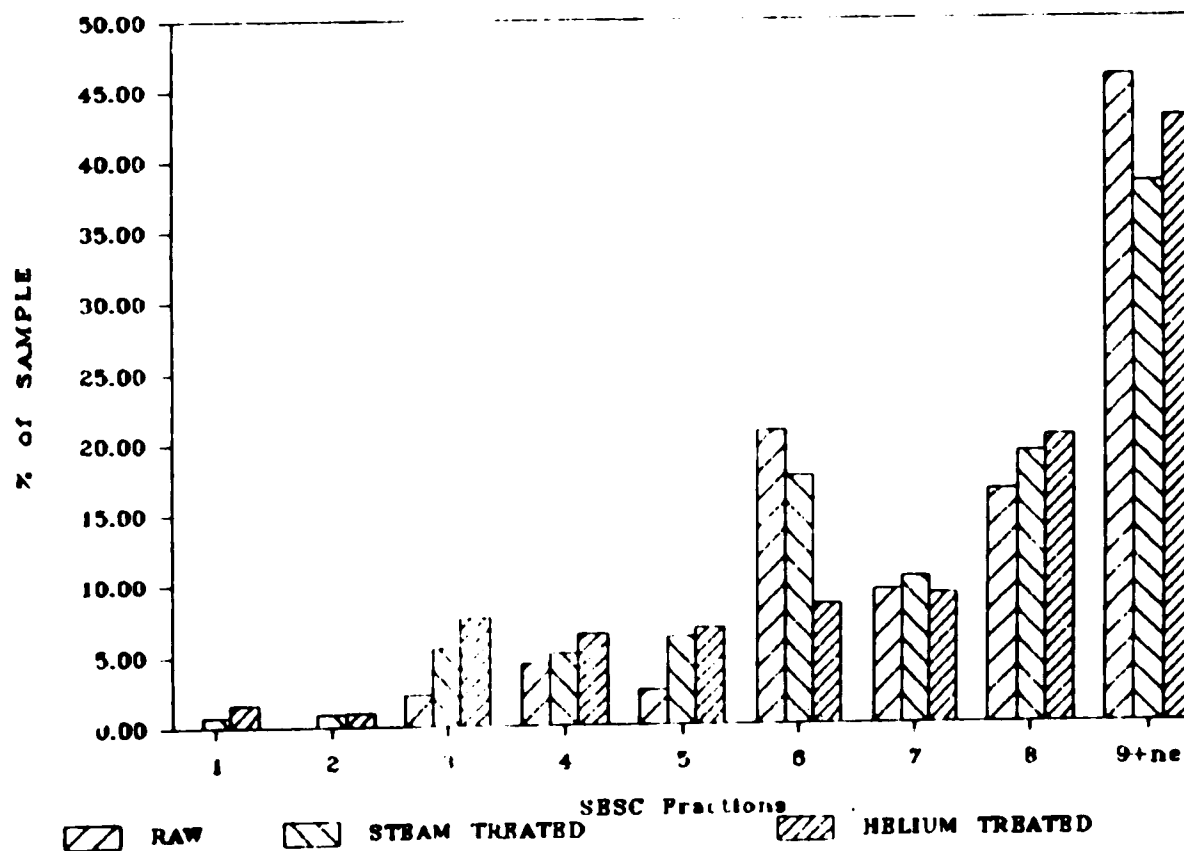


Fig.7.7.1 SESC Fractionation of Room Temperature Pyridine Extraction Liquids; Raw Steam Treated and Helium Treated Samples

the severe conditions in pyrolysis.

There is associated with these samples the same problems of the possible effects of sample handling (Sec. 7.6.1).

#### 7.7.2 GPC

The molecular weight distribution as determined by gel permeation chromatography of each of the SESC fractions is given in Figure 7.7.2. In fractions 3, 4, 7, and 8 the raw coal extract elutes later from the column, consequently it is lighter material. This is not a surprising result, especially in the later fractions. If it is considered that the room temperature extraction can not disrupt the coal, only remove from it small weakly bound structures, then the data shows that by treating the coal in steam or helium larger pieces have been dissociated from the major structure of the coal. These pieces can then be extracted from the treated sample.

Only in fractions 3, 4, 6 and 9 does the steam treated coal extract appear lighter than the helium treated coal extract.

#### 7.7.3 GC

The extracted liquids all proved to be too heavy to elute significantly from the GC column, even up to 350°C.

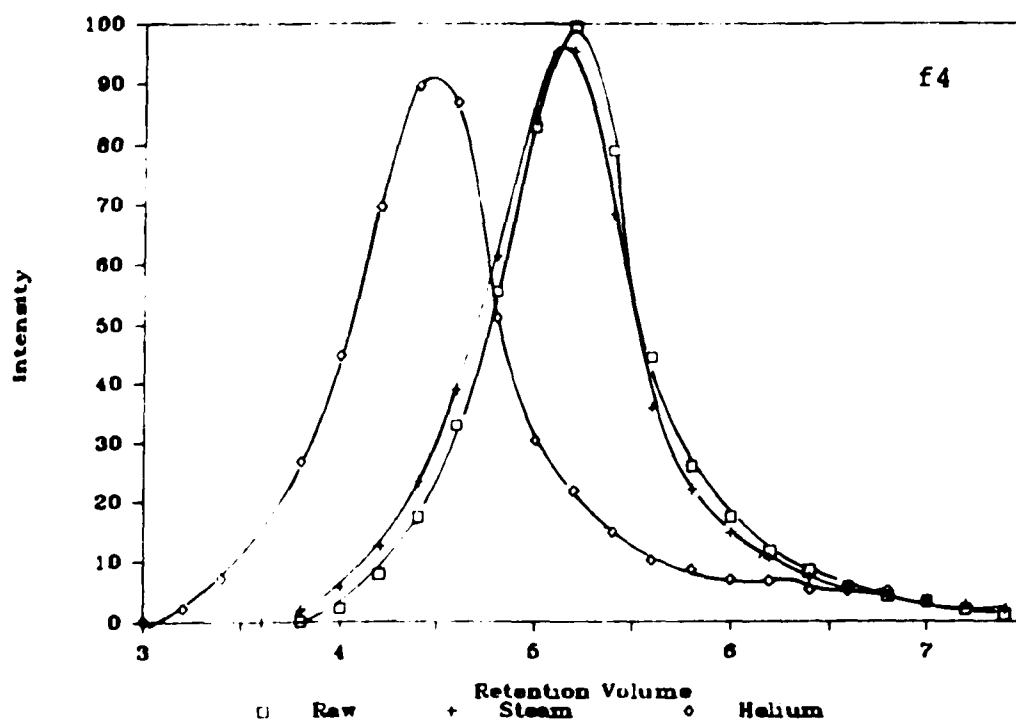
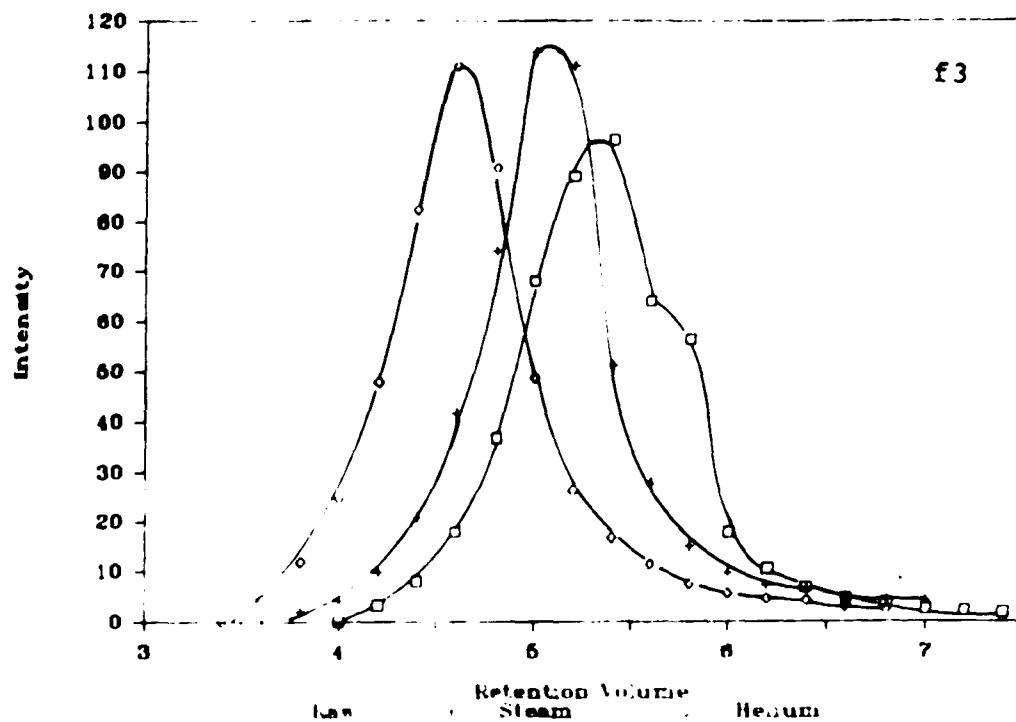


Fig.7.7.2 Molecular Weight Range of SESC Fractions,  
Illinois No.6 Coal Room Temperature  
Extraction Liquids

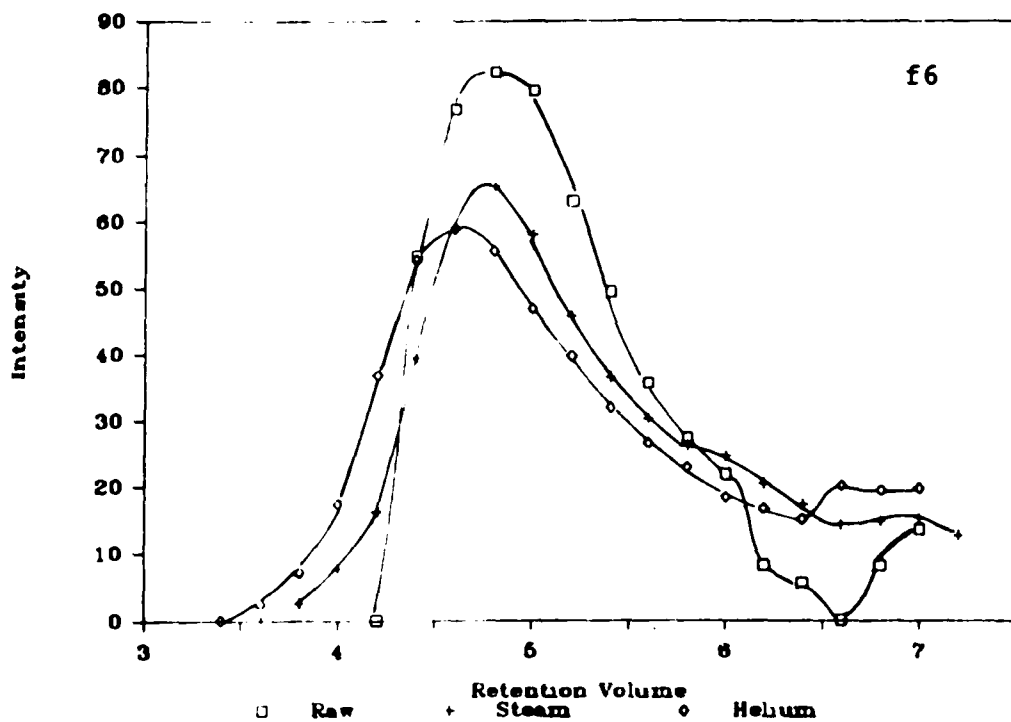
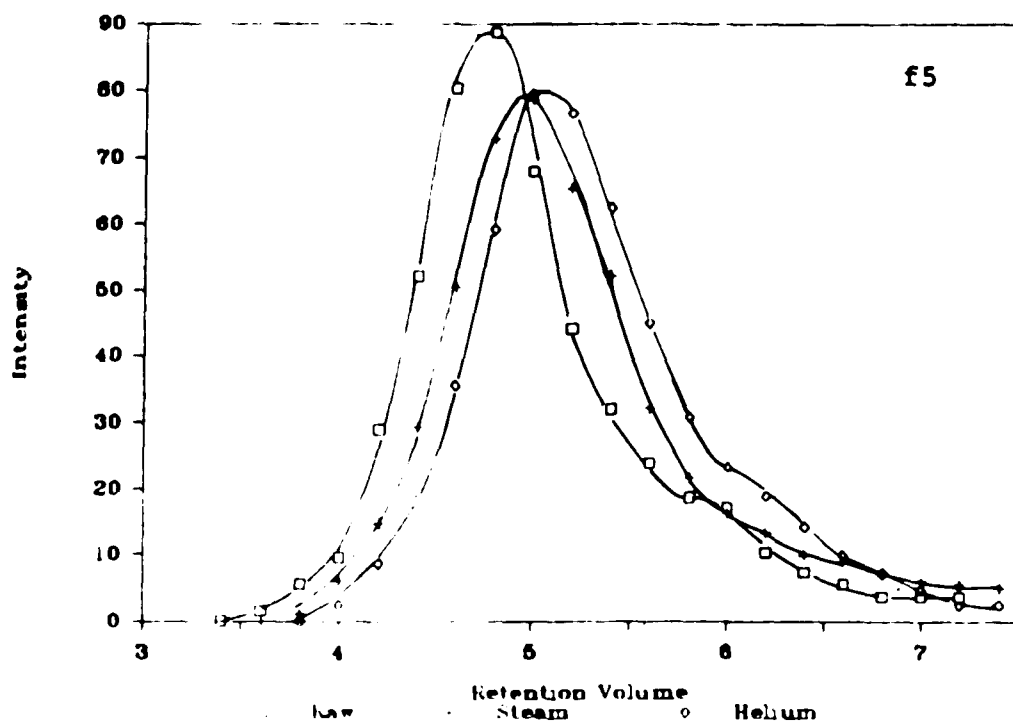


Fig.7.7.2 Molecular Weight Range of SESC Fractions,  
(cont.) Illinois No.6 Coal Room Temperature  
Extraction Liquids

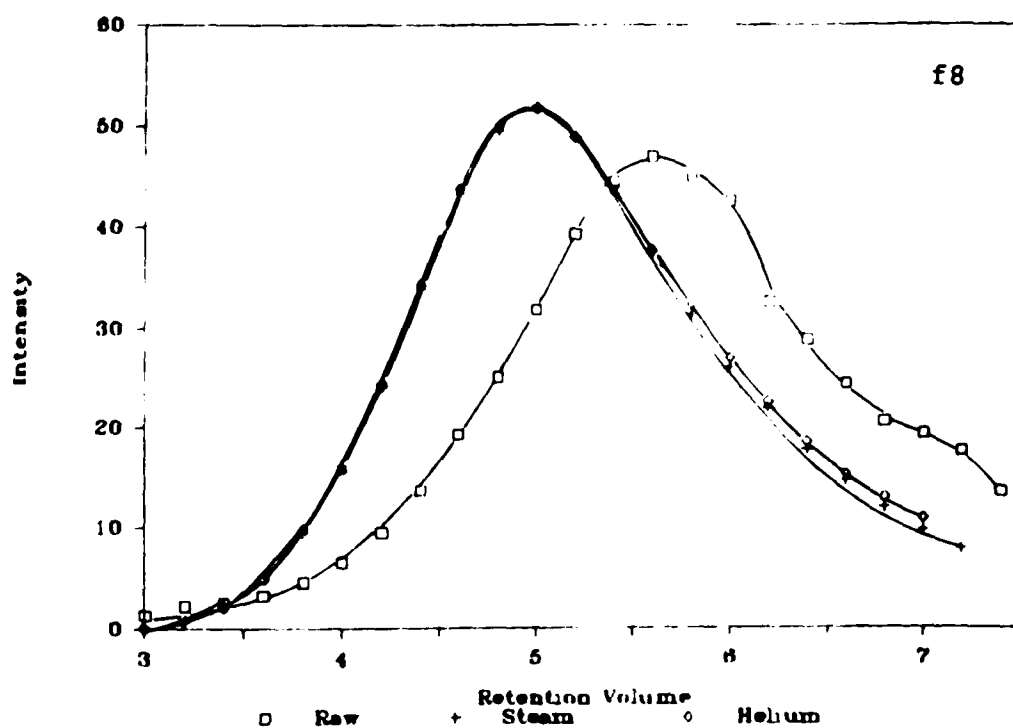
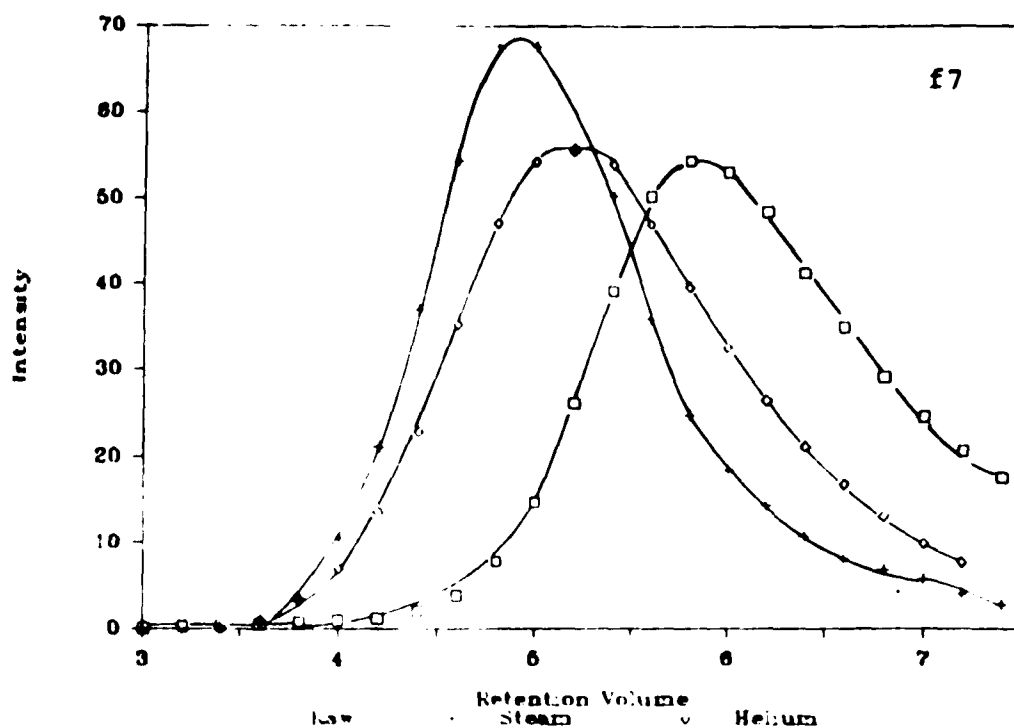


Fig.7.7.2 Molecular Weight Range of SESC Fractions,  
(cont.) Illinois No.6 Coal Room Temperature  
Extraction Liquids

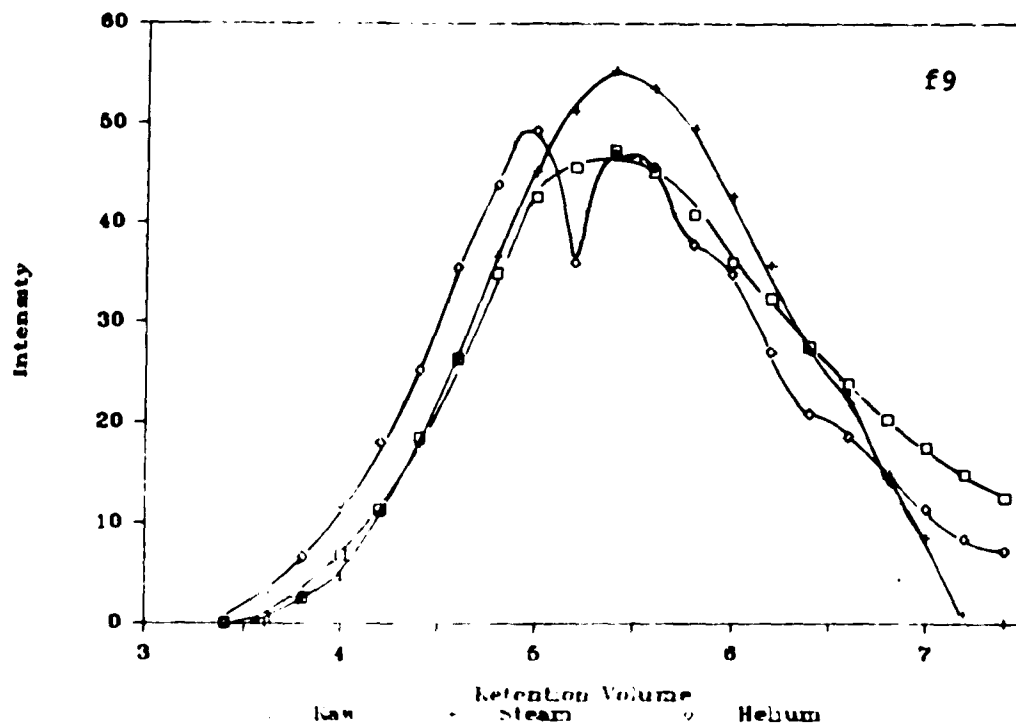


Fig.7.7.2 Molecular Weight Range of SESC Fractions,  
(cont.) Illinois No.6 Coal Room Temperature  
Extraction Liquids

## 7.8 FTIR

Diffuse reflectance infrared spectroscopy (DRIS) has been used to analyze the pretreated coal. Samples of coal pretreated under various conditions, raw coal, and raw coal dried under vacuum at 90°C were looked at. There are no apparent differences among the samples in the region attributed to carbonyl bonds ( $1600-1900\text{cm}^{-1}$ ) (Fig. 7.8.1). There does exist a shift in the ratio of the higher energy region attributed to -OH species and the lower energy region, also attributed to -OH. This is the  $3200-3700\text{cm}^{-1}$  region of the infrared spectrum (Fig. 7.8.2). There are two ways to interpret these peaks: the total number of -OH species remains fixed and the relative energy of the species changes, or there is a change in the total number of -OH species and more of a certain energy group are created or destroyed. The pretreated samples show relatively higher amount of more strongly (primarily) bound -OH (chemisorbed species) than does the raw coal. These materials have a relatively lower amount of hydrogen bond associations than do the lower energy (primarily) bound species. This finding indicates that there may be less hydrogen bonding in the pretreated coal, if the total number of species is held constant. If, however, the total number of -OH species increases with the increase found in

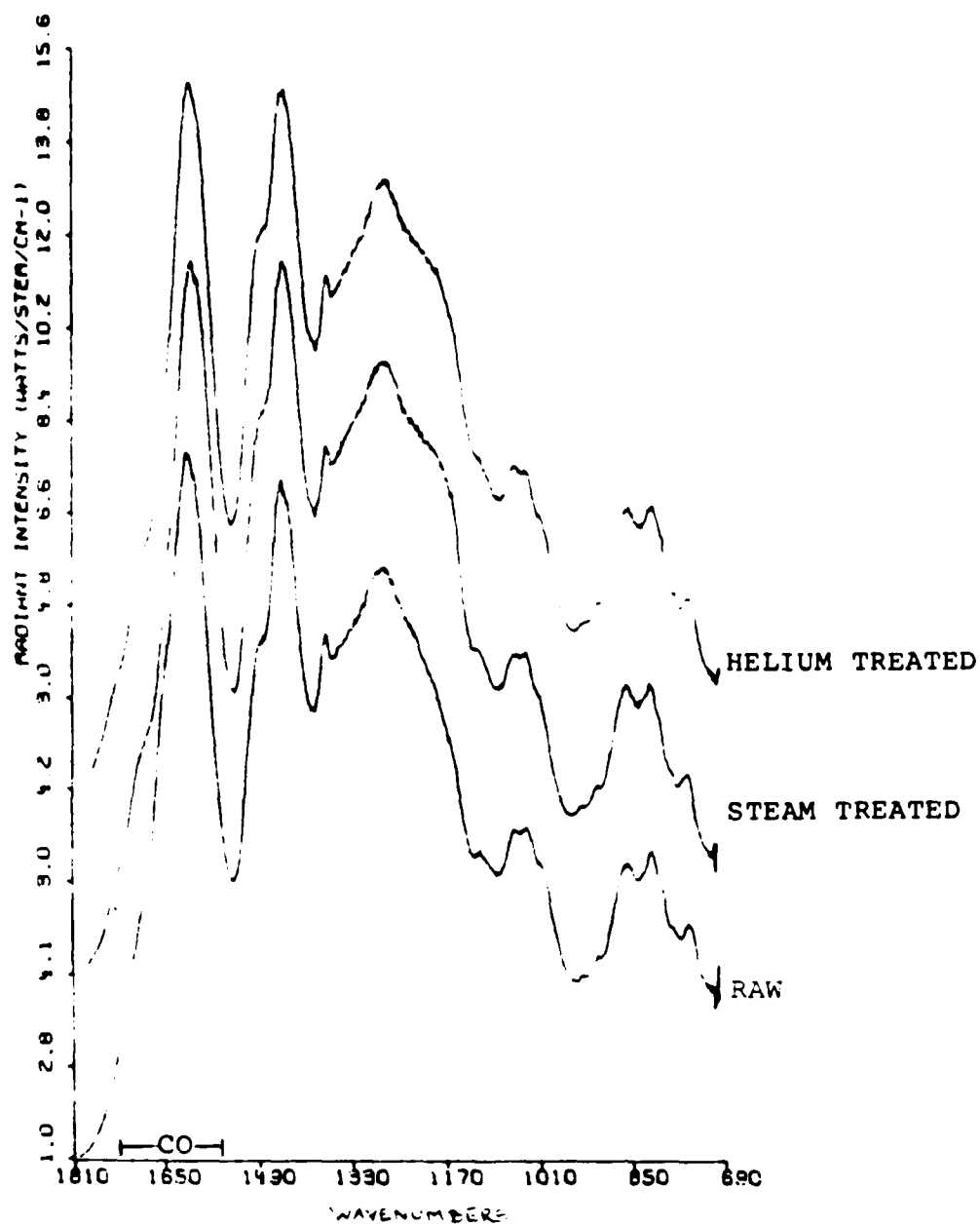
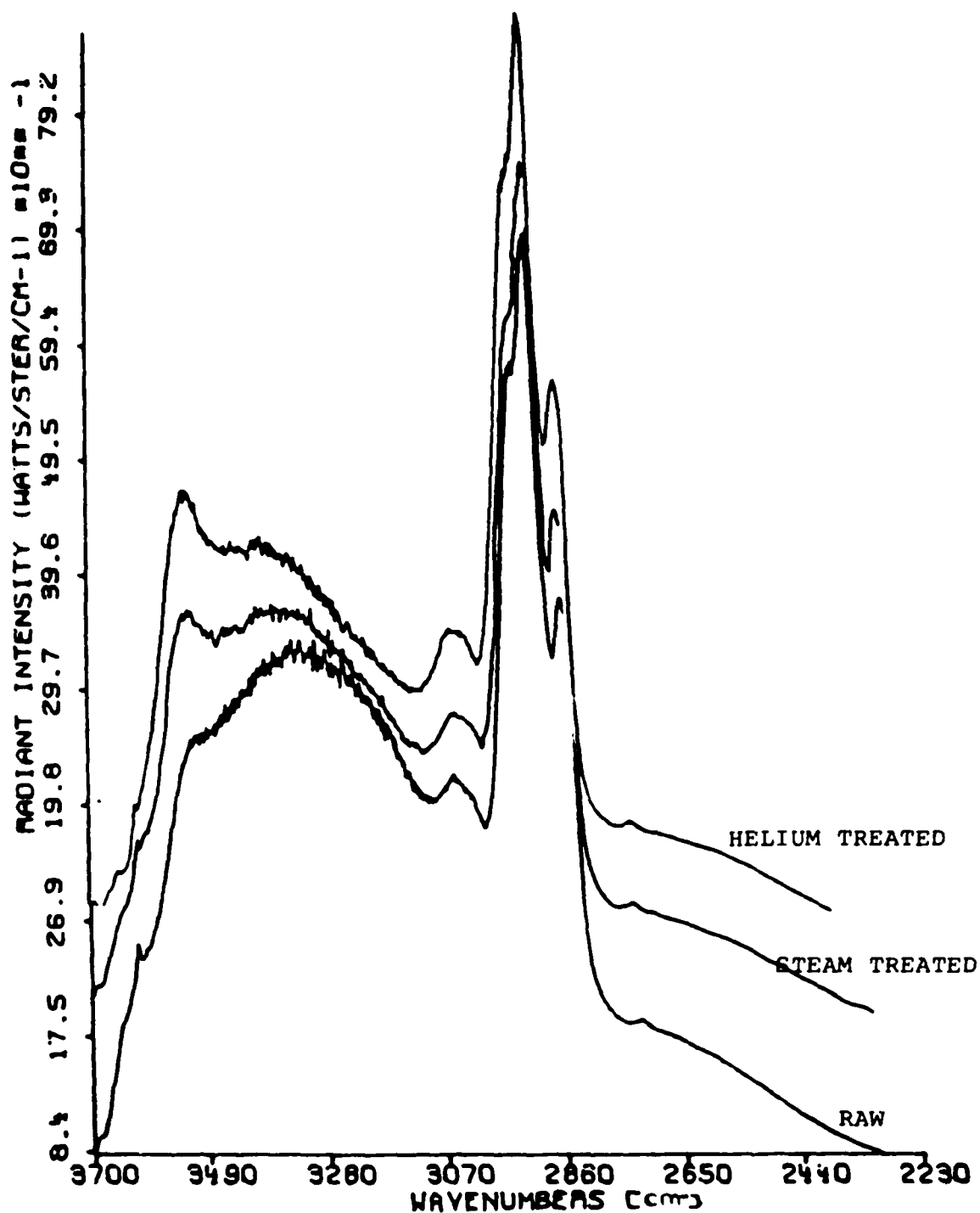


Fig.7.8.1 Diffuse Reflectance Fourier Transform Infrared Spectra, 600 - 1900  $\text{cm}^{-1}$ , Raw and Treated Illinois No.6 Coal



7.8.2 Diffuse Reflectance Fourier Transform Infra red Spectra, 2200 - 3700 cm<sup>-1</sup>, Raw and Treated Illinois No.6 Coal

strongly bound new -OH species the absolute amount of hydrogen bonding in the coal could actually increase.

A comparison of the spectra of raw coal and a coal pretreated at the optimum temperature, as found by pyrolysis experiments and extraction experiments, 340°C, in steam, shows no difference at any region except at the upper end of the spectrum (Fig. 7.8.3). All of the spectra generated (Table 7.8.1) display two bands in the hydroxyl region. The broader of the two, centered around  $3300\text{cm}^{-1}$ , is usually associated with phenolic, alcoholic, acidic, mineral and aqueous entities in the coal structure (Fuller and Smyrl, 1985). It has been shown to represent physisorbed water in oil shales. The higher energy peak at about  $3550\text{cm}^{-1}$  represents chemisorbed water in oil shales (Sheppard, 1986). This peak in our samples may be attributed to intramolecularly bound -OH, which are higher energy, more tightly primarily bound species. These materials have only a small amount of hydrogen bonding to other species.

In the raw coal sample the broad peak at  $3300\text{cm}^{-1}$  predominates and mostly occludes the one at  $3550\text{cm}^{-1}$ . Vacuum drying of the coal sample at 90°C does not alter this ratio (Fig. 7.8.4). In all the pretreated coal samples the peak height ratio of the two is reversed.

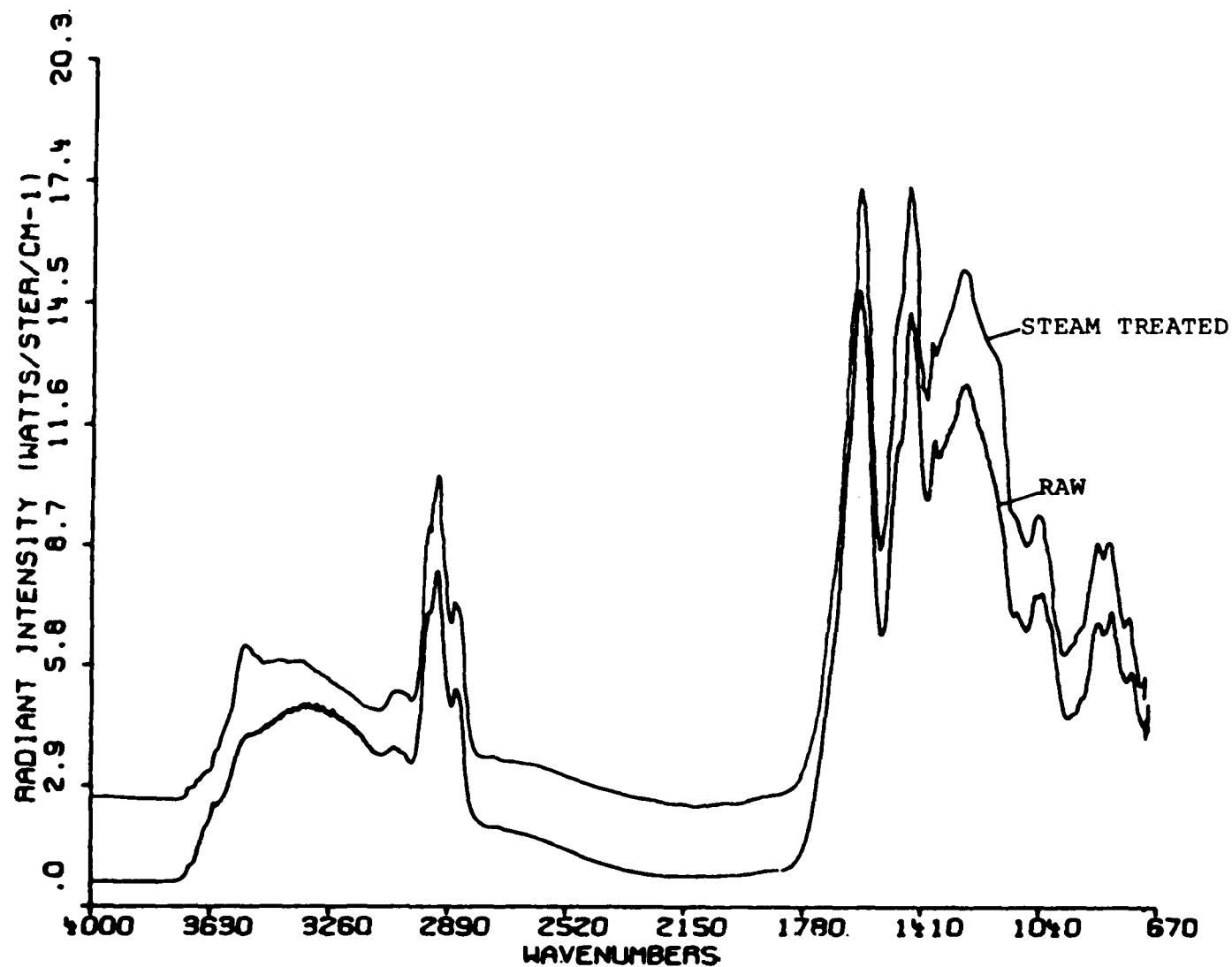


Fig.7.8.3 Comparison of DRIS Spectra for Raw and Steam Treated Illinois No.6 Coal, 670-4000cm<sup>-1</sup>

Table 7.8.1

Illinois No.6 Coal Samples Analyzed by Diffuse Reflectance  
Fourier Transform Infrared Spectroscopy

| <u>Sample ID</u>           | <u>Pretreat*<br/>Temp (°C)</u> | <u>Pretreat<br/>Atmosphere</u> | <u>Post Pretreat<br/>Handling</u>                   |
|----------------------------|--------------------------------|--------------------------------|-----------------------------------------------------|
| CFI#17 BGH<br>Raw          | -                              | -                              | -                                                   |
| CFI#17 BGH<br>Vacuum Dried | -                              | -                              | Dried in vacuum, 90°<br>Stored under N <sub>2</sub> |
| SP1 340                    | 340                            | Steam                          | Stored in N <sub>2</sub>                            |
| SP1A 340                   | 340                            | Steam                          | Exposed to Air<br>~5min, stored in N <sub>2</sub>   |
| SP2 340                    | 340                            | Steam                          | Stored in N <sub>2</sub>                            |
| SP2A 340                   | 340                            | Steam                          | Exposed to Air<br>~5min, stored in N <sub>2</sub>   |
| SP3 320                    | 320                            | Steam                          | Stored in N <sub>2</sub>                            |
| SP3A 320                   | 320                            | Steam                          | Exposed to Air<br>~5min, stored in N <sub>2</sub>   |
| SP4 360                    | 360                            | Steam                          | Stored in N <sub>2</sub>                            |
| SP4A 360                   | 360                            | Steam                          | Exposed to Air<br>~5min, stored in N <sub>2</sub>   |
| HP 340                     | 340                            | Helium                         | Stored in N <sub>2</sub>                            |
| HPA 340                    | 340                            | Helium                         | Exposed to Air<br>~5min, stored in N <sub>2</sub>   |

\* All samples treated for 15 minutes at 50 atm.

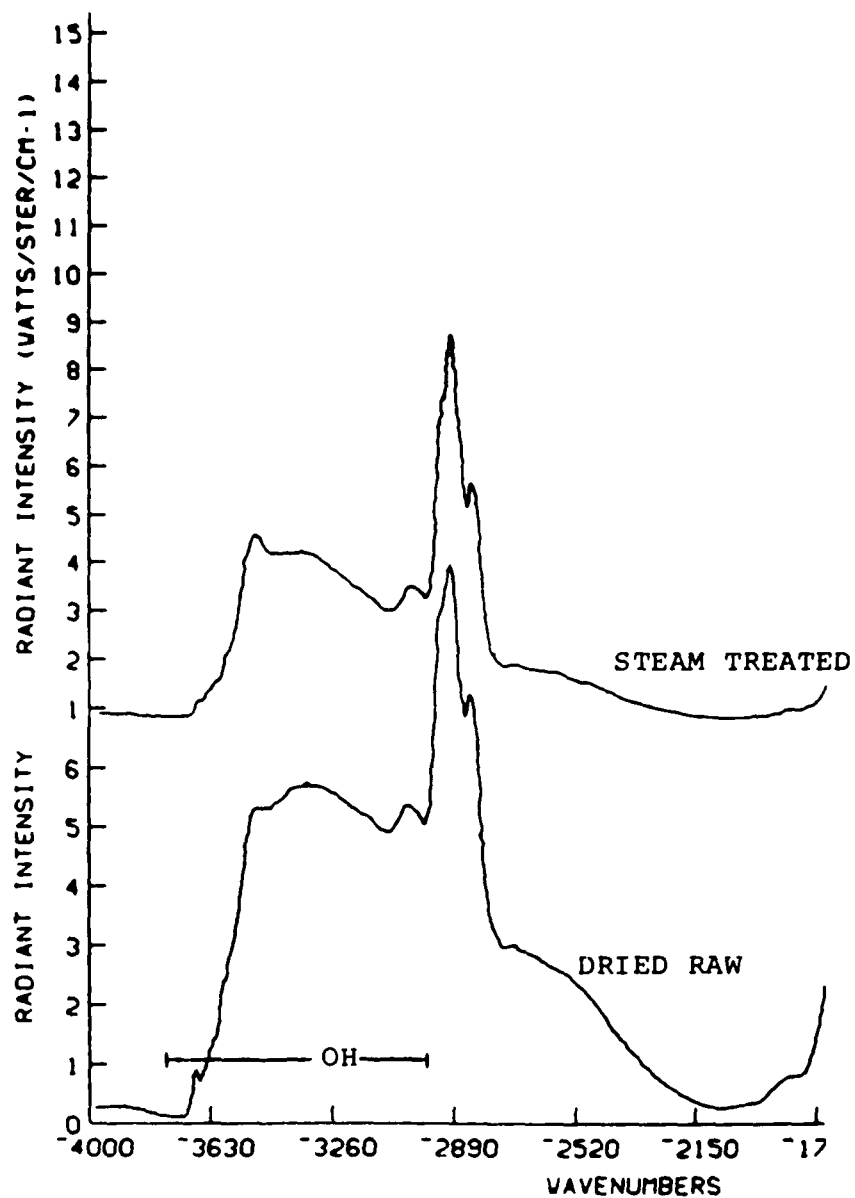


Fig.7.8.4 Comparison of DRIS Spectra for Dried Raw and Steam Treated Illinois No. 6 Coal, Expanded, Section 2200 - 3700  $\text{cm}^{-1}$

The peak at  $3550\text{cm}^{-1}$  is clearly visible (Fig. 7.8.5). When these two peaks are compared to the hydrocarbon CH resonance at  $2900\text{cm}^{-1}$ , which remains invariant, it appears that treatment of the coal somehow reduces the physisorbed (lower energy, more hydrogen bound) species, while leaving the chemisorbed (higher energy, less hydrogen bound) species intact. The effect is evident whether the coal is treated in helium or steam, and it is not effected by exposure of the samples to air for brief times (less than ten minutes). This is inconsistent with the previous findings for the behavior of the treated coal where it was found that the effects of helium treatment on liquid yields were not as significant as with steam treatment of the samples.

It was also established that exposure of steam pretreated samples to air for times as short as two minutes diminished both the liquid yields in flash pyrolysis and the amount of material extractable in pyridine. Since there is no difference in the ir spectra for preserved and air exposed samples it becomes apparent that the exposure to air reduces yields for reasons other than reformation of hydrogen bonds. It is conceivable, from this information, that the air exposure is solely responsible for ether bond formation as was discussed in Sec 4.6. The magnitude of the inclusion of oxygen must, however, be small because

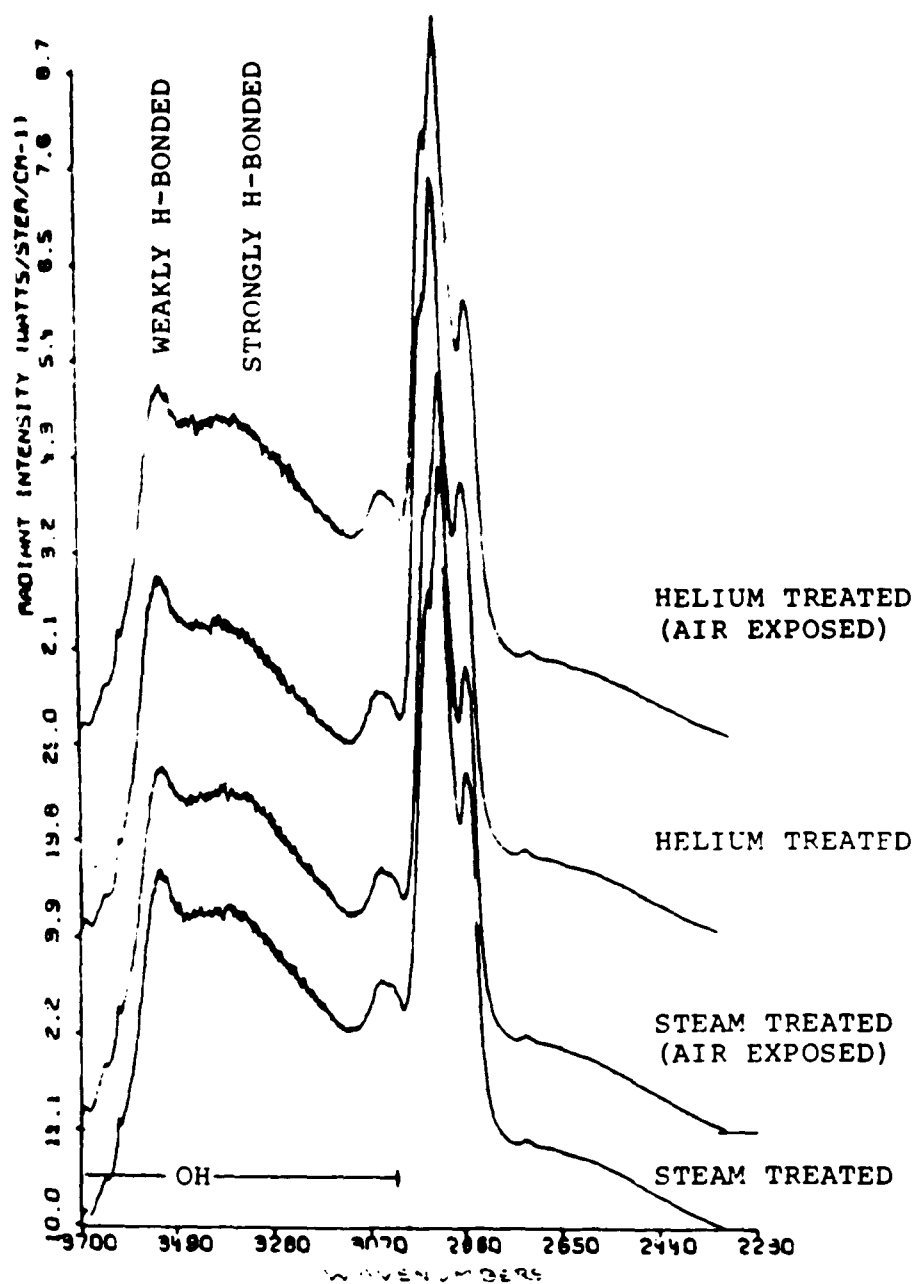


Fig.7.8.5 Comparison of DRIS Spectra for Illinois No.6 Coal Samples Treated in Steam and Helium, Preserved Under  $N_2$  vs Air Exposed

there is no evidence of it in the ir.

The reduction of the more hydrogen bonded species appears to be of the same magnitude for all the samples analyzed, irregardless of the pretreatment temperature. It is evident, because of the similarities of all the pretreated coal spectra, that the loss of these hydrogen bonded -OH species is not entirely responsible for the behavior of the pretreated coal samples in pyrolysis and extraction.

There are two ways to interpret this information. One way is that the total number of -OH species remains constant and thus with the loss of the hydrogen bonded species there would be an expected reduction of the hydrogen bonding in the structure. This is consistent with the concept that the pretreated coal exists in a partially depolymerized state. The second interpretation leads also to the conclusion that the coal is no longer in its original polymerized state. The total number of -OH species is considered to change, therefore the relative increase of the less hydrogen bonded (or more primarily bonded) species to the more hydrogen bonded (less primarily bonded) species could indicate the formation of tightly bound -OH species such as in the formation of phenolic groups. These groups, if formed at sites, which in the original coal were covalently bound, would hold the structure apart and prevent reformation

of the cross-linked structure, leaving a partially depolymerized coal bound only by hydrogen bonds at the new -OH functionalities. While there is no strong evidence to support or preclude either of these ideas at the present time, the swelling data, (Sec 7.9), indicate that there is an increase in the degree of hydrogen bond cross-links and would support the second of these two speculations. If the increase was found in strongly bound new -OH species, the absolute amount of hydrogen bonding in the coal could actually increase.

A comparison of the spectra of raw coal and a coal pretreated at the optimum temperature, as found by pyrolysis experiments and extraction experiments, 340°C, in steam, shows no difference at any region except at the upper end of the spectrum (Fig. 7.8.3). All of the spectra generated (Table 7.8.1) display two bands in the hydroxyl region. The broader of the two, centered around  $330\text{cm}^{-1}$ , is usually associated with phenolic, alcoholic, acidic, mineral and aqueous entities in the coal structure (Fuller and Smyrl, 1985). It has been shown to represent physisorbed water in oil shales. The higher energy peak at about  $3550\text{cm}^{-1}$  represents chemisorbed water in oil shales (Sheppard, 1986). This peak in our samples may be attributed to intramolecularly bound -OH, which are higher energy, more tightly bound species. These materials have only a

small amount of hydrogen bonding to other species.

In the raw coal sample the broad peak at  $3300\text{cm}^{-1}$  predominates and mostly occludes the one at  $3550\text{cm}^{-1}$ . Vacuum drying of the coal sample at  $90^{\circ}\text{C}$  does not alter this ratio (Fig. 7.8.4). In all the pretreated coal samples the peak height ratio of the two is reversed.

## 7.9 Swelling

A volumetric swelling technique developed by Liotta (1983) was applied to steam and helium treated samples. This study was implemented to gain some insight into the structure of the coal samples after steam treatment.

Values of the swelling ratios are given in Table 7.9.1. The values for the swelling ratio in pyridine have been corrected for the amount of material lost to the solvent phase by extraction. This correction is made by using average values of extractable material obtained from room temperature extraction of the same samples in pyridine (see Sec. 7.5)(Table 7.9.2). This was done because the swelling experiment measures the size of the solid sample. If a portion of the sample is no longer part of the solid phase the value for the degree of swelling of the solid is skewed. By accounting for the amount of material in the solvent the swelling values of the solid phase are comparable from one sample to the other.

In pyridine and in water the steam treated coal swells more than the raw coal or the helium treated coal by a considerable amount. In benzene the raw coal swells an insignificant amount more than the helium or steam treated coals. Pyridine is a strong hydrogen bond breaking solvent. Benzene is a non-hydrogen bond breaking solvent. The difference between the degree of

Table 7.9.1

Swelling Ratios (Q) for Raw and Treated\*  
Illinois No.6 Coal

| <u>Solvent</u> | <u>Raw</u>    |                  | <u>Steam Treated</u>       |               |                  | <u>Helium Treated</u>      |               |                  |
|----------------|---------------|------------------|----------------------------|---------------|------------------|----------------------------|---------------|------------------|
|                | <u>In Air</u> | <u>Extracted</u> | <u>Under N<sub>2</sub></u> | <u>In Air</u> | <u>Extracted</u> | <u>Under N<sub>2</sub></u> | <u>In Air</u> | <u>Extracted</u> |
| Pyridine       | 2.80          | 1.95             | 3.01                       | 2.46          | 1.88             | 2.24                       | 2.24          | 1.68             |
| Benzene        | 1.13          | 1.35             | 1.06                       | 1.00          | 1.12             | 1.00                       | 1.06          | 1.24             |
| Water          | 0.98          | 1.21             | 1.83                       | 1.84          | 0.98             | 1.56                       | 1.41          | 1.23             |

---

\*Treatments in steam and helium for 15 minutes at 50 atmospheres

Table 7.9.2

Correction for Pyridine Swelling Values

| Sample               | Swelling Ratio<br>in Pyridine<br>Uncorrected | Average %<br>Non-Extractable<br>In Room Temperature<br>Pyridine | Corrected<br>Swelling<br>Ratios |
|----------------------|----------------------------------------------|-----------------------------------------------------------------|---------------------------------|
| Raw                  | 2.32                                         | 83                                                              | 2.80                            |
| Steam                |                                              |                                                                 |                                 |
| Under N <sub>2</sub> | 2.11                                         | 70                                                              | 3.01                            |
| In Air               | 2.05                                         | 83                                                              | 2.46                            |
| Helium               |                                              |                                                                 |                                 |
| Under N <sub>2</sub> | 1.86                                         | 83                                                              | 2.24                            |
| In Air               | 1.86                                         | 83                                                              | 2.24                            |

swelling in pyridine and in benzene gives an indication of the amount of hydrogen bonds already dissociated in the unswollen coal. The smaller the difference the more H-bond dissociated the material is. In Table 7.9.3 the difference values are listed. The amount of hydrogen bond association goes up for the steam treated coal sample which is protected under nitrogen. The helium treated sample shows a lack of hydrogen bonding greater than the raw coal.

Extraction in pyridine destroys essentially all of the coal's hydrogen-bond cross-links so that subsequent swelling experiments reveal the backbone structure of the coal. It is apparent from these data that there is again a reduction of the degree of hydrogen bond dissociation in the pretreated coal as compared to the raw and helium treated samples even in the backbone of the coal after room temperature extraction. The helium treated coal, again, shows the least amount of hydrogen bond association.

When steam treated coal is exposed to air and then swelled in pyridine the swelling ratio is decreased. Exposure of helium treated coal to air has no effect on the swelling ratio. Although this method is geared toward the determination of hydrogen bond cross-links the decrease in swelling indicates an increase of cross-links of any kind. The formation of oxygen cross-links

Table 7.9.3

Difference in Swelling Ratio (Q)  
of Pyridine and Benzene Swollen Samples

|                |                      | $Q_{\text{pyr}} - Q_{\text{benz}}$ |
|----------------|----------------------|------------------------------------|
| Raw            | In Air               | 1.67                               |
|                | Extracted            | 0.60                               |
| Steam Treated  | Under N <sub>2</sub> | 1.95                               |
|                | In Air               | 1.46                               |
|                | Extracted            | 0.76                               |
| Helium Treated | Under N <sub>2</sub> | 1.24                               |
|                | In Air               | 1.18                               |
|                | Extracted            | 0.44                               |

is possible on exposure to air as was discussed in Sec 4.6.

When the swelling experiments were conducted in water the increase of swelling for the pretreated sample over the raw coal was startling. There is a twofold increase in the swelling value of the steam treated coal over the raw coal. In the work done on slurry formation it had been noted that it took almost twice as much water as the raw coal to make a pourable slurry. It was also found that it was very difficult to wet the steam treated coal with distilled water. Xanthum gum, a polymeric thickening agent was added to the distilled water to promote wetting of the coal.

It is apparent from this data that it is not a reduction of the hydrogen bonding in the steam treated sample that is responsible for the steam treated coal's behavior. On the contrary there is an increase in the hydrogen bonding of the steam treated coal ( Q value is largest for the steam treated sample). Because of the ability of water and water miscible solvents to swell the coal and the inability of water insoluble solvent to swell the coal the following conclusions have been drawn. The steam treated coal is not of the same structural makeup as the raw coal, nor as the helium treated coal. One may postulate two different structures for the modified coal. One interpretation of the data

which can be made does not include any chemical interaction of the water and the coal. Residual water not removed in the drying step of the pretreatment process acts to hold open the coal structure. The water is miscible in pyridine and water and thus the coal swells. A possible alternative structure consists of newly formed phenolic groups created in the high pressure steam treatment. The phenols may form hydrogen bonds to each other and to the coal structure. These sites readily accept the water or water miscible solvent and cause the coal to swell more than the native structure.

### 8. SUGGESTIONS FOR FUTURE WORK

A number of scoping studies should be performed to establish the limits on the pretreatment effect in steam pyrolysis:

- 1) Varying treatment steam pressure as a function of treatment temperature.
- 2) Establishing more clearly the effect on liquid yields of helium treatment at 50 atm.
- 3) Varying steam pyrolysis pressure.
- 4) Varying steam partial pressure in a steam/helium atmosphere for both treatment and pyrolysis.

Analysis of the treated solid samples should be continued in the following way, in addition to the already established screening by solvent extraction at room temperature:

- 1) Expanded use of Diffuse Reflectance Fourier Transform Infrared Spectroscopy.
- 2) Some scoping studies with solid state NMR.
- 3) Liquefaction bomb studies conducted under conditions where there is a rapid heat up of the sample to test conditions.
- 4) Measurement of the bulk density of raw coal and treated samples.

- 5) Diffusivity measurements of liquids (water) through the coal.
- 6) Measurement of pore size distribution and pore volume of both raw and treated coals.

Analysis of condensable materials from treatment, extraction liquids, and pyrolysis liquids should all be subjected to the following tests on a routine basis so that a change in process variables that manifests itself as a change in product can be detected and so that an overall material balance can be made:

- 1) Elemental Analysis
- 2) Infrared Spectroscopy
- 3) NMR ( $H^+$ )
- 4) Molecular Size Distribution (GPC)
- 5) FIMS (to check the GPC work at regular intervals)
- 6) Simulated Boiling Point Distribution (GC)
- 7) Functional group separation by liquid chromatography.
- 8) Implementation of supercritical fluid chromatography for the heavier material, not elutable from a GC column.
- 9) Collection of the condensable materials in an air free environment, and subsequently perform all the above tests excluding air.

All the above tests should, eventually be run on a suite of commercially interesting coals from around the world.

A series of tests should be performed to determine the limits on sample storage. It is at this time questionable whether the samples can be stored indefinitely under any conditions. Extraction experiments could be utilized to test the longevity of the samples which have been kept under different conditions (wet atmosphere, in darkness, under ultra violet light , in 100% O<sub>2</sub> free atmosphere, etc.)

The hypothesized water induced structures discussed in the body of this paper are to date not a proven structural entity. It would be of great interest to derive the methods needed to be able to support or disqualify this explanation for the treatment effect on the pyrolysis yields.

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