

1 of 2

Final Technical Report
The Effect of Selective Solvent Absorption
on Coal Conversion

prepared by

Dr. John W. Larsen
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania 18015

November 1993

Work performed under United State Department of Energy Contract No.
Fg-22-90PC-90304

INDEX

INTRODUCTION AND SUMMARY.....	Page i
LIST OF TABLES.....	Page ii
LIST OF FIGURES.....	Page iii
SECTION I.....	Page 1
Non-Selective Recycle Solvent Absorption by Illinois No. 6 Coal	
SECTION II.....	Page 24
The Role of Hydrogen Donor Diffusion in Direct Liquefaction	
SECTION III.....	Page 88
The Effect of Coal Conformation Change on Conversion in Tetralin	

INTRODUCTION AND SUMMARY

The work supported by this grant was directed at answering two related questions. 1) What is the composition of the solvent actually present in the coal during the early stages of direct liquefaction? 2) What is the effect of the presence or absence of hydrogen donors within the coal during the early stages of conversion. The answers to these questions will be found in Sections 1 and 2 respectively. Section 3 addresses another influence on coal reactivity; the structural change which occurs when coals are swollen by solvents.

Using a pair of different recycle oils from Wilsonville and ^1H NMR, ^{13}C NMR, gel permeation (GPC) chromatography, high pressure liquid chromatography (HPLC), and elemental analysis, no significant differences were observed between the composition of the recycle oil and that portion of the oil not absorbed by the coal. For these complex mixtures, coals are not selective absorbants. Since most of the hetroatoms responsible for most of the specific interactions have been removed by hydrogenolyses, this is perhaps not surprising.

To address the issue of the role of hydrogen bond donors in the coal, tetralin and 2-*t*-butyltetralin were used as hydrogen donor solvents. This work is reported in detail in Section 2. The basic idea is that the presence of the *t*-butyl group on the aromatic ring will hinder or block diffusion of the hydrogen donor into the coal

resulting in lower conversions and less hydrogen transferred with 2-t-butyltetralin than with tetralin. Observed was identical amounts of hydrogen transfer and nearly identical conversions to pyridine solubles for both hydrogen donors. Diffusion of hydrogen donors into the coal does not seem to play a significant role in coal conversion.

Finally, in Section 3 is discussed the unfavorable impact on conversion of the structural rearrangements which occur when Illinois No. 6 coal is swollen with a solvent. We believe this rearrangement results in a more strongly associated solid leading to the diminution of coal reactions.

This project has yielded a pair of surprises. Hydrogen donor diffusion does not seem to be a major factor in coal conversion while the structural rearrangement does. Both areas warrant further exploration.

LIST OF TABLES

Section I

Table 1. Elemental Analyses	Page 15
Table 2. Absorption of Recycle Oil	Page 16
Table 3. Temperature Dependence of Absorption	Page 17

Section II

Table 1. Response Factors for G. C. standards	Page 35
Table 2. Analytical Data on Illinois No. 6	Page 48
Table 3. Pyridine Solubility Data	Page 54
Table 4. Material Balance Data	Page 55
Table 5. Elemental Analysis of Liquefaction	Page 57
Table 6. Pyridine Solubility Data	Page 60
Table 7. Donor Solvent Recovery by G.C.	Page 62
Table 8. Data on Pyridine Soluble	Page 72
Table 9. G. C. Conversion and & Hydrogen data	Page 73
Table 10. Molecular Weight Distribution	Page 74
Table 11. Molecular Weight Distribution	Page 75

LIST OF FIGURES

SECTION I

Figure 1.	Filtration Apparatus	Page 19
Figure 2.	^1H NMR Spectrum of Recycle Oil	Page 20
Figure 3.	Diffuse Reflectance FTIR Spectrum	Page 21
Figure 4.	Gel Permeation Chromatograms	Page 22
Figure 5.	HPLC elution curves	Page 23

SECTION II

Figure 1.	Structural Model of Coal	Page 28
Scheme 1.	Flow Chart	Page 30
Figure 2.	Proton NMR of 2- <u>t</u> -butyltetralin	Page 41
Figure 3.	Gas Chromatography	Page 42
Figure 4.	GC-MS	Page 43
Figure 5.	FTIR	Page 44
Figure 6.	G.C.	Page 45
Figure 7.	Proton-NMR	Page 46
Figure 8.	GC-MS	Page 47
Figure 9.	Swelling of Illinois No. 6	Page 65
Figure 10.	Swelling of Illinois No. 6	Page 66
Figure 11.	Gel Permeation Chromatograph/1	Page 76
Figure 12.	Gel Permeation Chromatograph/2	Page 77
Figure 13.	Gel Permeation Chromatograph/3	Page 78
Figure 14.	Gel Permeation Chromatograph/4	Page 79
Figure 15.	Gel Permeation Chromatograph/5	Page 80
Figure 16.	Gel Permeation Chromatograph/6	Page 81

Figure 17. Gel Permeation Chromatography/7 Page 82
Figure 18. Gel Permeation Chromatography/8 Page 83

SECTION III

Figure 1. Conversion to Pyridine Extractables Page 95

SECTION I

Non-Selective Recycle Solvent Absorption by Illinois No. 6 Coal

Abstract

Argonne premium coals have been swollen with two Wilsonville process derived oils at temperatures between 150 °C and 275 °C. The magnitude of coal swelling varied with the oil used and with temperature for one of the oils. The whole oil and that portion of the oil not absorbed by the coals were compared using elemental analyses, NMR, IR, gel permeation chromatography, and high pressure liquid chromatography. Under all conditions, differences between the whole oil and the non-absorbed oil were not evident or minor. Bituminous coals are non-selective absorbents for these process-derived oils.

Introduction

The purpose of this work is to define more precisely the composition of the reacting system in the early stages of a direct liquefaction plant. In direct liquefaction plants, coals are introduced into mixing tanks with process derived solvent (recycle oil). Here they are stirred for a period of time at elevated temperatures before being pumped through the preheater into a reactor. In the mixing tank, the coal is often dried and always absorbs solvents and is swollen.¹ The time and temperature in mixing tanks is carefully controlled to achieve maximum pumpability. Coals which swell too much become rubbery and easily deformed and do not pump well. Some solvent swelling is thought desirable to provide reagent (hydrogen donor) access to the interior of the coal particles and to enhance gas diffusion rates. The material actually reacting in the preheater is not coal, but coal swollen by and in intimate contact with an unknown amount of recycle oil of unknown composition.

Coals are well known to be highly selective absorbents. When exposed to mixtures of polar molecules, one component is often preferentially absorbed. Illinois No. 6 coal preferentially absorbs a stoichiometric amount of methanol from mixtures of methanol and N-methylaniline.² Steric effects exist. Highly branched materials are less absorbed and more slowly absorbed than

their unbranched analogues.^{3,4} There are synergistic effects. The presence of small amounts of pyridine, a hydrogen bond breaker, increases the amount of chlorobenzene taken up by bituminous coals.²

Do coals selectively absorb certain components from recycle oils? From what is known about selective absorption by coals and about coal-solvent interactions, we expect that polar specifically-interacting molecules will be preferentially sorbed by coals. Molecules containing nitrogen or oxygen may be preferentially absorbed. On the other hand, most recycle oils have low heteroatom contents. But they do contain relatively large polynuclear aromatic molecules which also interact strongly with coals.⁵ Selective absorption from recycle oils by coals is a possibility and it is not known whether it occurs.

It is important to answer this question. Many attempts are being made to understand the chemistry occurring during direct liquefaction. The first step must be to define the reacting system. It is usually assumed to be coal, hydrogen donors (often modeled by tetralin), and hydrogen. This is not entirely correct.

It is coal, H_2 , and whatever components of the recycle oil have been absorbed by the coal. In general, aliphatic materials interact weakly with coals and coals will have a tendency to reject high H/C materials, among them many hydrogen donors.⁶

Experimental

The recycle oil (RO) was supplied by CONSOL Inc. and was sample V-131B from run 259 period E at the Wilsonville pilot plant. The coal used in the process was from the Pittsburgh seam (Ireland Mine). The average first stage temperature for period E was 440 °C, the second stage temperature was 420 °C, and Shell 324 catalyst was used in both stages. Consol solvent fractionation data using hexane, benzene, and pyridine gave 67.3% oils, 22.6% asphaltenes, and 10.1% preasphaltenes. Our data using cyclohexane, toluene, and pyridine are: oils 71.0%, asphaltenes 18.9%, and pre- asphaltenes 10.1%. The recycle oil contains 10.4% of material that is insoluble in 20 volumes of pyridine at room temperature. About half of this insoluble material is inorganic. When the oil is filtered through a 10-50 μ glass frit (see Fig. 1) at temperatures between 130 °C and 275 °C, 80 \pm 3% passes the filter. The amounts of oil absorbed by the coals are always corrected by the amount of oil which does not pass the filter at the temperature of the experiment.

A second oil was studied less thoroughly. This was a sample (R1235) obtained between the two reaction stages from Wilsonville run 260 period B using Wyoming sub-bituminous coal. It is a less heavily hydrogenated oil than the other and is designated throughout this paper as the interstage oil (IO). It contains 18%

pyridine insolubles.

Argonne premium coals were used for the solvent absorption measurements. Coals were exposed to the oils in the apparatus shown in Fig. 1. Weighed amounts of coal and solid oil were added above the glass frit (indicated by ~~XXXX~~ in the drawing) and a slow upward flow of dry N_2 was begun. The sample was warmed to the desired temperature (monitored by external thermocouples) by heating tape wrapped around the apparatus. At the desired time, the N_2 flow was reversed and the liquid was removed at the high temperature by filtration through the 10-50 μ glass frit. The swollen coal (filter residue) was dried under vacuum at room temperature. The amount of solvent absorbed was calculated using the initial weight of the dried coal used and the weight of the dried swollen coal and was corrected for the amount of oil which did not pass the filter at the temperature of the experiment. After cooling, the solid filtered oil was removed from the apparatus by scraping and washing with toluene. The material obtained was sticky and very difficult to work with. A procedure was developed which gave a powdery material which was much easier to handle. A similar procedure has been used by Maciel.⁷ A pyridine solution of the filtered oil was poured into 20 volumes of 4% aq HCl forming a flocculent powder. This was filtered, washed with water, 40% aq methanol, again with water, and dried under vacuum. Recovery was 97-99%. By elemental analyses (see Table 1), 1H NMR, and HPLC of the chloroform soluble portion,

flocculation does not change the chemical composition of the oil. All analyses were carried out on samples so treated.

^1H NMR spectra were obtained on a Bruker AM5 instrument operating at 500.135 MHz with a tip angle of 15 (3 μs) using D_5 -pyridine solutions.

IR spectra were obtained with a Mattson Sirius 100 spectrometer by diffuse reflectance using procedures which have been described in detail elsewhere.⁸

Gel permeation chromatography using pyridine solvent was carried out as described except that a series of 4 μ -Styragel columns (100, 500, 1000, 10,000 \AA) was used.⁹

HPLC was performed using an IBM Model 9533 liquid chromatograph equipped with a 20 μL loop valve injector and a variable wavelength UV detector which was operated at 254 nm. A Nucleosil NO_2 column (150 mm, 4.6 mm i.d., 5 μm particle diameter) purchased from Alltech was used. A gradient elution changing at 4 vol%/min from hexane to chloroform followed by 30 min of 100% chloroform was used. The flow rate was 1 mL/min. 20 μL of chloroform solutions (5 mg/mL) of the oils were injected onto the column. Reproducible retention times were obtained only when chloroform was run through the column for 30 min at the end of each run.

Results

The effect of coal particle size, exposure time, and oil:coal ratio on solvent absorption were explored. At 150 C, the absorption of recycle oil by -100 mesh Pittsburgh No. 8 coal was constant at 34.9 ± 1.5 % using oil:coal ratios of 2.5:1, 2.3:1, 2.0:1 and 1.8:1. At an oil:coal ratio of 2.3:1, varying the coal mesh size between -20 and -100 and the exposure time between 2 hr and 6 hr had no effect on the amount of oil absorbed at 150 C. Normally, -100 mesh and 2 hr exposures were used.

We encountered problems handling the sticky, clingy, gummy filtered oil. These were solved by pouring a pyridine solution of the oil into 4% aqueous HCl giving a solid precipitate which was easy to handle. Careful spectroscopic and elemental analysis of the oil before and after such treatment (see Table 1) demonstrated that the difference was only physical. The chemical composition remained unchanged.

The amounts of oil absorbed were different for different coals and for the two oils used. These data are in Table 2. The effect of temperature on amount absorbed differed sharply for the two oils, with only the interstage oil showing a temperature effect (see Table 3).

The oils and that portion of them not absorbed by the coals

were analyzed by ^1H NMR. The solvent used was D_5 -pyridine which dissolved all of the filtered oils. The spectra were identical as can be seen in Figure 2. The elemental analyses of the oils before and after the removal of a fraction by the coals were also the same (Table 1).

Diffuse reflectance IR spectra of the recycle oil before and after swelling Pittsburgh No. 8 coal are shown in Figure 3. The spectra are identical.

To investigate the possibility of molecular size effects on solvent uptake by coals, the oils were analyzed before and after coal swelling by gel permeation chromatography. Pyridine was the solvent and a series of four u-Styragel columns was used as previously described.⁹ Typical elution curves are shown in Figure 4. Gel permeation chromatography reveals no significant difference between the original oils and the oils after a portion of them had been absorbed by a coal.

We next analyzed the oils by high pressure liquid chromatography. Following the work of Matsunaga, we chose a Nucleosil NO_2 column.¹⁰ The eluting solvent was a gradient varying at 4 vol%/min from hexane to chloroform, A UV detector operating at 254 nm was used. Here at last we found a difference caused by sorption of the solvent by coals. The elution curves are shown in Figure 5. The peak at 21 min present in the starting

recycle oil is nearly absent after exposure to coal. A component is being selectively absorbed. It is a very minor component.

Discussion

Two different oils were used. The interstage oil was less severely hydrotreated than the recycle oil. The interstage oil swells the coal more. This could be due to a greater ability to disrupt noncovalent cross links (hydrogen bonds for example) or a stronger overall interaction with the coal. Like dissolves and swells like. Having been less severely treated, the interstage oil is more like coal. The interstage oil also contains significantly more phenolic hydroxyl (0.79 meq/g vs 0.46 meq/g). It is not surprising that the interstage oil is the better swelling solvent.

The two coal/oil systems are quite different in their response to temperature. Coal swelling in the interstage oil increases with increasing temperature while swelling in the other oil is temperature independent. Over the temperature range used in this work, the swelling of Illinois No. 6 coal containing up to 32% tetralin is temperature independent.¹¹ Similar results have been obtained for other coals in pyridine.¹² Theory predicts that coal solvent swelling will be independent of temperature.¹² It is clear that the two oils must be interacting differently with the coal and that it is the interstage oil that is unusual. There is

not enough information to determine the origin of the temperature dependence.

Except for small differences in the HPLC elution curves, no differences were found between the starting oil and the oil after removal of a portion through absorption by the coals. There are two explanations. The trivial one is that the experimental techniques were insensitive to changes caused by removal of at least 20% of the sample. Consider the NMR spectra in figure 2 for example. There is so much fine structure and it is so accurately reproduced that it is hard to believe that the missing material is in any way different than the whole. A great many differences can be hidden behind the elemental analyses of mixtures, but NMR and chromatography are much more revealing. Our conclusion is a negative one: the analytical data reveal no differences in the oils before and after coal swelling. Based on only this information, our conclusion would be that the coals extract a representative sample of the oil and the composition of the oil in the coal is the same as the composition of the oil outside of the coal.

The only data which conflict with this are the HPLC results. For both oils, one peak is lost, selectively absorbed by the coal. The amount of material is small and our attempts to collect the peak and characterize it by mass spectrometry failed. The similarities between the curves are much greater than the

differences. Not having characterized the selectively absorbed fraction, no conclusions can be drawn as to its significance. It is a very minor component.

Different individuals may reach different conclusions based on the importance given to the HPLC results. We believe the data reported here justify the assertion that these coals are not significantly specific absorbents for these oils and that the compositions of the oil inside and outside of the coals are essentially the same. We do not know whether this will be the same for other coals and oils. We believe this behavior can safely be extrapolated to non-polar oils and bituminous coals. Oils of higher polarity and low rank coals probably should be individually investigated. We have no plans for such investigations.

References

1. Berkowitz, N. An Introduction to Coal Technology, Academic Press; New York: 1979.
2. Green, T. K.; Larsen, J. W. Fuel 1984, 63, 1538-1543.
3. Larsen, J. W.; Lee, D. Fuel 1985, 64, 981-984.
4. Aida, T.; Fuku, K.; Fujii, M; Yoshihira, M.; Maeshima, T.; Squires, T. G. Energy Fuels 1991, 5, 79-83.
5. Derbyshire, F. J.; Varghese, P.; Whitehurst, D. D. Fuel 1982, 61, 859-864. Derbyshire, F. J.; Oderfer, G. A.; Varghese, P.; Whitehurst, D. D. Fuel 1982, 61, 899-904.
6. Larsen, J. W.; Green, T. K.; Kovac, J. J. Org. Chem. 1985, 50, 4729-4735.
7. Davis, M. F.; Quinting, G. R.; Bronnimann, C. E.; Maciel, G. F. Fuel 1989, 68, 763-770.
8. Flowers, R. A.; Gebhard, L. A.; Larsen, J. W.; Silbernagel, B. G. Energy Fuels 1989, 3, 762-764; 1992, 6, in press.

9. Larsen, J. W.; Wei, Y.-C. Energy Fuels 1988, 2, 344-350.
10. Matsunaga, A. Anal. Chem. 1983, 55, 1375-1379.
11. Eser, S.; Jenkins, R. G.; Wei, G.; Schobert, H. H.; Joseph, J. T. Fuel 1991, 70, 1445-1455.
12. Cody, G. D.; Eser, S.; Hatcher, P.; Davis, A.; Sobkowiak, M; Shenoy, S.; Painter, P. C. Energy Fuels in press.

Table 1. Elemental Analyses

Substance	%C	%H	%O ^a	%S	%N	%Ash
Recycle Oil (RO)	83.9	6.8	1.6	1.1	0.3	6.3
Filtered Recycle Oil	89.5	7.9	1.4	0.2	0.5	0.4
Flocculated Filtered RO	89.5	7.6	1.6	0.4	0.5	0.1
RO After Swelling Pgh. Coal ^b	89.5	7.7	1.9	0.3	0.5	<0.2
Interstage Oil (IO)	78.3	6.1	0.1	1.6	0.7	13.3
Pyridine Soluble Part of IO	88.3	6.8	2.2	0.3	0.8	1.6
IO After Swelling Pgh. Coal ^c	88.1	6.7	3.6	0.4	0.7	0.5

a. By difference except for Recycle Oil

b. 150 C, 2 hr, Recycle Oil:Coal 2.3:1

c. 150 C, 2 hr, Interstage Oil:Coal 2.0:1

Table 2. Absorption of Recycle Oil and Interstage Oil By Argonne
Premium Coals at 150 °C for 2 Hours

Coal	Recycle Oil ^a (% of Coal)	Interstage Oil ^b (% of Coal)
Beulah-Zap Lignite	22	102
Wyodak Sub-bituminous	20	132
Illinois No. 6	31	98
Pittsburgh No. 8	35	80
Upper Freeport	38	82
Pocahontas No. 3	38	65

a. Recycle Oil:coal 1.8:1

b. Interstage Oil:Coal 2.0:1

Table 3. Temperature Dependence of Absorption of Oils by
Pittsburgh No. 8 Coal

Temperature °C	Recycle Oil ^a % of Coal	Interstage Oil ^b % of Coal
130	26	76
150	34	80
180	35	100
200	33	104
275	31	118

a. Recycle Oil:Coal 1.8:1

b. Interstage Oil:Coal 2.0:1

LIST OF FIGURES

Figure 1. Filtration Apparatus Used for High Temperature Absorption Measurements

Figure 2. ^1H NMR spectrum of the Recycle Oil (B) and of the Oil after 19% of it was absorbed by Pittsburgh No. 8 coal at 150 °C using a solvent:coal ratio of 1.8:1 (A)

Figure 3. Diffuse Reflectance FTIR Spectrum of the Recycle Oil (B, filtered at 150 °C) and of the same oil after 19% of it was absorbed by Pittsburgh No. 8 coal at 150 °C using a solvent:coal ratio of 1.8:1 (A)

Figure 4. Gel permeation chromatograms of the Recycle Oil (A) and the same oil after 14% of it had been removed by exposure to Pittsburgh No. 8 coal at 150 °C using a solvent:coal ratio of 2.3:1 (B)

Figure 5. HPLC elution curves for the chloroform soluble portion of the recycle oil (A), that same oil after exposure to Pittsburgh No. 8 coal at 150 °C and solvent:coal ratio 1.8:1 (B), and the chloroform extract of the treated coal (C)

Figure 1.

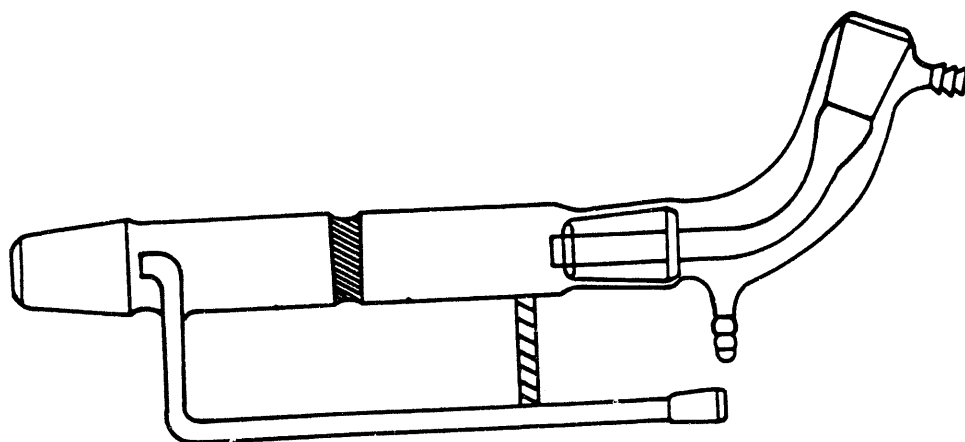


Figure 2.

Figure 2.

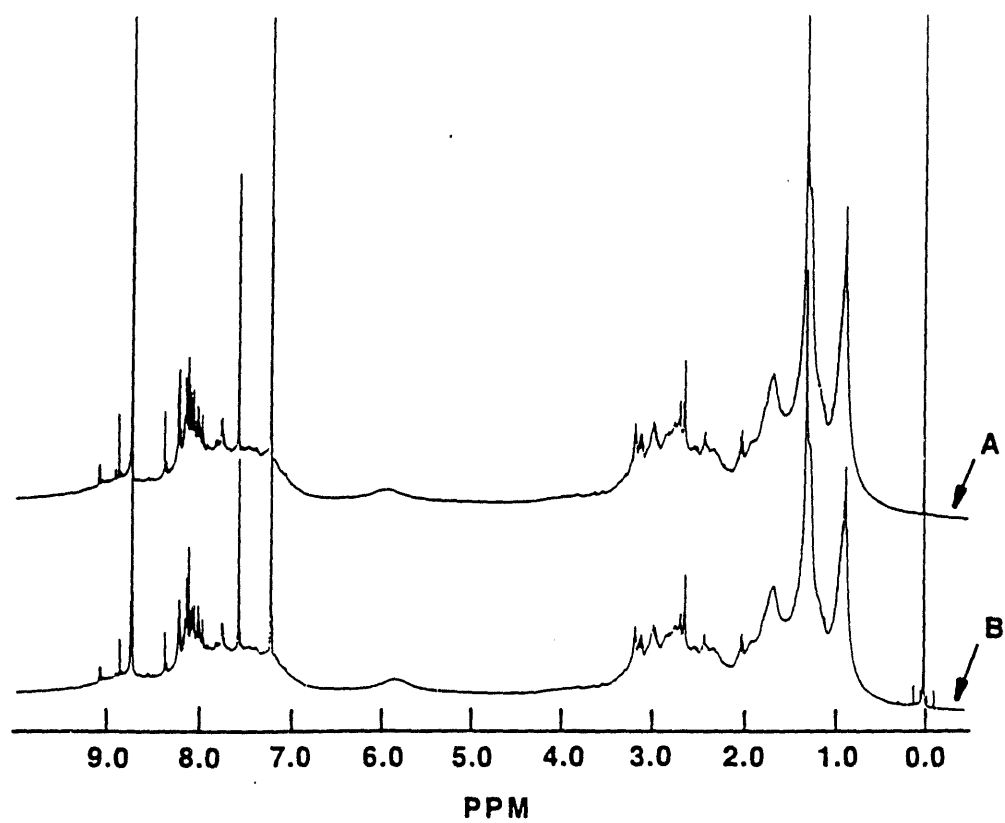


Figure 3.

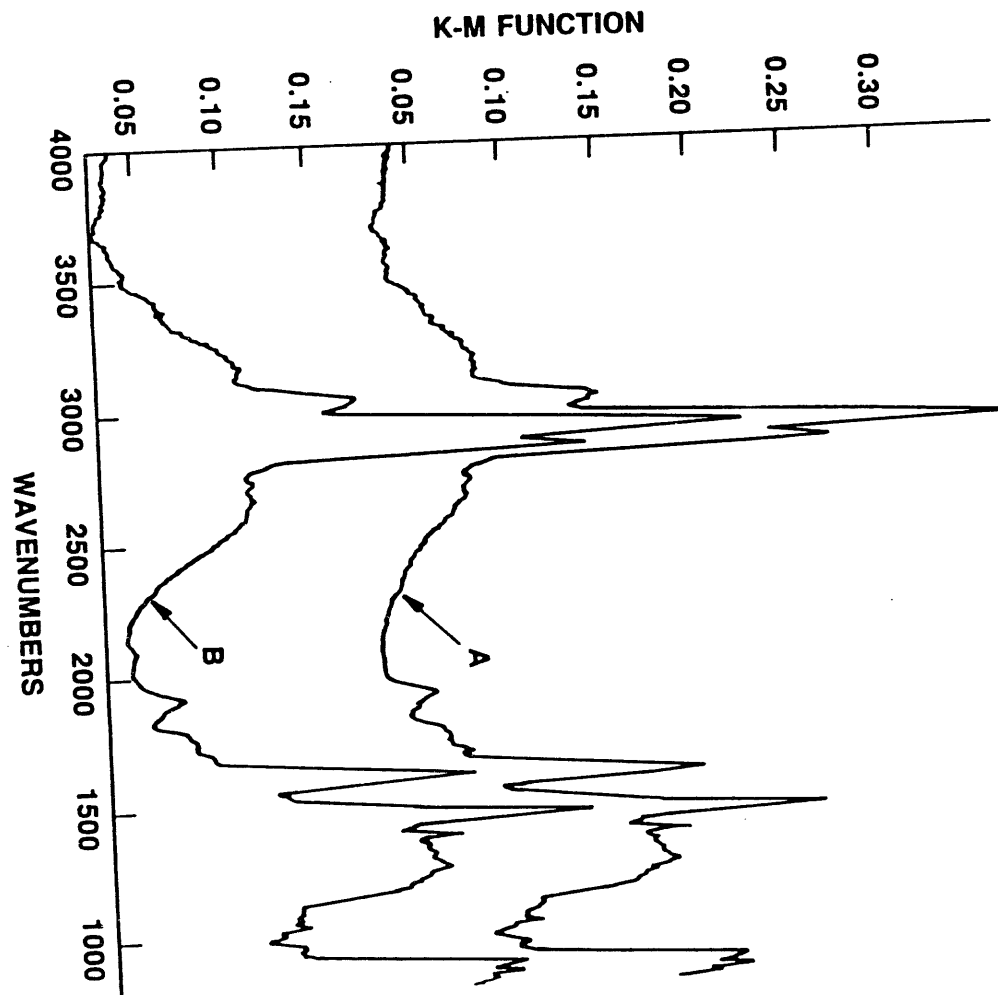


Figure 3.

Figure 4.

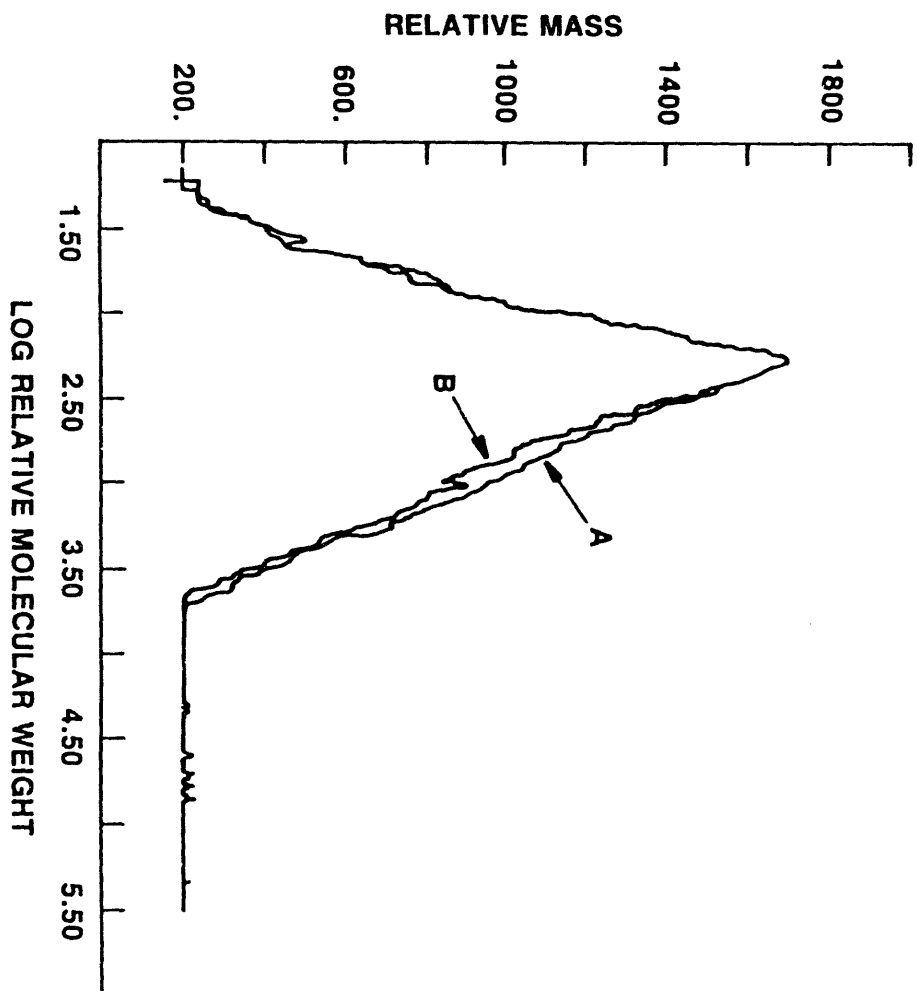


Figure 4.

Figure 5.

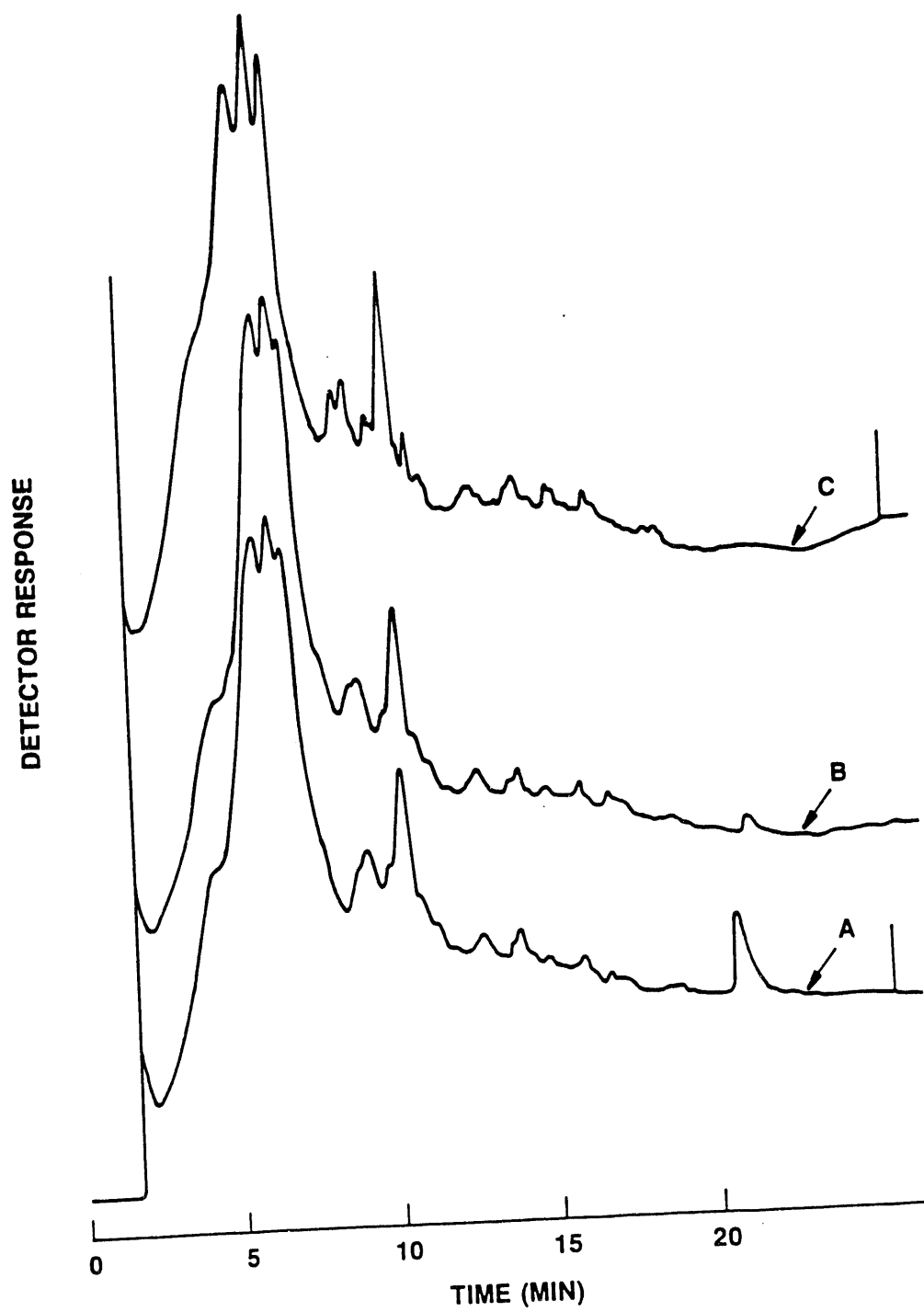


Figure 5.

SECTION II

The Role of Hydrogen Donor Diffusion in Direct Liquefaction

ABSTRACT

The diffusion limitations of donor solvents in coal liquefaction is studied. The liquefaction experiments were 10 minute parallel experiments using tetralin and 2-t-butyltetralin as donor solvents. 2-t-butyltetralin was synthesized in excess of 98% purity. The reaction conditions employed were 1 atmosphere nitrogen at room temperature and reaction temperatures on the order of 400°C. Conversion of coal to pyridine solubles is reproducible and correlates with the amount of hydrogen transferred per dry ash free coal. Conversions in both donor solvents are strikingly similar. Swelling experiments in tetralin and 2-t-butyltetralin show discrimination against the branched 2-t-butyltetralin.

I. INTRODUCTION:

This work is aimed at understanding the diffusion limitations of hydrogen donor solvents during the early stages of coal liquefaction. In coal liquefaction, coal is converted to soluble products by transfer of hydrogen from donor solvents and from hydrogen gas. The hydrogen donating solvent may or may not be present, depending on its ability to diffuse into the coal. The goal of this study is to compare the effect on coal conversion of a good hydrogen donor when dissolved in coal and when it is excluded from the coal interior.

Coal is a heterogenous carbonaceous fossilized material with a macromolecular structural network.¹ It is a porous sedimentary rock composed largely of macerals (phytogenic organic substances)², and to a lesser extent, of minerals, trace elements, water and gases.^{3,4} The organic components are called macerals and the inorganic components, mineral matter. The mineral matter in coal produces ash on complete combustion.^{5,45} Others have described the coal macromolecular network as groups of heteroatomic-containing polycyclic, aromatic and hydroaromatic ring structures joined by hydrogen bonds, and covalent linkages.⁶⁻⁸ Shin's structural model of coal (Fig. 1) is based on coal conversion products.⁹ The components of Shin's coal model were based on the distribution of aromatic and aliphatic groups from ¹H, ¹³C spectroscopy, elemental analysis, and functional group analysis. Nishioka and others have disputed the proposed coal structure on the basis of the strong

intra- and intermolecular physical associations of coal molecules.⁴⁶ Nonetheless, the structure of coal can be described as a non-homogenous crosslinked matrix with covalent and noncovalent interactions.^{10-14,47} This feature renders coal insoluble¹⁵ unless its molecular network is broken down.

One method of breaking down the coal macromolecular structure to obtain useful products is by coal liquefaction. Coal liquefaction is the conversion of solid coal into liquid and solid fuel by three processes: pyrolysis, indirect liquefaction, and direct liquefaction.⁵ In pyrolysis coal is devolatilized in an inert or a hydrogen-rich environment to obtain tars and oils. Indirect liquefaction involves the formation of liquid products from the reaction of gasified coal over a catalyst, and direct liquefaction involves the production of soluble products from the reaction of coal with H₂ or with a hydrogen-rich donor solvent in the presence or absence of a catalyst.⁵

In direct liquefaction, hydrogen from a hydrogen-rich donor solvent, hydrogen gas, or recycle solvent is added to coal in the presence or the absence of a catalyst to convert coal to soluble products. The mixture of coal, recycle solvent and/or the hydrogen donor is preheated, and reacted at high temperatures and pressures in the liquefaction reactor. A typical liquefaction reaction involves the following: (i) initial coal dissolution to produce primarily a heavy nondistillable residuum, (ii) hydrogen transfer

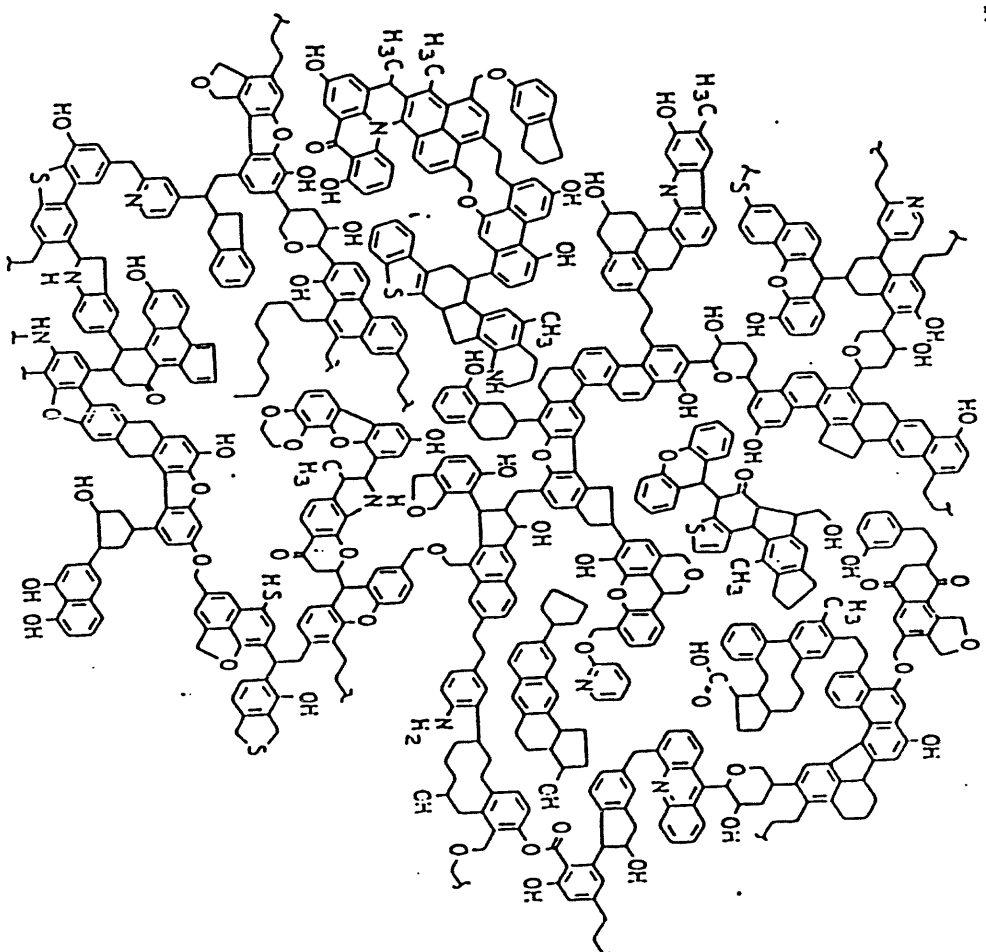
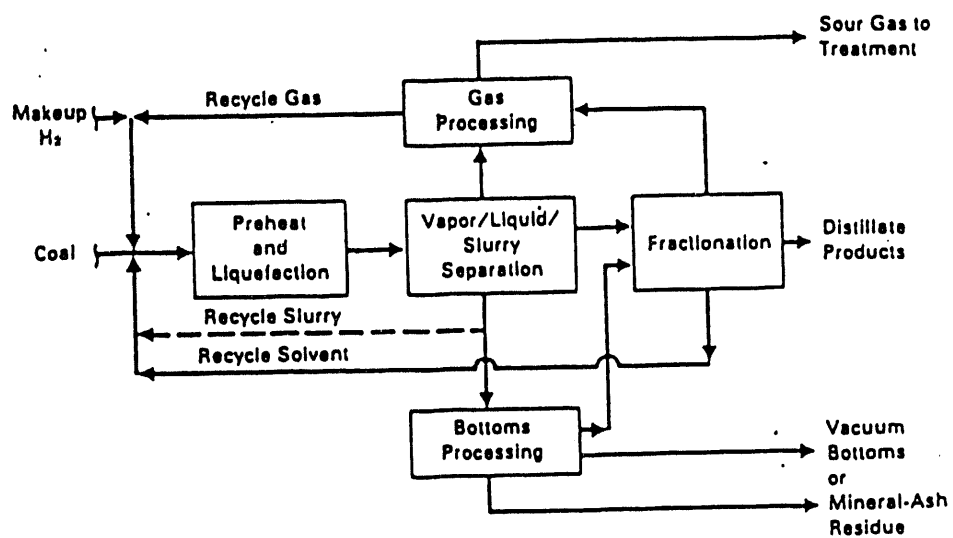


Fig. 1. Structural model of coal by Shin⁹

that stabilize the dissolved coal-derived residuum, (iii) hydrogen attack to form distillable hydrocarbons and to remove heteroatoms from the depolymerizing coal, and (iv) rehydrogenation by addition of hydrogen to the donor solvent molecules (Scheme 1.).⁵

Much of the initial coal dissolution occurs in the slurry preheater.^{6,16-18} Dissolution of the coal proceeds first by the cleavage of the most labile bonds in coal. Bond thermolysis results in hydrogen transfer from H₂ or from the donor solvent to the coal free radicals.^{2,4} Ouchi¹⁹ and Aida²⁰ have speculated that donor solvents rapidly diffuse into the coal particle and that the hydrogen transfer reactions take place between the solvent and the radical species within the coal itself. The donor solvent enters the coal particle to provide a source of free radicals generated thermally within the coal matrix. At temperatures on the order of 400°C, thermally induced bond cleavage breaks up the crosslinked macromolecular framework. Bond breaking occurs at significant rates near 400°C generating free radicals by bond fission.²⁰⁻²²

Hydrogen shuttling, hydride transfer, pericyclic and chain reactions have been postulated as possible pathways to the fragmentation of coal during liquefaction^{18,23}. But to a large extent, hydrogen donors have been postulated to convert the radical centers to stable-end groups. These reactions yield coal solids, liquids and gases of modest molecular weight.



Scheme 1. Flow Chart for a Simplified nonCatalytic Coal Liquefaction Process⁵

In coal liquefaction, the solvent functions as the transport medium, the hydrogen donor and the solvent for the heavy liquefaction products.¹⁶ The absence of hydrogen atom donors cause the coal radicals to undergo condensation reactions which lead to solid residues that are more crosslinked and robust than the starting coal. These are described as 'retrogressive' reactions. In the absence of hydrogen donors, and at temperatures that support combustion, the coal particles melt, give off volatile gases, and harden to form the porous cellular substance called coke or char.^{18,22} The carbon content of coke renders it valuable as a fuel and as a reducing agent in many metallurgical and chemical processes, however, in coal processing plants and direct liquefaction, coke formation retards liquefaction yields. Coke plugs the process lines and/or reactors and retards the pumping action of each stage of liquefaction process. Donor solvents suppress coke formation during liquefaction, and enhance the conversion yields.⁵

The actual role that hydrogen donors play in the early stages of coal conversion is not totally defined. Several studies have investigated the reacting system at the initial stages of coal liquefaction, yet none of these has addressed the question of whether the donor solvent goes into the coal to donate its hydrogen or whether the coal molecule breaks apart before abstracting hydrogen from an external donor solvent.²³⁻²⁶ Coals themselves are hydrogen donors^{20,24}, and the relative importance of external

hydrogen donors and internal donation has never been determined.

This work is aimed at determining the effects of good hydrogen donors dissolved within the coal matrix when solid coal is rapidly heated in a solvent to reaction temperatures on the order of 400°C. Our strategy for exploring the importance of the presence of hydrogen donors in the coal during liquefaction is to compare two materials of identical hydrogen donor ability, only one of which can penetrate the coal. Two such donor solvents were used in parallel liquefaction experiments to determine the extent of conversion of Illinios #6 (Ill. #6) coal.

The literature suggests that molecules substituted with highly branched groups are either not absorbed by the coal, or that they are absorbed only slowly.²⁷⁻²⁹ Fowkes et. al. studied the adsorption of phenols and amine bases on coals, and discovered that unless they were t-butyl substituted, phenol and pyridine rapidly penetrated the coal.²⁷ Larsen and Lee studied the equilibrium swelling of coals by aniline, pyridine, 4-t-butylaniline, and 4-t-butylpyridine. It was found that equilibrium swellings were significantly smaller with the tertiary butyl derivatives than with pyridine and aniline.²⁸ These results were also confirmed by Aida and coworkers. They showed that discrimination against penetration of coal by branched groups is even greater in binary solvents systems where one of the solvent components, a good coal swelling solvent, is expected to open up the structure for the bulky

component.²⁰

Based on the interaction of coal and branched groups, the donor solvents chosen were tetralin and 2-t-butyl tetralin. Tetralin is a good donor solvent^{13,20}, but not a good swelling solvent. It does swell coal by 10 - 30 % depending on the coal.^{11,48} 2-t-butyltetralin is not expected to penetrate the coal, but will serve as a hydrogen donor to the species that are liberated from the coal.

II. General Experimental

A)(i) Gas Chromatography

Gas chromatographic analyses were performed using a Hewlett Packard Model 5880A gas chromatograph equipped with a flame ionization detector (FID). The column used was a 15m X 0.25mm id. AT-5 capillary column (Alltech). The stationary phase was polydimethyldiphenyl (5%)siloxanes with 0.45 μ m film thickness. A typical temperature program consisted of a 1-min hold at 100°C, a 3°C ramp to 130 °C and a 6 minute hold at 130 °C. The G.C carrier gas, flow rate and split ratio are Helium, 1.06ml/min, and 113:1, respectively. The injection port temperature was 250°C and the detector temperature was set at 275°C. The detector response was demonstrated to be linear over the range 2.5×10^{-3} to 3.8 Molar using 0.4 μ L injections. These conditions were sufficient to elute all the injected materials. Areas from the electronic integration of the FID signal were converted to molar units by response factor calibration. With cis-decalin as the internal standard, standard solutions of tetralin, naphthalene, 2-t-butyltetralin and 2-t-butylnaphthalene and cis-decalin were made in pyridine to determine the G.C. response factors. The concentration of the standard solution ranged from 4.13×10^{-2} M to 6.49×10^{-2} M. A typical response factor for each component in the standard solution is summarized in Table 1 below. The formula used for the calculation of response factors³⁰ is summarized.

$$\text{Response Factor} = \frac{(\text{Mass of Internal Standard}) \times (\text{Area of Unknown})}{(\text{Mass of Unknown}) \times (\text{Area of internal standard})}$$

Table 1: Response Factors for G.C. standards used for Quantitation of the Liquefaction Products.

<u>Compound</u>	<u>Molarity</u> <u>/ (x 10⁻²M)</u>	<u>Response</u> <u>Factor^a</u>
Tetralin	5.33	1.037 ± 0.006
Naphthalene	5.48	1.080 ± 0.010
2- <u>t</u> -Butyltetralin	4.13	0.870 ± 0.027
2- <u>t</u> -Butylnaphthalene	4.35	0.574 ± 0.024
<u>Cis</u> -Decalin	6.49	1.000

a) Errors are standard deviation

(ii) ^1H NMR, GC-MS and FTIR

^1H NMR spectra were obtained using a Joel FX 90Q Fourier Transform Spectrometer. The NMR spectra were recorded as chloroform- d or acetone- d_6 solutions with tetramethylsilane as the internal reference at room temperature and pressure. The chemicals and solvents used were obtained from Aldrich and Fischer. GC-MS spectra were obtained on a Hewlett Packard 5890A interfaced with an HP5970 Mass Selective detector. Transmission Infra Red spectra were obtained as neat samples on KCl pellets on a Mattson Polaris FTIR spectrophotometer.

(iii) Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed on a Waters ALC 201 GPC unit equipped with refractive index and mass sensitive detectors. The GPC columns were each 32cm long by 1.2cm o. d. The chromatographic column consists of four micro-styragel columns connected in series and calibrated with polystyrene standards. The particle size of each of the μ styragel column was arranged from the injector to the detector in the following order: 10^4A^* , 10^3A^* , 500A^* , and 100A^* . The columns were operated at ambient temperature at a flow rate of 1 ml/min. HPLC grade pyridine was used as the mobile phase.

The molecular weight distribution of the soluble coal products had previously been measured^{31,32} using this system. The system is equipped with a digital thermal pulse flow meter and the mass

detector output is obtained as a function of elution volume. The mass detector was an ACS model 750/14 mass detector that operated by nebulization, evaporation, and light scattering detection. The nebulizer gas flow was nitrogen. The solute in the solvent is nebulized in the gas stream through an evaporator at 60°C. The solvent is evaporated leaving a fine mist of solute particles which are detected by a photomultiplier placed at a fixed angle to the light beam. A photomultiplier detects the particle cloud at a 120°C angle, and displays the amplified signal on the computer interfaced Asyst program. The molecular weight distribution data are calculated as a function of the elution volume of the injected sample.

The equations used to calculate the number average (M_n) and weight average (M_w) molecular weights are illustrated below.^{33,34}

$$M_n = \frac{\sum h_i}{\sum (h_i/M_i)}$$

$$M_w = \frac{\sum h_i M_i}{\sum h_i}$$

where h_i = the gpc curve height at the i th volume increment and
 M_i = the molecular weight of the species eluted at the i th time retention volume.

The GPC curves are presented in the appendix of this report.

Solvent Purification Prior to Synthesis

Vacuum dried (1mmHg & 430°C) Davison molecular sieves, (4A*) and 10 - 16 mesh (Fischer Scientific) were used to dry the CS₂, the t-butylchloride, and the tetralin used for the 2-t-butyltetralin synthesis (Aldrich Chemical Co. Inc., Milwaukee, WI). ACS grade KOH (Fischer Brand) was used to dry the pyridine (Aldrich)³⁵. All other reagents were obtained from Aldrich or Fischer and used without further purification. The solvents used were stored under nitrogen.

B) Synthesis:

(i) Synthesis of 2-t-Butyltetralin

2-t-butyltetralin was synthesized by a slight modification of the method of Whitmore et. al.³⁶ A one-liter, three necked round bottom flask was equipped with a magnetic stirrer, a thermometer, a reflux condenser connected to the HCl exit trap, and a Claisen adapter. The Claisen adapter contained a rotating solid addition apparatus for the AlCl₃, and an addition funnel that contained CS₂ solution.

The CS₂ solution was prepared by mixing 1.56 mol (146g) of t-butyl chloride, 1.52 mol (201 g) of tetralin, and 170 ml of CS₂ in a

flask. Fifty milliliters of CS_2 and 25 ml of the CS_2 solution were added to the reaction flask which was cooled in ice-water bath. The contents of the reaction flask were stirred as the AlCl_3 and the CS_2 solutions were added. HCl evolution was observed as the reaction begun. The temperature was maintained at $0 - 5^\circ\text{C}$ throughout the reaction. A total of 75 minutes was allowed for the addition of all the AlCl_3 and the CS_2 solution. The resulting mixture was red and was allowed to stir until the evolution of HCl had stopped. After 2 hours of stirring, the reaction was quenched with 400cc of ice-cold water (0°C). The resulting solution looked off-white with some red droplets. After stirring for 15 minutes the aqueous layer was separated from the organic layer.

The resulting solution was washed with 200 mL of water followed by 200ml of 12 % Na_2CO_3 . The yellow organic solution was dried over 25 g of anhydrous calcium chloride for 24 hours and then over 5 grams of K_2CO_3 for another 24 hours. The clear yellow solution was decanted and filtered from the drying agent. Carbon disulfide was removed by rotary evaporation under vacuum at ambient temperature. The crude product obtained was 90% (wt) pure by gas chromatography.

The crude product was then subjected to fractional vacuum distillation in a vacuum jacketed column (68cm X 1.6cm i.d. x 3.0cm o.d.). The Fenske rings used for packing the column were 0.5cm o.d. Distillation of the crude product yielded five fractions. The least pure fraction contained 74% of 2-t-butyltetralin (by G.C.)

Fraction 5 was in excess of 98% pure by G.C. and represented a 47% yield based on the tertiary butyl chloride used. The boiling point of the pure 2-t-butyltetralin at 8mm Hg was 109 - 110°C. Proton NMR, and G.C, analysis of the pure 2-t-butyltetralin showed the exclusive formation of 2-t-butyltetralin in excess of 98% purity (Fig. 2 and Fig. 3.) GC-MS (Fig. 4) and FTIR (Fig. 5) were used to further characterize 2-t-butyltetralin.

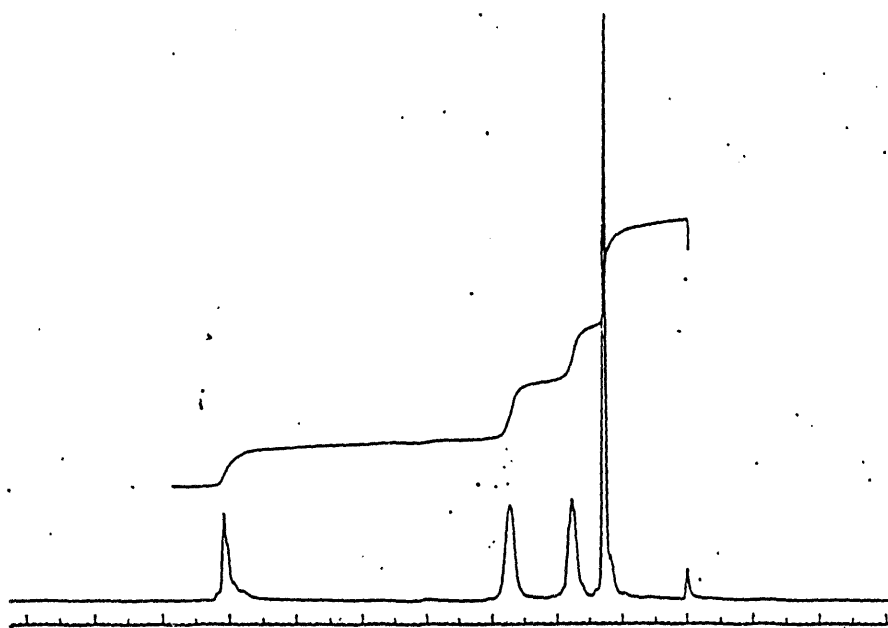
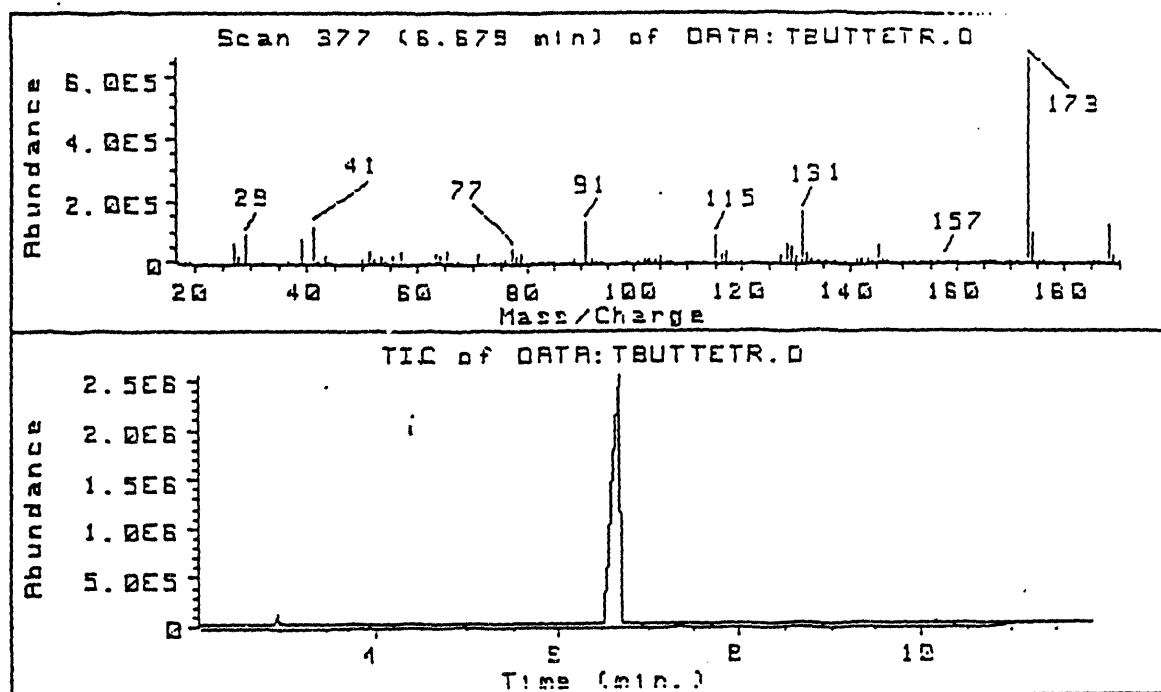


Fig. 2. Proton NMR of 2-t-butyltetralin



DRAW done
[MS1]

T: Scan 69 (2.975 min) of DAT
Z: TIC of DATA:TBUTTETR.D
Y: Scan 68 (2.963 min) of DAT
X: Scan 377 (6.679 min) of DA

Fig. 4. GC-MS of 2-t-butyltetralin

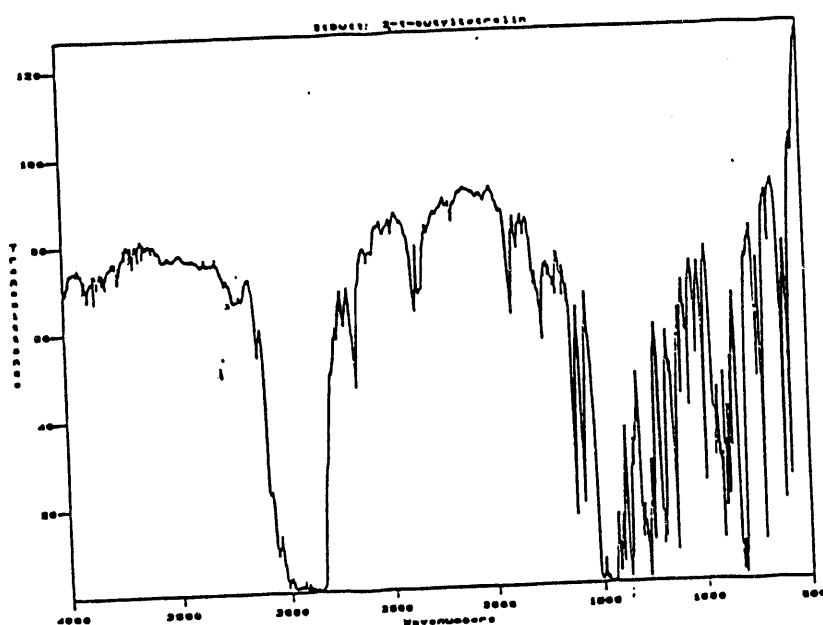
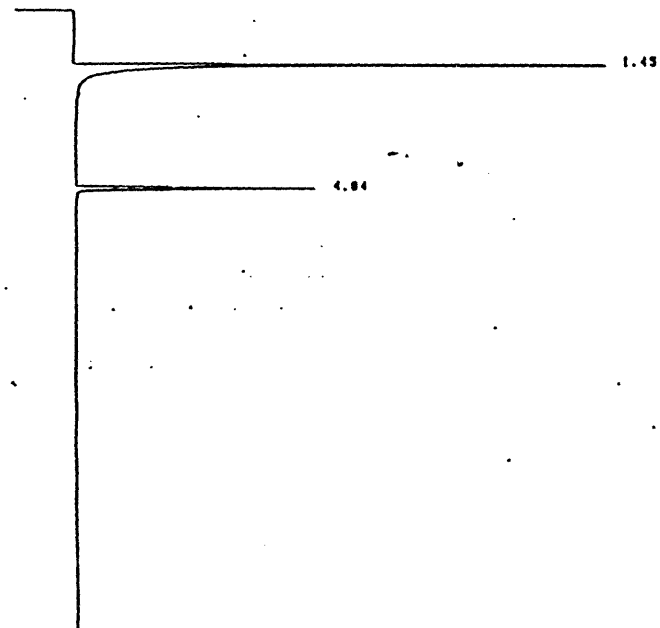


Fig. 5. FTIR of 2-t-butyltetralin

START
 READY FOR INJECTION
 1ST OVEN TEMP
 OVEN TEMP=160°C SETPT=160°C LIMIT=405°C



EXP 3 3800A MANUAL INJECTION 0 04:11 SEP 10, 1991
 AREA %

RT	AREA	TYPE	AREA %
1.45	50309.30	00	99.237
4.04	367.04	00	0.763

TOTAL AREA = 50676.40
 MULTIPLIER = 1

Fig. 6. G.C.Trace of 2-t-butyl-naphthalene

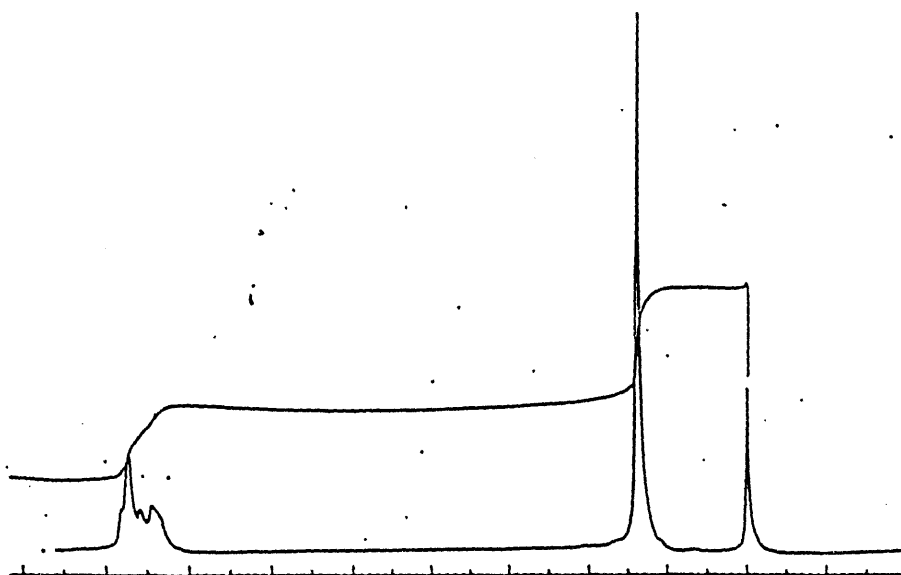
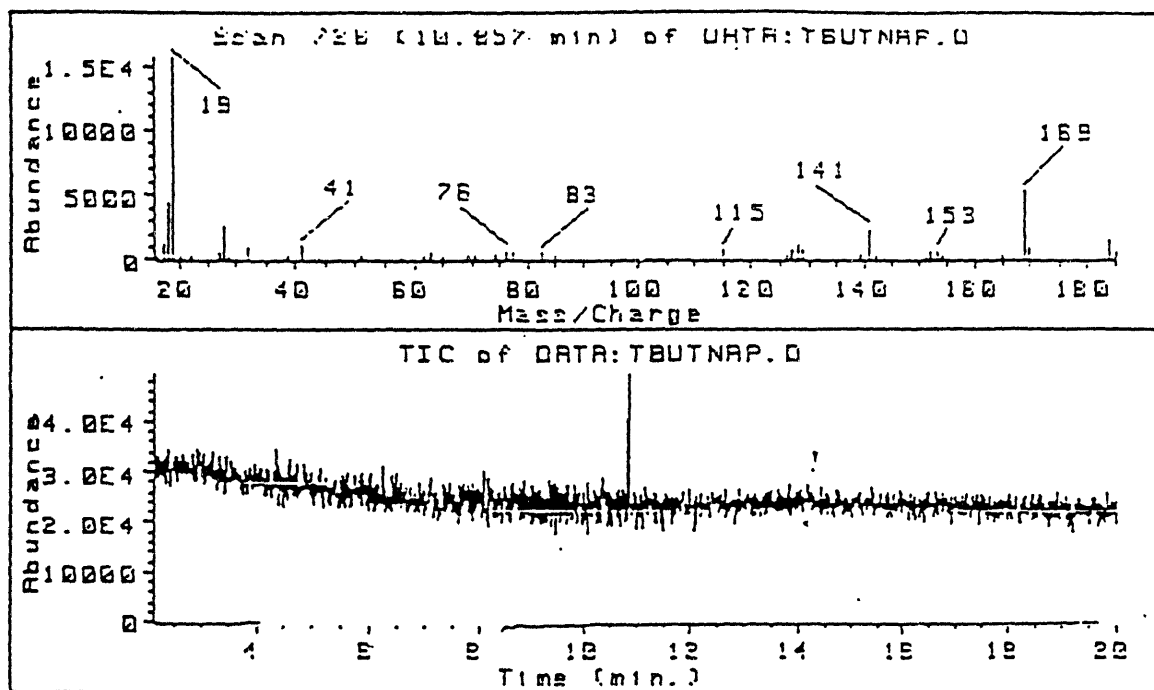


Fig. 7. Proton-nmr of 2-t-butylnaphthalene



T: null.
 Z: TIC of DATA:TBUTNAP.D
 Y: null.
 X: Scan 726 (10.857 min) of D

[MS1] _____

Fig. 8. GC-MS of 2-t-butyl-naphthalene

C).Illinois #6 Coal Pretreatment Prior to Liquefaction

The coal used was 100 mesh Ill #6 coal from the Argonne Premium Coal Sample program. Each sample of 'as-recieved' Ill #6 coal was dried to constant weight in a vacuum oven (Fisher Scientific Model 280) at 110°C. The dried coal was then stored in the N₂ filled glove box. Elemental analysis of the 'as received' Ill#6 coal sample is summarized in Table 2³⁷. The data is presented for moisture and ash free (maf), and dry mineral matter free (dmmf) coal. The thimbles used (Whatman Extraction thimbles) for Soxhlet extraction were dried at 110°C in a vacuum oven to constant weight.

Table 2: Analytical Data on Ill#6 'as-recieved' Coal from the Argonne Premium Coal Sample Program³⁷

<u>Elemental Composition</u>	<u>MAF</u>	<u>DMMF</u>
Carbon	77.67	80.73
Hydrogen	5.00	5.20
Nitrogen	1.37	1.43
Org Sulfur	2.38	2.47
Chlorine	0.06	0.06
Fluorine	0.00	0.00
Oxygen	13.51	10.11
Dry ash	15.48	-

D. Liquefaction Reactions in 5mL and 22mL Autoclaves

Two parallel sets of liquefaction reactions in tetralin and 2-t-butyl tetralin were performed at temperatures on the order of 400°C. One set of experiments was performed in 5 mL minibombs and the second set was performed in autoclaves with an approximate volume of 22 mL.

For the 5 mL minibombs, four mini-reactors were operated simultaneously. The same number of moles of 2-t-butyltetralin and tetralin were used in the matched pairs of experiments. Each reactor was charged with coal and donor solvent under 1 atmosphere of dry nitrogen, and plunged into the preheated fluidized sandbath. The desired reaction temperature was achieved within one minute of plunging the reactors into the fluidized bath. The reactors were shaken axially at a speed of 200 - 250 cycles per minute. All liquefaction reactions were performed for 10 minutes. The time temperature profile was measured using an iron constantan (J-type) thermocouple attached to the reactor.³⁸ After 10 minutes, the reactors were quickly cooled in an ice water bath.

The contents of each reactor was washed out with pyridine into a beaker under nitrogen. A weighed amount of the internal standard (cis-decalin) was added and thoroughly mixed using a magnetic stirrer. Less than 1% of each pyridine-coal mixture was filtered through a 0.45µm millipore filter and analyzed by G.C. Yields of naphthalene and 2-t-butylnaphthalene were obtained by gas

chromatography to determine the amounts of hydrogen transferred from the donor solvents. Dealkylation of 2-t-butyltetralin was also observed.

The reaction products were Soxhlet extracted with pyridine in a dry nitrogen atmosphere.^{39,40} The pyridine soluble fraction was rotary evaporated, and both the soluble portion and the residue were vacuum dried to constant weight. Conversion was determined by pyridine extractibility in comparison to the non-reacted coal.^{41,42,50} The percent pyridine soluble coal on a daf basis was calculated based on the amount of dried pyridine extracts and dried coal residue. The overall material balance ranged between 90-105%.

Extraction Yield (wt. % daf) =

$$\frac{(\text{Mass of Whole Coal} - \text{Mass Residue}) \times 100}{\text{Mass daf coal}}$$

The liquefaction and work-up procedure for the 22 mL autoclave experiments were similar to those used in the 5 mL minibomb experiments except the following: 2 runs were made for each 22mL autoclave experiment, and, when extraction was complete, 500 μ L of the filtered pyridine soluble fraction were subjected to gel permeation chromatography. Results for the 22mL liquefaction experiments can be found in the Appendix of this report.

E. Swelling of Ill#6 Coal with Tetralin and 2-t-Butyltetralin

6.0 mm o.d. glass tubes were used for the swelling experiment. One end of each tube was sealed such that the inside bottom of the tube was flat. An average of about 140 mg of 100 mesh Ill#6 coal was weighed into each tube and the open end was sealed with parafilm.

The tubes were centrifuged in a Fischer Centrifuge for 15 minutes and gently tapped so that the top layer of the coal lay flat with respect to the bottom of the sealed tube. The height H_1 of coal was measured with a ruler (0.5mm minimum measurement), and centrifuged again for another 15 minutes. The new height was identical to H_1 . Using the Thermolyne shaker (Sybron), the coal particles were allowed to disperse in each tube. An average of 1.40 g of solvent was added to each tube by means of a syringe through the parafilm sealed tube. Each tube was immediately immersed in liquid nitrogen (-196°C).

Each frozen coal-solvent mixture in the glass tube was evacuated using a vacuum manifold vacuum source and sealed using a torch. The swelling experiments were performed at room temperature in the fume hood, at 50°C in a constant temperature water bath, and at 100°C , and 150°C in a Techne sandbath. The swelling ratio was obtained according to the formula.^{37, 48}

$$Q_v = H_2/H_1$$

where H_1 was the initial height of the coal after centrifugation, but before solvent addition, and H_2 is the coal height exposed to

solvent after a certain period of time. Q_v is the volumetric swelling index.³⁷

The average of three measurements was used at each reaction temperature and for each swelling solvent. The standard deviations of the swelling ratios observed were within 4% of the mean values.

Results and Discussion

Liquefaction of Coal in 5mL Minibombs

Table 3 presents pyridine solubility data based on the amounts of solvent to coal weight ratio at 350°C . On the whole, the total extraction yields (residue based) are higher when tetralin, rather than 2-t-butyltetralin is used as donor solvent. Though differences in residue based pyridine solubles are not very large, it is evident that conversions to pyridine solubles are slightly higher with tetralin as donor solvent than with 2-t-butyltetralin. Beta tert-butyltetralin may be too bulky to penetrate the coal and may only serve to donate its hydrogens to the depolymerizing coal.

Pyridine solubles based on the dried extracts however, are markedly high and misleading. The material balance data in Table 4 clearly show solvent incorporation into the recovered coal. The extract based pyridine solubles are larger than the residue based pyridine solubles. Conversions greater than 100% are impossible and the higher values obtained must be due to solvent incorporation to varying extents.

To probe the differences in pyridine solubility based on the dried residue and dried extracts, elemental analyses of the coal products which had 101% and 159% coal mass balance were determined by Galbriath Laboratories (Table 5).

Table 3: Pyridine Solubility Data on 10 minute liquefaction Experiments at 350°C.

<u>Donor Solvent</u>	<u>Coal Mass/g</u>	<u>Solvent:Coal Ratio (g/g)</u>	<u>Pyridine Soluble/daf Ill#6 Coal</u> <u>(Residue Based) (Extract Based)</u>	
Tetralin	0.34	5.3	51%	81%
Tetralin	0.34	5.3	54%	55%
2- <u>t</u> -ButylT**	0.37	5.7	48%	118%
2- <u>t</u> -ButylT**	0.34	6.3	49%	120%

2-t-ButylT** -2-t-butyltetralin

Table 4: Material Balance Data on 10 minute Liquefaction
Experiments at 350°C

<u>Ill #6 whole</u> <u>Dried Coal/g</u>	<u>Solvent</u> <u>/g</u>	<u>%Pyridine Soluble*</u> <u>(Extract based)</u>	<u>Material Balance</u>		
			<u>Coal</u>	<u>Solvent</u>	<u>Overall</u>
0.338	1.800 Tetralin	81 (51)	125	90	104
0.340	1.820 Tetralin	55 (54)	101	90	90
0.369	2.099 2- <u>t</u> -BuT ^b	118 (48)	160	97	106
0.340	2.134 2- <u>t</u> -BuT ^b	120 (49)	159	96	105

^b Solvent used is 2-t-Butyltetralin

* Pyridine solubility data, Residue based data in parenthesis

Compared to the dried whole coal, and the DAF coal, the H/C ratios of the tetralin, 2-t-butyltetralin extracts and residue are significantly higher. In addition to pyridine incorporation into the tetralin extract and 2-t-butyltetralin residue, there is significant donor solvent incorporation. When compared to the (DAF coal), 4.5% and 8.7% of donor solvent are respectively incorporated into the tetralin and butyltetralin extracts. The 2-t-butyltetralin residue has a 6.6% donor solvent incorporation. The 2-t-butyltetralin residue does not seem to have pyridine incorporation. Calculations of the amounts of solvent incorporated can be found in Appendix E of this report.

Elemental analysis of the tetralin extract and 2-t-butyltetralin residue show a 0.6% and a 1.2% pyridine incorporation respectively. Clearly the 2-t-butyltetralin extract has enormous solvent incorporation indicated by the large H/C ratio.

In Table 6, percent conversions and hydrogen transfer as a function of solvent to coal ratio and reaction temperature are reported. As shown, without donor solvent, conversions to pyridine solubles are small (28%). This observation is consistent with those of Ouchi⁴³ and Nishioka.⁴⁴

Table 5: Elemental Analysis of Liquefaction Products carried out at 350°C (mole%).

<u>Coal Sample</u>	<u>Coal Balance</u>	<u>%C</u>	<u>%H</u>	<u>%N /10⁻²</u>	<u>H:C Ratio</u>
Whole Dried Coal ³⁷		5.47	4.23	8.29	0.77
DAF Coal ³⁷		6.47	5.00	9.79	0.77
Tetralin Extract (101%)		6.45	5.52	10.6	0.86
2- <u>t</u> -BuT** Extract (159%)		7.12	7.93	<3.57	1.11
2- <u>t</u> -BuT** Residue (159%)		5.52	5.01	9.86	0.91

DAF Dry-Ash-Free
2-t-BuT** -2-t-butyltetralin

The data in Table 6 demonstrate the requirement of a donor vehicle for better conversion. At 382°C, cis decalin gives an average conversion yield of 50% whereas tetralin and 2-t-butyltetralin at 385°C give a minimum conversion yield of 75%. The reaction with cis-decalin (382°C) and that with the donor solvents tetralin and 2-t-butyltetralin (385°C) stress the necessity of hydrogen donation to enhance conversion yields. Tetralin and 2-t-butyltetralin are good hydrogen donors due to the benzylic type free radical intermediate and the subsequent loss of four hydrogen atoms to yield stable aromatic compounds.

Slightly higher conversions are observed when tetralin is used as donor solvent. At 350°C, the conversion yields in both tetralin and 2-t-butyltetralin solvents are similar (approximately 50%). A similar correlation is observed at 385°C (75% and 82%): 2-t-butyltetralin and tetralin give similar pyridine soluble yields. This implies that hydrogen donation by tetralin and butyltetralin are similar, and since butyltetralin is not expected to penetrate the coal, hydrogen donation must be external to the depolymerizing coal. Under similar conditions coal conversions in tetralin and butyltetralin were found to stress the importance of external hydrogen donation in these experiments.

Conversions with 2-t-butyltetralin as donor solvent are generally slightly lower than those with tetralin, except for the 5.5:1 of 2-t-butyltetralin to coal weight ratio (Table 6). This data

conflicts with the observed trend. A repeat of the 5.5:1 parallel reaction of the 2-t-butyltetralin to coal ratio needs to be performed to determine whether there is a critical solvent to coal ratio which gives higher conversions with 2-t-butyltetralin.

Higher temperatures yield better conversions. This observation is expected⁴⁹ since greater physical dissociation and bond cleavage of the coal molecular network occurs at higher temperatures. When this occurs, the hydrogen donor solvent has easy access to the depolymerizing coal.

The conversion yeilds at 437°C in naphthalene are similar to that with tetralin at 350°C. This observation is not surprising since Neavel²⁴ obtained 27% benzene solubles after reacting 78 %daf coal with naphthalene at 400°C. At this temperature, repolymerization of the radical coal molecules resulted in the low conversion data. Naphthalene only serves as a hydrogen shuttler since no hydronaphthalenes were formed from the G.C. trace of the reaction products.

The hydrogen transfer data (Tables 6 and 7) at 350°C are fairly constant irrespective of the solvent to coal ratio used. At higher temperatures, 385°C, a three fold increase in hydrogen transfer is observed irrespective of the donor solvent and the solvent to coal weight ratio used. Though tetralin and 2-t-butyltetralin have essentially identical hydrogen donor abilities, hydrogen donation

Table 6: Pyridine Solubility Data in 5 mL minibombs

<u>Donor Solvent</u>	<u>Solvent:Coal Ratio (g/g)</u>	<u>Temp. /°C</u>	<u>% Pyridine Soluble (Residue based)</u>	<u>% H, per daf Coal</u>
NS	-	25	28	-
NSL	-	357	28	-
Tetralin	3.8	350	55	0.17
Tetralin	3.9	350	57	0.16
2-t-BuT	5.4	350	-	0.13
2-t-BuT	5.5	350	74	0.14
Tetralin	5.3	350	51	0.16
Tetralin	5.3	350	54	0.16
2-t-BuT	5.7	350	48	0.16
2-t-BuT	6.3	350	49	0.15
Tetralin	3.9	385	82	0.45
2-t-BuT	5.4	385	75	0.46
2-t-BuT	5.9	385	76	0.44
Cis-Decalin	6.3	382	51	-
Cis-Decalin	6.2	382	45	-
Cis-Decalin	6.7	382	44	-
Cis-Decalin	6.1	382	48	-
Naphthalene	3.7	437	63	-
Naphthalene	3.3	437	53	-
Naphthalene	3.5	437	54	-
Naphthalene	3.6	437	54	-

NS No Solvent, only extraction.

NSL Liquefaction without Solvent

by 2-t-butyltetralin during liquefaction, is expected to be lower since tertiary butyl groups are known^{17, 24-26} to sterically hinder penetration into the coal macromolecular network. Table 7 also shows that at a specified temperature, identical amounts of hydrogen transfer are obtained by either solvent. One possible explanation for the identical hydrogen transfer and liquefaction yields is that tetralin and 2-t-butyltetralin are equally effective at donating hydrogen to the depolymerizing coal. This is true in these sets of experiments. Hydrogen donation in liquefaction must be external. In other words hydrogen donation by a donor solvent occurs after the coal molecules have been thermally broken down.

Table 7: Donor Solvent Recovery by G.C. (mole %) and % H₂ Transfer Data.

<u>Coal:Solvent</u> <u>Ratio (g/g)</u>	(Product Recovery -mole %)				<u>%H₂/daf</u> <u>Coal</u>
	<u>Tetralin</u>	<u>Naph[*]</u>	<u>2-t-BuT^{**}</u>	<u>2-t-BuNaph^{***}</u>	
3.9 ^d	96.6	1.16	-	-	0.17
3.8 ^d	95.9	1.20	-	-	0.16
5.4 ^e	0.18	-	83.9	0.92	0.13
5.5 ^e	0.14	-	90.1	0.98	0.14
5.3 ^d	89.3	0.86	-	-	0.16
5.3 ^d	88.8	0.86	-	-	0.16
5.7 ^e	0.12	-	95.1	0.97	0.16
6.3 ^e	0.14	-	95.5	1.11	0.15
3.9 ^f	89.5	3.20	-	-	0.45
5.9 ^g	0.08	-	85.4	3.14	0.46
5.4 ^g	0.18	-	85.9	3.19	0.44

- * Naph - Naphthalene
 ** 2-t-BuT - 2-t-butyltetralin
 *** 2-t-BuNaph - 2-t-butyl-naphthalene
 d Reaction at 350°C in Tetralin
 e Reaction at 350°C in 2-t-butyltetralin
 f Reaction at 385°C in Tetralin
 g Reaction at 385°C in 2-t-butyltetralin

Swelling of Ill#6 Coal with Tetralin and 2-t-butyltetralin

The swelling of Illinois #6 coal in tetralin and 2-t-butyltetralin at several temperatures is shown in Fig. 9 and Fig 10. The swelling of Ill#6 coal with tetralin is greater than with 2-t-butyltetralin, except for the coal swelling experiment done at ambient temperature. At room temperature a greater swelling ratio is obtained with 2-t-butyltetralin than with tetralin.

At 50°C and 100°C, the swelling of Ill#6 coal with tetralin has a swelling ratio of 1.2 whereas that with 2-t-butyltetralin has a swelling ratio of 1.1. Equilibration is reached at about the 8th day and the swelling of Ill#6 coal with tetralin was always higher than with 2-t-butyltetralin. This supports the trend of slightly higher conversions in tetralin than in 2-t-butyltetralin. The steric effects due to the branched 2-t-butyl group is clearly observed at these swelling temperatures.

The coal swelling tubes that had equilibrated at room temperature and at a 100°C were used for the swelling experiments conducted at 150°C (Fig. 10). At 150°C, equilibration was achieved at about the third day in either solvents. In all cases and at 150°C, swelling with 2-t-butyltetralin was less than tetralin. At 150°C, the average swelling ratio obtained was 1.3 with tetralin and 1.2 with 2-t-butyltetralin, showing decreased swelling ratio with the bulky solvent. Though the differences between swelling with tetralin and butyltetralin are not large, swelling at 150°C shows steric

hinderance by the 2-t-butyl group.

The swelling results observed in 2-t-butyltetralin are interesting since they indicate penetration to some extent by the bulky non-polar 2-t-butyltetralin, especially, at higher temperatures.

The swelling results nonetheless do show that 2-t-butyltetralin penetrates the coal to a lesser extent than tetralin.

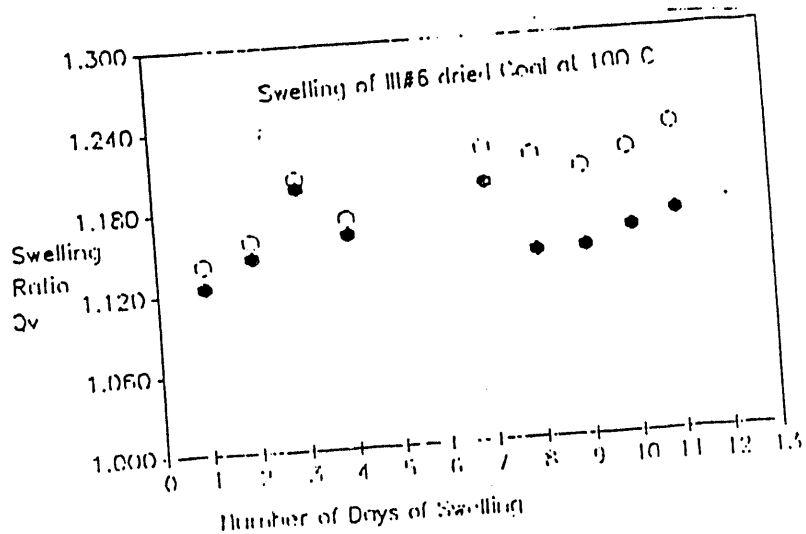
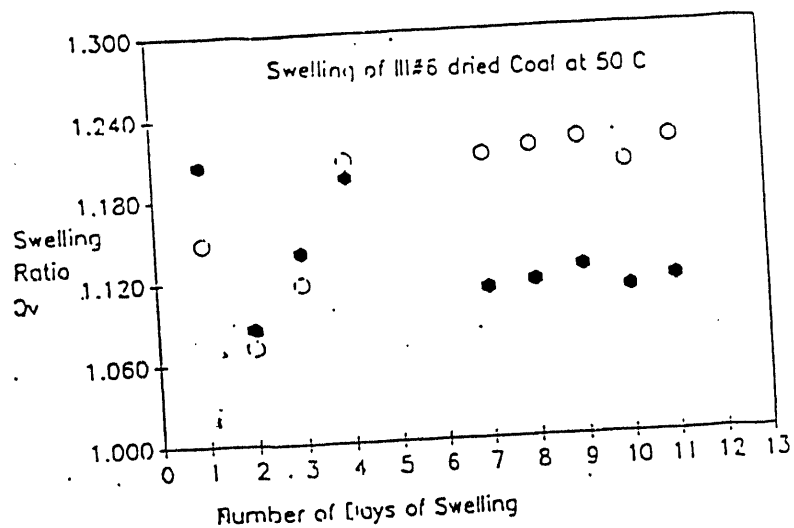
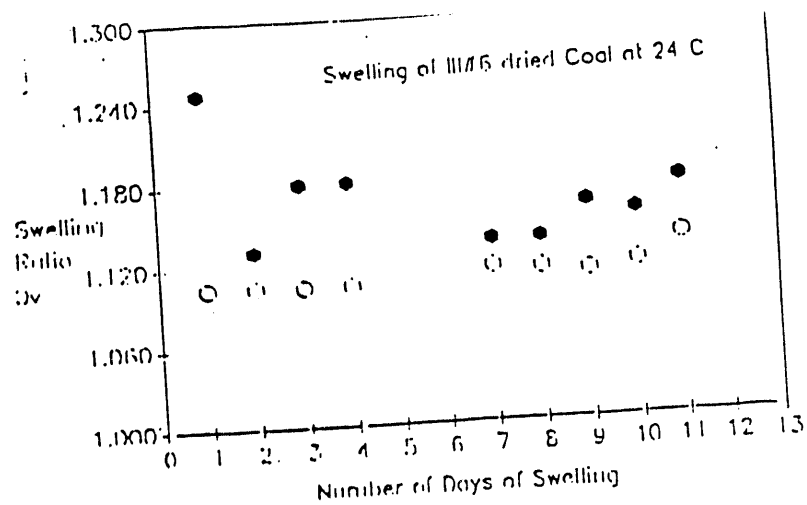
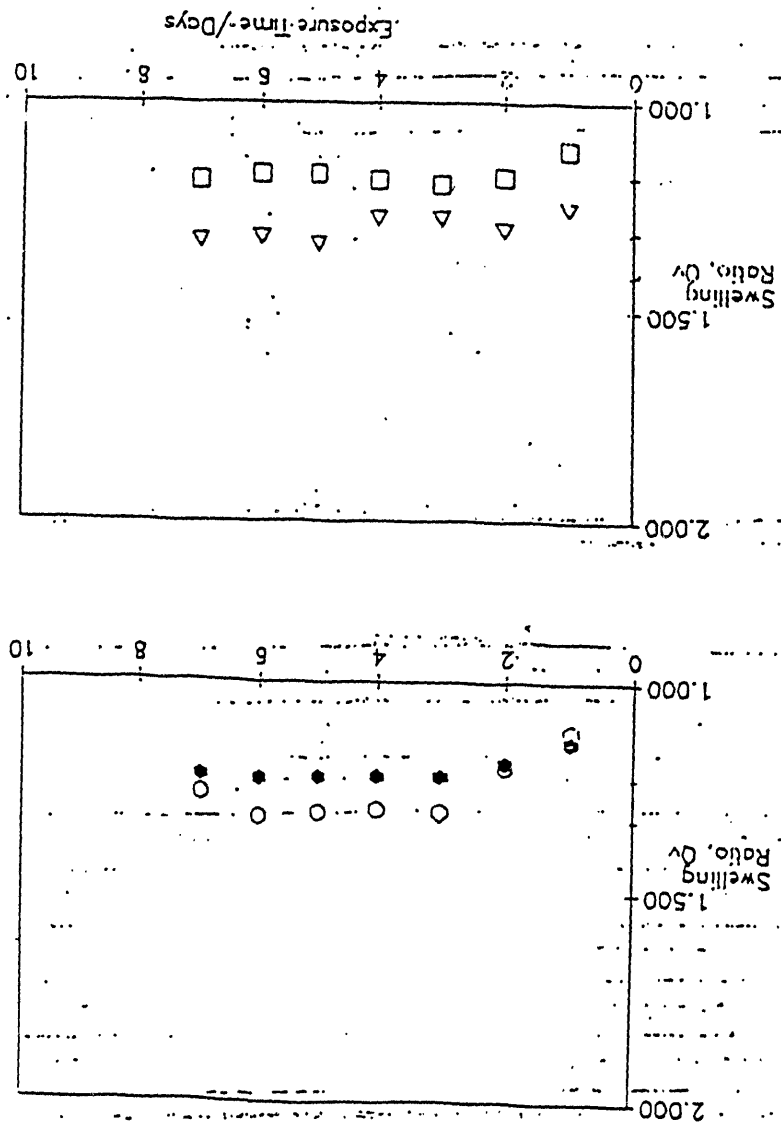


Fig. 9. Swelling of Ill#6 Coal at 24°C, 50°C and 100°C

(○) Tetralin
(●) 2-t-Butyltetralin

Fig. 10. Swelling of ILL#6 coal at 150 °C

Swelling from room temperature in Tetralin (\diamond), in 2-E-Buyltetralin (\bullet)
 Swelling from 100°C in Tetralin (\triangle), in 2-E-Buyltetralin (\square)



Conclusions:

At varying solvent to coal ratios, conversion to pyridine solubles in tetralin and butyltetralin are slightly higher for tetralin than for 2-t-butyltetralin. Higher temperatures enhance the conversion yields and subsequently increase the %H₂ transferred per daf coal. Also, the amount of hydrogen transferred at a particular temperature are similar. This demonstrates that similar amounts of hydrogen transfer occur when 2-t-butyltetralin, or tetralin is used as donor solvent in the liquefaction experiments.

The swelling data indicates that 2-t-butyltetralin penetrates coal to a lesser extent than tetralin. The steric effects are clearly evident. The mechanism of hydrogen donation to the coal must be external, that is the coal macromolecular structure must break apart before abstracting hydrogen from the solvent.

The above experiments show that hydrogen donation by tetralin and 2-t-butyltetralin are strikingly similar in the coal liquefaction studied. The coal swelling experiments suggest discrimination against the branched 2-t-butyltetralin. External hydrogen donation is therefore important in the liquefaction experiments studied.

Recommendations

Further work to support the mechanism of external hydrogenation during liquefaction are the following:

I. Tetralin and 2-t-butyltetralin should be used to hydrogenate benzophenone to determine their relative hydrogen donor abilities.

II. Additional donor solvents like Pyrene, and tert-Butylpyrene should be used in liquefaction experiments to determine differences in conversion yields and %H₂ transfer/daf coal.

III. The coal used must be swollen at the liquefaction temperatures employed to determine exactly whether the coal absorbs either solvents to a similar extent.

IV. Sequential solvent extraction in cyclohexane, toluene and pyridine should be used to remove the donor solvent from the depolymerized coal products to give better conversion data.

REFERENCES:

1. Zimmerman, E. R.; in Evaluating and Testing the Coking Properties of Coal, Miller Freeman Publications Inc., San Francisco (1979) 11 - 15
2. Hershkowitz F., in Chemistry of Coal Conversion, Scholsberg R.A. Ed., Plenum Press, New York (1985), 45 - 57
3. Van Krevelen, D.W. Coal, 2nd Ed. Reprint, Elsevier Scientific Publishing Co. New York NY (1981)
4. Joseph T. J.; Fisher, R. B.; Masin C. A.; Energy and Fuels (1991) 5, 724 - 729
5. Fillo, J. P.; Craun, J. C.; Later, D. W.; Wilson B. W.,; Haugen, D. A.; in Toxicology of Coal Conversion Processing, Gray, Druker and Massey, Ed. Wiley and Sons, New York (1988), 13 - 470
6. Stephans H. P. and Kottenstette, R. J.,; Fuel (1991), 70, 386 - 392
7. Haggin, J. Chem. Eng. News, 60 (1982) 17 - 26
8. Heredy, L. A. and Wender, I.; Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem. 25, (1980), 38 - 45
9. Shin, J. H.; Fuel 63 (1984) 1187 - 1196
10. Brenner, D. Fuel 64 (1985), 167 - 173
11. Larsen, J. W. and Shawver, S. Energy & Fuels 4, (1990), 74 - 77
12. Larsen, J. W. and Mohammidi, M., Energy and Fuels 4, (1990), 107 - 110
13. Larsen, J. W., Green K. T., Kovak, J.; J. Org. Chem., 50, (1985), 4729 - 4735
14. Quinga, M. Y. E. and Larsen, J. W.; Energy and Fuels 1, (1987), 300 - 304
15. Given A. P.; in Coal Science Gorbaty, M. L., Larsen J. W., Wender, I.; Editors. Academic Press Inc. NY (1984), 179-180
16. Gorin E.; Seymore, B.; Wolk, R.H.; in Chemistry of Coal Utilization Elliot, M. A. Ed. (1981), 1845 -1930
17. Snape, C.E. Fuel (1991), 70, 285 - 288

18. Whitehurst, D. D.; Farcasiu M.; Mitchell, O. T.; Lin, N. H.;
in Coal Liquefaction: The Chemistry and Technology of Thermal Processes, (1980) 1 - 370
19. Ouchi, K. and Gorbaty, M. L.; Coal Structure Ed. (1981), 37-288
20. Aida, T.; Fuku, M.; Energy Fuels (1991), 5, 79 - 83
21. Larsen, J. W.; Gorbaty, M. L. et al., Editors. Coal Science
Academic Press Inc., (1983), 2, 65 - 120
22. Hessley, K. R.; Reasoner, J. W.; Riley, T. J. Coal Science,
An Introduction to Chemistry and Technology and Utilization.
Wiley Interscience, NY. (1986) 137 - 214
23. Buchanan, A. C.; Dunstan, D. J.; Douglas, C. E.; Poustma, M.
L.; J. Am. Chem. Soc. 108, (1986), 7703 - 7715
24. Neavel, R. C., Fuel (1976), 55, 237 - 241
25. Ouchi, K.; Makabe, M.; Yoshimoto I.; Fuel, 63, (1984),
449 - 452
26. Skowronski, R. P.; Ratto, J. J.; Goldberg, I. B.; Heredy, A.
L.; Fuel (1984) 63, 440 - 448
27. Fowkes, F. M.; Llyodd, T. B.; Jones, K. L. ; Energy Fuels
(1989), 3, 97
28. Larsen J. W.; Lee, D. Fuel (1985), 64, 981
29. Barr-Howell, B. D.; Howell, J. M.; Peppas, N.; Energy Fuels
(1987), 1, 181
30. Katritzky, R. A.; Lapucha, R. A.; Franz, J. F.; Musumarra, G.;
et. al. Tetrahedron Computer Methodology (1989), 2, 17 - 36
31. Larsen, J. W.; and Lapucha, R.A.; Quarterly Report DE-AC22-
89PC89883 (January 1992, March 1992) Also, Larsen, J. W.;
Yamada, O. ; Azik, M.; Quarterly Report DE- FG22-87PC79926
32. Kirkland, J. J.; Yon, W. W.; Bly, D. D.; Modern Size-Exclusion
Liquid Chromatography J. W. & Sons (1979), 8
33. Billmeyer, F. W.; TextBook of Polymer Science 2nd. Ed. J.W. &
Sons (1971), 78
35. Perring D. D.; Armargo W. L. F.; and Perring D. R.
Purification of Laboratory Chemicals, Pergamon Press, New
York. (1966)

36. Whitmore, F. C.; Holden W. J.; J. Am. Chem. Soc. (1943), **65**, 2088 - 2092
37. Vorres, S. K.; Users Handbook for the Argonne Premium Coal Sample Program. (10/89), 11
38. Korda, A. and Larsen, J.W. Quarterly Report DE-FG22-87PC79926-12
39. Karr, C.Jnr.; Analytical Methods For Coal and Coal Products Academic Press, New York (1978), 556 - 568
40. Furniss, B.S.; Hannaford, A.J.; Rogers V.; et. al. Vogel's Textbook of Practical Organic Chemistry 4th edition. Longman London and New York. (1986), 132
41. Yamada, O. and Larsen, J. W. Quarterly Report DE-FG22-87PC79926-9
42. Awadalla, A. A.; Cookson, D. J.; Smith, E. B.; Fuel (1985), 1097 - 1107
43. Ouchi, K; Satoshi, I; Masataka, M; Hironori, I. International Conference on Coal Science (1987), **11**, 363
44. Nishioka, M.: Fuel (1991), **70**, 1413
45. Damberger, H. H.; Harvey, R. D.; Ruch, R.R.; Thomas J.; in The Science and Technology of Coal and Coal Utilization Cooper, B.R., and Ellingson, W.A., Editors, Plenum Press NY (1984), 22 - 30
46. Nishioka, M. Fuel (1992), **71**, 941 - 948
47. Peppas, N. A.; Lucht, L. M.; Hooker, D. T.; Ind. Eng. Chem. Fundam. (1986), **25**, 103 - 108
48. Larsen J.W.; Kovac, J.; Green, T. K.; Fuel (1984), **63**, 935 -938
49. Vlieger ,J.; Gelan, J : Franco, D.; Macjchrowicz, B; Fuel (1989), **68**, 696
50. Ouchi, K.; Makabe, M.; Itoh, H.; Ohe, S.; Fuel (1985), **64**, 1108 - 1111

APPENDIX

Data in the appendix of this report represent the liquefaction experiment results of the 22 mL autoclaves. These experiments were not reproduced.

Appendix A

Only one set of experiments were done at each temperature, and the amounts of reactant the reactor were small. This may have caused mixing problems in the reactors. The data however shows that at constant solvent to coal ratio, coal conversions to pyridine solubles increased when the temperature was raised from 350 - 400°C. This observation implies that tetralin is better able to donate its hydrogen to the radically formed coal faster than 2-t-butyltetralin does. This is also consistent with the mass transfer effects expected since the less bulky donor solvent, tetralin is better able to reach the rapidly forming radicals.

Table 8: Data on Pyridine Soluble Argonne Premium Ill#6 Coal in 22mL Autoclaves

<u>Solvent</u>	<u>Ill#6 Coal</u> <u>/g</u>	<u>Solvent</u> <u>/mmol</u>	<u>Solvent</u> <u>/Coal(g/g)</u>	<u>Rxn. Temp.</u> <u>/°C</u>	<u>% Pyridine</u> <u>Solubles</u>
Tetralin	1.06	16.0	2.0	350	45
	1.02	16.0	2.0	377	66
	1.05	18.0	2.3	400	78
2- <u>t</u> -BuT*	1.07	16.0	2.8	350	35
	1.02	16.0	2.8	377	52
	1.07	18.0	3.2	400	82
2- <u>t</u> -BuT*	2- <u>t</u> -Butyltetralin				

Appendix B

The hydrogen transfer data in Table 9 show a greater amount of hydrogen transfer when 2-t-butyltetralin is used than when tetralin is used as donor solvent. This set of data is conflicting with the pyridine solubility data in Table 8.

Table 9: G.C. conversion and % hydrogen transfer data mole% for reactions in 22mL Autoclaves.

<u>Rxn Temp</u> <u>/°C</u>	<u>Tetralin</u>	<u>Naphthalene</u>	<u>2-t-BuT</u>	<u>2-t-BuNaph</u>	<u>%H/daf</u> <u>Coal</u>
<u>A: Tetralin as Solvent</u>					
350	89.4	3.21	-	-	0.23
377	82.9	6.21	-	-	0.46
400	77.2	9.31	-	-	0.74
<u>Rxn Temp</u> <u>/°C</u>	<u>Tetralin</u>	<u>Naphthalene</u>	<u>2-t-BuT</u>	<u>2-t-BuNaph</u>	<u>%H/daf</u> <u>Coal</u>
<u>B. 2-t-Butyltetralin as solvent</u>					
350	0.49	-	92.7	3.80	0.26
377	0.50	-	94.3	7.50	0.56
400	0.49	-	79.6	12.9	1.00

Appendix C

The molecular weight distribution data indicates that higher temperatures yield higher weight and number average molecular weight species. The number of bonds broken are similar at each temperature, except at 400°C with tetralin as donor solvent.

Larger amounts of pyridine solubles are observed at increasing temperatures.

Table 10: Molecular Weight Distribution, Pyridine Solubility and %H₂ Transfer Data for reactions done in 22mL Autoclaves

<u>Rxn Temp</u> <u>/°C</u>	<u>Mw</u>	<u>Mn</u>	<u>Mw/Mn</u>	<u>%Pyridine</u> <u>Soluble</u>	<u>%H₂/daf</u> <u>Coal</u>
<u>Tetralin as Donor Solvent</u>					
350 (Fig.11) ^h	5600	1340	4.18	45	0.23
377 (Fig.13) ^h	32,900	7400	4.48	66	0.46
400 (Fig.15) ^h	97,100	35,400	2.74	78	0.74
<u>2-t-butyltetralin as Donor Solvent</u>					
350 (Fig.12) ^h	14,100	3190	4.42	35	0.26
377 (Fig.14) ^h	18,900	3980	4.74	52	0.56
400 (Fig.16) ^h	83,700	19,200	4.37	82	1.00

The molecular weight distribution graphs are presented on page 59 to page 66.

Appendix D

Pyridine solubility is enhanced with increased reactant amounts. The molecular weight distribution data and the pyridine solubility data are enhanced

Table 11: Molecular Weight Distribution on the Degree of Filling of 22 mL Autoclaves at 350°C

<u>Solvent</u> <u>: Coal (g/g)</u>	<u>Coal</u>	<u>Mw</u>	<u>Mn</u>	<u>Mw/Mn</u>	<u>%PS</u>	<u>%H/daf</u> <u>coal</u>
2.0 ⁱ (Fig.11)	1.06	5600	1340	4.18	45	0.23
2.0 ^j (Fig.12)	1.07	14,100	3100	4.42	35	0.23
2.0 ⁱ (Fig 17)	3.00	54,900	8000	6.86	51	0.26
2.0 ^j (Fig.18)	3.03	79,900	16,000	5.01	41	0.23

%PS - % Pyridine soluble
i - Solvent is Tetralin
j - Solvent is 2-t-butyltetralin

$M_n = 1340.0678$
 $M_w = 5602.3213$
 $M_w/M_n = 4.1806$

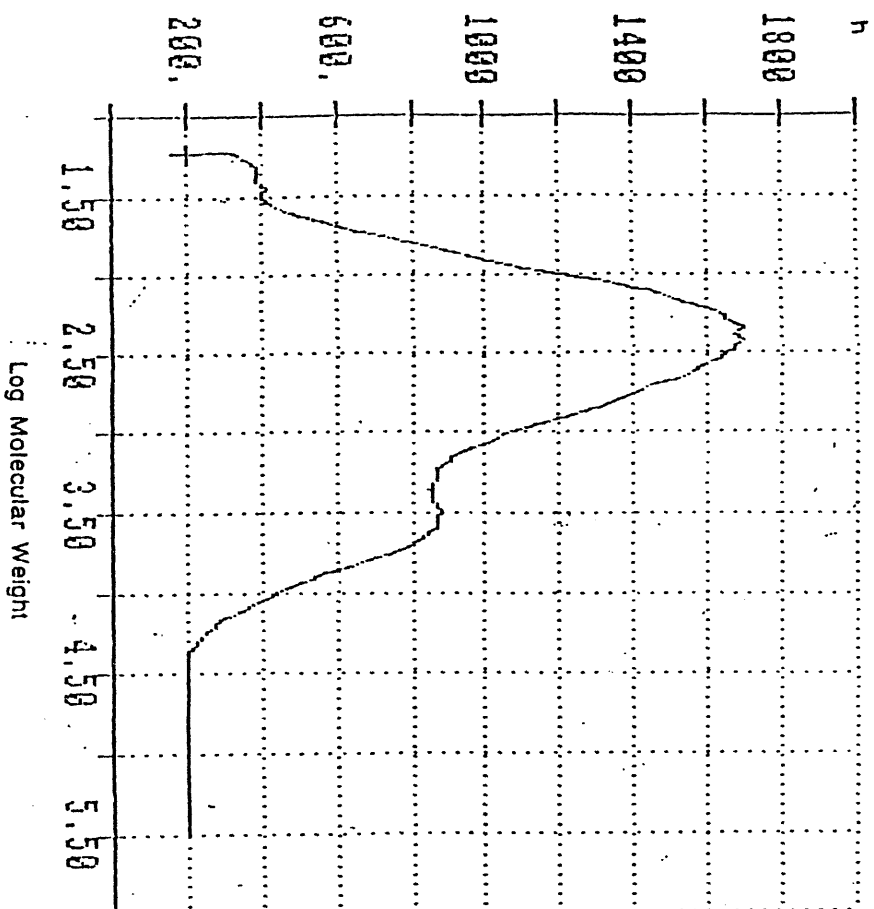


Fig. 11 Gel Permeation Chromatograph- Molecular Weight Distribution
 of Pyridine Extract #1

Mn=
3193.4463
Mw=
14143.0928
Mw/Mn=
4.4288

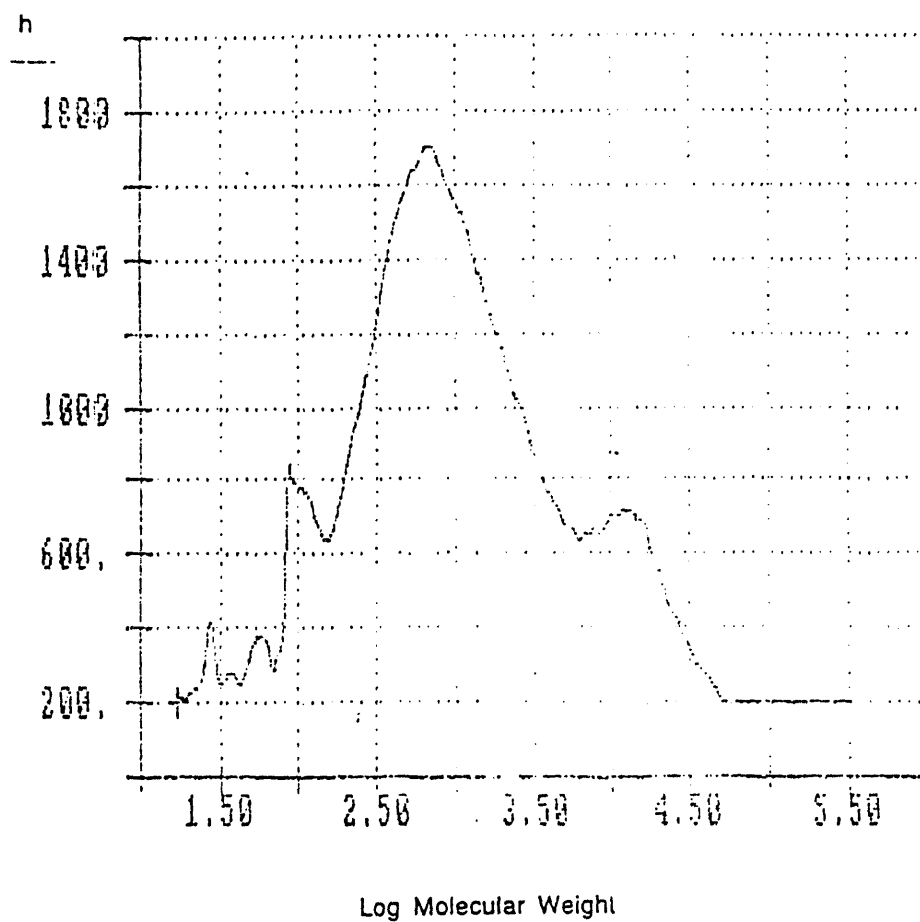


Fig. 12 Gel Permeation Chromatograph- Molecular Weight
Distribution of Pyridine Extract #2

$M_n = 7353.1562$
 $M_w = 32916.6508$
 $M_w/M_n = 4.4765$

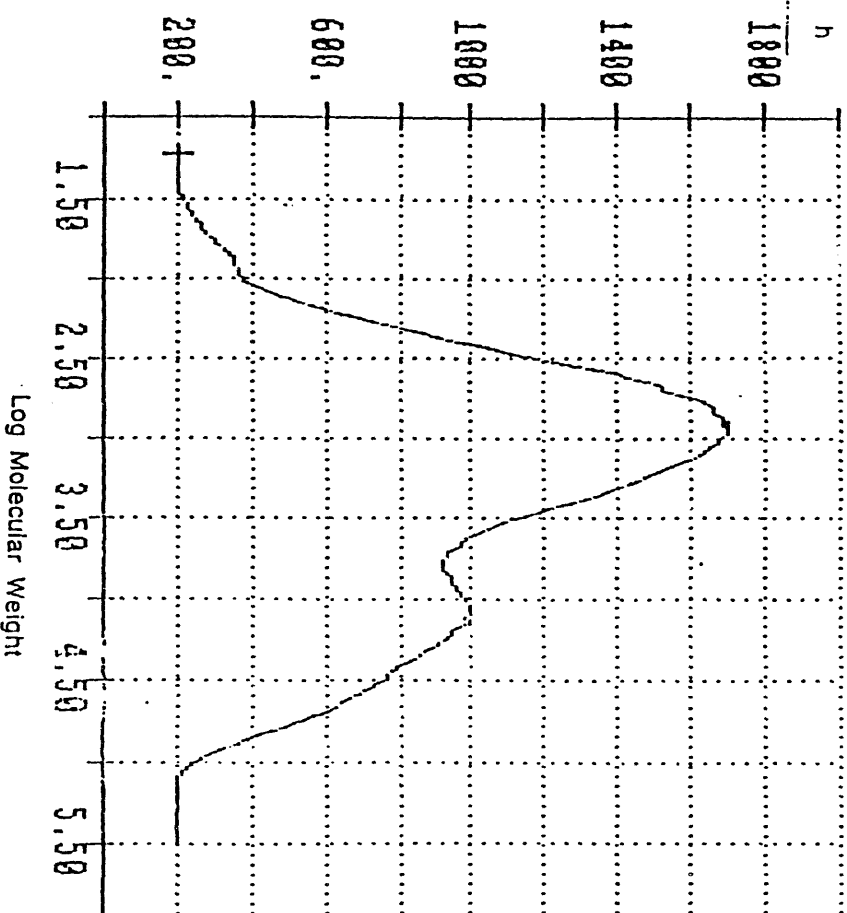


Fig. 13 Gel Permeation Chromatograph- Molecular Weight Distribution
 of Pyridine Extract #3

$M_n = 3980.5249$
 $M_w = 18864.0059$
 $M_w/M_n = 4.7391$

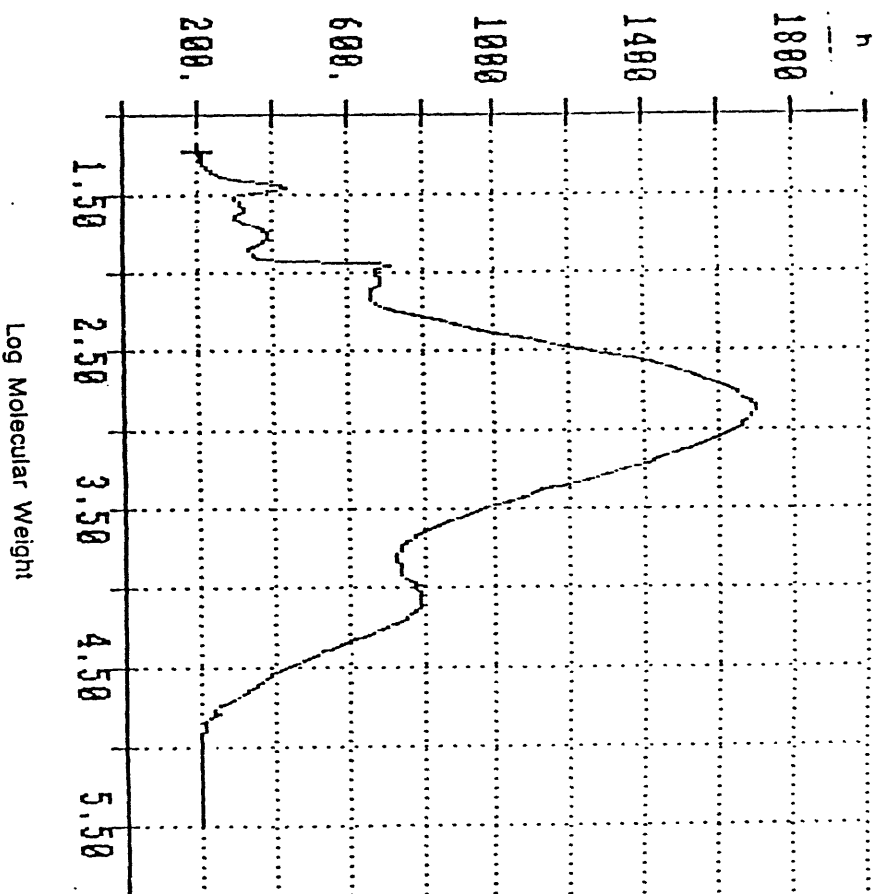


Fig. 14 Gel Permeation Chromatograph- Molecular Weight Distribution
 of Pyridine Extract #4

$M_n =$
 35449.7578
 $M_w =$
 97136.2656
 $M_w/M_n =$
 2.7401

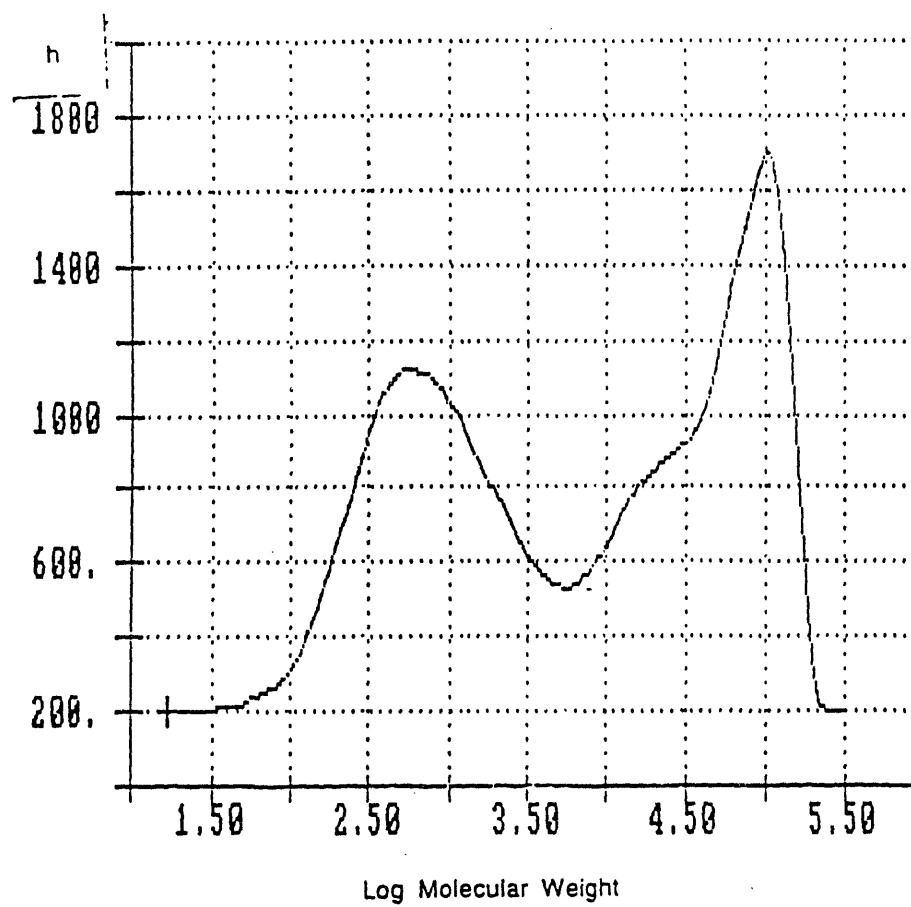


Fig. 15 Gel Permeation Chromatograph- Molecular Weight Distribution
 of Pyridine Extract #5

$M_n = 19154.5039$
 $M_w = 83710.9156$
 $M_w/M_n = 4.3703$

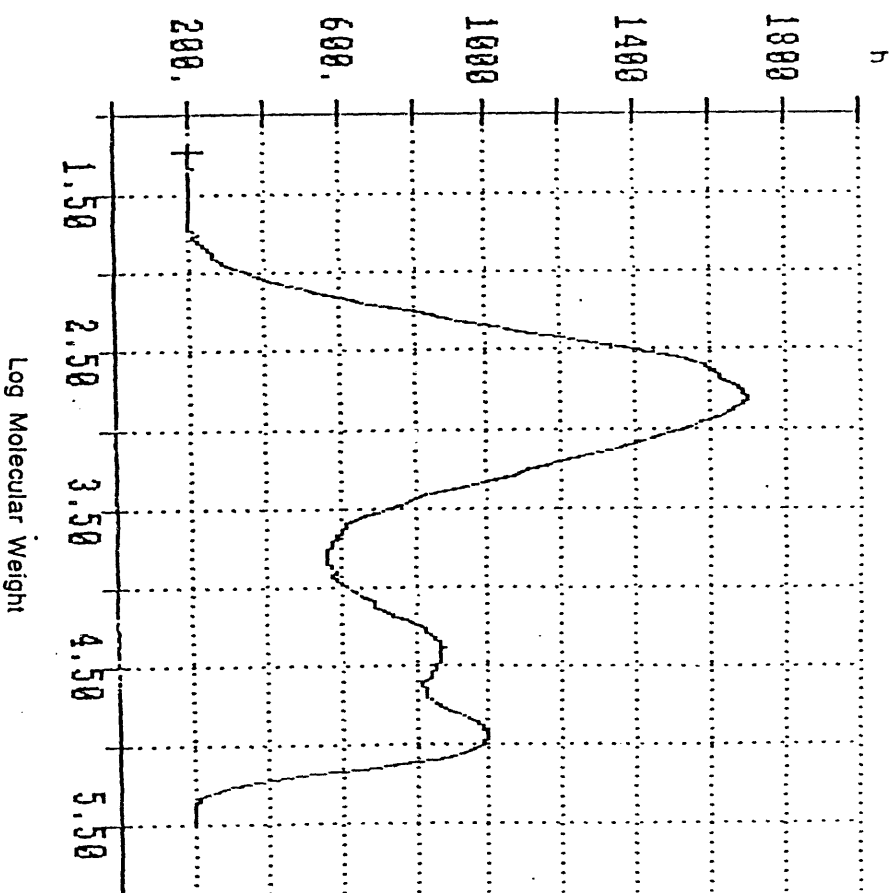


Fig. 16 Gel Permeation Chromatograph - Molecular Weight Distribution of Pyridine Extract#6

Mn=
8003.8325
Mw=
54888.0859
Mw/Mn=
6.8577

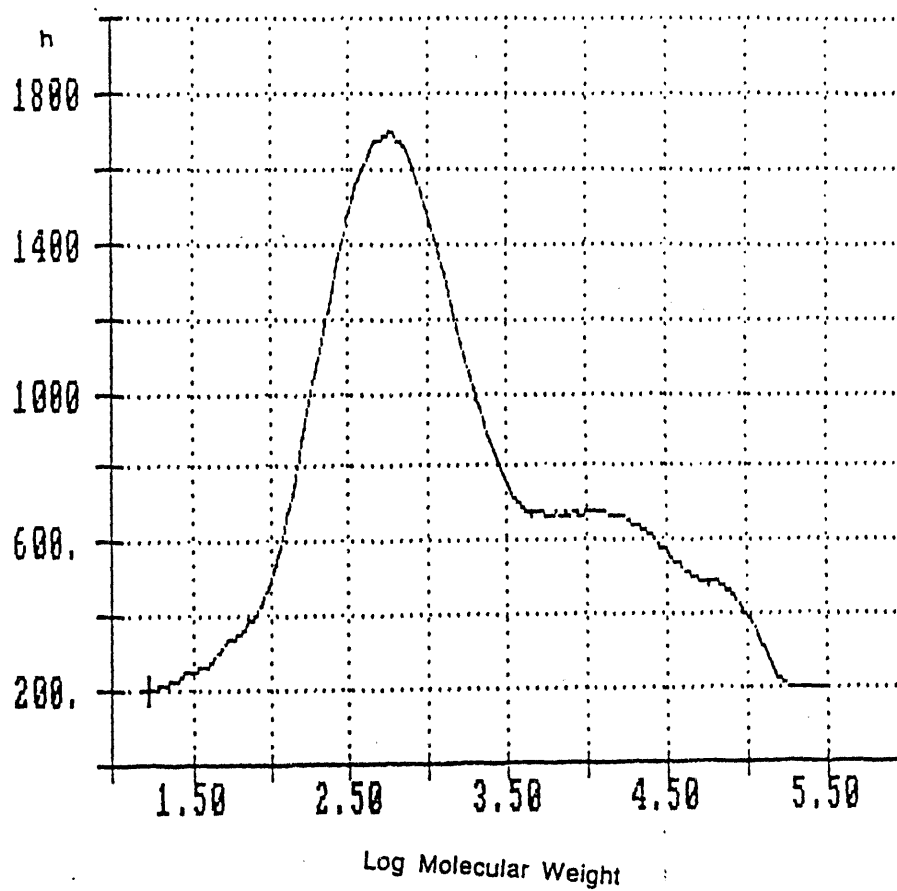


Fig. 17 Gel Permeation Chromatography - Molecular Weight Distribution of Pyridine Extract #7

$M_n = 15966.3799$
 $M_w = 79924.4862$
 $M_w/M_n = 5.0058$

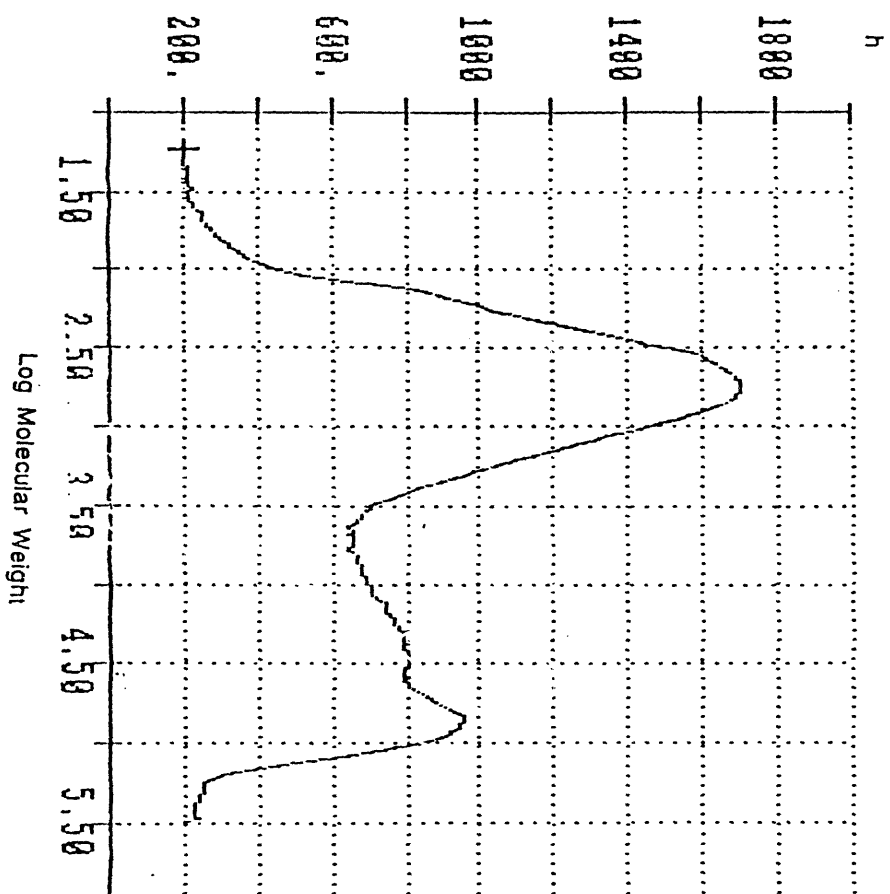


Fig. 18 Gel Permeation Chromatograph - Molecular Weight Distribution of Pyridine Extract #8

Appendix E: Calculation of Solvent Incorporation for 5ml minibomb:

Elemental Analysis of Liquefaction Products carried out
at 350°C (Wt%)

<u>Coal Sample</u>	<u>Coal Balance</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>
Whole Dried Coal ³⁷		65.65	4.23	1.16
DAF Coal ³⁷		77.67	5.00	1.37
Tetralin Extract (101%)		77.40	5.52	1.48
2- <u>t</u> -BuT** Extract (159%)		85.40	7.93	<0.5
2- <u>t</u> -BuT** Residue (159%)		66.21	5.01	1.38

From Table 5:

Appendix E: Elemental Analysis of Liquefaction Products carried out
at 350°C (mole%).

<u>Coal Sample</u>	<u>Coal Balance</u>	<u>%C</u>	<u>%H</u>	<u>%N /10⁻²</u>	<u>H:C Ratio</u>
Whole Dried Coal ³⁷		5.47	4.23	8.29	0.77
DAF Coal ³⁷		6.47	5.00	9.79	0.77
Tetralin Extract (101%)		6.45	5.52	10.6	0.86
2- <u>t</u> -BuT** Extract (159%)		7.12	7.93	<3.57	1.11
2- <u>t</u> -BuT** Residue (159%)		5.52	5.01	9.86	0.91

Appendix E:

Calculation of Solvent Incorporation for 5mL minibomb experiments:

1. For the Tetralin Extract, the weight increase in Nitrogen is from the table in Appendix E is

$$\begin{aligned}\text{Weight increase in Nitrogen} &= (1.48 - 1.37) \text{ g} / 100\text{g coal} \\ &= 0.11\text{g} / 100\text{g coal}\end{aligned}$$

Therefore, the amount of pyridine incorporated is

$$\begin{aligned}\frac{(0.11\text{g Nitrogen})}{(100\text{g Coal})} &\times \frac{(79\text{g pyridine})}{(14\text{g N}_2 \text{ in pyridine})} \\ &= \underline{0.62\text{g pyridine} / 100\text{g coal}}\end{aligned}$$

The weight increase in hydrogen from the pyridine will therefore be

$$\begin{aligned}\frac{(0.62 \text{ g pyridine})}{(100\text{g coal})} &\times \frac{(5 \text{ g hydrogen})}{(79 \text{ g of pyridine})} \\ &= 0.039\text{g H}_2 \text{ from pyridine} / 100\text{g coal}.\end{aligned}$$

The weight difference in hydrogen of the tetralin extract is

$$(5.52 - 5.00)\text{g} = 0.52\text{g} / 100\text{g of coal}.$$

If the amount of hydrogen due to coal is 0.039g, then the weight increase of hydrogen due to tetralin is

$$(0.52 - 0.039)\text{g} = 0.481\text{g of H}_2 / 100\text{g coal}$$

Therefore weight of tetralin per 100 g of coal is

$$\begin{aligned}\frac{(0.481\text{g H from tetralin})}{(100\text{g coal})} &\times \frac{(132 \text{ g tetralin per mol of tetralin})}{(14 \text{ g of H}_2 \text{ per mol of tetralin})} \\ &= \underline{4.5 \text{ g of tetralin per 100g coal.}}\end{aligned}$$

Appendix E:

Calculation of Solvent Incorporation for 5mL minibomb experiments:

2. All residue contain all ash. Therefore, the weight increase in nitrogen of the 2-t-butyltetralin residue comes from nitrogen comes from pyridine. From Appendix E, the whole dried coal, and the 2-t-butyltetralin residue data,

$$\begin{aligned}(1.38 - 1.16)\text{g} &= 0.22\text{g wt. N}_2 / 100\text{g coal.} \\ 14 \text{ g of N}_2 \text{ is equivalent to} & 0.22\text{g wt. N}_2 / 100\text{g coal} \\ \text{Therefore 79g of pyridine} &= \frac{0.22 \times 79}{14} \\ &= \underline{1.24\text{g of pyridine} / 100\text{g coal.}}\end{aligned}$$

3. The weight increase in carbon of the 2-t-butyltetralin extract when compared to the dry ash free coal shows the following:

$$\begin{aligned}\text{Weight increase in MAF coal} &= (85.40 - 77.67) \text{ g carbon} \\ &= 7.73\text{g increase in C/ 100g coal}\end{aligned}$$

Therefore, the amount of 2-t- butyltetralin in the coal extract is

$$\begin{aligned}&\frac{(7.73\text{g Carbon})}{(100 \text{ g coal})} \times \frac{(188 \text{ g 2-t-BuT/mol of 2-t-BuT})}{(168\text{g C in 1 mole of 2-t-BuT})} \\ &= \underline{8.65\text{g 2-t-BuT/ 100g of coal}}\end{aligned}$$

The amount of Nitrogen incorporated into the 2-t-butyltetralin residue is very small from the data above.

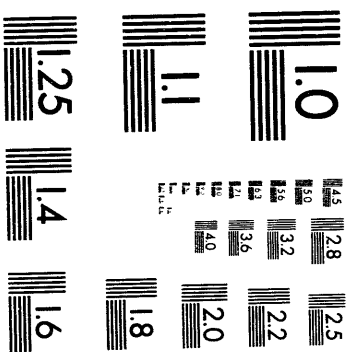
that stabilize the dissolved coal-derived residuum, (iii) hydrogen attack to form distillable hydrocarbons and to remove heteroatoms from the depolymerizing coal, and (iv) rehydrogenation by addition of hydrogen to the donor solvent molecules (Scheme 1.).⁵

Much of the initial coal dissolution occurs in the slurry preheater.^{6,16-18} Dissolution of the coal proceeds first by the cleavage of the most labile bonds in coal. Bond thermolysis results in hydrogen transfer from H₂ or from the donor solvent to the coal free radicals.^{2,4} Ouchi¹⁹ and Aida²⁰ have speculated that donor solvents rapidly diffuse into the coal particle and that the hydrogen transfer reactions take place between the solvent and the radical species within the coal itself. The donor solvent enters the coal particle to provide a source of free radicals generated thermally within the coal matrix. At temperatures on the order of 400°C, thermally induced bond cleavage breaks up the crosslinked macromolecular framework. Bond breaking occurs at significant rates near 400°C generating free radicals by bond fission.²⁰⁻²²

Hydrogen shuttling, hydride transfer, pericyclic and chain reactions have been postulated as possible pathways to the fragmentation of coal during liquefaction^{18,23}. But to a large extent, hydrogen donors have been postulated to convert the radical centers to stable-end groups. These reactions yield coal solids, liquids and gases of modest molecular weight.

SECTION III

The Effect of Coal Conformation Change on Conversion in Tetralin



2 of 2

Abstract

When warmed at 115° in chlorbenzene, Illinois No. 6 coal undergoes a conformational rearrangement. Similar structure changes occur during pyridine extraction. Both warming in chlorobenzene and pyridine extraction decrease conversion of this coal to pyridine extractables when it is heated in tetralin.

Conformational rearrangements of the organic portion of Illinois No. 6 coal caused by mild solvent treatment sharply reduce its reactivity with tetralin at 350°C. Illinois No. 6 coal was heated in tetralin (N₂ atmosphere) at 350°C for periods of up to 1 hour and its conversion to pyridine extractable material was measured. The conversion data were compared with the results of analogous reactions of the pyridine extract and of the insoluble extraction residue. Pyridine extraction is known to cause conformational rearrangements.¹ The conversion of the whole coal was significantly (between 10% and 20%) greater than the sum of conversions of the extract and the residue. Another sample of Illinois No. 6 was heated in chlorobenzene for 300 hr at 115°C, conditions known to induce conformational rearrangements within coals.² Subsequent reactions of this rearranged coal with tetralin at 350°C gave significantly lower conversions to pyridine solubles than did the whole coal. For shorter reaction times, the conversions were the lowest of the three systems and were as much as 25% less than those of the unaltered coal.

A number of different experimental approaches have shown that coals undergo conformational rearrangements when exposed to solvents. Brenner demonstrated that rapid rearrangements occur in coal thin sections swollen with THF.³ Hsieh and Duda showed that diffusion rates were sensitive to the previous exposure of coals to solvents.⁴ Cody and co-workers observed that the first swelling of

six coals was anisotropic and that the coals rearranged to a new shape when the solvent was removed.⁵ Two papers are directly relevant to the present work. It has been argued that extraction with pyridine causes conformational rearrangements in coals, rearrangements which result in enhanced association through increased non-covalent interactions between aromatics.¹ Evidence has also been presented that warming a coal in chlorobenzene at 115°C results in similar conformational rearrangements leading to a more highly associated, lower free energy coal.^{2,6}

The effect of these conformational rearrangements on coal reactivity is the subject of this paper. Two recent papers report the enhancement of coal liquefaction by pre-swelling with organic solvents or tetrabutylammonium hydroxide.^{7,8} Both studies used hydrogen donor solvents, H₂ atmospheres, and removal of the swelling solvents before liquefaction.^{7,8}

Illinois No. 6 coal from the Argonne Premium Coal Sample Bank was used. Dry pyridine Soxhlet extractions of previously dried coal were carried out under a slight positive pressure of dry N₂ until the solvent draining from the coal was clear and water white. The extractability of the coal was 31% (wt) measured as the weight loss of the solid. It is well known that small and variable amounts of pyridine are tenaciously retained by coals.⁹ Small amounts of pyridine added to the reactions of the whole coal with tetralin had no effect, showing that the retained pyridine does not influence the measured reactivity. Reactions were carried out in tubing bombs using 2g of coal and 4g of tetralin in dry N₂ atmospheres.

The bombs were heated at 350°C in a Techne sand bath and reached 75% of their reaction temperature in 40 sec. Vertical agitation at 220 cycles/min was used. Reaction times were measured from the moment of immersion in the hot bath. After the reaction, the bombs were rapidly cooled in a blast of cold air. Coal samples were warmed in chlorobenzene at 115°C for 300 hr. The chlorobenzene was removed under vacuum and analysis for chlorine showed that less than 0.1% (wt) of the rearranged coal was retained chlorobenzene. All handling of substrates and reaction products was performed in dry N₂ atmosphere.

The figure shows the conversion of Illinois No. 6 coal to pyridine extractables by heating in tetralin at 350°C for the indicated times. Conversion reaches a maximum of 90% after 40 minutes and then decreases to 82% after 1 hour, probably due to retrograde reactions occurring. Independently, the pyridine extract and the insoluble extraction residue were reacted under the same conditions and their independent conversions are shown. It is noteworthy that for longer reaction times, the extract undergoes retrograde reactions which decrease its pyridine extractability. The sum of conversions of these two materials, weighted by their relative amounts in the coal, is also plotted in the figure. The pyridine treated material is significantly less reactive than the unextracted coal. Also shown in the figure are conversion data for the reactions which used chlorobenzene rearranged coal as a substrate. For shorter reaction times this is the least reactive material studied. However, its conversion after 1 hour approaches

that of untreated coal.

Both pyridine extraction and chlorobenzene treatment have been reported to induce the conformational rearrangement of coals to more highly associated, lower free energy states. The data presented here demonstrate that, under the mild reaction conditions used in this work, the rearranged coal is much less reactive than the parent coal. Whether this is due to alterations in mass transfer or chemical effects is not known at present and is under active investigation. All who carry out chemical reactions on coals should be aware that exposure to solvents can have significant effects on reactivity. In a forthcoming series of papers we will be discussing the nature and thermodynamics of the conformational rearrangements of coals.

Acknowledgement: This material was prepared with the support of the U. S. Department of Energy, Grant No. DE-FG22-87PC79926. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE. We are grateful to Drs. Peter Hall and Robert Flowers for many stimulating discussions and wise suggestions.

John W. Larsen*, Murat Azik, Anna Korda
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania 18015

REFERENCES

1. Larsen, J.W.; Mohammadi, M. Energy Fuels 1990, 4, 107-110
2. Nishioka, M.; Larsen, J.W. Energy Fuels 1990, 4, 100-106
3. Brenner, D. Fuel 1985, 64, 167-173
4. Hsieh, S.T.; Duda, J.L. Fuel 1987, 66, 170-178
5. Cody, G.D.Jr.; Larsen, J.W.; Siskin, M. Energy Fuels 1990, 2, 340-344
6. Larsen, J.W., Proc. ICCS Intl. Conference on Coal Science, Tokyo, Japan 1989, Vol. 1, 9-12
7. Joseph, J.T. Fuel, 1991, 70, 139-144
8. Baldwin, R.M.; Kennar, D.R.; Nguanprasert, O.; Miller, R.L. Fuel, 1991 70, 429-433.
9. Collins, C.J.; Hagaman, E.W.; Jones, R.M.; Raaen, V. F. Fuel, 1981, 60, 359-360

Figure legend

Figure 1.

Conversion to pyridine extractables in tetralin at 350° C in an N₂ atmosphere for Illinois No.6 coal and products.

□ Pyridine extract; ○ Residue from pyridine extraction; △ Weighted sum of extract and residue; ▲ Illinois No.6 coal; ● Illinois No.6 coal heated in chlorobenzene at 115° C for 300 hr.

CONVERSION [% daf]

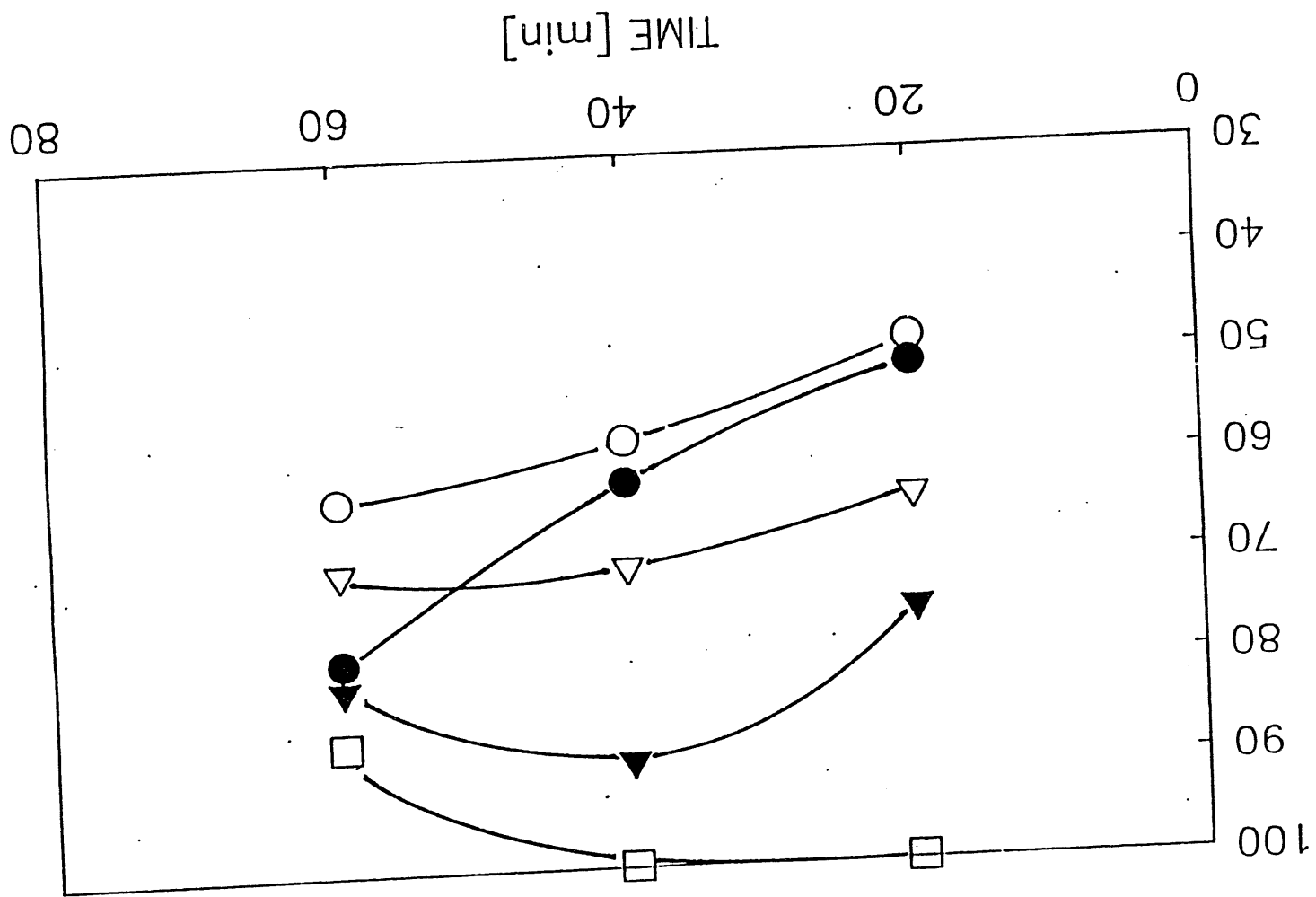


Figure 1.

DATE

FILMED

4 / 14 / 94

END

