

**CORRELATION OF COAL PROPERTIES WITH HYDROLIQUEFACTION
REACTIVITY: A BRIEF REVIEW**

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ABSTRACT

Since the earliest days of coal liquefaction processing and research, the desirability of correlation of coal properties with coal reactivity under direct hydroliquefaction conditions has been recognized by coal scientists. This article traces the history of reactivity correlations from the earliest work of Bergius through the classic work at the Bruceston Bureau of Mines during the 1940's to the most recent advances in this subject. Particular emphasis in this review is placed on an examination of the contributions of Professor Peter Given and his co-workers. Reactivity methodologies and techniques for correlation are presented and critically evaluated for utility and applicability as predictive tools.

Early Studies

The first attempts to hydrogenate coal in the laboratory were carried out by Marcelin Berthelot (1) in 1868. The results of subsequent experiments were published by Ipatiev (2) and his co-workers in 1904, in which it was demonstrated that the yield of liquids via high pressure pyrolysis of numerous organic constituents could be markedly enhanced by application of hydrogen. Emil Fischer suggested in 1912 that if coking operations were carried out in a hydrogen atmosphere, an increased yield of hydrocarbons might result. This hypothesis was later confirmed by Franz Fischer and Keller (3), who distilled a bituminous coal in hydrogen under pressure and found that the tar yield was significantly enhanced. Further research on coal hydrogenation was carried out by Fischer and his co-workers at the Kaiser-Wilhelm Institute using for the most part sodium formate and carbon monoxide in the presence of water (4).

Research which would eventually lead to the first "commercial" process for coal liquefaction was in progress as early as 1910 under the direction of Friedrich Bergius. Bergius initially studied the conversion of cellulose and peat in the presence of water, and only later turned his attention to coal. Coals were found to behave in a similar fashion, and Bergius was granted a process patent in 1914 for conversion of coal and other carbonaceous substances. Much of the work of Bergius is summarized in a document published in 1925 (5). In this paper, Bergius first describes the effect of the nature of the coal on the yield of liquid and tars from coal and states that coals

containing more than 85% carbon (d.a.f.) gave unacceptably low yields and were hence unsuitable for hydrogenation. In laboratory investigations on a series of 29 British coals of different rank (lignite through anthracite) published in 1928, Graham (6) indicated that no such arbitrary reactivity division was justified. Correlations for hydrogenation yields with coal properties were attempted by Graham using such factors as ultimate carbon, C/H ratio, C/(H-(O/8)) ratio, moisture, oxygen, and fixed carbon. All correlations were deemed to be unsuitable. Beuschleim and Wright (7) in a study of the hydrogenation of 14 U.S. coals and later Gordon (8) also reported similar findings. Francis (9) suggested that the reactivity of coal toward oxidizing agents was an excellent measure of their reactivity towards hydrogen.

Macroscopic and Microscopic Coal Constituents

Bergius stated that fusain was the most difficult of the constituents of coal to liquefy. Shatwell and Bowen (10) reported the oil yield from a sample of hand-picked fusain from bituminous coal to be negligible. Wright and Sprunk (11) microscopically analysed the residues from batch hydrogenation of several different U.S. coals, and determined the relative reactivities of the various petrographic constituents. Both Gordon (12) and Heinze (13) stressed the need for reducing the fusain content of coals processed in continuous liquefaction plants in order to minimize handling problems in the solids/liquid separations unit operations. Other studies on the effect of the macroscopic properties of coal (vitrain, fusain, clarain, durain) were reported by Shatwell and Graham (14) and Horton et al. (15), with contradictory results.

The first systematic study on the effect of the macroscopic and microscopic coal constituents on coal reactivity was conducted at the Bruceton Bureau of Mines Research Station (now Pittsburgh Energy Technology Center of the US Department of Energy). An extensive treatise on the effect of the petrographic constituents on the reactivity of coal for direct hydrogenation was published by Fisher et al. (16) in 1942. As an integral portion of this research, the behavior of individual maceral groups was determined experimentally, and a correlation developed for liquefaction reactivity. A parity plot for predicted vs. actual yield of residue was presented by Fisher, where "residue" denoted the yield of acetone insolubles after reaction at 445 - 450 °C for 2 hours (initial hydrogen pressure of 2000 psi). Here, the yield of residue was predicted by assuming that the coal constituents would react as follows:

- ash and fusain = 100% residue
- opaque attritus = 38% residue
- all other constituents = 0% residue

While this correlation was deemed to be more adequate than previous relationships based solely on rank or carbon

content, the deficiencies in terms of chemical differences between macroscopic and microscopic coal constituents for coals of varying rank was recognized by these researchers.

The Work of Peter Given

During the 1970's, Professor Peter Given and his co-workers at Penn State University began a very extensive study of the effect of coal composition on coal reactivity utilizing 104 coals from the U.S. To date, a series of ten papers have been published concerning the coal reactivity studies of Given et al., of which two pertain directly to the subject of reactivity correlations. The first paper (17) dealt with correlations between properties of 104 coals from the Penn State/DOE coal sample bank and conversion of coal to ethyl acetate solubles measured after reaction at 400 °C for one hour in tetralin. This paper introduced the concept of cluster analysis to the subject of reactivity correlation. It was reported that partitioning the samples into three distinct groupings (clusters) markedly improved the total variation accounted for by the multiple linear regression models employed for correlation of conversion and coal properties. The groupings recommended had the following characteristics:

Group 1: medium sulfur, high rank

Group 2: high sulfur, medium rank

Group 3: low sulfur, low rank

The regression equations developed for correlation of liquefaction conversion and coal properties for each of these groups were as follows:

Group 1: $\text{Conv} = 34.8 R_o + 50.7 \text{H/C} + 0.16 V + 30.5$

Group 2: $\text{Conv} = 0.86 \text{VM} - 22.8 R_o + 1.39 S_t + 39.0$

Group 3: $\text{Conv} = 0.93 \text{VM} + 0.28 \text{TRM} - 1.7$

where: R_o = vitrinite reflectance

H/C = atomic hydrogen-to-carbon ratio

V = vitrinite content of coal

VM = volatile matter

S_t = total sulfur

TRM = total reactive macerals

The adequacies of these reactivity correlations, expressed as a percentage of the total variation in the data set explained by the model, were 80.0%, 79.2%, and 47.5% respectively. A later paper in the series (18) concentrated on the development of reactivity correlations for a set of 26 high volatile bituminous coals with high sulfur contents, and extended the models previously developed in include analyses of the liquefaction products and coal structural features. These structural features included the usual compositional parameters as well as data from FTIR, ^{13}C -nmr, and the products of oxidation with trifluoroperoxyacetic acid. No significant correlations between liquefaction yields and structural features of the coals were found from this study.

Reactivity Definitions

The traditional parameter that has been used for coal liquefaction reactivity correlations is the point-yield conversion. This parameter is defined by measuring the yield of some solvent-soluble material (THF, pyridine, toluene, etc.) at a fixed reaction time and fixed temperature. This single parameter has been widely utilized by many researchers as the dependent variable in reactivity correlations with coal properties such as volatile matter, H/C and O/C atomic ratios, vitrinite reflectance, maceral distribution, etc. (19,20,21,22,23,24,25,26). As has been recently demonstrated by Shin et al. (27), this parameter can provide meaningful correlations with coal properties for a narrow suite of reasonably homogeneous coals, but the correlations weaken significantly or even disappear if either the time or temperature is changed. Use of a rate constant as a correlational parameter for coal reactivity was proposed by Furlong (28) and Gutmann (29), and was found to be generally satisfactory for a particular suite of coals within a single rank. This parameter, however, also fails to hold if the temperature is changed (27). An attempt to derive a more universal parameter that could be employed for definition of coal reactivity was made by Shin et al. (30), who combined both static and dynamic reactivity parameters into a single variable.

Many of the compositional parameters utilized as independent variables in the work cited above represented derived coal properties rather than fundamental chemical features which, as pointed out by Neavel (31), limits their utility in correlational models. Instrumental techniques such as pyrolysis/mass spectrometry (32,33) ^{13}C -n.m.r., FTIR, and ^1H -n.m.r. have also been employed in an attempt to generate a larger data base of compositional information for use in correlation with reactivity. In some cases, the parameters developed from these data are derived from statistical techniques such as principal component and factor analysis, and thus have little if any interpretation or meaning chemically. In this regard, the later work of Neill, Shadle, and Given (34) represents a significant departure from this philosophy in that an attempt was made to correlate both liquefaction chemical properties and coal structural features with the observed liquefaction reactivity.

The lack of significance often found with single-parameter reactivity models has been interpreted to reflect the need for development of multi-parameter models containing functional dependence for reactivity on several compositional parameters. Recently, the use of activation energy as a fundamental parameter for correlation of liquefaction reactivity data has been proposed. Prasad (35) collected reported values for activation energies from other studies, and found a direct correlation between

hydroliquefaction activation energy and the H/C ratio of the coal. Shin et al. (36) measured the hydroliquefaction activation energies for conversion of 5 bituminous coals from the Argonne Premium coal collection to THF and toluene solubles. Correlation of these data with fundamental coal chemical properties as determined from ^{13}C -n.m.r. (CP/MAS with dipolar dephasing) and ^1H -n.m.r. (CRAMPS) was successful in developing single parameter reactivity models with very high levels of significance (90%+) between the following variables:

Ea (toluene) <---> total oxygen
Ea (THF) <---> aliphatic hydrogen
Ea (toluene) <---> protonated aliphatic carbon

Observations and Conclusions

Coal is an extremely heterogeneous material, both from a macroscopic and microscopic point of view. Correlation of liquefaction reactivity with coal properties is, as a result, inherently difficult and any truly "universal" correlations that will be developed will need to be based on fundamental coal chemical and structural information. Lack of this type of information has been a severe limitation for all of the correlational efforts cited in this brief review. If truly predictive models are to be developed, basic data on coal structure will be invaluable. Choice of a reactivity definition employed as the dependent variable in these correlations is probably relatively arbitrary, and may be based totally on purely operational considerations (rate of reaction or extent of reaction) rather than any fundamental considerations. The role of pretreatment processes on reactivity modification (drying, grinding, etc) and mineral matter and matrix effects caused by organic/inorganic interactions needs to be better defined. This is especially true for low rank coals, where the inherently high reactivity of these materials can cause severe processing difficulties leading to artificially low levels of conversion.

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INFLUENCE OF ORGANIC COAL STRUCTURE ON LIQUEFACTION
BEHAVIOUR UNDER LOW-SEVERITY CONDITIONS

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ABSTRACT

The influence of coal structure on primary conversions and oil yields in thermolytic extraction with different H-donor and non-H-donor solvents and in dry catalytic hydrogenation has been investigated. Pre-soaking of coal/H-donor solvent slurries at 250°C increased conversions and the level of hydrogen transfer at short contact times (SCT ≤ 10 min.) with 9,10-dihydrophenanthrene demonstrating the importance of solvent accessibility. However, contrary to other studies, prior removal of THF-extractable material (mobile phase) from one bituminous coal actually gave rise to higher conversions to pyridine-solubles for non-donor polynuclear aromatic compounds (PAC), such as naphthalene, phenanthrene and pyrene. These findings highlight the difficulties in relating primary conversions to coal characteristics. In contrast, oil yields have been found to broadly increase with decreasing rank in both H-donor solvent extraction with a process solvent and dry catalytic hydrogenation. However, in SCT tetralin extraction where poor physical contact between coal and solvent exists, neither total conversion nor oil yield correlates with rank.

INTRODUCTION

The correlation of coal characteristics with liquefaction behaviour has received considerable attention (see, for example refs 1-7) particularly since the renewed interest during the 1970s in the production of liquid fuels and chemical feedstocks directly from coal. As early as 1940, Storch and coworkers (8,9) demonstrated that coals containing up to ~87% dmmf C give high yield of soluble products (albeit under severe conditions) and materials which today would be classified as vitrinite and inertinite liquefy readily. More recently, the work of the late Peter Given and coworkers (2,3) on tetralin extraction of US bituminous coals is particularly noteworthy; high sulphur coals of intermediate carbon content gave the highest conversions. However, apart from the lack of precise structural information on the nature of aromatic, aliphatic and heteroatomic groups and low molecular weight (MW)

material (mobile phase) in coals, research has been hampered by the fact that the rate and extent of conversion are heavily dependent on the conditions used. Indeed, the recent review by one of the authors⁽¹⁾ indicated that a clear distinction has to be made between overall or primary conversions (typically pyridine, quinoline or THF-solubles) and distillate or oil yields (toluene or alkane soluble material). The profound influence of low MW material and the nature of H-donor and non-donor solvents on primary conversions were also highlighted. In contrast, distillate or oil yields often correlate with parameters reflecting the aliphaticity of coals (H/C ratio - ref. 5, decreasing vitrinite reflectance - ref. 6, CH₂ content - ref. 7), better correlations being achieved for low-rank coals if yields are expressed on a "CO₂ free" basis⁽⁵⁾. The effects of coal characteristics on conversions are generally much less pronounced under high-severity conditions when a combination of vehicle solvent, hydrogen overpressure is catalyst are employed.

In this paper, a number of low-severity liquefaction regimes are considered. The influence of different H-donor and non-donor solvents on primary conversions without a hydrogen overpressure is discussed in the light of other recent work⁽¹⁰⁻¹³⁾. Also, it is demonstrated that oil yields broadly increase with decreasing coal rank in both H-donor extraction and dry catalytic hydrogenation provided that retrogressive reactions are avoided in the initial stages of coal dissolution.

EXPERIMENTAL

Conditions used for the extraction and hydrogenation experiments are summarised in Table 1. H-donor solvent extractions of a Wyodak sub-bituminous coal (73% dmmf C), an Illinois No.6 coal (78% dmmf C) and a UK bituminous coal (Pt. of Ayr, 87% dmmf C) were conducted using (i) a Lummus process - derived distillate (nominal boiling range of 340 to 400°C) containing approximately 1% donatable hydrogen) as described previously⁽¹⁴⁾ and (ii) tetralin with a short contact time (SCT, 10 min). The relatively high temperature of 450°C was used with the process distillate to achieve high oil yields without having a hydrogen overpressure.

To investigate factors affecting the initial stages of coal dissolution, extractions were conducted on two UK coals (Linby, 82% dmmf C and Pt of Ayr) at 400°C using a number of model compounds including tetralin, naphthalene, 9,10-dihydrophenanthrene, phenanthrene and pyrene for periods up to 30 min. For Linby coal, the effect of prior Soxhlet extraction with THF on conversions was investigated (extract yield, 6% daf coal). Also, coal/solvent slurries were pre-soaked at 250°C in a number of experiments. For the model hydroaromatic compounds, the amount of H transferred during extraction was determined by GC analysis of the products.

Dry hydrogenations with and without a dispersed sulphided molybdenum (Mo) catalyst (1% loading of Mo) were carried out at 350 and 400°C⁽¹⁵⁾ (Table 1) on a suite of five coals comprising a Spanish lignite (Utrillas, 60.4% dmmf C), a sub-bituminous coal (PSOC-1408, 72.9% dmmf C), two h.v.A bituminous coals (PSOC-1266 and 1296, 83% and 87 dmmf C, respectively) and a l.v. bituminous coal (PSOC-1325, 90% dmmf C). To investigate the role played by low MW solvent extractable material (mobile phase) in dry catalytic hydrogenation, a series of experiments were conducted with Utrillas lignite and an Illinois No.6 coal in which the coals were first extracted with chloroform prior to catalyst impregnation. The quantities of chloroform-soluble material extracted were 2.5 and ~5.0% dmmf coal for the lignite and the bituminous coal, respectively.

RESULTS AND DISCUSSION

Primary Conversions and Influence of Mobile Phase

Yields for the various H-donor and non-donor solvent extractions of Linby coal at 400°C are summarised in Table 2; the conversions for the THF-extracted coal include the extracted material. Surprisingly, pre-extraction with THF significantly increases primary conversions in the polynuclear aromatic compounds (PACs) investigated. These findings appear to be contrary to those of other liquefaction⁽¹⁶⁾ and pyrolysis⁽¹⁷⁾ studies where prior removal of chloroform-extractable material significantly reduced conversions. However, Rincon and Cruz⁽¹⁸⁾ have reported recently that pre-swelling coals in THF increases conversions for both anthracene oil and tetralin. The fact that Pt. of Ayr (87% dammf C) coal yielded over 80% pyridine-solubles in pyrene (C.E. Snape, unpublished data) without pre-extraction is consistent with the earlier results of Clarke et al⁽¹⁹⁾ for anthracene oil extraction where UK coals containing ~85-87% dmmf C gave the highest conversions. It was suggested previously by one of the authors that this could correspond to a minimum in the cross-linking density of bituminous coals⁽¹⁾. However, these latest findings infer that the mobile phase is merely limiting accessibility for larger PACs, such as pyrene, within lower rank bituminous coals, such as Linby.

Conversions to pyridine-solubles for non-THF-extracted Linby coal were much greater with naphthalene than with phenanthrene and pyrene (Table 2, pre-soaking at 250°C has little effect on conversions) and, even after THF extraction, naphthalene conversions are comparable to those of pyrene. Although Neavel obtained high yields of pyridine solubles with naphthalene at short contact times for some US bituminous coals⁽²⁰⁾, conversions were much lower after longer extraction times. This trend is not evident for Linby coal where little variation in conversion to pyridine and THF-solubles is found for residence times between 10 and 30 min for both the initial and THF-extracted coal samples (Figure 1 and Table 2). The trends reported here were certainly not anticipated from previous studies with model PACs^(1,21) but yields of THF-solubles for pyrene were considerably greater than those obtained with both phenanthrene and naphthalene (Table 2, Figures 1 and 2). This evidence provides strong support for pyrene being an effective "hydrogen-shuttler"⁽²¹⁾; the available hydrogen in Linby coal is utilised more effectively with pyrene than with naphthalene and phenanthrene, generating significantly higher yields of THF-solubles.

As expected, tetralin and 9,10-dihydrophenanthrene gave much higher yields of THF-solubles after THF extraction than the PACs with the exception of pyrene (Table 2). Pre-soaking the coal/solvent slurries at 250°C increased SCT conversions for 9,10-dihydrophenanthrene but not tetralin (Figures 3 and 4) presumably due to poorer physical contact of tetralin with the coal; Narain et al⁽²²⁾ found similar improvements in SCT hydroliquefaction with 1-methylnaphthalene. For 9,10-dihydrophenanthrene, the higher conversion to THF-solubles was not accompanied by an increase in H consumption. However, the conversion at SCT (Figure 3) was no more than that obtained after prolonged extraction (30 min, Table 2) with pyrene where no H donation can occur. This agrees with the work of Baldwin and coworkers⁽²³⁾ which showed that oil yields (dichloromethane - DCM; toluene or alkane-solubles) provide more reliable indicators of H utilisation than overall conversions to pyridine (or quinoline) or THF-solubles. The lower yields of pyridine-solubles obtained with tetralin compared to 9,10-dihydrophenanthrene (Table 2) and even to naphthalene and pyrene for the THF-extracted coal (Table 2, Figures 1 and 2) again are probably attributable to tetralin being largely vaporised at liquefaction temperatures. Indeed, different trends in primary conversion are evident for the SCT tetralin and the higher temperature process-solvent extractions (Table 3). The sub-bituminous coal (Wyodak) gives the highest yield of quinoline-insolubles with tetralin consistent with the general trend found in SCT hydroliquefaction by Whitehurst^(1,24). In the case of the process solvent, yields of THF-insolubles increase with increasing rank (Table 3) although the trend is much smoother

than could be realistically expected for a larger suite of coals. Nitrogen containing solvents, such as indoline have also been found to give significantly higher primary conversions for Wyodak coal (25) than tetralin presumably due to the more effective disruption of hydrogen bonds in the coal. Clearly, solvents which provide good physical contact are essential to minimise retrogressive reactions particularly for low-rank coals.

In view of the compelling arguments recently put forward by McMillan and coworkers (12) in support of solvent-mediated hydrogenolysis, it is pertinent to consider whether chemical or physical factors for the different H-donors investigated are responsible for inefficient hydrogen utilisation and, in particular, whether different conversions are evident for a given level of hydrogen donation. Majchrowicz et al (26) demonstrated that by increasing the filling factor for tetralin in autoclaves so that more of the tetralin is in the liquid phase, conversions to THF-solubles increased but the level of hydrogen transfer remained constant. Table 2 indicates that when 0.5% daf hydrogen has been consumed, the yields of THF-solubles obtained with 9,10-dihydrophenanthrene are considerably higher than with tetralin. Also, the maximum obtainable yield of THF-solubles at 400°C is significantly higher for 9,10-dihydrophenanthrene (Figures 3 and 4). Despite the reservations over the use of THF-soluble yields as indicators of H utilisation, these findings clearly indicate that cleavage of relatively stable C-C bonds via hydrogen radical transfer occurs to a significantly greater extent in 9,10-dihydrophenanthrene.

The results summarised in Table 4 (27) suggest that removal of some of the mobile phase prior to dry catalytic hydrogenation does not adversely affect chloroform-soluble yields obtained at long reaction times and, in the case of the lignite, the initial rate of conversion may actually be enhanced. Thus, the breakdown of the macromolecular network of coals is not strongly dependent on the presence of mobile species.

Oil Yields

Figure 5 gives the yields of chloroform-soluble liquid products obtained from the dry hydrogenation experiments at 400°C with the sulphided Mo catalyst. Table 3 lists oil and gas yields from the process solvent extractions at 450°C. In both regimes, oil yields (chloroform or n-heptane-soluble liquids) generally increase with decreasing rank. Again, the trends are probably much smoother than could be anticipated for a larger suite of coals. For lignites and sub-bituminous coals, it is probably more appropriate to express oil yields on a "CO₂ plus CO free" basis (5) (Table 3), a higher yield then being obtained for Wyodak sub-bituminous coal compared to Illinois No.6 coal in the process solvent extractions (Table 3). Reducing the hydrogenation temperature from 400 to 350°C amplifies the effect of rank on the yields of chloroform-soluble liquids (27) (Figure 6) because of the greater thermal sensitivity of low-rank coals. For catalytic hydrogenation, the trends would not be so acute in the presence of H-donor solvents where conversions tend to be considerably higher.

Although the yield of DCM-insolubles increases with increasing rank in SCT tetralin extraction (Table 3, Q1 + QS/DCM insols), the actual estimated yields of DCM-soluble liquid product are similar for Wyodak and Pt of Ayr coals even after correcting for the carbon oxides. Thus, retrogressive reactions encountered in SCT extraction with tetralin for Wyodak coal limit both primary conversions and oil yields. The relatively high concentration of solvent extractable material in Illinois No.6 coal may be responsible for this coal giving the highest oil yield in SCT liquefaction. Also, for dry hydrogenation without catalyst, oil yields do not correlate with rank (Figure 5), the sub-bituminous coal giving a significantly lower oil yield than one of the h.v.A bituminous coals. Thus, the catalyst is needed to limit retrogressive reactions by promoting cleavage reactions probably by hydrogen radical mediated hydrogenolysis(12). These findings are in broad agreement with trends obtained under typical SRC-II processing conditions (6) where addition of pyrite is needed to give high oil yields for low-rank coals and clearly show the importance of limiting retrogressive reactions in the initial

stages of liquefaction for low-rank coals.

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TABLE 1 Summary of Liquefaction Experiments

Experiment	Temp °C	Solvent	Solvent to Coal Ratio	Gas	Atmosphere Pressure (Gold)
H-donor Solvent extraction					
1.	450	Lummas process-derived distillate	2:1	H ₂	30
2.	400	Tetralin ⁺ 9,10 dihydrophenanthrene ⁺	2:1	H ₂	1
Non-donor PAC extraction ⁺	400	Naphthalene, phenanthrene, Pyrene ⁺	2:1	H ₂	1
Dry catalytic hydrogenation	400	-	-	H ₂	70
Experiment					
Extraction time, min					
Solvents used to determine conversions					
H-donor solvent extraction					
1. 450°C	30	THF, n-heptane,			
2. 400°C	7-30	Pyridine, quinoline, THF			
Non-donor PAC extraction⁺					
	7-30	Pyridine/quinoline, THF			
Dry catalytic hydrogenation					
	60	Chloroform			

+ = with and without a pre-soak period of 60 min. at 250°C

* = before and after THF-extraction of Linby coal

TABLE 2 Primary conversions for Linby coal at 400°C

Solvents	Coal treatment	Time min.	Yields ^a		Hydrogen consumption (% daf coal)
			Pyridine sols.	THF sols.	
naphthalene	None	10	51	25	
	"	30	58	29	
	THF-ext.	7	81	24	
	"	30	76	26	
Phenanthrene	None	7,30	22	15	
	THF-ext.	7,30	38	30	
Pyrene	None	7,30	24	14	
	THF-ext.	10	60	47	
	"	30	83	60	
9,10 Dihydro-phenanthrene	THF-ext.	5	55	34	0.5
	"	30	88	83	2.1
	Pre-soak	5	88	53	0.4
	"	30	93	80	1.9
Tetralin	THF-ext.	7	38	25	0.5
	"	30	78	65	1.2
	Pre-soak	7	43	35	0.5
	"	30	75	66	1.3

+ % daf coal

TABLE 3 H-Donor Solvent Liquefaction Results

Coal	Pt of Ayr	Illinois No.6	Wyodak
SCT Tetralin			
% daf coal	Qls	8	5
	QS/DCM insols	69	60
	DCM liquids ^a	20	32
			26
			35
			20
			(24)
Process Solvent			
% daf coal	THF insols.	17.0	3.6
	THF sol ^b /C ₇ insols.	47.5	47.1
	C ₇ liquids ^b	27.6	41.5
			2.1
			35.3
			39.5
			(47.5)
	CO + CO ₂	1.6	1.5
	C ₁ -C ₃ gases	5.5	5.9
			16.8
			6.0

Ql - quinoline insolubles QS - quinoline solubles
 C₇ - n-heptane * - includes water
 () - "CO₂ + CO" free basis DCM - dichloromethane

TABLE 4 Influence of Chloroform Pre-extraction on Oil Yields (Chloroform-Soluble Liquids) in Dry Catalytic Hydrogenation at 400°C

Reaction Time (Mins.)	Utrillas Lignite		Illinois No. 6	
	Original	Pre-extracted	Original	Pre-extracted
5	50.0	63.7	24.4	8.6
10	59.0	74.3	53.8	22.6
60	66.0	77.8	77.8	73.2

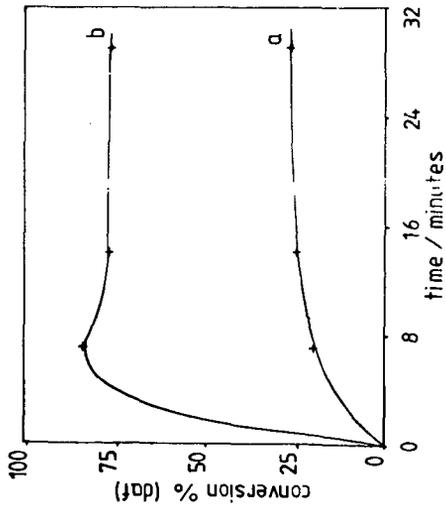


Figure 1 Conversion of THF-extracted Linby coal with naphthalene at 400°C
 (a) THF - solubles
 (b) Pyridine - solubles

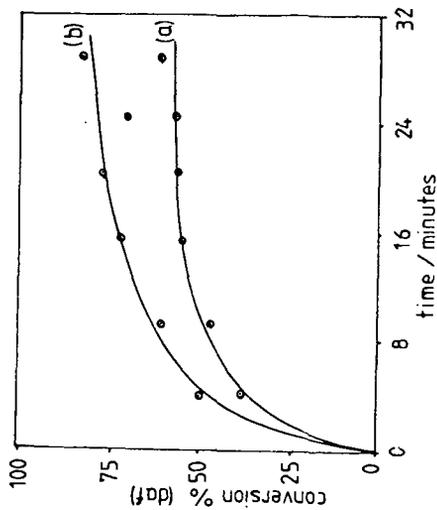


Figure 2 Conversion of THF-extracted Linby coal with pyrene at 400°C after pre-soaking at 250°C for 1 hour.
 (a) THF - solubles
 (b) Pyridine - solubles

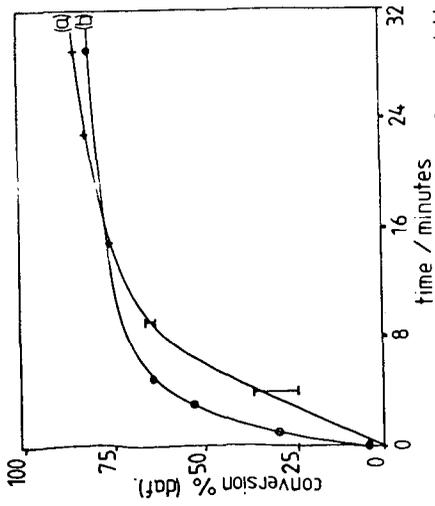


Figure 3 Conversion of THF-extracted Linby coal with 9,10-dihydrophenanthrene at 400°C to THF-solubles.
 (a) Normal extraction
 (b) After pre-soaking at 250°C for 1 hour

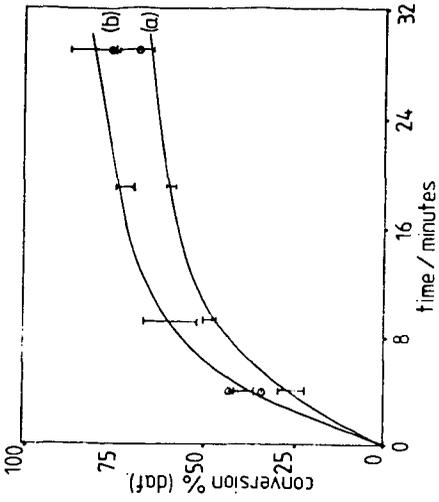


Figure 4 Conversion of THF-extracted Linby coal with tetralin at 400°C after pre-soaking at 250°C for 1 hour.
 (a) THF-solubles
 (b) Pyridine-solubles

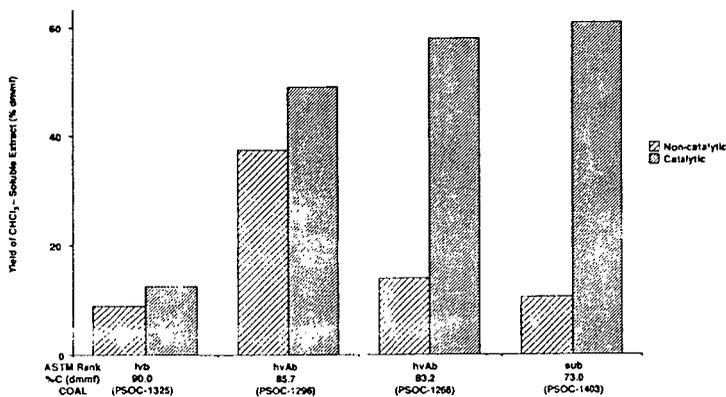


Figure 5 Effect of coal rank and sulphided Mo. catalyst on yield of chloroform-soluble liquids in solvent-free hydrogenation at 400°C

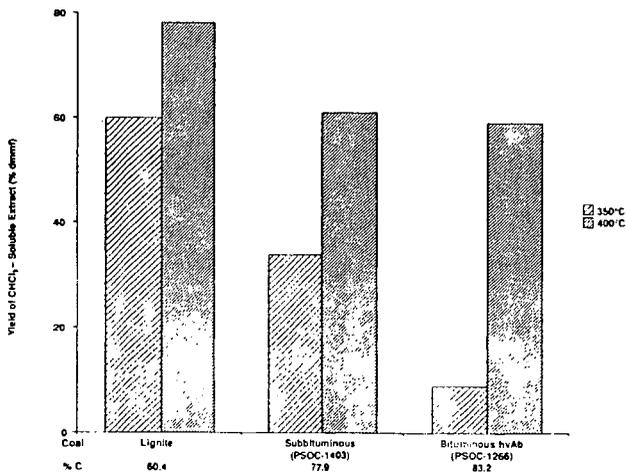


Figure 6 Influence of temperature and coal rank on yield of chloroform-soluble liquids in dry catalytic hydrogenation with a sulphided Mo. catalyst.

AN INVESTIGATION OF THE CHEMISTRY OF CATALYTIC PRELIQUEFACTION

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INTRODUCTION

Direct coal liquefaction processes which have been developed over the years have been based on the philosophy of high temperature homolytic cleavage of bonds to yield free radicals which are capped by hydrogen from the donor solvent or hydroaromatic structures in coals. While low rank coals offer the potential of high oil yields because of their small aromatic ring cluster size, it has been observed that under conditions optimized for bituminous coals, low rank coals appear harder to liquefy (1,2). For example, Derbyshire and Whitehurst (3) demonstrated that low rank coals produce very low conversions in short contact time liquefaction in a donor solvent or in long time liquefaction in a non-donor solvent. For low rank coals and lignites, it appears likely that crosslinking reactions associated with oxygen functional groups (4,5) occur before the homolytic cleavage reactions, and if not controlled, can limit the maximum conversion of coal to liquids.

It has been observed that in single stage coal liquefaction, bond breaking, crosslinking and hydrogen transfer reactions are carried out simultaneously. This does not enable each individual reaction to be optimized. Recent research on "temperature staged liquefaction" routes, exploring the effects of catalyst and solvent has been pursued using tubing bomb experiments at Penn State University by Derbyshire, Davis, Schobert and co-workers (6-12). The tubing bomb results (6) showed that liquefaction of a low rank coal at 350°C in naphthalene with a Mo catalyst resulted in improved yields with higher fractions of oils in subsequent liquefaction at 425°C.

The objective of this work was the identification and optimization of the beneficial preliquefaction chemistry through the application of advanced analytical techniques and theoretical models which have been previously employed to understand and predict coal pyrolysis and fluidity behavior. The analytical techniques include three methods to determine the functional group composition of the preliquefaction products: 1) Quantitative Fourier Transform Infrared (FT-IR) spectroscopy (13-16); 2) Cross-polarization-magic angle spinning (CP/MAS) NMR with dipolar dephasing (17-21); and 3) Thermogravimetric analysis with detection of the evolved products by FT-IR spectroscopy (TG-FTIR) (22,23); 4) Field Ionization Mass Spectroscopy (FIMS), a method to determine the molecular weight distribution of soluble products (24-27); and 5) Solvent swelling to determine the degree of crosslinking in the preliquefaction residue (28,29).

The theoretical model describes the break up of the coal macromolecular network under the influence of bond cleavage and crosslinking reactions using a Monte Carlo statistical approach (30-34). A similar statistical approach for coal decomposition using percolation theory has been presented by Grant et al. (35). Such statistical methods have been used for the inverse problem in the polymer literature, i.e., the formation of a macromolecular network by polymerization (36-40).

EXPERIMENTAL

SAMPLES - Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank and the Argonne Premium Sample Bank. The Penn State coals were obtained undried and in lump form about 12 mm diameter and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffing into a number of 10 g representative samples and sealed in vials under nitrogen. The Argonne coals were provided in sealed vials under argon. Properties of the coals are shown in Table 1.

Preliquefaction and Liquefaction Experiments - Preliquefaction and liquefaction experiments were carried out at Penn State University and at Advanced Fuel Research, Inc. The procedure was that described by Derbyshire et al. (6). The preliquefaction was carried out in a tubing bomb at temperatures between 275 and 350°C. Coal was impregnated with MoS₂ catalyst and mixed in a

ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent. Reactions were carried out in tubing bomb reactors of about 20 cm³ capacity which were heated by immersion in a fluidized sandbath.

Following preliquefaction, the bomb was cooled and vented to determine the gases evolved by volumetric measurement and gas chromatographic analysis. The solid and liquid products were worked-up to obtain the yields of insoluble residue (either chloroform or tetrahydrofuran (THF) insoluble), asphaltenes (hexane insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene was part of the hexane solubles.

ANALYSES - Quantitative FT-IR Analysis - Selected samples of the liquefaction products, total product, the chloroform extracts, the asphaltenes, and the solid residues were analyzed as KBr pellets by FT-IR. The methods employed for quantitative analysis have been described previously (13-16).

TG-FT-IR - Pyrolysis analyses were performed on the preliquefaction solids using thermogravimetric (TG) analysis with on-line analysis of the evolved products (including an infrared spectrum of the condensables) by FT-IR. The TG-FTIR method has been described previously (22,23).

Solvent Swelling and Extraction - The residue samples were extracted with pyridine at the boiling point to obtain the amount and composition of the extract. A portion of the dried, extracted solids was swelled in pyridine in order to estimate the density of crosslinks introduced by the liquefaction process. The solvent swelling measurements were carried out according to the method of Green, Kovac, and Larsen (28,29).

FIMS Analysis - Selected extracts were sent for analysis in the Field Ionization Mass Spectrometry (FIMS) apparatus at SRI International. This technique was described by St. John, et al. (24) and has been used extensively in our development of the network model for coal decomposition (30-34,41,42). The Field Ionization induces little fragmentation and so provides a determination of the sample's molecular weight.

NMR - NMR analyses were performed on selected samples using dipolar dephasing and off magic angle spinning methods developed at the University of Utah (17-21). This work was performed at the University of Utah under the direction of Professor Ronald Pugmire.

Model Compounds - Model compounds were employed to provide well known materials to study specific chemical reactions or to provide standards to calibrate the analytical techniques. These included 1-naphthoic acid and 2-naphthoic acid to study the reaction of aryl carboxyl groups under preliquefaction conditions.

RESULTS

PRODUCTS DISTRIBUTION - Both the products of the preliquefaction and liquefaction stages were analyzed. Variations were made in coal type, (lignite, subbituminous, and bituminous), preliquefaction temperature (275-350 °C), gases present (hydrogen, nitrogen, helium), catalyst (Mo or none), solvent (naphthalene, tetralin or dry) preliquefaction time (30 min - 60 min), and liquefaction time at 425 °C (10 min - 30 min). Results for PSOC 1401 (a Wyodak subbituminous, which was the most frequently studied coal) are presented in Fig. 1. The figure compares liquefaction data (10 min at 425 °C) for no preliquefaction, preliquefaction at 275 °C (with H₂ and catalyst) and preliquefaction at 350 °C (with H₂ and catalyst). **The results show that preliquefaction at 350 °C does have a positive effect on the total yield and product quality in liquefaction (much lower residue) while preliquefaction at 275 °C causes a negative effect (higher residue).** The results for other coals and conditions are summarized as follows:

- 1) Preliquefaction at 275 °C appears to have a negative effect on subsequent liquefaction when compared to results without a preliquefaction step. Preliquefaction results in up to 10% of the coal converted to gases and chloroform solubles. Most coals behaved the same and there was little effect due to the presence of either the catalyst or hydrogen.

The solvent was, however, necessary to produce the chloroform extracts as none were produced by a thermal treatment in the absence of a solvent.

- 2) Preliquefaction at 350°C in the presence of a catalyst appears to have a strong positive effect on liquefaction for low rank coals. The largest change due to preliquefaction (high chloroform extract yield, high CO₂ yield) is produced by both hydrogen and catalyst. Nitrogen and catalyst produce smaller but similar changes, while no catalyst produces much less change and as shown by Derbyshire et al. (6) produces little change in liquefaction. Preliquefaction with no solvent or catalyst produces the least change in the product. Preliquefaction in tetralin produces no improvement over preliquefaction in naphthalene.

FT-IR FUNCTIONAL GROUP ANALYSIS - Quantitative FT-IR functional group analysis was performed on the starting coals, preliquefaction residua, chloroform extracts, oils, and asphaltenes.

Residua - Results for PSOC 1401, preliquefaction with H₂ and Mo at 350°C, are presented in Fig. 2. The preliquefaction step produces the following changes: 1) decreases the carbonyl (1700 cm⁻¹) and hydroxyl regions (3400 cm⁻¹) (presumably carboxyl loss); 2) decreases the aliphatic hydrogen (2900 cm⁻¹); and 3) substantially increases the aromatic hydrogen (750-850 cm⁻¹).

The quantitative functional group analysis for PSOC 1401 from these and other spectra are summarized in Fig. 3 and Table 2. The aliphatic hydrogen (Fig. 3a) is found to decrease for solvent treated residues compared to residues formed in the absence of the solvent. The most drastic changes are in the aromatic hydrogen (Fig. 3b), the carbonyl (Fig. 3e), and the one adjacent aromatic hydrogen (Fig. 3g). As can be seen, the major changes are brought about with the catalyst and solvent. These are changes which presumably lead to the improved liquefaction yields.

There are three other cases of interest. The first is HCD 1401-350° which is identical to HC 1401-350° in using hydrogen and a catalyst but no solvent was present. The quantitative functional group analysis is presented in Table 2. It shows the loss in aliphatics and carboxyl, but not the same dramatic increase in the aromatic hydrogen. The second case is NCT 1401-350 which was preliquefied in tetralin with a catalyst under a nitrogen atmosphere. The results in Table 2 are very similar to HCD 1401-350 (low aliphatics and low carboxyl). The third case is for the HC 1401-350 residue after it was subsequently heated to 400°C. This was done to see whether the high aromatic peaks are due to adsorbed naphthalene. The data in Table 2 show that the functional group composition is almost identical to that in the starting residue. So heating to 400°C does not change the chemistry and adsorbed naphthalene is not likely.

Our initial conclusion from the FT-IR data on the residua is that it is the reduction in the carboxyl concentration which is most important to the improvements brought about by preliquefaction, and this reduction requires the catalyst but not the solvent and probably not the hydrogen. The major reasons for these conclusions are: 1) pretreatments dry, with naphthalene (with hydrogen and nitrogen) and with tetralin, all reduced the carboxyl concentration, and the dry and naphthalene cases both produced improved liquefaction yields; 2) the presence of hydrogen does not appear to make much difference between HC 1401-350 and NC 1401-350; and 3) the increased aromatics were not present in the dry preliquefaction residue (HCD 1401-350) and so, do not appear necessary for the improvement in liquefaction.

The increase in the aromatic hydrogen appears to result from adducted naphthalene for the following reasons: 1) the peak positions are consistent with adducted naphthalene; 2) the increase is too large to have come from conversion of aliphatic hydrogen to aromatic hydrogen, no increase was seen for NT 1401-350 which had a similar decrease in aliphatic hydrogen; 3) increased aromatic hydrogen due to removal of the carboxyls would not be likely to increase the one adjacent hydrogen peak; and 4) the peak must be due to a tightly bound chemical because it is not removed at 400°C.

Extracts - Quantitative spectra were obtained for the soluble products of the preliquefaction process. Results for the THF extracts of the residue (asphaltene 1) for HC 1401-350 is presented in Fig. 4 and Table 2. The asphaltenes are very high in carboxyl groups, methyl groups, and aliphatic or

hydroaromatic hydrogen. The spectrum does not show very large aromatic peaks; the material appears to contain less than 50% aromatic carbon based on the amount of aliphatic carbon and oxygen present. The THF solubles appear to have carboxyl concentration comparable to the original coal but much larger than the residue. They contain significantly less ether oxygen.

TG-FTIR ANALYSIS - The analysis of the volatile products are related to the functional group composition of the sample, so the TG-FTIR analysis provides a good complement to the FT-IR functional group analysis. Since the FT-IR analysis showed the carbonyl region to change drastically in preliquefaction, we consider the CO₂ evolution which results from the thermal decomposition of the carboxyl groups. Figure 5 compares the CO₂ evolution from a number of residua. The major change occurs for the catalytic preliquefaction at 350°C (HC 1401-350 and NC 1401-350). Here a drastic reduction is observed in the CO₂ evolution at all temperatures. **This suggests a major chemical change in the carboxyl groups.** The nitrogen thermal case shows less of a change.

SOLVENT SWELLING - The results showed that there was less or comparable loss in solvent swelling for a catalytic preliquefaction compared to thermal treatment without a catalyst. But since the catalytically treated samples show much greater removal of the carboxyl groups, these samples will undergo much less crosslinking upon further thermal treatment.

FIMS ANALYSES - FIMS analyses were performed on the extracts from HC 1401-350 which were separated into hexane solubles (oils plus naphthalenes) and hexane insoluble, THF soluble (asphaltene 2). The oil fraction is very volatile with an average molecular weight of 303 AMU on a number average basis. **The results show that there is significant chemistry going on involving naphthalene dimerization and probably addition.**

NMR ANALYSIS - NMR analysis was performed on the residue from HC 1401-350. The results are presented in Table 3. The data confirm the lower aliphatic content and higher aromatic content in the preliquefaction samples determined in FT-IR. The increase in the aromatic content is in protonated carbon (0.28 for the residue compared to 0.17 for the coal). The major decrease in the aliphatics is in the CH₂ groups (0.27 in the coal vs. 0.16 in the residue). The cluster size in the preliquefaction coal (12.3 carbons) appears to be higher than for the raw coal (9.7). The carboxyl carbon (f_c) in the preliquefaction product (0.05) is also lower than in the raw coal (0.08) consistent with the FT-IR and TG-FTIR results.

STUDIES WITH MODEL COMPOUND - Since the results of the preliquefaction experiments with a subbituminous coal at 350°C in the presence of a catalyst showed a significant role of carboxyl groups in preliquefaction chemistry, model compounds with aryl carboxyl groups (1-naphthoic acid and 2-naphthoic acid) were studied. The preliquefaction was carried out at 350°C for 1 hour in nitrogen with ammonium tetrathiomolybdate (1% Mo on dmmf basis) as the catalyst. The starting reaction mixture used was 50% naphthalene, 25% of 1-naphthoic acid and 25% of 2-naphthoic acid (weight basis). The FT-IR spectra (dry, uncorrected) of the starting reaction mixture and the residue after preliquefaction were compared. There is a strong loss in the carbonyl and hydroxyl bands due to the loss of carboxyl groups during the preliquefaction in the presence of the catalyst. A blank run was done without the catalyst which indicates that the catalyst is necessary to cause excessive decarboxylation. The CO₂ formation was more than a factor of three higher, due to the presence of the catalyst. The CO₂ evolution in absence of the catalyst is due to the higher decarboxylation.

MODELING

The liquefaction model is based on AFR's FG-DVC model of coal devolatilization (30-32). The model describes the decomposition or condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions. Our model employs a simple macromolecular network in the computer consisting of aromatic ring clusters (monomers) linked by bridges. The bridges are either broken by bond scission reactions or are formed by crosslinking. In the model, the break-up or solidification of the molecule occurs near a "gel point" where the number of unbroken bonds per ring cluster (monomer), α , reaches a critical value $\alpha_c \approx 0.95$. For bituminous coals, this critical value can be achieved in pyrolysis and the coal melts and becomes fluid. The effects of low temperature crosslinking which occurs for low rank coals is to increase α so that in some cases the network

cannot come apart by normal pyrolytic reactions.

For liquefaction, the hydrogen consumption in the pyrolysis process (which required hydrogen donation from the aliphatic and hydroaromatic hydrogen in the coal) was modified to allow donation from the solvent. In addition, the external and internal transport steps in devolatilization (which describe vaporization of small molecules and gas phase transport) are modified to describe small molecules becoming liquid and mixing with the solvent. The details of AFR's FG-DVC model can be found in Ref. 32.

From the analysis of the results on the preliquefaction chemistry, it was found that the preliquefaction process results in reduction of carboxyl groups, partial crosslinking of the structure and some bond breaking resulting in higher chloroform extractables. The effect of this preliquefaction process on subsequent liquefaction is high yields of liquids.

The preliquefaction chemistry and its effect on subsequent pyrolysis were simulated by the FG-DVC model. The starting polymer structure of Wyodak coal was modified by putting additional crosslinks (0.13/monomer) to account for partial crosslinking of the structure. The original coal had pyridine solubles of 7.4% but the residue after preliquefaction has THF solubles of 21.5%. To account for this change in the molecular weight distribution of the starting polymer, the oligomer length was decreased from 10 to 4. The donatable hydrogen was kept constant in both cases. The carboxy content (responsible for early crosslinking) was reduced from 6.9% to 2.9%. The results of the simulation are shown in Fig. 8.

Comparing Figs. 8a and 8c for the original and modified coals respectively, we find that while the number of bonds/bead α for the unmodified coal do not go below the critical value of 0.95, the value of α for the modified coal does. This results in the opening of the macromolecular structure and better penetration of the liquefaction solvent in subsequent liquefaction resulting in high liquid yields. Figures 8b and 8d compare the fluid fraction of the mixture on pyrolysis at 440°C for original and modified coals respectively. The modified coal shows a much higher fluid fraction which results in greater fluidity during subsequent liquefaction.

DISCUSSION

There are three suggested modifications which could lead to improved liquefaction. They are: 1) reduced crosslinking; 2) hydrogenation; and 3) increased bond breaking. The experimental results suggest that modification 1 is the most likely, 2 does not occur and 3 appears to happen to some extent.

Having identified the probable chemical changes responsible for improvements in yield and quality in liquefaction, attention was focused on the reactions which produce the chemical changes. The results raise the following questions and possible answers.

Question 1. What is the chemistry of carboxyl removal? Partial answer. **There are carboxyls removed from the residue by conversion to CO₂ and with the extract.** This occurs only in the presence of the catalyst but with or without the solvent or hydrogen. Fewer crosslinks are formed than would otherwise have been formed with the amount of carboxyl removed. This is confirmed by FT-IR, TG-FTIR, NMR, the model simulation, and experiments with model compounds. Naphthalene adduction could have occurred in the HC 1401-350 case to produce the high aromatic, but carboxyl removed occurred in other cases without this effect. Most of the carboxyl removed is by the formation of CO₂. Decarboxylation is seen for the model compounds in the presence of the catalyst.

Question 2. What happens to aliphatics? The most probable answer. **There is a reduction in the aliphatics, most likely produced by removal (with the chloroform solubles) of long chain polymethylene and small fragments high in methyl.** This is confirmed by FT-IR, TG-FTIR, and NMR.

Question 3. Where do the increased aromatics come from? The most probable answer. **Large increases in aromatics were observed in some cases, which are probably due to naphthalene**

adduction. Conversion from aliphatics is unlikely. The evidence comes from FT-IR, NMR, FIMS and the model compound studies which show that naphthalene adduction occurs.

Question 4. What kind of bonds hold the preliquefaction insoluble products together? The most probable answer. **The bonds remaining in the residue appear similar to those in the parent coal based on the liquefaction and TG-FTIR data.** But there is no really good experiment which determines the kinds of bonds. Based on the FT-IR spectra of the residue there is enough aliphatic hydrogen for $-\text{CH}_2\text{CH}_2-$ bonds.

Question 5. Why is the preliquefied insoluble product so easily liquefied? The most probable answer. **The preliquefaction product with the reduced carboxyl groups content is more easily liquefied than the parent coal.** Based on the product distribution and solvent swelling data and the model simulation, this improvement results from a reduction in the CO_2 associated crosslinks and from the bond breaking which produces the chloroform solubles. Both effects reduce the total number of bonds linking the network so that the coal can become fluid. If the chloroform soluble fraction is removed after preliquefaction and the residue liquefied, the drastic improvement in the liquefaction is not observed. The model simulation confirms that the residue alone will liquefy slightly better than the parent coal, but not as good as the mixture.

CONCLUSIONS

- 1) Preliquefaction of a Wyodak subbituminous coal at 350°C with solvent, catalyst and hydrogen produced the best results, (highest yields and best quality) in subsequent liquefaction for 10 minutes. The preliquefaction step produced substantial changes in the functional group composition of the residue, (low aliphatic, low carboxyl, and high aromatic), a large chloroform extract yield and a high CO_2 yield.
- 2) Other preliquefaction treatments at 350°C produced results which were not as good as the best case.
- 3) The preliquefaction step did not appear to induce appreciable hydrogenation of the residue even with tetralin as a solvent or a hydrogen gas atmosphere.
- 4) The improvement in liquefaction behavior appears to be due to loss of the functional groups usually responsible for crosslinking without the associated crosslink formation; probably carboxyl.
- 5) Experiments were carried out to test whether carboxyl groups on a model compound were removed under preliquefaction conditions (350°C , Mo, naphthalene solvent and nitrogen or hydrogen gas). Results showed that almost all of the carboxyl groups were converted to CO_2 . Almost no decarboxylation occurred in the absence of the catalyst.
- 6) Simulations show that the reduction in the carboxyl group concentration in the preliquefaction step for the Wyodak coal is capable of significantly enhancing the subsequent decomposition of the macromolecular network in the liquefaction step, thus improving the liquefaction yields.

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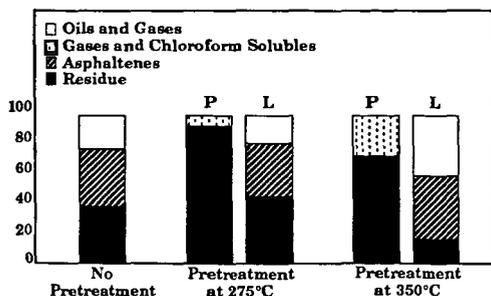


Figure 1. Product Distributions for Preliquefaction and Liquefaction Comparing Results for No Preliquefaction, Preliquefaction at 275°C and Preliquefaction at 350°C. P = Pretreatment and L = Liquefaction. Liquefaction Conditions - 425°C, Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (10 min.). Preliquefaction Conditions - Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (275°C - 30 min., 350°C - 60 min.).

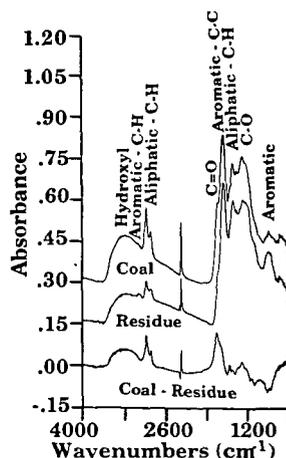


Figure 2. Comparison of FT-IR Spectra for Residue and Parent Coal for PSOC-1401 Wyodak Subbituminous Coal.

Table 1 - Coal Properties.

Coal	PSOC-1504	PSOC-1401	PSOC-1482	Beulah Zap	Wyodak
Seam	Upper Sunnyside	Lower Wyodak	Hagel	Beulah Zap	Wyodak-Anderson
State	Utah	Wyoming	North Dakota	North Dakota	Wyoming
ASTM Rank Class (apparent)	HVA	Subbituminous	Lignite	Lignite	Subbituminous
Moisture Content (wt. % (a.r.))	3.4	16.3	34.5	32.2	28.1
Mineral Matter	8.6	6.5	9.7	11.1	10.0
Elemental Composition Wt.% dmmf					
C	82.9	72.7	72.2	74.1	76.0
H	5.8	4.5	4.4	4.9	5.4
O ^a	8.7	21.4	21.6	19.1	17.0
N	1.8	1.1	1.1	1.2	1.1
S	0.8	0.3	0.7	0.7	0.5
Sulphur Forms (% dry coal)					
Organic	0.71	0.26	0.61	0.63	0.43
Pyritic	0.04	0.01	0.09	0.14	0.17
Sulphate	0.02	0.00	0.02	0.03	0.03
Total	0.77	0.27	0.72	0.80	0.63

^a by Difference

Table 2. Quantitative FT-IR Analysis of PSOC-1401 Residues at 350°C. (wt. % dmmf)

Sample	Hydrogen			Aromatic Hydrogen			C _{al}	Units (Abs. x cm ⁻¹)	Oxygen				
	H _{al}	H _h	H _{ar}	H _{total}	H _{ar} /H _{total}	1Adj			2Adj	3+	O _h	O _{ether}	O _{total}
PSOC-1401	2.57	.37	1.44	4.38	.33	.40	.74	.30	17.13	31.33	5.96	4.88	10.84
PSOC-1401	2.85	.36	1.49	4.70	.32	.47	.65	.37	19.00	33.32	5.74	5.40	11.14
HC1401-350	1.54	.25	2.27	4.06	.56	1.07	.82	.38	10.27	13.03	4.00	5.25	9.25
HC1401-350	1.50	.26	2.39	4.15	.58	.93	.99	.47	10.00	13.73	4.10	6.25	10.35
HC1401-350	1.25	.23	2.64	4.12	.64	.99	1.19	.46	8.33	12.89	3.75	6.00	9.75
HC1401-350	1.37	.23	2.27	3.87	.59	.80	1.04	.43	9.13	12.83	3.75	6.40	10.15
NC1401-350	1.29	.28	2.14	3.71	.58	.79	.92	.43	8.60	16.15	4.50	4.75	9.25
NC1401-350	1.22	.30	2.29	3.81	.60	.88	1.01	.40	8.13	18.50	4.75	5.25	10.00
NT1401-350	1.42	.41	1.57	3.40	.46	.46	.65	.46		24.81	6.50	9.00	15.50
NT1401-350	1.10	.42	1.26	2.79	.45	.34	.59	.33	7.33	20.91	6.75	6.50	13.25
NC1401-350/Tet	1.82	.18	1.70	3.70	.46	.57	.78	.35	12.13	12.94	2.90	5.50	8.40
NC1401-350/Tet	2.04	.22	1.63	3.89	.42	.48	.68	.47	13.60	13.60	3.60	5.60	9.20
HeD1401-350	2.03	.25	1.37	3.65	.38	.38	.69	.30	13.53	31.82	4.00	6.00	10.00
HeD1401-350	2.07	.25	1.27	3.59	.35	.36	.64	.27	13.80	31.09	4.00	6.00	10.00
HCd1401-350	2.09	.14	1.30	3.53	.37	.38	.61	.31	13.93	12.73	2.20	6.40	8.60
HCd1401-350	2.38	.16	1.59	4.13	.38	.53	.68	.38	15.87	12.49	2.60	6.90	9.50
HC1401-350	7.01	.51	1.18	8.70	.14	.35	.35	.48	46.73	25.30	8.20	2.50	10.70
HC1401-350	6.60	.51	1.27	8.38	.15	.40	.36	.51	44.00	22.21	8.20	2.10	10.30

Nomenclature

- HC - Hydrogen Catalytic
- NC - Nitrogen Catalytic
- HT - Hydrogen Thermal
- NT - Nitrogen Thermal
- HCD - Hydrogen Catalytic Dry
- HeD - Helium Dry
- Tet - Tetralin

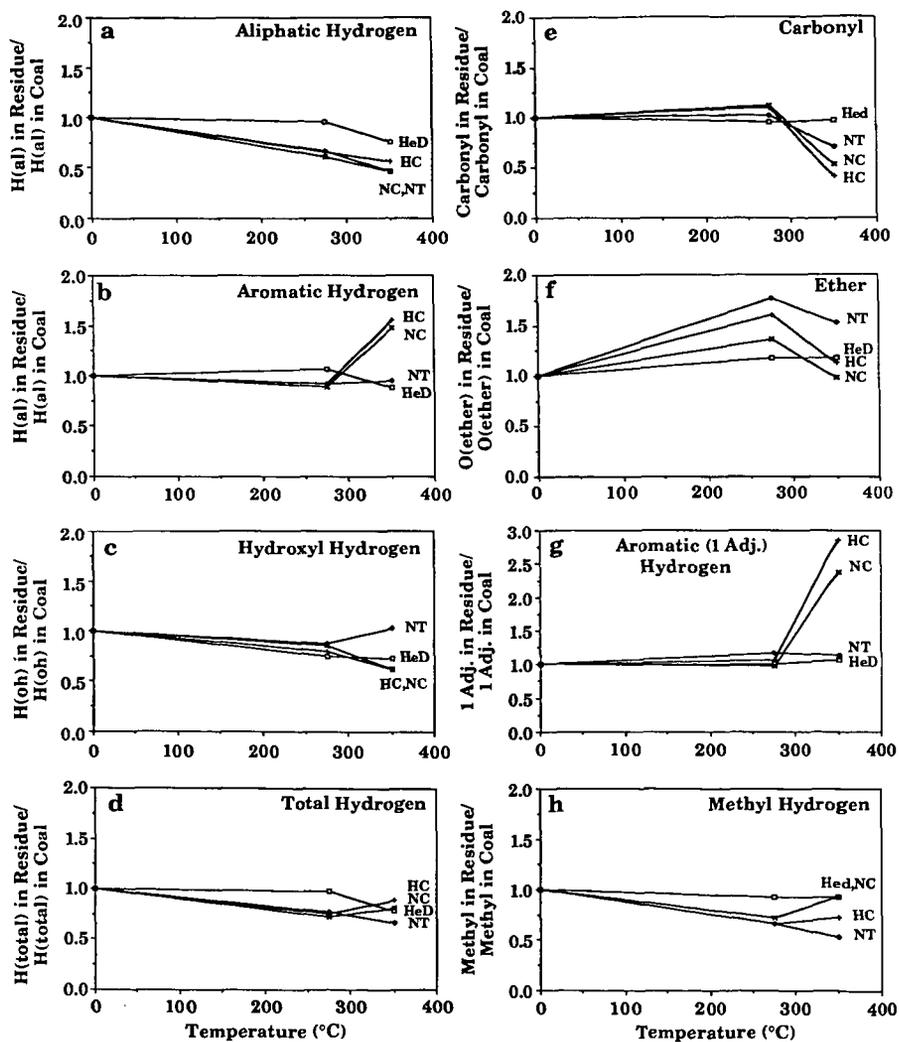


Figure 3. Variations in Functional Group Compositions with Preliquefactions.

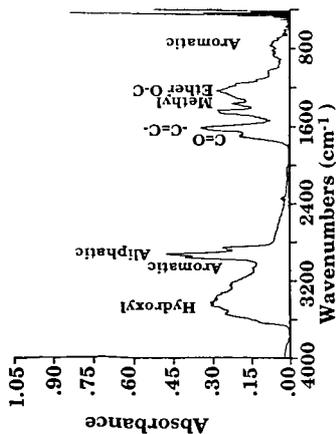


Figure 4. Comparison of FT-IR Spectra of THF Extracts of the Residue (Asphaltene) Formed at 350°C in the Presence of Catalyst and the Presence of Hydrogen.

Table 3 - Carbon Structural Distribution of the Wyodak Subbituminous Coal and the Preliquefaction Residue Formed at 350°C in the Presence of Catalyst and Hydrogen

Sample	f_a	f_a^C	f_a^H	f_{al}	f_{al}^H	f_{al}^*	Carbons/Clusters
Coal	.63	.08	.17	.37	.27	.10	9.7
Char	.75	.05	.28	.25	.16	.09	12.3

Fractions of sp^2 hybridized carbon and (error estimate).
 f_a = total carbon. (± 0.03).
 f_a^C = carbonyl. $\delta > 165$ ppm. (± 0.02).
 f_a^H = protonated and aromatic. (± 0.03).
 Fraction of sp^3 hybridized carbon and (error estimate).
 f_{al} = total carbon (± 0.02).
 f_{al}^H = CH or CH₂. (± 0.02).
 f_{al}^* = CH₃ or nonprotonated. (± 0.03).

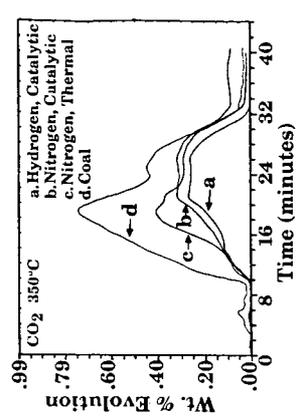


Figure 5. Comparison of CO₂ Evolution Profiles for PSOC-1401 Samples of Coal and Preliquefaction Residue at 350°C from the TG-Plus.

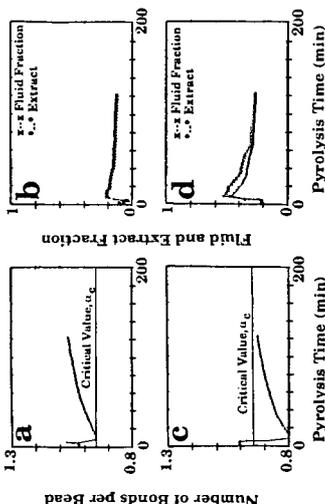


Figure 6. Comparison of Number of Bonds per Bead for a) Original Wyodak Coal (initial crosslinks = 290, initial extract yield = 7.4%, oligomer length = 10 and hard bonds = 200) and c) Modified Wyodak Coal (initial crosslinks = 600, initial extract yield = 21.5%, oligomer length = 4 and hard bonds = 0). b and d Compare the Fluid Fraction and Extract Yield for Original Wyodak Coal and Modified Wyodak Coal, Respectively.