

STUDIES OF THE INITIAL REACTIONS THAT OCCUR
DURING DIRECT COAL LIQUEFACTION*

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INTRODUCTION

Reactions that occur during preconversion processing of coal in direct liquefaction can be either beneficial or harmful. If the thermally or catalytically produced fragments are rapidly stabilized with hydrogen, the resulting compounds have lower molecular weights than the original coal molecules and can be easily upgraded. However, if stabilization is inefficient, the fragments can undergo retrogressive reactions resulting in formation of higher molecular weight materials that are more difficult to upgrade. In current Wilsonville integrated two-stage direct coal liquefaction processes, the initial reactions of coal, which are grouped together under the term preconversion chemistry, occur between the time the coal is mixed with recycle solvent and the time the coal slurry enters the first-stage reactor. This includes the preheating step in which the coal slurry is heated up to first-stage reaction temperatures. The initial temperature for preconversion processing is about 180°C (the temperature of the solvent-coal mixture in the slurry blend tank). The final temperature has not been reported because the temperature of the feed to the first-stage reactor is proprietary. However, it must be less than the average first-stage temperature, which is approximately 425°C.

The objectives of this work are to identify the types of compounds and process conditions that give rise to retrogressive reactions during preconversion processing. Experiments have been performed to evaluate the impacts of temperature, catalysts, mineral matter, and hydrogen donors on these reactions. Initial studies have been carried out using dibenzyl ether (DBE) because ether linkages represent one type of bonding believed to be present in coal (1). Previous studies have analyzed the kinetics and mechanism of thermolysis of DBE (2,3) and have also used DBE to study effects of process variables in coal liquefaction (4). Results of thermal reactions with DBE have shown that the main reaction products are toluene, benzaldehyde, benzyl alcohol and benzene (2). In the presence of catalysts such as $ZnCl_2$, the product distributions are more complicated and can contain significant amounts of material with higher molecular weights than DBE (5,6).

EXPERIMENTAL

Materials

The commercial hydrotreating catalyst for these experiments was Shell 324M, a NiMo/Al₂O₃ catalyst with 12.4 wt% Mo and 2.8 wt% Ni. Prior to use, this catalyst was presulfided with a 10 mol% H₂S/H₂ mixture at 380°C and atmospheric pressure for 2 h, and was then

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ground to -200 mesh. $ZnCl_2$ was used as received. Three types of fine-grained mineral matter were also utilized in experiments: mineral matter separated from an Argonne Illinois #6 Premium Coal by low-temperature ashing, kaolinite ($Al_2Si_2O_5(OH)_4$) in the form of a Georgia kaolin, and an acid-cleaned pyrite sample from the Robena mine.

Hydrotreating Experiments

Hydrotreating experiments and thermal reactions with dibenzyl ether (DBE) were performed in 26 cm³ batch microreactors with 1000 psig H₂ cold charge pressure. All reactions were performed for 15 minutes at temperatures of 180°C, 230°C or 300°C. The catalytic reactions were carried out both with and without the addition of a hydrogen donor (hexahydropyrene, H₆Py) or a hydrogen donor precursor (pyrene). Reactant and catalyst loadings for most experiments consisted of about 100 mg DBE, 50 mg catalyst or mineral matter, and 50 mg of pyrene or H₆Py. One set of four experiments at 300°C, which was aimed at determining the impact of clays on retrogressive reactions, had 425 mg DBE and kaolinite loadings ranging from 26 to 207 mg.

Product Analyses

Products from the microreactor experiments were dissolved in CS₂ and analyzed using a combination of gas chromatography (GC) and GC/mass spectrometry (GC/MS). Recoveries of products from several runs were determined quantitatively by GC using dodecane as an internal standard and response factors determined for DBE, toluene, pyrene and H₆Py. Recoveries of products from the DBE reactions included quantitation of all non-solvent and non-pyrene peaks that were detected on the gas chromatogram. Quantitation of the recoveries of pyrene and H₆Py included all detectable hydrogenated pyrene species. The amount of high molecular weight material formed by retrogressive reactions in each run is defined in this work as the amount of material that could not be detected by GC.

RESULTS and DISCUSSION

Products of the reaction of DBE that were identified in these 300°C experiments include toluene, which is the main product, benzaldehyde, benzyl alcohol, bibenzyl and other C₁₄H₁₄ compounds, and diphenylmethane. No gaseous hydrocarbon products were detected in these runs.

Results of experiments performed at 300°C with Shell 324M are shown in Table 1. Two thermal runs at 300°C with DBE yielded some reaction, giving average values of 86 wt% unreacted DBE, 4 wt% toluene, 4 wt% benzaldehyde, 1 wt% benzyl alcohol, and 5 wt% material (100% minus total recovery) that could not be vaporized in the GC, thus showing the presence of high molecular weight material formed by retrogressive reactions. A similar reaction with Shell 324M as a hydrotreating catalyst gave 27 wt% toluene and no detectable DBE. The total recovery of products derived from DBE for this reaction was only 46 wt%. Therefore, 54 wt% of the reaction products were high molecular weight materials. When pyrene, a hydrogen donor precursor, was added to a reaction with Shell 324M (run 3), the toluene yield doubled compared to run 2. However,

23 wt% of the reaction product was still comprised of high molecular weight material. Addition of H₆Py instead of pyrene gave increases in toluene yield and DBE product recovery compared to pyrene addition. Even with this good hydrogen donor present at the start of the reaction, 17 wt% of the DBE product could not be detected by GC. The recoveries of all detectable pyrene species from experiments 3 and 4 were significantly less than 100%, suggesting an interaction between these compounds and either DBE or products derived from DBE.

Reactions were also performed with ZnCl₂ as a catalyst at 300°C with and without pyrene or H₆Py. These reactions all gave almost complete conversion of DBE, but the GC patterns showed very little intensity. Thus, the recoveries of products derived from DBE and the recoveries of pyrene and H₆Py (including all hydrogenated pyrene species) were low (<10 wt%) indicating the formation of more high molecular weight material than obtained in runs with Shell 324M. A GC/MS analysis of the products from experiments with ZnCl₂ plus pyrene and ZnCl₂ plus H₆Py showed the presence of peaks with molecular weights of 292 and 298, respectively, suggesting the presence of benzylpyrene and benzylH₆Py compounds, respectively. These identifications are supported by previous work (5), using DBE and toluene, in which benzyltoluene was identified as a product. If all the unrecovered pyrene (from the ZnCl₂ plus pyrene run) was converted to a benzylpyrene compound, the weight of the benzyl group present in this compound would only account for about 25% of the unrecovered DBE products. The same holds true for the reaction with H₆Py.

If these benzylation compounds are also present in the products for reactions 3 and 4 (Table 1) with Shell 324M, the weight of benzyl groups tied up in the benzylpyrene and benzyl-H₆Py compounds would account for 14 wt% additional recovery of DBE products in run 3 and an additional 6 wt% for run 4. Thus the total recoveries of DBE products would be about 90 wt% for these two reactions, suggesting that up to 10 wt% of the product could be due to high molecular weight material not detected by GC. However, elemental analyses of the catalysts are not yet available and may show that some of the missing material has been deposited on the catalyst.

GC analyses of the experiments with mineral matter separated from the Illinois #6 Premium Coal Sample only accounted for about 9 wt% of the amount of DBE in the feed. Coal-derived mineral matter contains many different components, including clays, pyrite (FeS₂), quartz and carbonates. Therefore, additional experiments were performed with pyrite and kaolinite to determine the impact of these two components on DBE. Pyrite was chosen because it has known catalytic activity. Kaolinite was chosen because it is a clay mineral present in coal and clays usually are the most abundant minerals in coal. In addition, a previous study (7) has shown that the acidic components of coal mineral matter enhance DBE conversion. The products of the reaction with pyrite have not yet been quantified, but the GC area counts suggest that pyrite gave a high recovery of DBE products and a toluene yield similar to those obtained with Shell 324M in runs 3 and 4 of Table 1. In contrast, a reaction with kaolinite gave a recovery of DBE products of only 7 wt%, suggesting that the clay components of the mineral matter are primarily responsible for the retrogressive reactions that occur.

All of the products from the DBE experiment with kaolinite were soluble in CS₂. Filtration and weighing of the kaolinite from the reactor gave a good recovery with only a minor weight gain, which accounted for <2.5% of the non-recovered material. In addition, evaporation of the CS₂ from the reaction products yielded most of the weight that could not be detected by GC. Therefore, the poor recovery of DBE products had to be due to formation of high molecular weight materials. A set of four reactions was performed with different feed/kaolinite ratios. The results, shown in Table 2, indicate that even small amounts of clay can have a significant impact on recovery and hence on the formation of compounds by retrogressive reactions.

At 230°C, a thermal reaction and reactions catalyzed by Shell 324M, ZnCl₂, and mineral matter from the Illinois #6 coal gave results similar to those obtained at 300°C; pyrite yielded only about a third the toluene of the 300°C reaction.

At 180°C, a thermal run showed very little reaction and had a total recovery of 100 wt%. A reaction with Shell 324M gave 73% recovery of products derived from DBE including 55 wt% toluene. Comparison of these results with those of run 2 in Table 1 shows that the toluene yield is double that obtained at 300°C and the overall recovery is about 50% higher. The reaction with Shell 324M therefore appears to be more efficient at the lower temperature, and suggests that it would be beneficial to measure the rates of the reactions occurring at both 300°C and 180°C. Pyrite gave very little reaction at 180°C, which is not surprising since the pyrite - pyrrhotite transition does not occur at this low temperature and pyrrhotite is believed to be the active phase (8). A reaction with a feed containing 2:1 DBE:kaolinite gave only 15 wt% recovery of DBE products. Therefore, even at this low temperature, retrogressive reactions yielded 85 wt% high molecular weight products with kaolinite.

CONCLUSIONS

The results of these experiments indicate that retrogressive reactions of DBE occur in the presence of a good hydrogenation catalyst (Shell 324M), a Lewis acid (ZnCl₂), and coal-derived mineral matter. ZnCl₂, coal-derived mineral matter, and kaolinite (a clay present in coal) cause the greatest yield of high molecular weight products from retrogressive reactions. These results suggest that detrimental reactions can occur in the low temperature initial stages of coal liquefaction when coal mineral matter is present. Although the amount of retrogressive products is less in reactions with Shell 324M, it is still significant even with a good hydrogen donor and high pressure hydrogen. Therefore, the addition of a hydrogenation catalyst, such as Shell 324M, will not eliminate these low temperature reactions. The best way to minimize these reactions may be to use coals that have been extensively cleaned to remove the clays. Future studies will involve determining if these effects are also obtained with coal.

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Table 1. Results of quantitative analyses of 300°C 15 minute reactions.

Run #	Catalyst	Additive	Product Recoveries*			Recovery (Wt %)** Additive
			DBE	Tol	Total	
1	-	-	86	4	95	
2	Shell	-	0	27	46	
3	Shell	Pyrene	0	54	77	42
4	Shell	H6Py	1	61	83	72

- * Based on weight % of DBE in feed.
 ** Based on weight % of pyrene or H₆Py in feed. Recoveries include all pyrene species detectable by GC.

Table 2. Effects of feed/kaolinite ratio on product recovery.

Feed/Kaolinite	Product Recovery*
2.2	7
4.9	7
15.6	17
38.5	87

- * Based on weight % of DBE in feed.

LIQUEFACTION BEHAVIOR OF HIGH-SULFUR LIGNITES

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INTRODUCTION

Previous work in this laboratory has investigated the hydrodesulfurization of Mequinenza (Spanish) lignite, a coal which is of interest for its remarkable organic sulfur content of about 11% on a daf basis. In experiments using impregnated molybdenum catalysts, sulfur removals of up to about 70% were obtained (1,2). In an ideal process configuration, the hydrodesulfurization reaction would remove the organic sulfur as H_2S , leaving a sulfur-free or low-sulfur char suitable for combustion. However, it is inevitable that the reaction of a highly reactive lignite with hydrogen in the presence of a good hydrogenation catalyst will produce some liquids as by-products. In fact, in the experiment in which a sulfur reduction of 70% was achieved, 48% of the lignite was converted to liquid products, although most of the sulfur removed did appear as H_2S . This behavior prompted an examination of the liquefaction reactivity of this lignite, with particular concern for the formation of liquids at relatively mild conditions and short reaction times.

Given's study of the liquefaction behavior of 104 high volatile bituminous coals included coal samples of up to 7.3% total sulfur (dry basis) (3). Examination of the data by cluster analysis showed that a factor representing sulfur had a major role in separating the coals into statistically separate groups. Subsequent work, using a set of 26 high volatile bituminous coals with a maximum sulfur content of 7.9% (dry basis), showed no significant relationships of the yields of oils, asphaltenes, or gas to sulfur content (4). The highest organic sulfur content of the coals used in that work was 3.3% (dry basis). The final comment in the 1988 paper (4) was that, "the role of sulphur in coals clearly merits further intensive study."

The work reported here used coals of different rank and much milder reaction conditions. Furthermore, a much smaller sample set was used. Therefore, our results are not intended to be a direct extrapolation of previous work (3,4), but rather represent a collateral line of investigation. The results presented here offer some insights into the exploitation of the relatively weak C-S bond for obtaining good liquids yields at mild conditions which might be typical of the low-temperature stage of a temperature-staged liquefaction system.

EXPERIMENTAL

Three lignites were used in this work: Hagel seam lignite from the United States, Cayhira lignite from Turkey, and the Spanish Mequinenza lignite mentioned above. Some of the characteristics of these lignites are shown in Table 1. The principal criterion for the choice of these lignites was to obtain as wide a range of organic sulfur contents as possible. A secondary consideration, having first obtained the desired organic sulfur contents, was to obtain lignites with reasonably comparable carbon and hydrogen contents.

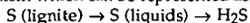
The procedure for conducting the reactions was the same regardless of the gas atmosphere or whether a catalyst was used. All reactions were carried out in microautoclave reactors (tubing bombs) of nominal 30 mL capacity. A 5 g lignite sample of dry lignite was used. No solvent was used in these experiments. The reactor was flushed three times with the desired gas, either nitrogen or hydrogen, before being pressurized to 6.9MPa. The pressurized reactor was then immersed in a sandbath preheated to 275° C. The reactor was subjected to vertical oscillation of 2.5 cm at 200 cycles/min for 30 min. At the end of an experiment the reactor was rapidly quenched by immersion in cold water.

The cooled reactor was vented into a glass expansion bulb from which samples could be withdrawn for gas chromatographic analysis. The reactor contents were washed with tetrahydrofuran (THF) into a dry Soxhlet thimble and were then extracted with THF for about 24 hr under nitrogen. The THF was removed from the extract by rotary evaporation. The solid residue was dried at 100° for 18-20 hr before weighing. The gas yield was calculated by difference from the weights of the liquids and the THF-insolubles.

For experiments in which a catalyst was used, the lignites were impregnated with reagent grade ammonium tetrathiomolybdate, $(\text{NH}_4)_2\text{MoS}_4$. An amount of this salt sufficient to give a 1% molybdenum loading (expressed on a daf basis as elemental molybdenum, not the molybdate salt) was dissolved in sufficient distilled water to give a 1:1 lignite:water ratio. The lignite was slurried in the aqueous solution and stirred for at least 2 hr. Excess water was removed by vacuum freeze drying to a lignite moisture content below 1%. Typically the impregnation procedure was carried out with a large enough batch of lignite to suffice for a series of experiments. The dried, impregnated lignites were stored under nitrogen.

RESULTS AND DISCUSSION

An analysis of the yields of sulfur-containing liquids and H_2S , and of the selectivities to these products, as functions of conversion suggests that the net hydrodesulfurization process for the Mequinenza lignite occurs via a sequential mechanism which can be represented as



This analysis has been discussed previously (5) and is presented in detail elsewhere (6). Assuming that the reaction follows pseudo-first order kinetics allows calculation of the apparent activation energy for hydrodesulfurization by the standard Arrhenius approach (e.g., 7). The apparent activation energy calculated in this way is 28.5 kcal/mole, which is in very good agreement with a value of 27.9 kcal/mole determined for the HDS of a coal-derived recycle solvent on a carbon-supported molybdenum catalyst (8). These results, particularly the indication of a sequential mechanism involving an initial production of liquids which are subsequently hydrotreated on the molybdenum catalyst, were the experimental basis for probing further into the first step - liquids formation - with particular interest in whether the unusually high concentration of organic sulfur in the Mequinenza lignite might have some effect on the liquefaction behavior.

The C-S bond is significantly weaker than the C-C bond. Although data in various reference sources vary slightly, values of 66 and 83 kcal/mole, respectively, are typical (9). These values were the basis for a hypothesis that a coal structure containing a high proportion of relatively weak C-S bonds may be more easily broken apart, relative to a structure with small concentration of C-S bonds, in either thermolysis or hydrogenolysis. To test this hypothesis the three lignites, with organic sulfur contents ranging from 0.8 to 11.3%, were reacted in both hydrogen and nitrogen atmospheres with and without a catalyst.

The relevant experimental results are summarized in Table 2. The results for reaction in hydrogen atmosphere show that the liquid yield increases as organic sulfur increases, regardless of whether the lignite was first impregnated with a catalyst. Similar results have been reported for other lignites (with the highest organic sulfur content being 6.0%), but that data was obtained at reaction temperatures of 380-460°C (10). The magnitudes of conversions and product yields in the experiments with catalyst and hydrogen gas are comparable to results obtained in the dry (i.e., without added solvent) catalytic liquefaction of a subbituminous coal at comparable reaction conditions (11). For reactions in nitrogen atmosphere, where presumably the decomposition of the coal structure would be due entirely to thermal effects, liquid yield also increased with organic sulfur for experiments in the absence of catalyst. This trend was not followed for reactions in nitrogen with the impregnated molybdenum catalyst, for reasons which are not clear. However, the Cayhiran lignite was the only one of the three to produce measurable quantities of H_2S during the reaction in nitrogen atmosphere, suggesting that the organic sulfur functional groups in this lignite might be different from those of the Hagel and Mequinenza lignites. The composition

of the gas produced in the treatment of the Cayhiran lignite was 77% CO₂ and 23% H₂S, suggesting that some of the sulfur functional groups in this lignite are readily susceptible to catalytic hydrogenolysis directly to H₂S, rather than breaking apart to form sulfur-containing liquids. For example, diaryl disulfides readily undergo reductive cleavage of the S-S bond to H₂S around 300°C (12).

For experiments in the absence of catalyst, both the Hagel and Cayhiran lignites showed an increase in liquid yield for reactions run in hydrogen relative to those run in nitrogen. In the case of the Mequinenza lignite, the liquid yields were essentially identical, within experimental error. This result suggests that the extensive array of C-S bonds enables a facile, thermally induced breakdown of the coal structure which is able to proceed without the intervention of hydrogen.

When reactions were carried out using lignites impregnated with the molybdenum catalyst, a greater yield of liquids was observed, from all three lignites, for experiments in hydrogen relative to those in nitrogen. Furthermore, the improvement in liquid yield, expressed as the difference between the yield in hydrogen and that in nitrogen, itself increased as a function of the organic sulfur content of the lignite. Thus for Hagel lignite the increased liquid yield in hydrogen was 0.7% (i.e., 3.0% in hydrogen vs. 2.3% in nitrogen), while for the Mequinenza lignite the increased yield in hydrogen was 4.5%.

We hypothesize that the key steps which facilitate the formation of liquids in high yield from the high organic sulfur lignites are the generation of thiols and the subsequent role of thiols in cleaving disulfide structures. The relative thermal instability of the S-S bond, which is even weaker (51 kcal/mole) than the C-S bond (13) is offered as an argument that disulfides should not be present in coals, because of the inability of the disulfide group to survive coalification (12). However, the lignites have not experienced extensive coalification. Thiols are easily formed, as for example, by hydrolytic cleavage of disulfides (14) or other organic sulfur functional groups. Once some thiols have been generated in the reaction, they can then facilitate the further reaction of disulfides. A mixture of disulfides and thiols will equilibrate (assuming no species are removed) to produce all possible reaction products; e.g.



If steps are taken to prevent the complete equilibration of the mixture, then the reaction of the thiol with the disulfide can be exploited to achieve essentially permanent cleavage of the latter. In fact, such a disulfide cleavage by thiols is used in biochemical reactions, where such reagents as 2-mercapto-1-ethanol or dithiothreitol (Cleland's reagent) are used to cleave the disulfide linkage in proteins to the free thiol group in cysteine (15). Provided that the disulfide linkages in the lignites are bridging groups, rather than components of cyclic structures (a proviso analogous to the concept of open ethers and closed ethers among oxygen functional groups), the thiols formed by the initial reduction of some of the sulfur groups could then facilitate further depolymerization of the coal structure by reaction with the disulfides.

It has been suggested that organic sulfur is uniformly distributed throughout a coal sample, on the basis of solvent extraction work (16). Specifically, the sulfur content of extracts produced with various solvents is about the same from one solvent extract to another, indicating that even though individual solvents may be able to dissolve different portions, or extents, of the coal structure, approximately the same amount of sulfur is removed in each case. It is also recognized that in dry liquefaction a good dispersion of the catalyst is of special importance in obtaining good conversions (17). The dispersion of the catalyst obtained by the impregnation technique, combined with the inherent dispersion of the sulfur throughout the lignite structure, facilitate the initial reactions of the sulfur functional groups with hydrogen to generate thiols. Even though hydrogenolysis of the disulfide linkages may be continuing throughout the reaction, the cleavage of the disulfide linkage is further enhanced by the disulfide-thiol reaction.

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TABLE 1

Ultimate and sulfur forms analyses (dry, ash-free basis) of lignites used in this work.

	Hagel	Cayhıran	Mequinenza
Ultimate			
Carbon	71.34	68.15	64.81
Hydrogen	4.50	5.50	5.72
Nitrogen	1.14	2.21	0.96
Organic sulfur	0.79	4.91	11.32
Oxygen (difference)	22.23	19.23	17.19
Sulfur forms			
Total sulfur	0.93	7.34	12.64
Pyritic sulfur	0.10	1.97	1.15
Sulfate sulfur	0.02	0.52	0.14
Sulfide sulfur			0.04
Organic sulfur	0.81	4.91	11.32

TABLE 2

Results of experiments in hydrogen and nitrogen atmospheres at 275^o, 6.9MPa gas pressure (cold) for 30 min. Results are expressed on a dry, ash-free basis.

	Hagel		Cayhıran		Mequinenza	
	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂
Thermal (no catalyst)						
Total conversion	6.0	6.3	4.2	3.0	11.1	11.2
Liquid yield	1.8	1.6	2.4	1.8	11.9	12.1
Gas yield	4.2	4.7	1.9	1.2	-	-
Catalytic						
Total Conversion	7.3	5.5	3.5	1.9	16.0	12.6
Liquid yield	3.0	2.3	3.2	1.8	16.4	11.9
Gas yield	4.3	3.2	0.3	0.1	-	0.7

TEMPERATURE PROGRAMMED AQUEOUS LIQUEFACTION EXTENDED TO SUPERCRITICAL CONDITIONS

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INTRODUCTION

Since coal contains highly diverse molecular structures with chemical bonds of various dissociation energies, the use of one single preselected reactor temperature to accomplish liquefaction is difficult to defend. Isothermal reactor conditions will likely result in the rapid rupture of weak bonds, a modest rate of cleavage of intermediate strength bonds, and probably leave the strong ones untouched. In attempts to address the chemical diversity within coals, the concepts of staged liquefaction and temperature programmed liquefaction have been devised (1-5) and the success of these efforts are encouraging.

Staged liquefaction is defined as using two or possibly more different temperatures over a specified time period to accomplish liquefaction. Temperature programming is defined as the raising of the reactor temperature through a defined sequence of temperatures over the liquefaction time period. In essence, the latter is staged liquefaction with up to an infinite number of temperature stages. The terminology for the latter is adapted from its common usage in chromatography.

The concept of temperature programming was developed as a technique to match the slurry medium's ability to donate hydrogen atoms with the rate of radical production from the coal. The specific objective is to prevent the newly formed coal radicals from undergoing retrograde dimerization reactions by allowing adequate time for the slurrying medium to donate hydrogens to them.

Temperature programming for liquefaction reactors using H₂O-H₂S and Indian Head lignite in the subcritical temperature region, 300-350°C, gave higher yields than comparable ones using either 300°C or 350°C isothermal conditions (1,2). The temperature program profile was designed with the aid of thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (1-3,7,8).

The objective of this study is to extend the use of temperature programming of liquefaction reactions beyond the subcritical temperature region of the slurrying liquid, H₂O-H₂S (1,2,9). ESR, TGA and DTA data are employed in the design of the temperature programs. The critical temperature of water in these reactors is approximately 374°C. However, since it is known to vary with the gaseous composition of mixtures.

EXPERIMENTAL

A 12-ml bath autoclave was used for these experiments (10). For all reactions, 1 g of as-mined Indian Head lignite (Zap, ND) ground to 200 mesh was charged along with 1 g H₂O, 0.117 g pyrrhotite ground to 200 mesh, 1.73 MPa H₂S, 3.39 MPa CO and 3.39 MPa H₂ into the autoclave. The heating block was preheated to the initial temperature, and the autoclave, when inserted into the heating block, reached 300°C 2.0 min. after insertion. Then, the heating block temperature was manually varied from 300 to the final temperature with the appropriate temperature program. After reaction, the products were washed with the desired solvent into a glass fiber soxhlet extraction thimble and extracted until constant weight was achieved. The yields were calculated using the mass of undissolved solid on the moisture- and ash-free basis. The proximate and ultimate analyses of Indian Head lignite are: moisture 29.5%, ash 9.0% moisture-free(mf), carbon 65.0% mf, hydrogen 4.2%, nitrogen 1.9% mf, sulfur 0.8% mg and oxygen 19.1% mf by difference.

RESULTS AND DISCUSSION

The rapid progression of temperature profiles (rapid profiles) employed herein are portrayed in Figure 1, and the slow progression of temperature profiles (slow profiles) used for this study are defined in Figure 2. The results obtained from using various temperature programs to liquefy Indian Head lignite are shown in Figures 3-9. Figure 1 illustrates the rapid profiles used to obtain the yield data of Figures 3-7 (points A through P). Figure 2 similarly portrays the slow profiles used to obtain the yield data of Figures 8 and 9 (points Q through T). Hereafter, when three percentage yields are given as the data from a given set of conditions, the three percentages refer to THF-, toluene-, and cyclohexane-solubility yields, respectively. The selection of the plateau temperatures of the temperature program used herein, 300°, 350°, 400° and 450° is discussed in the preceding article (2).

The isothermal data illustrated in Figure 3 and Table 1 serve as the baseline liquefaction yield data against which the yield data of the temperature programmed runs can be compared for relative effectiveness. When the residence time at 300°C is increased (programs A to D of Figure 1), the conversion to tetrahydrofuran (THF)-soluble products is enhanced (Figure 3).

When the liquefaction reactor temperature is isothermally kept at 350°C for 37.5 minutes, the conversions are improved by 22%, 23% and 11% (program G of Figure 1 Figure 4) from that of the 37.5-minute, 300°C isothermal reaction (program C of Figure 1, Figure 3). No appreciable further increases in the soluble product yields occurred by extending the residence time at 350°C from 37.5 to 60 minutes (programs G to H of Figure 1, Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C over 60 minutes using the rapid profile (program L of Figure 1, Figure 5), the yields improved from that of the 350°C isothermal reaction (program H of Figure 1) by an additional 9%, 23% and 22%. When compared to the 400°C, 60-minute isothermal reaction, the 400°C programmed reaction gave yields which were improved by 8%, -14%, and 14%. When residence time at 400°C was increased from 0 to 40, minutes the cyclohexane-soluble product yields further improved (programs J to L of Figure 1, Figure 5) but the THF- and toluene-soluble product yields were essentially unchanged.

When the liquefaction reactor temperature was programmed to proceed from 300 to 450°C over 60 minutes using the rapid profile (program O of Figure 1, Figure 6), the product yields further increased from that of the 60-minute, 300 to 400°C program L by an additional 4%, 30%, and 9% (Figure 5). The residence time at 450°C (programs N to O of Figure 1) enhanced the toluene-soluble yield but had little effect on the THF- and cyclohexane-soluble product yields. The 300 to 450°C temperature programmed product yields at 37.5 minutes are +20%, -4%, and +8% changed from the yields obtained under comparable 450°C isothermal conditions (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 480°C over 60 minutes using the rapid profile (program P of Figure 1, Figure 7), the cyclohexane-soluble product yield is enhanced and the THF-soluble product decreased from that of the 300-450°C reaction (program O of Figure 1, Figure 6). The 300-480°C, 60-minute programmed reaction provides 7% greater THF-soluble product yield than that of isothermal reaction of 480°C for 60 minutes (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 350°C over 37.5 minutes using the slow profile (program Q of Figure 2, Figure 8), the product yields are 4%, 2%, and 1% increased from that of the comparable 350°C, 37.5-minute isothermal reaction (Figure 4). However, the differences are not statistically significant. At 60 minutes (programs Q to R of Figure 2), the corresponding yields are increased by 14%, 13%, and 6% from that of the related isothermal program H of Figure 1 (Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C using the slow profile (program T of Figure 2, Figure 9), the yields are increased by 7%, 14%, and 4% from that of the comparable related rapid profile (program L of Figure 1, Figure 5) and 14%, 9%, and 20% from that of the 60-minute, 400°C isothermal reaction (Table 1). Residence time at 400°C was valuable in enhancing both the toluene- and cyclohexane-soluble yields (Figure 9).

In summary, the slow 300-400°C profile gives 95%, 83%, and 57%, the rapid 300-400°C profile gives 88%, 59%, and 53%, and the 400°C isothermal run produces 81%, 72% and 37% soluble product yields for the 60-minute reaction time.

CONCLUSIONS

Temperature programmed liquefaction gives superior yields compared to the corresponding isothermal counterpart and is dependent upon the nature of the temperature program profile. In a H₂O/H₂S medium using CO/H₂/pyrrhotite/Indian Head coal over the 300-450°C temperature range, the use of two designed temperature program profiles is examined: one with a rapid progression of temperatures and a second with a slow progression. The liquefaction efficiency is measured by the yields of cyclohexane-, toluene-, and tetrahydrofuran-soluble products formed. The relative liquefaction yields for 60-minute reactions are: slow profile > rapid profile > isothermal. The rate of temperature progression through the three sequential 50-degree temperature segments influences the three yields differently. The residence time at 300°C is important in producing respectable yields of THF-soluble products, the 300-350°C temperature range further improves all three product yields, the 350 to 400°C temperature range primarily improves the yields of toluene- and cyclohexane-soluble products, and the 400-450°C temperature region further improves the toluene-soluble product yields. No special yield effects are observed on going from subcritical to supercritical aqueous conditions in the course of the temperature programs.

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Table 1. Conversion Yields Using Isothermal Conditions

Temp. °C	Time, min	Conversion yields, % ^a		
		THF	Toluene	Cyclohexane
300	60	68	10	10
350	60	81	10	10
400	60	81	72	37
450	37.5	70	67	54
480	60	76	na	na

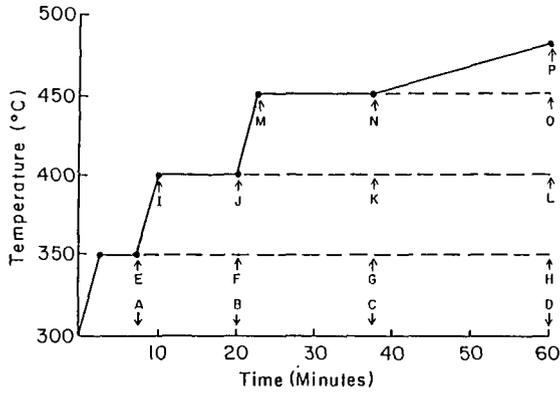


Figure 1. Rapid temperature progression programs (rapid profile) used to liquefy Indian Head lignite.

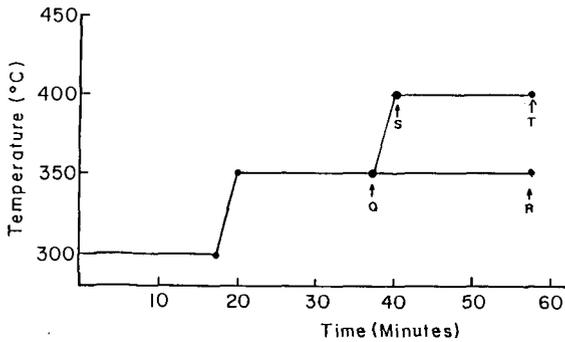


Figure 2. Slow temperature progression programs (slow profile) used to liquefy Indian Head lignite.

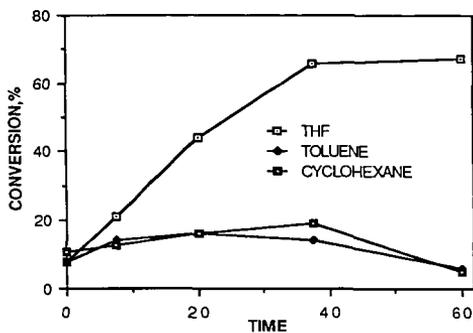


Figure 3. The yields of soluble products obtained as a function of time isothermally at 300°C.

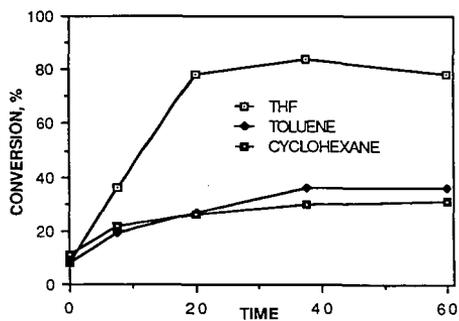


Figure 4. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 350°C.

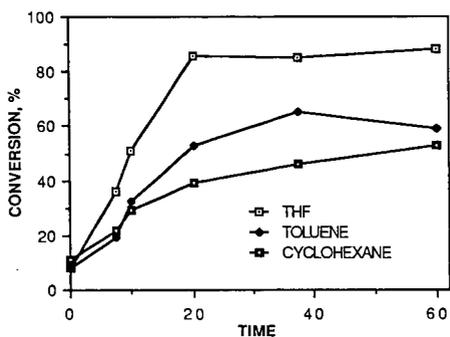


Figure 5. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 400°C.

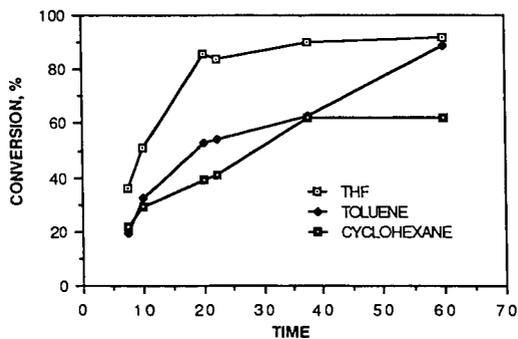


Figure 6. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 450°C.

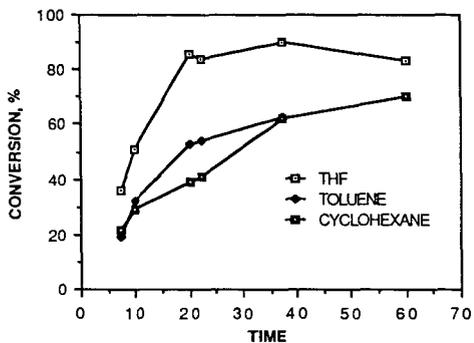


Figure 7. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 480°C.

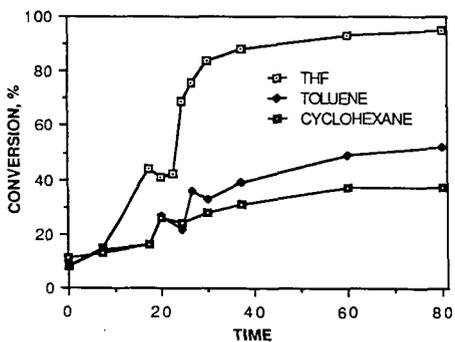


Figure 8. The yields of soluble products obtained as a function of time using the slow profile from 300 to 350°C.

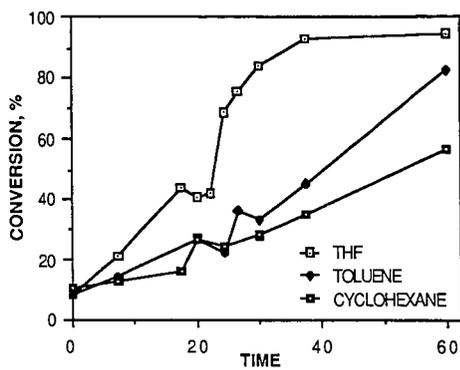


Figure 9. The yields of soluble products obtained as a function of time using the slow profile from 300 to 400°C.

UNEXPLORED PRODUCTS FROM
REACTIONS OF LOW-RANK COAL IN AQUEOUS SYSTEMS

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INTRODUCTION

Processing of coal in aqueous systems has been investigated for a variety of purposes. The aqueous processing conditions can be divided into three temperature regimes. Temperatures over 375°C are considered to be liquefaction conditions. The liquefaction of coal in water and carbon monoxide at 400°C was demonstrated in 1921 by Fischer and Schrader (1). Appell applied aqueous processing to lignites and Bruceton coal in 1968 (2). An organic vehicle was also added in much of their study. Further development of aqueous carbon monoxide (CO-Steam) processing was conducted at the Grand Forks Energy Technology Center (3). Stenberg has reported the processing of low-rank coals in water-hydrogen sulfide mixtures (4). The chemistry of aqueous conversions of bituminous coals at 400°C has been investigated by Ross (5) and Ruether (6). Supercritical aqueous systems have also been investigated for low-rank coal liquefaction (7). Temperatures less than 300°C have been studied for coal activation in staged processing (8,9). Intermediate temperatures (300 to 370°C) are used in processes such as hot water drying of low-rank coals (10).

Our studies were directed toward elucidating the transformation of oxygen functional groups during processing of low rank coals. This paper reports the results from a matrix of reactions conducted in aqueous systems in the intermediate temperature range (300 to 325°C). The objectives were to determine the extent of conversion with an emphasis on decarboxylation and dehydration reactions under these mild conditions and to investigate the cleavage of oxygenated organic compounds, such as phenolics and ketones, from the coal structure. The effects of phase transfer catalysts in improving the conversion were studied. Also, the question of whether a submicron-particle-size dispersion of the coal in an alkaline medium has any effect on reactivity in the liquefaction was investigated.

In this intermediate temperature range, the changes in the coal were extensive enough so that conversion to soluble and volatile products was obtained, and detailed analyses of the products were carried out. The products were in some cases different from those obtained at higher temperatures. Some of these products are not stable at 375°C. In conducting experiments at the intermediate temperatures, there is less uncertainty about whether products resulted from primary or secondary reactions.

EXPERIMENTAL

A matrix of reactions were carried out under different conditions with a high sodium Beulah (ND) lignite (11). The lignite (850 micron size) was mixed with the aqueous medium in a 1:25 ratio. Reactions were carried out in a 300 ml Parr bomb reactor with magnetic stirring. The reactor was heated at the desired temperature (with cold charge) for one hour. At the end of the reaction period, the reactor was cooled to room temperature and the product

gases removed. The solid product was recovered by filtration. Percent conversion was reported as 100 minus the percent of the insoluble solid recovered (mf basis).

The basic filtrate was extracted with ether to give an ether-soluble extract of neutral components. Acidification of the filtrate and extraction with dichloromethane gave the base-soluble fraction (mainly phenolics and lactones). The physical and product yield data are given in Table 1. Along with various yield comparisons, the reaction products were examined with solid state ^{13}C NMR, PAS-FTIR, and GC/FTIR/MS (12). Analyses of catechols were performed with an HPLC method.

One experiment involved testing a colloidal dispersion in aqueous 5% sodium hydroxide. The dispersions were made by blending the as-received coal with the aqueous base at high speed at ambient temperatures with a kitchen-style blender (11). These dispersions are very stable and are resistant to separation by centrifugation as well as filtration.

RESULTS AND DISCUSSION

The reaction of Beulah lignite in water (no reducing agent or catalyst) at 325°C was examined first as the basis for further investigations. Duplicate runs gave very low conversions (21%). The PAS-FTIR spectrum of the coal residue showed that some loss of carboxylic acid groups had occurred, and a small residual pressure of carbon dioxide was obtained as a result of the thermal decarboxylation. The ^{13}C NMR spectrum of the residue showed it to be considerably deficient in aliphatic carbons in comparison with that of the unreacted Beulah. Analysis of the soluble products showed that the phenolic fraction consisted mainly of phenol and guaiacol, with smaller amounts of cresols and the series of methyl-, ethyl-, and propylguaiacol, and even smaller amounts of the other alkylphenols commonly found in coal pyrolysis products. This distribution of the phenolics, with the guaiacols in abundance, is unusual and therefore remarkable. Traces of catechols were also present. The portion of the coal structure which is most like lignin is evidently the most easily cleaved under neutral conditions. The neutral product fraction consisted mainly of cyclic ketones, such as substituted cyclopentanones and cyclopentenones, and small amounts of alcohols (13). These polar organic compounds were qualitatively analyzed with the GC/FTIR/MS.

Aqueous processing was next investigated by adding a mixture of formic acid and sodium formate to the suspension of coal in water and heating at 325°C for one hour. A significant increase (doubling) in the conversion was observed. A residual pressure of 200 psi was observed in the reactor after cooling. The gas contained CO_2 formed from the decomposition of formate, and CO_2 from decarboxylation and possibly the water gas shift reaction. FTIR spectroscopy of the unconverted residue confirmed the loss of carboxylic acid groups. The weight of soluble products was 75% of that predicted by the conversion data. In addition to the CO_2 from decarboxylation, water may be lost from the coal structure via dehydration reactions. The soluble products from the reaction were the phenolics and ketones. In this experiment with the added formate, the distribution of phenolics was more typical of low-rank coal pyrolysis or high temperature liquefaction product, with very small amounts of guaiacol and the alkyl-substituted guaiacols and large amounts of cresols and alkylphenols.

A similar liquefaction reaction was performed with the formate under basic conditions (5% aqueous NaOH). The conversion after heating at 325°C was about the same as that obtained in the formic acid/formate system above. Less decarboxylation was observed in this case. This finding is consistent with that observed at higher temperatures, that base retarded the decarboxylation, and acid conditions promoted the decarboxylation.

The phenolic products were typical of pyrolysis products with small amounts of guaiacols. Another class of compounds was found in significant amounts in these products from the alkaline reaction conditions. A series of lactones was observed in the material obtained by acidification of the base-soluble fraction. In the basic solution, the lactones are present in the hydroxy acid carboxylate form, which then closes up to the lactone during acidification. Four lactones were identified by matching mass spectra and infrared spectra (13). The identified lactones are γ -butyrolactone, α -methyl- γ -butyrolactone, γ -valerolactone, and γ -caprolactone. These lactones were absent in the previous experiments, which were run under neutral and acidic conditions.

A study of reactivity of colloidal dispersions of lignite was performed for comparison with the reactivity of the larger particle coal systems described above. The submicron dispersion of Beulah lignite in aqueous sodium hydroxide was prepared and heated with sodium formate at 325°C. The product yield data indicated that the conversion was roughly the same as that obtained from particulate coal suspensions in base under identical liquefaction conditions. It was concluded that conversion is dependent upon reaction temperatures, times, reducing agents, and catalysts and is independent of the particle size of the coal. This is probably because either the coal breaks down sufficiently or the reactions are not diffusion controlled.

The reaction of Beulah lignite at 325°C in aqueous sodium hydroxide, with no formate present, was also investigated. The conversion dropped considerably and was comparable to that obtained for the reaction in water with no reducing agent. Products were similar to those obtained in the alkaline formate reaction.

To study the effects of temperatures on conversion, decarboxylation and nature of products being formed, several reactions were carried out with the alkaline lignite dispersion with added formate at temperatures of 250 and 300°C. The conversions at 250°C were very poor (0 and 7%) and the conversion at 300°C (34%) was considerably lower than that obtained at 325°C. FTIR studies indicated that very little decarboxylation occurred at temperatures less than 300°C. Phenols were the major products as before.

Several possible coal structures may be considered as precursors for the lactone products obtained. The lactones were obtained under basic conditions even in the absence of formate; thus, a hydrolytic cleavage would seem to be more probable than a reductive cleavage. Hydrolysis of an ester linkage could liberate the γ -hydroxyacids at either the acid or alcohol end, or hydrolysis of a polyester could also give the hydroxyacids. Poly(β -hydroxybutyric acids) are storage polymers of bacteria, and one could speculate on the incorporation of γ -hydroxyacids into coal structures as poly(γ -hydroxyacids), as a result of the same bacterial polymerase enzyme activity during the degradation of woody material. However, attempted acid hydrolyses of coals and treatment with methoxide at lower temperatures, which are normally appropriate for

transesterification, did not give the lactone or the transesterification product, the methyl ester of the hydroxyacid. In fact, no evidence exists for the presence of esters in the low-rank coals.

A more likely possibility is an ether hydrolysis, which would involve cleavage of a bond to the oxygen of the precursor to give the lactone or the hydroxyacid, as shown in Scheme 1. This could be initiated by attack of the carboxylate anion on one side of the ether linkage (substitution mechanism) (1A) or attack of base on groups on the other side of the ether linkage (elimination mechanism) (1B, 1C).

The origin of the cyclic ketones is also intriguing, and few clues are available for deducing the precursors. The most likely possibility is that an extensive thermal rearrangement liberates the ketone. An example of such a deep-seated transformation is the production of acetone during lignin pyrolysis at similar temperatures, where aromatic carbons are incorporated into the acetone structure.

The similarity between the γ -lactone products and the muconolactones involved in the fungal metabolism of alkylbenzoic acids and catechols derived from lignin may generate an opportunity to construct new models for coal structures and the coalification process. Further work is in progress to establish this theory.

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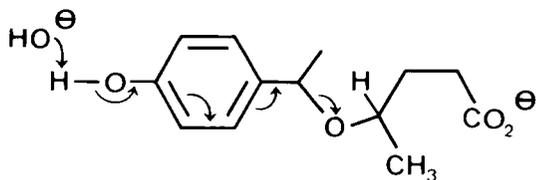
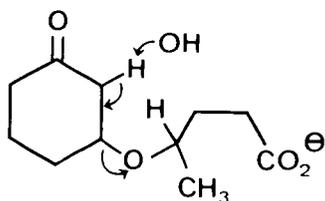
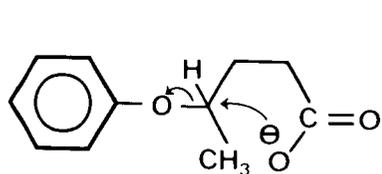
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TABLE 1

REACTIONS OF BEULAH LIGNITE IN AQUEOUS SYSTEMS

Run Number	Solvent	Temp (°C)	Pressure (psi)	Catalyst	Conversion wt%
1.	H ₂ O	325	1460	NaOOCH NaOH	50
2.	H ₂ O	325	1450	none	21
3.	H ₂ O	325	1720	NaOOCH	47
4.	H ₂ O	325	1460	NaOOCH NaOH	50
5.	H ₂ O	325	1470	NaOOCH NaOH	--
6.	H ₂ O	325	1400	NaOOCH NaOH (Disp.)	50
7.	H ₂ O	325	1530	NaOH (Disp.)	23
8.	H ₂ O	250	460	NaOOCH NaOH	--
9.	H ₂ O	300	1000	NaOOCH NaOH	34

SCHEME 1



COMPARISON OF APPROACHES FOR MONITORING H-DONOR CONTENTS
UTILISING REPRESENTATIVE MODEL COMPOUNDS

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ABSTRACT

The content of donatable hydrogen in hydrogenated samples of phenanthrene, pyrene, fluorene, 1-methylnaphthalene and 2-methylnaphthalene have been calculated from ^{13}C nmr spectroscopy, gas chromatography and a chemical test using sulphur as an hydrogen acceptor. Good agreement between the three approaches was found for all the samples except hydrogenated fluorene where the value from the sulphur approach was much higher. However, the ease of carrying out the sulphur approach would suggest that it is a good method for monitoring the donatable hydrogen content of process recycle solvents.

INTRODUCTION

As well as producing good conversions to low boiling point material, a coal liquefaction process on present concepts needs to regenerate its own solvent which should have a content of hydrogen donor compounds sufficient to maintain effective dissolution of coal. In two stage liquefaction processes the solvent is regenerated during the second stage where the coal liquid is catalytically hydrocracked. Conditions must be set in this second stage to ensure that the solvent fraction mass balance and its hydrogen content are maintained on recycling the solvent to the first dissolution stage. Consequently, monitoring the amount and changes in composition of the recycle solvent is an important role in liquefaction processes.

Since the recycle solvent fraction contains many different compounds, a detailed assessment of changes in composition is difficult. However, an evaluation of the 'dissolving power' can be made if the hydrogen donor content of the recycle solvent is measured. Several methods have been proposed for measuring the hydrogen donor content with probably the most popular approach adopting quantitative nmr spectroscopy⁽¹⁻⁸⁾. Amongst the other approaches, the use of hydrogen acceptors in chemical tests have been suggested. For instance, Bockrath et al⁽⁹⁾ used dibenzylmercury as a source of benzyl radicals to which hydroaromatic compounds would donate hydrogen. Aiura et al⁽¹⁰⁾ used sulphur as the hydrogen acceptor and found good agreement with results calculated from nmr spectroscopy.

In this paper, a modified chemical test using sulphur is compared with quantitative nmr for hydroaromatic mixtures produced by catalytic hydrogenation of the parent aromatic compound; the donor content was also estimated from the glc analysis of the hydrogenated product. The aromatic compounds used were phenanthrene, pyrene, 1-methylnaphthalene, 2-methylnaphthalene and fluorene whose hydroaromatic derivatives have boiling points consistent with that of the recycle solvent.

EXPERIMENTAL

Hydrogenation of model aromatic compounds

All the hydrogenations were carried out in a 500ml capacity spinning/falling basket autoclave manufactured by Baskerville Scientific Ltd and used a 15% Mo/

3% Co commercial catalyst supplied by Akzo Chemie, the Netherlands. Typically, 75g of the model compound were hydrogenated with 5.0g of catalyst at a feed pressure of hydrogen of 10MPa for 2h at 400°C.

Glc analysis of hydrogenated products

The products were analysed as ~1% solutions in cyclohexane using a Perkin Elmer Sigma 3B Dual FID Chromatograph attached to a JJ Model CR 600 Pen Recorder and a LDC Model 300 Peak Area Integrater. 0.5 µl of the solution was injected through a pneumatic seal onto an OV 101, 25 m x 0.32 mm capillary column over a temperature program of 80°C initial temperature and 5°C min⁻¹ ramp rate. Identification of the peaks was assisted by gc/ms analysis, kindly carried out by British Coal, Coal Research Establishment.

Nmr spectroscopy analysis

Proton and ¹³Cnmr spectra were recorded on a Jeol Model PFT-90Q spectrometer fitted with a 10 mm probe. All solutions were made up in chloroform-d and TMS was added as an internal standard for the proton spectra; the chloroform-d peak at 76.99 p.p.m. was used as the standard for ¹³C spectra. To facilitate quantification of ¹³Cnmr, the paramagnetic relaxation agent, chromium acetylacetonate was added and 10,000 acquisitions were gathered at a 3s delay between the 90° pulses. A gated decoupling sequence was used during acquisitions.

Chemical testing of hydrogenated products with sulphur

0.2-0.3g (weighed to four decimal places on an analytical balance) was reacted with 0.5g of elemental sulphur in a 10ml capacity bomb-type autoclave (manufactured by Baskerville Scientific Ltd) fitted with a 0-10 bar Schaevitz pressure transducer linked to a digital readout. The bomb was maintained at temperature (250°C) until no further increase in the H₂S pressure was observed. The measured pressure was related to the H-donor content using a calibration graph produced from similar experiments with known amounts of 9, 10 dihydrophenanthrene.

RESULTS AND DISCUSSION

Table 1 shows the contents of starting material, hydroaromatic, saturate and non-donor compounds for the hydrogenated products. Where the glc peaks could not be identified they were assigned to the non-donor heading. For phenanthrene the hydroaromatic content was 50% octa, 31% tetra and 3% dihydrophenanthrene with the remaining 16% being made up of butyltetralin, tetralin and the isomerisation compound cyclohexylmethylindan; of the non-donor compounds 14% was identified as biphenyl. The breakdown of the hydroxyrenes was di, 25.5%; hexa, 57.9%; tetra, 5.4% and deca, 11.2%. The hydroaromatic content of the hydrogenated methylnaphthalenes contained both methyltetralins and tetralin and the non-donor compounds mainly consisted of decalin and naphthalene. For fluorene only 80% of the peaks were identified; the hydroaromatic content was all hexahydrofluorene and 49% of the non-donor material was diphenylmethane.

An estimation of the hydrogen donor content was made from glc using the integrated peak areas of the assigned peaks and multiplying by the number of donatable hydrogen. An example of the peak assignment is shown in figure 1 for hydrogenated pyrene. The values calculated are shown in table 2 as wt% donatable hydrogen product. The estimation of donatable hydrogen from ¹³Cnmr spectroscopy followed

the method of Clarke et al⁽¹⁾ and the calculated results are shown in table 2 which also contains the values determined from the sulphur chemical test and values of aromaticities calculated directly from ¹³Cnmr spectroscopy; aromaticities were also calculated indirectly from proton nmr spectroscopy (following Brown and Ladner⁽¹¹⁾) and from glc analysis (denoted by the heading theoretical). A sample ¹³Cnmr spectrum for hydrogenated 1-methylnaphthalene is shown in figure 2 which clearly shows the aromatic and aliphatic regions separated by the peaks from the chloroform-d solvent.

Agreement between the three approaches is generally good, the S-method tending to produce the higher values and ¹³Cnmr the lower values. The donatable hydrogen content obtained from glc is compared with that from nmr in figure 3 and with that from the S-method in figure 4. It can be seen that for figure 3 the points tend to the left of the theoretical line and for figure 4 they tend to the right of the line.

The values for hydrogenated fluorene do show a wide variation compared with the other samples. The value obtained from glc could be an underestimate because of the relatively large proportion of the peaks that remained unidentified. Some of these peaks could have resulted from hydroaromatic compounds and might account for the difference between the glc and nmr spectroscopy methods but is not large enough to account for the difference to the value for the S-method. However, the product from the sulphur test did contain some black insoluble material, probably indicative of the occurrence of some polymerisation. Glc analysis of the soluble part of the product did show the formation of some higher boiling point material (retention time 1918s) and the disappearance of some of the lower boiling point material. Therefore, other reactions than dehydrogenation of hexahydrofluorene to fluorene occurred; these reactions may have produced gaseous alkanes which would contribute to the pressure rise. Unfortunately, analysis of the gas mixture after the reaction was not possible. Further experiments are now in hand to assess the other reactions occurring but the fact that these reactions occur even at 250°C (cf 400°C used for coal dissolution) may suggest that hydrofluorenes may not be good hydrogen donors.

CONCLUSIONS

Apart from the hydrogenated fluorene, the chemical test method using sulphur as an hydrogen acceptor has proved to be a good method for determining donatable hydrogen contents. The method requires only a small amount of sample, can be carried out in a few hours and used relatively inexpensive material. The glc approach would be unsuitable for recycle solvents because of the complex chromatograms and the difficulty in identifying all the peaks. The ¹³Cnmr approach needs more expensive equipment, a separate saturates determination and will take much longer in order to accumulate a good spectrum. The S-method has been tried with recycle solvents and has, on first estimations, shown good agreement with values calculated from ¹³Cnmr⁽¹²⁾. The method is also more representative of the situation in coal dissolution in that it places the recycle solvent under hydrogen donation conditions.

ACKNOWLEDGEMENTS

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STARTING COMPOUND	G.L.C. Analysis of Hydrogenated Product (wt%)			
	Compound remaining	Hydro-Aromatic	Saturates	Non-donor
	24.2	72.2	-	3.6
	28.3	58.1	3.0	10.6
	16.7	74.7	4.8	3.8
	26.4	59.2	4.5	9.9
	28.6	25.8	-	45.6

TABLE 1. ANALYSIS OF THE HYDROGENATED MODEL COMPOUNDS

STARTING COMPOUND	DONATABLE HYDROGEN (%)			AROMATICITIES		
	* S METHOD	G.L.C.	¹³ C N.M.R.	¹³ C N.M.R.	¹ H N.M.R.	THEORETICAL
	1.87	1.84	1.77	0.77	0.85	0.75
	2.09	1.94	1.86	0.75	0.78	0.68
	2.09	2.07	2.08	0.60	0.68	0.63
	1.87	1.65	1.62	0.64	0.69	0.65
	2.44	0.96	1.23	0.61	0.78	0.78

* CHEMICAL DEHYDROGENATION USING SULPHUR AS AN HYDROGEN ACCEPTOR

TABLE 2 Donatable Hydrogen Content and Aromaticities of Hydrogenated Model Compounds

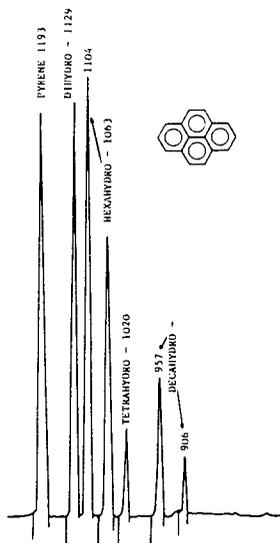


FIGURE 1 Gas Liquid Chromatogram of Hydrogenated Pyrene Showing Retention Times in Seconds

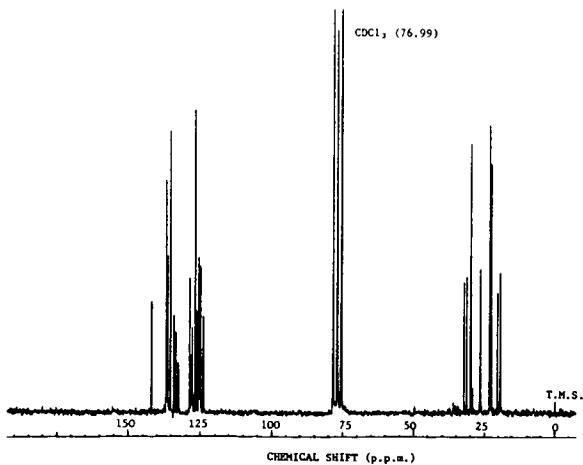


FIGURE 2 ¹³C nmr Spectra of Hydrogenated 1-Methylnaphthalene

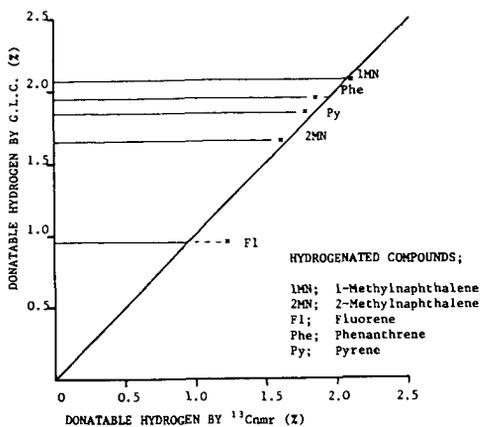


FIGURE 3 Comparison of G.L.C. and $^{13}\text{Cnmr}$ for the Determination of Donatable Hydrogen

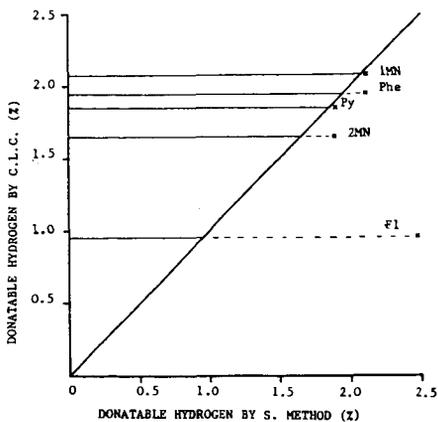


FIGURE 4 Comparison of G.L.C. and S Method for the Determination of Donatable Hydrogen

AUTOClave STUDIES INTO THE HYDROLIQUEFACTION OF COAL LIQUIDS:
THE EFFECT OF RECONTACTING THE CATALYSTS

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ABSTRACT

Fresh and used catalysts (CoMo, NiMo, ZnMo and ZnW) were used in hydro-liquefaction experiments with a Point of Ayr coal liquid over five contacts (2h, 400°C, 19MPa hydrogen) in spinning/falling basket autoclaves. For all catalysts conversions to low boiling point material, H:C ratios of distillation fractions, sulphur contents of the hydroliquefied liquids and carbon contents and specific surface areas of the catalysts were unaffected by repeat contact. However, the sulphur contents of the Mo-containing catalysts did increase with contact reflecting gradual sulphidation of the catalysts by the H₂S produced by desulphurisation of the coal feed; the sulphur content of the ZnW catalyst did not increase after the first contact.

INTRODUCTION

Aspects of coal liquefaction have been much researched, particularly with the re-emergence of interest caused by the oil crises in the 1970's. The types of reactors used in the studies have been various, ranging from small 'bomb' type microautoclaves through larger autoclaves and bench-scale continuous reactors to larger scale pilot or demonstration plants. The use of differently sized and designed high pressure equipment for liquefaction studies further complicates an already complex system and allows only limited comparison of results.

In a continuous reactor, particularly of the trickle bed type, intimate contact between the coal liquid and the catalyst will be maintained throughout the pass of the liquid feed. In an autoclave, particularly of the stirred design, the contact between the liquid and the catalyst will not be as intimate. The action of the stirrer will induce a centrifugal force which will tend to throw the liquid away from the catalyst surface. Consequently, it can be visualised that less strongly adsorbed molecules will spend a shorter time at the catalyst surface so that reaction rates and mechanisms could be very different from those observed in continuous reactor studies. In addition, steady state conditions can be readily investigated in a continuous reactor whereas, for a single contact in an autoclave, steady state conditions may not have been established and changes in catalyst activity will become more relevant.

EXPERIMENTAL

The coal liquid was one of two batches supplied by British Coal Research Establishment (CRE) and was produced by dissolving Point of Ayr coal in a process recycle solvent. The catalysts were prepared by the technique of incipient wetness using an alumina support supplied by Akzo Chemie, the Netherlands following a procedure described previously (1).

The hydroliquefaction experiments were carried out in spinning/falling basket autoclaves manufactured by Baskerville Scientific Instruments; a full

description of the autoclaves is given elsewhere⁽²⁾. The experiments used 100g of the coal liquid and 4.0g of catalyst at a hydrogen pressure of 19MPa at a reaction temperature of 400°C for 2h. After the experiment the liquid product was transferred to a glass jar and stored under nitrogen; the catalyst was removed from the autoclave basket, rinsed with tetrachloroethane in an ultrasonic bath, air dried and stored in glass vials. In order to ensure that sufficient catalyst was available to take samples for analysis the following number of experiments were carried out for the five contacts: 1st contact, 5; 2nd contact, 5; 3rd contact, 4; 4th contact, 3; and 5th contact, 2 experiments making a total of 19 experiments per catalyst.

The hydrocracked product was separated into various boiling point fractions by vacuum distillation before analysis by gas chromatography using a Perkin Elmer Model Sigma 3B Chromatograph attached to a JJ Model CR 600 Pen Recorder and a LDC Model 300 Computing Integrator; 0.5 µl of a 1 wt% solution of the fraction in cyclohexane was injected onto a 25m x 0.32 mm OV 101 capillary column using a temperature program of initial temperature 80°C, ramp rate 5°C min⁻¹. Some carbon, hydrogen and sulphur analysis was carried out on the liquid products and used catalysts. A Leco Model CHN Determinator was used for carbon and hydrogen analysis and a Leco Model SC 132 Sulphur Determinator was used for sulphur analysis. The specific surface area analysis of the used catalysts was by nitrogen adsorption using a Micromeritics instrument.

RESULTS AND DISCUSSION

Repeat contact experiments were carried out with the bimetallic catalysts CoMo, NiMo, ZnMo and ZnW; the catalysts were prepared to contain 15 wt% of Mo or W (as its common oxide) to the mass of the alumina support and 3 wt% of the oxides Co, Ni or Zn. The amounts of material bpt <260, <275, 275-450 and >450°C (calculated from a combination of the masses of the distillation fractions and their g c analysis) are expressed as wt% of the hydrocracked liquid (HL) for CoMo-catalysed experiments in the bar chart figure 1; the bar chart in figure 2 shows similar values for the average of the four catalysts. Both figures show that the amounts of the various bpt fractions were not significantly dependent upon repeat contact. Overall there was a tendency for conversion to low bpt material (<260 or <275°C) to be slightly higher after the first contact, i.e. with fresh catalyst and to fall after the 5th contact; the high first contact value would result from the initial higher surface area of the fresh catalyst and the low 5th contact value could have resulted from gradual catalyst sintering causing some of the catalyst to pass through the holes in the basket mesh.

The bar chart in figure 3 shows the wt% of hydrophenanthrenes (excluding perhydrophenanthrene), phenanthrene and material boiling below naphthalene in HL for ZnMo-catalysed experiments; the zero contact refers to the coal liquid feed (CL). It can be seen that the amounts were not influenced by repeat contact. The amounts of hydrophenanthrenes and material bpt below naphthalene were more than those in CL and the amounts of phenanthrene tended to be lower.

The values of the H:C ratios for the boiling point fractions obtained after vacuum distillation of the HL's from CoMo-catalysed experiments, shown in figure 4, again indicate no dependence on repeat contact. The H:C ratios decreased with increasing bpt of the fraction. The sulphur contents of the HL's for all the four catalysts are shown in figure 5 with no dependence on repeat contact. The lower values for the two Zn catalysts only reflected the use of a different batch

of CL whose sulphur content was less. In terms of the sulphur contents of the distillation fractions for NiMo and CoMo the average values, for the five contacts were 0.01, 0.02, 0.03 and 0.27% for the cold trap, the <250°C, the 250-275°C and 275-450°C fractions respectively, i.e. most of the sulphur in the recoverable material residing in the 275-450°C fraction which would represent the recycle solvent. There was very little change in the values with repeat contact showing that the solvent fraction will be recycled with a relatively high level of sulphur but that the sulphur concentration would not increase with recycle and the catalyst desulphurisation capacity would not be impaired. The level of sulphur in the recycle solvent is quite surprising bearing in mind the relative ease of desulphurisation compared with the denitrogenation or deoxygenation. Most, if not all, of the sulphur remaining will be in a ring in clusters and the likelihood is that some preferential adsorption on the catalyst surface has prevented some of the sulphur-containing molecules from reaching the catalyst surface.

The values for carbon contents and specific surface areas for the used ZnMo catalysts are shown in figure 6 and the sulphur contents of all the used catalysts are shown in figure 7. Only the sulphur contents of the catalysts showed any dependence on repeat contacts and the increase in sulphur content for Mo-containing catalysts indicated gradual sulphidation of the metal content of the catalysts. For the W-containing catalyst, ZnW, the sulphur contents remained relatively constant after the first contact, probably indicating that only the Zn content was sulphided and that the level of H₂S produced by desulphurisation was inadequate to cause sulphidation of the W content. Since it is accepted that presulphidation of Mo and W-containing catalysts enhances their activity, it might have been expected that catalyst activity would increase with contact because of sulphidation. However, it has been reported that 'in situ' sulphidation of catalysts does not lead to enhanced activity for autoclave studies⁽¹⁾, probably because of rapid carbon deposition, and hence increasing sulphidation with contact would be unlikely to enhance activity. In addition, it has been shown in further experiments with a presulphided CoMo catalyst that repeat contact did not affect conversion to low bpt material.

CONCLUSIONS

The investigation has shown that constant catalyst activity was attained after a single contact in the autoclaves. (Other work has shown that this situation also exists at longer reaction times and at different temperatures.) The conversions to low bpt material (hydrocracking), the H:C ratios (hydrogenation) and the carbon deposited on and the specific area of the catalysts (deactivation) as well as the contents of specific materials, e.g. phenanthrene and hydrophenanthrenes, were all unaffected by repeat contact in the autoclaves. Consequently, single contacts for hydroliquefaction investigations should be representative of steady state conditions. However, the results obtained from autoclave studies would not necessarily be reproduced in other types of reactors.

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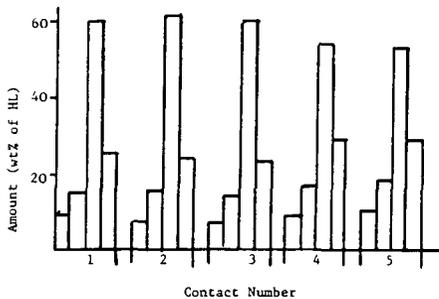


Figure 1. Variation of amounts of fractions with repeat contact with CoMo
 For each contact: 1st bar - $<260^{\circ}\text{C}$;
 2nd bar - $<275^{\circ}\text{C}$; 3rd bar - $275\text{-}450^{\circ}\text{C}$;
 4th bar - $>450^{\circ}\text{C}$. HL = hydrocracked liquid.

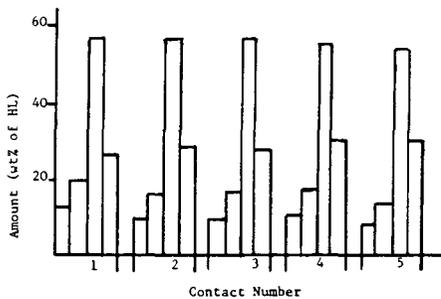


Figure 2. Variation of amounts of fractions with repeat contact - average values for all catalysts.
 For each contact: 1st bar - $<260^{\circ}\text{C}$;
 2nd bar - $<275^{\circ}\text{C}$; 3rd bar - $275\text{-}450^{\circ}\text{C}$;
 4th bar $>450^{\circ}\text{C}$. HL = hydrocracked liquid.

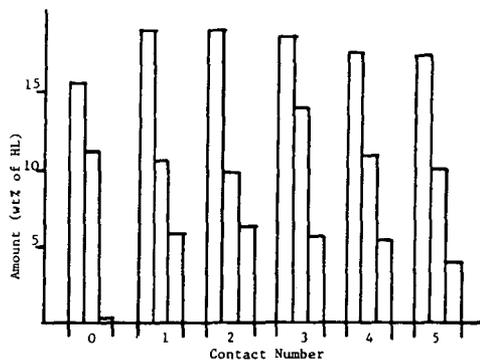


Figure 3. Variation in amounts of hydrophenanthrenes (1st bar), phenanthrene (2nd bar) and material bpt < naphthalene (3rd bar) with repeat contact. HL = hydrocracked liquid; 0 contact indicate coal liquid feed.

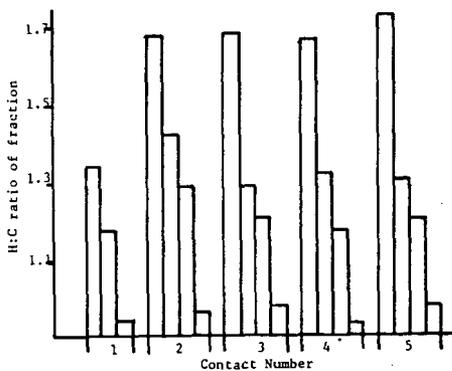


Figure 4. Variation of H:C ratio of distillation fractions with repeat contact. For each contact: 1st bar - cold trap; 2nd bar - 250°C; 3rd bar - $250\text{--}275^{\circ}\text{C}$; 4th bar - $275\text{--}450^{\circ}\text{C}$

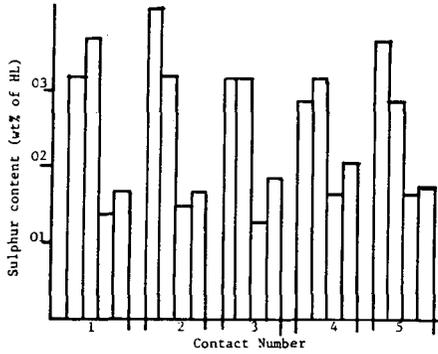


Figure 5. Variation of sulphur content of hydrocracked liquid (HL) with repeat contact. For each contact: 1st bar - CoMo; 2nd bar - NiMo; 3rd bar - ZnMo; 4th bar - ZnW.

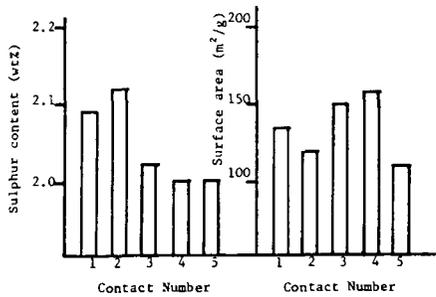


Figure 6. Variation of sulphur content and specific area of catalysts with repeat contact.

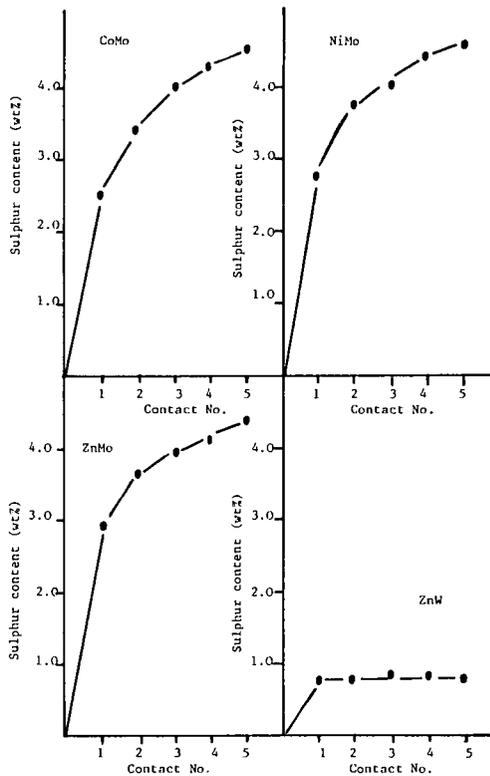


Figure 7. Variation of sulphur content of catalysts with repeat contact.