

COAL GEL CHEMISTRY 2. COAL LIQUIFACTION BY BINARY SOLVENT SYSTEM

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INTRODUCTION

Although the importance of the accessibility of hydrogen donor solvents like a tetralin into coal matrix has long been emphasizing to the primary coal liquifaction of coal(1), not many efforts have been devoted to the study on the penetration mechanism of penetrants into coal, and developing practical devices of improving the accessibility.

Recently, we developed a new method for accurately measuring both the dynamic and equilibrium solvent swelling behaviors of coal(2), and revealed that the coal behaved as a molecular sieve which discriminated among molecules diffusing into the pore system of coal on the basis of size, shape and functionality.

Based on our observations, tetralin is one of the penetrants which show significantly low degree of penetration rate into coal matrix, probably because of its steric hindrance. Meanwhile during the investigation of the synergistic effect on the solvent swelling of coal in the binary solvent system, of which one component was more less bulky than other, we also found that the steric requirement of coal could be released by forming "Coal Gel" under such condition.

Here we report the results of the study on the improvement of the accessibility of hydrogen donor like a tetralin into coal matrix, and the primary liquifaction of coal by using binary solvent systems.

EXPERIMENTAL

The swelling measurements were carried out as described into previous paper (2). Coal, Illinois #6, used in thses studies were from the Ames Laboratory Coal Library. Prior to use, the coal was ground, sized, dried at 110°C overnight under vacuum and stored under nitrogen atmosphere. The solvents were distilled by ordinary procedures before use.

The coal liquifaction were carried out by using a stainless steel tubing micro-autoclave(8.0ml capacity). A typical coal liquifaction procedure is as follows: Coal(500mg; 50-60 mesh) and solvent(3.0ml) were taken into the auto-clave with a stainless ball. After a nitrogen gas was bubbled through the mixture, it was heated for 2 hours in an electric oven maintaining temperature at 370 °C, which was shaken for 3 minutes with 30 minutes intervals. After the re- action, the autoclave was cooled at room temperature, and carefully opened. The content was washed out with 50ml of distilled pyridine, and the mixture was immersed in an ultrasonic cleaning bath for 2 hours. Then it was filtered through 3 μ m Millipore-filter.

RESULT AND DISSCUSSION

1. Swelling of Illinois #6 Coal in Hydrocarbons

Table 1 shows the swelling data of Illinois #6 coal obtained with hydro- carbon solvents.

These data clearly indicate that there is a steric component to the swell- ing rate for solvent penetration of the coal matrix, for example, in the branch- ed isomer, that is, in iso-propylbenzene the coal swelled aproximately 9 times slower than in n-isomer. On this point of view, it seems to be quite understand- able that t-butylbenzene or tetralin are belonging to the slowest group of the penetrants. Actually, the molecular model of tetralin shows that the saturated ring system in this molecule makes a significant steric barrier upon the planer aromatic ring system.

2. Swelling of Illinois #6 Coal in Binary solvent System

Figure 2 shows the Illinois #6 coal in benzene / tetralin solvent system. There is a obvious synergistic effect on the equilibrium swelling ratio (Q-value) which means that the addition of certain amount of benzene to tetralin can make a significant increase of tetralin in the coal matrix in terms of the quantity and the penetration rate. As we reported previously (3), in this case also, the relative concentrations of each components, benzene and tetralin, in the supernatant of the coal-solvent mixture was varied through swelling, that is, the concentration of benzene was sharply decreased at the initial stage of swelling and then maintained almost constant value which was a little below the initial concentration.

These observations clearly indicate that less bulky benzene molecule penetrated predominantly into coal matrix, and formed so-called "Coal Gel" which will not possess such rigid steric requirement as the raw coal.

Table 2 shows the equilibrium swelling ratio (Q-value) obtained various solvent systems. It is obvious that the net volume of tetralin in the coal matrix in the binary solvent systems are significantly increased compared to tetralin alone.

3. Coal Liquifaction by Binary Solvent System

Figure 2 shows the pyridine solubles obtained from the liquifaction by the various binary solvent systems, in which the results by tetralin and THQ (1,2,3,4-Tetrahydroquinoline) are also illustrated.

Here, some arguments may come to the penetration mechanism at the liquifaction temperature, 370°C, and the swelling measurement temperature, 21°C.

However the results shown in this Figure strongly suggest that the enhancements of the yields of the liquifaction of coal were caused by the improvement of the accessibility of hydrogen donor like tetralin.

A curious phenomenon was also observed in the case of pyridine / tetralin system in which the addition of pyridine seemed to have induced a negative

effect on the coal liquifaction. It is quite interesting contrast to our common understandings that pyridine was one of the best solvents in the coal chemistry, i.e., extraction or swelling.

ACKNOWLEDGEMENTS

We wish to thank Professors Toshihisa Maeshima and Masakuni Yoshihara for their useful discussions and encouragements.

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Table 1. Swelling Behaviors of Illinois #6 Coal in Hydrocarbons ^{a)}

Hydrocarbons	Q-Value ^{b)}	V _{Ret.} ^{c)}
n-Pentane	1.022	0.8
Benzene	1.046	1.0 ^{d)}
Ethylbenzene	1.038	4.0
n-Propylbenzene	1.024	17.0
i-Propylbenzene	1.008	153
t-Butylbenzene	1.003	> 10 ³
Tetralin	1.003	> 10 ³

a) 100-200 mesh, measured at 21 °C

b) After one month

c) Rate Retardation Factor : $V_i(\text{benzene}) / V_i(\text{hydrocarbome})$

d) $V_i = 2.73 \times 10^{-4} \text{ min.}^{-1}$

Table 2. Swelling of Illinois #6 Coal in Binary Solvent System ^{a)}

Solvent System	Q - Value ^{b)}
Tetralin	1.003
n-Pentane	1.022
n-Pentane / Tetralin ^{c)}	1.025
Benzene	1.046
Benzene / Tetralin ^{c)}	1.030
Methanol	1.323
Methanol / Tetralin ^{c)}	1.110
Pyridine	2.734
Pyridine / Tetralin ^{c)}	1.482
NMPDN ^{d)}	3.063
NMPDN ^{d)} / Tetralin ^{c)}	1.625

a) Coal: 100-200 mesh, measured at 21°C

b) After one month

c) Solvent / Tetralin (1 : 2 vol.)

d) N-Methylpyrrolidinone

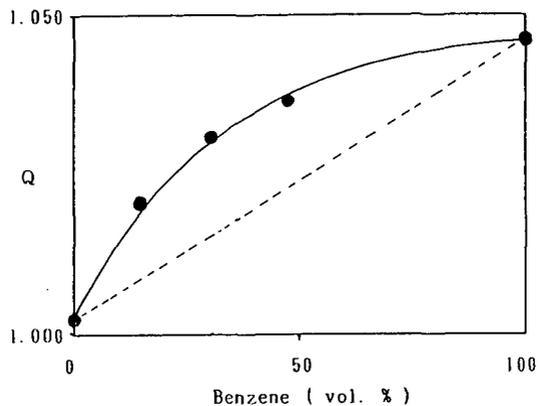


Figure 1 Swelling of Illinois #6 Coal in Benzene / Tetralin System (Coal: 100-200 mesh, 21 °C)

Solvent System	Pyridine Soluble (%, dmmf)		
	0	50	100
Tetralin		43	
THQ ^{a)}			93
n-Pentane / Tetralin ^{b)}		74	
Benzene / Tetralin ^{b)}		71	
Methanol / Tetralin ^{b)}			83
Pyridine / Tetralin ^{b)}		10	
NMPDN ^{c)} / Tetralin ^{b)}			92

- a) 1,2,3,4.-Tetrahydroquinoline
- b) Solvent / Tetralin (1:2 vol.)
- c) N-Methylpyrrolidinone

Figure 2. Coal Liquifaction (Coal : 50-60 mesh, 370 °C, 2 hrs.)

STUDIES OF COAL PYROLYSIS AND COAL
EXTRACTION USING IN-SITU ESR SPECTROSCOPY

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ABSTRACT

Important features of recent results on the pyrolysis and solvent extraction of American coals (H/C between 0.55 and 0.81) using in-situ ESR spectroscopy are presented. In the pyrolysis studies, the temperature variation of the free radical density between 25°C and 650°C establishes the presence of four distinct stages in about a dozen coals studied. Extraction of the coals with N-Methyl Pyrrolidone shows an inverse correlation between percentage extraction and room temperature free radical density. Significance of these results is discussed.

INTRODUCTION

Electron spin resonance (ESR) due to free radicals in coals was discovered in 1954 [1,2]. Since then, some correlations between the ESR parameters of the free radicals in coals and various properties of coals (such as rank [3], heteroatom content [4], liquefaction [5] and coking behavior [6]) have been reported. Recently we developed a heated gas-flow system in which in-situ ESR spectroscopy of samples could be carried out between room temperature and 650°C. This apparatus has been used to study pyrolysis behavior of about a dozen American coals with atomic H/C varying between 0.55 and 0.81. One of the most significant results of this study is the discovery of four distinct temperature regions in these coals from the temperature variation of the free radical density [7-9]. Following this work, Fowler et al [10] have confirmed the presence of similar regions in some British coals. Although some explanations have been advanced for these regions in earlier studies [7-10], additional discussion on these temperature regions or stages as well as some details of the high-temperature apparatus used in this work, are presented in this paper. We also examine the use and limitations of ESR in the studies of the extraction and de-ashing of coals with N-Methyl pyrrolidone (NMP), a subject of considerable current interest [11,12].

THE HIGH TEMPERATURE CAVITY SYSTEM

A block diagram of the high-temperature microwave cavity system used for the in-situ ESR studies for temperatures to 650°C is shown in Fig. 1. All parts with prefix 'WG' are made of quartz and they were obtained from Wilmad Glass Co. The system uses a flowing nitrogen gas passing over a heater (powered by a Variac) to heat the sample located in a TE₁₀₂ mode cavity. To obtain various temperatures, first the voltage in the Variac is adjusted. Additional control is provided by adjusting the gas pressure and flow rate. Temperature stability of ±1°C was obtainable in the whole temperature range studied. Because of the isolation provided by the quartz dewar, the external temperature of the TE₁₀₂ cavity, even at 650°C sample temperature, did not exceed 50°C. Since a thermocouple cannot be placed inside the cavity next to the sample during an ESR experiment, a separate experiment was carried out to calibrate the thermocouple placed at the sample position, but without making ESR measurements. Finally, a screw is used (Fig. 1) to keep the microwave coupling to the cavity constant at different sample temperatures. Further details of this apparatus are given elsewhere [13]. Details of the other experimental procedures are given in our earlier publications [7-9].

RESULTS AND DISCUSSION

A typical variation of the free radical density N_s with temperature for a representative coal (Matewan coal with $H/C \approx 0.71$) is shown in Fig. 2. The data is from Ref. 9 and it shows the four distinct temperature regions mentioned above in the Introduction. In region 1 ($\sim 25^\circ$ - 250°C) and in region 3 ($\sim 400^\circ$ - 600°C), the spin concentration N_s increases with increasing temperatures whereas in region 2 (250° - 400°C) and region 4 ($>600^\circ\text{C}$), N_s decreases with increasing temperatures. Although the locations of these regions or stages differ slightly from coal to coal on the temperature scale and relative changes in N_s with temperature are also different for different coals, the qualitative features of the variation of N_s noted above are the same for all of about dozen coals studied in our work [7-9]. Recent work of Fowler et al [10] on some British coals have yielded similar variations for N_s even though their experiments were done under slightly different conditions viz. flowing N_2 gas through the samples versus evacuated samples in our case. Note that N_s represents the spin density corrected for the Curie variation [7-10].

As an aid to interpret the results, we show in Fig. 2b the schematic variation of the CO_2 internal surface area as a function of the charring temperature for a bituminous coal (Saline County, Illinois) [14] and in Fig. 2c the temperature variation of the sample weight for a British coal [10]. Although the results in Figs. 2a, 2b and 2c are for different coals, sufficient evidence exists [7-10,14] that qualitatively features of these curves are the same for different coals. It is evident from Fig. 2 that these different measurements all point to the distinct temperature stages first highlighted in our ESR work [7]. We now critically examine the nature of these distinct stages.

The average activation energies, evaluated for stage 1 assuming Arrhenius variation is ≈ 4 kcal/mol. Since the magnitude is much smaller than that necessary for bond fission [3,15], stage 1 probably corresponds to the decomposition of the substituted groups, resulting in the release of CO_2 , CO and H_2O [7,15]. Some decrease in the weight of the samples observed in this region supports this finding. Fowler et al [10] have noted that increase of N_s in their samples may partly be due to desorption of oxygen. However this cannot be the case in our samples because our samples were evacuated and vacuum sealed prior to experiments.

The decrease in N_s with increasing temperatures in stage 2 is perhaps one of the more interesting results of these recent studies. Several mechanisms could contribute to a decrease in N_s :

- a. Recombination of free radicals by thermally activated mobility within the pore network;
- b. Previously stable radicals become very reactive, become short-lived and hence are not observed;
- c. Quenching of radicals by internally transferred hydrogen; and
- d. Decrease in the surface area leading to the blocking of the pore network and recombination.

It is noted that there is no significant loss in the sample weight in this region so that some kind of quenching or recombination of the radicals is most likely the cause for the decrease of N_s . We tend to disfavor explanation b since if this was the mechanism, a broadening of the ESR lines should be observed. This certainly is not the case [9]. Explanations a and d are related and they receive strong support from the observed decrease in the surface area

(Fig. 2b and Ref. 14). It is noted that stage 2 is observed even in treated samples [10] and in residues and extracts after treatment with NMP [12] although the location of the peaks and valleys are affected by the treatment. Swelling of coals which is observed in many coals in this temperature range is partially due to release of gases such as H_2 and may cause the observed decrease in the internal surface area. H_2 gas is known to quench the free radicals [16]. Thus it is very likely that explanations a, c, and d are simultaneously operative in stage 2, perhaps at different levels in different coals.

In stage 3, the sharp decrease in the sample weight accompanied by the sharp increase in N_s has been interpreted to be due to breaking and rearrangement of the aromatic rings of the coal structure. The activation energies determined from the temperature dependence of N_s are in the range of 15 kcal/mol [9]. These energies are sufficient for bond fission [3,15]. The fact that the volatiles in this stage contain free radicals further supports this interpretation [17]. In stage 4, the decrease in N_s is most likely to be recombination of free radicals and formation of chars.

The use of ESR spectroscopy in coals treated with solvents such as NMP [12] has led to considerable understanding of the mechanism of coal extraction with these solvents. There is strong evidence that treatment with NMP extracts exinites and to a lesser degree vitrinites present in coal samples whereas the inertinites and ash are left in the residue [12]. This conclusion is partly based on the observation of the inverse correlation between N_s and percent extraction as exinites have lower free radical density [12].

CONCLUDING REMARKS

In this paper we have discussed some of the recent results obtained with in-situ ESR spectroscopy on coal pyrolysis and coal extraction. Although many interesting results have been obtained and we have now the capability of measuring ESR due to free radicals at high temperatures at time intervals of one minute or so, the short-lived free radicals are not observed by the steady-state ESR spectroscopy. The next advance in this area is likely to come from an understanding of the role of short-lived free radicals in coal conversion processes.

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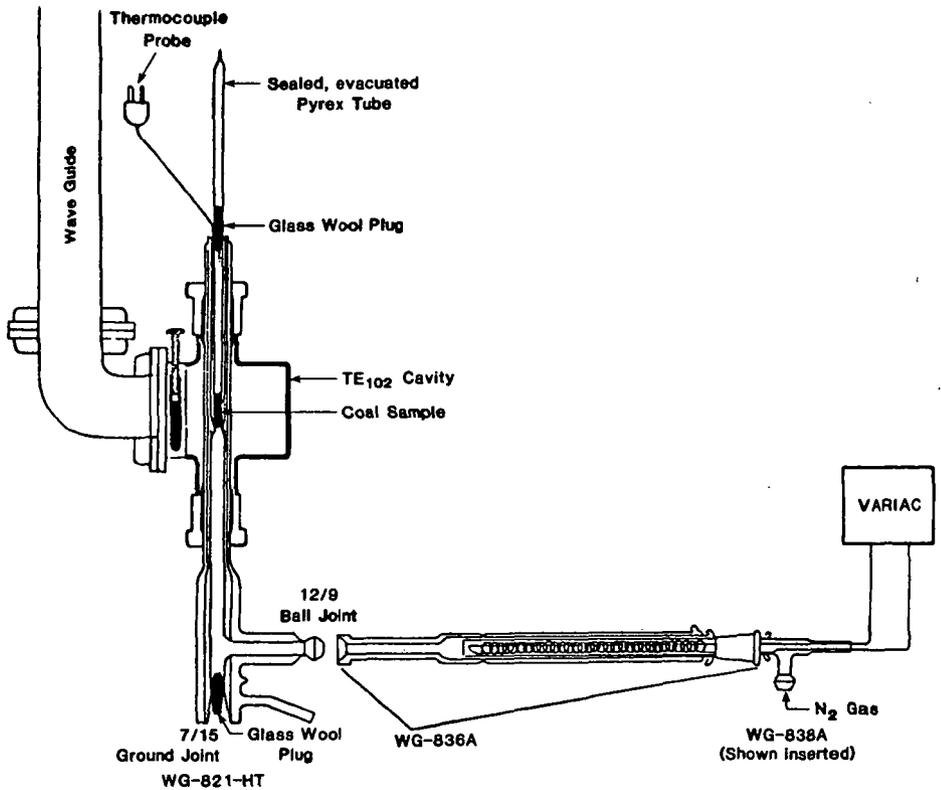


Fig. 1. A block diagram of the high-temperature microwave cavity system for in-situ ESR studies to 650°C with $\pm 1^\circ\text{C}$ stability. Components labelled with prefix 'WG' are made of quartz and they were obtained from Wilmad Glass Co. (see text for details).

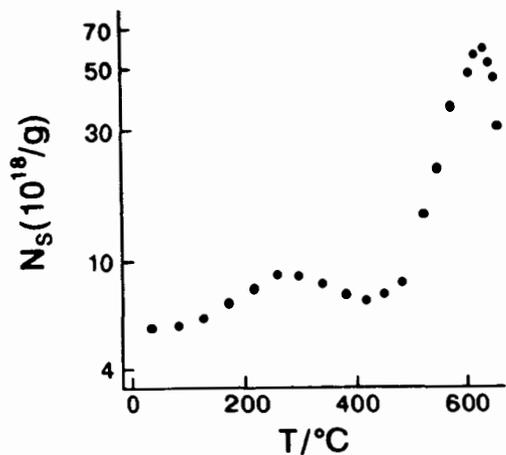


Fig. 2a. Free radical density N_s vs temperature for Matewan coal (Based on Ref. 9).

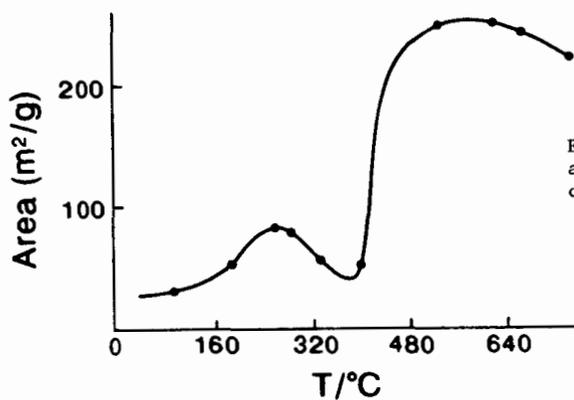


Fig. 2b. Internal CO_2 surface area vs temperature for a coal (Based on Ref. 14).

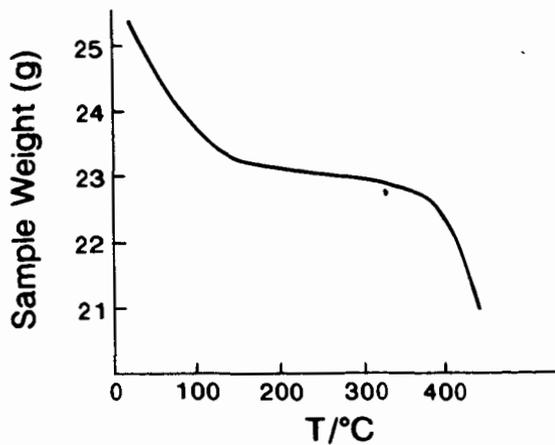


Fig. 2c. Sample weight vs temperature for a British coal (Based on Ref. 10).

THE IMPACT OF LIQUEFACTION SOLVENT COMPOSITION ON
HYDROGEN UTILIZATION EFFICIENCY

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INTRODUCTION

Hydrogen utilization efficiency in coal liquefaction is important not only because of the direct cost of H_2 , but more particularly because of the cost of the high pressure equipment that is required to hydrogenate solvent and coal structures even in the presence of catalysts. The effects of solvent composition on H-utilization efficiency would most readily be obtained from batch autoclave studies, where solvent composition can most easily be treated as an independent variable. However, such data are scarce because the rate of coal conversion is often the primary, if not the only, observable addressed.

In previous mechanistic work directed at understanding the modes of bond scission available for relevant coal structures, we observed experimentally that the selectivity and efficiency with which donatable hydrogen is used to cleave aryl-alkyl linkages in coal surrogates is highly dependent on the degree of hydrogenation of the donor (1-3). The observed variations in efficiency were well reproduced by a mechanistic numerical model incorporating the various competing H-transfer processes (3). The basic trend elaborated by the model is that an increase in the level of polycyclic aromatic hydrocarbon in the solvent can increase the efficiency of H-utilization markedly, at a minor expense in H-transfer rate. Conversely, solvents which are very low in the fully aromatic PCAH component tend to transfer hydrogen faster, but do it less discriminately, such that a much smaller fraction of the hydrogen transferred goes to produce hydrogenolysis, and more goes to simple ring hydrogenation. At that time we proposed that this trend in efficiency could have substantial implications for actual coal liquefaction, but we had no obvious examples at hand to cleanly support this assertion. The recent results of Mochida and coworkers (4) provide a very clear illustration of the relevance of our earlier projections. This demonstration of relevance includes the premise on which these conclusions were based, namely that H-transfer-induced bond scission plays a substantial role in coal liquefaction. In this paper we discuss Mochida's results in light of our earlier findings, and elaborate on the interactive effects of the H-donor and acceptor components of liquefaction solvents.

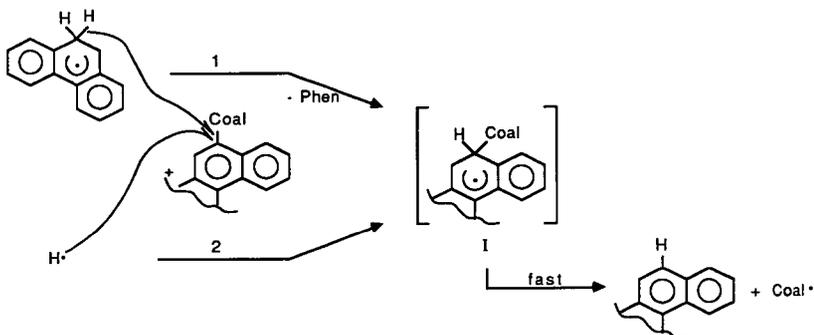
RESULTS AND DISCUSSION

Mochida et al. recently described the liquefaction of an Australian brown coal in tetrahydrofluoranthene (THFL), a donor solvent, containing varying amounts of fluoranthene (FL), a non donor (4). Their results show that although the conversion rates decrease as FL is added to the reaction mixture, the selectivity to oils (vs. gases) goes up somewhat, and the efficiency of H-utilization for oil production increases substantially. In Table 1 are shown the yields reported by Mochida for conversion in two media: 100% THFL and in a mixture of 75% THFL and 25% FL. In each case, the values shown are those reported at the time of maximum oil yield.

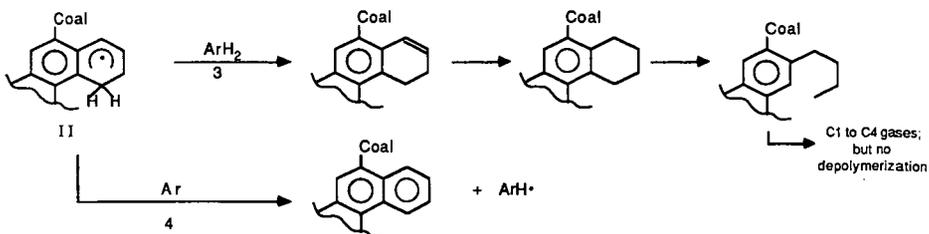
Replacement of 25% of the donor THFL with an equal amount of the non donor FL in the starting solvent increases the oil yield by five percentage points at the "expense"

of the gas yield. Substantially more pronounced is the impact of FL addition on the H-utilization efficiency (the ratio of oil produced to THFL consumed). As Table 1 shows, this value increases by 60%.

The origin of this change in efficiency cannot be understood without understanding the modes of H-transfer that lead to hydrogenolysis and/or hydrogenation. For this purpose, it is necessary to review some of our earlier findings. First, we can make the general statement that a shift in the utilization of hydroaromatic hydrogen could not occur without there being a shift in the mode of H-transfer. Specifically, if the addition of free H-atoms to positions on aromatic clusters bearing linkages (Reaction 1) were not in competition with the recently elucidated (1,2,5,6) radical hydrogen-transfer process (Reaction 2), there would be no basis for such a shift.



In Figure 1, we show previously presented (3) experimentally observed and numerically modeled H-utilization efficiency data for dinaphthylmethane cleavage. The reactions depicting the efficiency-determining competition in H-transfer processes are shown below:



It is not sufficient to consider merely the manner of formation of the ipso-substituted cyclohexadienyl radical I, because this intermediate, once formed at coal conversion temperatures, has an extremely short lifetime before elimination of virtually any linkage (as Coal•). In other words, cleavage will result no matter how I was formed.

Efficiency is determined by what happens to all of the radical species produced by H-transfer to positions not bearing linkages, II. When the concentration (and effectiveness) of polycyclic aromatic hydrocarbons that can act as hydrogen acceptors, transferring H-atoms back from non-ipso radicals, is low, then the non-ipso radicals are more likely to abstract a second hydrogen (e.g., from hydroaromatic in an "over hydrogenated" solvent). This dihydro intermediate is very reactive and will quickly be reduced to a tetrahydro intermediate. The tetrahydro intermediate can then receive additional hydrogens to open the aliphatic ring and crack off the 4-carbon chain as light hydrocarbons. In the example shown, this would mean that 6 or more hydrogens were consumed and no linkages were broken.

In contrast, when the concentration of H-acceptors is sufficient, the otherwise wastefully transferred hydrogen is recovered from the non-ipso radicals by the bimolecular RHT process, regenerating the hydrogen carrier radicals ArH^{\cdot} , so that the hydrogen transfer activity is maintained and there can be another chance at transfer to an ipso position. Ideally, this could result in having the only irreversible H-transfer being that to positions bearing linkages. In fact, the observed and computed hydrogen utilization efficiencies shown in Figure 1 indicate that, at least in the model system, a utilization efficiency approaching 90 to 100% can be achieved by merely adjusting the degree of hydrogenation.

When the original model compound studies were performed several years ago, we were surprised to observe that not only did the rate of hydroaromatic consumption go down when the solvent initially contained a significant amount of the respective aromatic, but that the absolute amount of hydroaromatic remaining at various reaction times could actually be larger when starting with less!

The final point to be recalled from our earlier studies is (as mentioned above) that the increase in H-utilization efficiency is achieved at some expense in terms of reaction rate. In the case of the data in Figure 1, when the efficiency showed a six-fold increase from 15% to 90%, the cleavage rate declined by about 60%. Closer examination of Mochida's data, as discussed below, shows that all of these trends are observed in the real coal liquefaction system.

Figure 2 shows the gas, oil, asphaltene, preasphaltene, and residue yields observed by Mochida as a function of time, when the starting solvent contained no fluoranthene, and when it contained 25% fluoranthene (4). In the 0% FL case, the oil yield develops faster, and the residue disappears more quickly, but in the 25% FL case, the more slowly developing oil yield reaches a 8% higher value at its maximum (which is at 30 min rather than 10 min), and the gas yield is only about 2/3 of that produced when the starting solvent is 100% THFL. This moderate advantage that results from starting with 25% FL becomes quite marked when the ratio of oil yield to THFL consumption is computed, revealing, as shown above in Table 1, a 60% increase in H-utilization efficiency.

The evolution of the solvent composition for these same two cases also shows the curious trend that there is equal or greater THFL remaining when the starting solvent contained less. For example, at 20 minutes the THFL concentration in the recovered solvent is 30% when starting with pure THFL and 35% when the starting with only 75% THFL. The extent of crossover is small and could easily be assigned to experimental scatter, were it not for the fact that similar crossovers were also observed in our studies. The faster THFL decline is associated with a greater rate of production of perhydrofluoranthene. Thus in Mochida's case, as in our earlier model system studies, the absence of a significant initial concentration of PCAH allows multiple H-transfers and full reduction of some of the hydroaromatic species; one can infer that similar reduction without cleavage, followed by ring opening and gas production, are also occurring within the coal structures themselves.

A year ago, we presented a similar explanation (7) for excessive gas production when high temperature excursions occurred during coal hydrolysis as reported by Gorbaty and Maa (8). In this case the effectiveness of the PCAH systems as H-acceptors evidently decreased as a result of increasing temperature, thereby allowing greater ring reduction and ring opening. The chemistry we proposed was criticized as being excessively speculative. We find it gratifying to note that in the present case, careful analysis by Mochida of the recovered liquefaction solvents provides direct evidence for the anticipated wasteful reduction of aromatic systems.

Finally, we wish to suggest that the trend in H-utilization efficiency noted here is not merely a fortuitous result of scattered behavior. In an earlier publication, Mochida et al. described in less detail the liquefaction of three subbituminous coals in the fluoranthene solvent system (9). For two of the coals, a decrease in the starting THFL content from 100% to 67% resulted in an oils plus asphaltenes yield decrease of only 3%. Although THFL consumption was not detailed, given that the decreases in THFL consumption found in the more recent studies on brown coals were generally on the order of 40 to 45%, it can be presumed that in the case of subituminous coals too, the decrease in THFL consumption was much more than 3%. Thus, a trend in H-utilization efficiency similar to that observed for the brown coal probably also occurred for the subbituminous coals. Despite the fact that concern with conversion rate has tended to overshadow consideration of H-utilization efficiencies, other examples undoubtedly exist. For example, Derbyshire et al. earlier reported increased conversions in tetralin/pyrene mixtures as compared to pure tetralin (10). Although they did not report the consumptions of hydroaromatic, it once again is very likely that consumption decreased upon addition of pyrene. Similarly, more recent results of Cassidy et al (11) showing a substantial increase in absolute oil yields upon partial replacement of tetralin with pyrene probably also reflect increased H-utilization efficiency. Thus, we anticipate that a more thorough examination of the literature will provide many other examples.

We recognize that the apparent advantage of lower THFL concentration cannot be expected to transfer unchanged from the batch autoclave to continuous units. For example, the somewhat longer time required for disappearance of the THF-insoluble residue in the 75% THFL case (Figure 2b) could have a detrimental impact under large-scale continuous processing conditions, where persistence of an insoluble phase in the preheater could exacerbate coking on heat-transfer surfaces.

SUMMARY

The recent results of Mochida and coworkers, showing that modest decreases in conversion rate are accompanied by very substantial increases in hydroaromatic hydrogen utilization efficiency when 25% of the hydroaromatic in the starting solvent is replaced by the corresponding aromatic, provide significant confirmation of projections we had made earlier. These predictions were based on the premise that solvent-mediated hydrogenolysis of strong bonds plays an important role in coal liquefaction, and they required an understanding of the role of competitive H-transfer processes in these hydrogenolyses.

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Table 1

EFFECT OF REPLACEMENT OF PART OF TETRAHYDROFLUORANTHENE (H-DONOR) BY
FLUORANTHENE (NON-DONOR) ON EFFICIENCY OF H-UTILIZATION AND SELECTIVITY TO OILS

THFL Content	PRODUCT YIELD*	
	100%	75%
Gas	18	13
Oil	63	68
Asph.	13	14
PA + Res.	6	5
Oil Yield	1.1	1.7
THFL Consumption	1.1	1.7

* Optimal yield for coal conversion at
450°C/N₂/Solvent:Coal 3:1

Data from Mochida, 1988

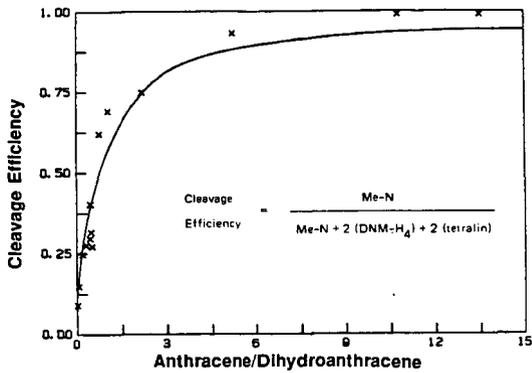


Figure 1. Experimental and Computed cleavage efficiency as a function of aromatic/hydroaromatic ratio

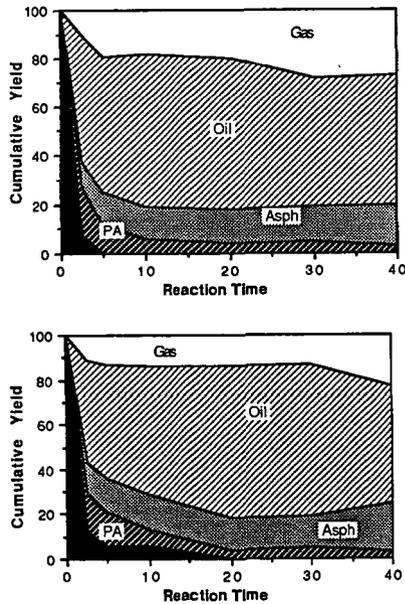


Figure 2. Product yields from conversion of an Australian Brown Coal In (a) 100% tetrahydrofluoranthene, and (b) a 75/25 mixture of tetrahydrofluoranthene and fluoranthene.

Data from Mochida, 1988

INVESTIGATION OF LIQUEFACTION MECHANISMS USING MOLECULAR PROBES

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INTRODUCTION

The mechanisms of coal liquefaction have been investigated using 1,3-dimethylnaphthalene and decalin as molecular probes. These two pure compounds have been added to various mixtures composed of a coal, a liquefaction solvent, and a high molecular weight alkane. In all cases, the amount of the probes added to the reaction mixture of coal, solvent, and alkane is small enough that the probes themselves are unlikely to perturb the reaction chemistry to a measurable degree.

The mixtures were heated in small autoclaves to liquefaction conditions, and the products recovered for analysis by quantitative gas chromatography. From the analysis of the products from the added probes, it is possible to draw conclusions about the relative amount and kind of intermediates that were created by the liquefaction conditions. For example, cis-decalin is transformed to the equilibrium mixture of the cis-and trans-isomers by the abstraction of hydrogen from either tertiary position by a free radical (1,2). The extent to which the equilibrium has gone to completion is then a measure of the exposure of decalin to radicals of sufficient reactivity to abstract the tertiary hydrogen. In the case of 1,3-dimethylnaphthalene, it is the monomethyl products that are of particular interest. Dealkylation of aromatic compounds is known to proceed under liquefaction conditions by the attack of free hydrogen atoms (3,4) or by the transfer of a hydrogen atom from a reactive donor (5). The total amount of demethylation is then a measure of the exposure of 1,3-dimethylnaphthalene to the total of free hydrogen atoms plus hydrogen atom donors. The use of the 1,3-isomer also allows the selectivity of the attack of hydrogen atoms to be measured. Loss of the methyl group from the 1-position leaves 2-methylnaphthalene as the product, whereas loss of the methyl group from the 3-position leaves the 1-methylnaphthalene as the product. The ratio of these easily separated isomers is then a measure of the weighted average of the selectivities of the entire population of hydrogen atom donors to which the probe is exposed.

In the present application of this approach, it is of particular interest to probe the effect of using petroleum residua as the liquefaction solvent in conjunction with coal. A combination of coal and resid was selected that has previously been used at the Pittsburgh Energy Technology Center for detailed evaluation of coprocessing schemes (6). The results

described below show that the interaction of coal and residua may lead to a reaction environment wherein the exposure of the probes to free radicals is enhanced over that expected based on additive behavior alone. The addition of coal, in particular, also has a very large influence on the selectivity of demethylation of dimethylnaphthalene.

EXPERIMENTAL

The 8-gram reaction mixtures contained 2.5% cis-decalin, 2.5% 1,3-dimethylnaphthalene, 0-20% Illinois No. 6 coal, 0-20% Maya atmospheric tower bottoms (ATB), and 57-95% n-octacosane or n-dotriacontane as solvent. The 40-mL reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and held at temperature for 15, 60, or 180 minutes. The reaction products were washed from the reactors with tetrahydrofuran, and the soluble products were analyzed by quantitative capillary gas chromatography using internal standards. Selected samples were analyzed by GC/MS. The proximate and ultimate analyses of the coal and ATB are given in Table 1.

RESULTS AND DISCUSSION

The isomerization of cis-decalin is initiated by the free radical abstraction of the tertiary bridgehead hydrogen. Subsequent hydrogen transfer to the near planar radical intermediate leads to a mixture of cis- and trans-decalin. Thus, decalin can be used as a probe for radical activity in general, since its isomerization is initiated by any radical capable of abstracting the tertiary hydrogen. Since the isomerization is reversible, the ratio of decalin isomers eventually approaches its equilibrium value. If the rates of isomerization are constant over time, the rate of approach to equilibrium can be described by the expression for first-order reversible reactions

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = kt \quad (1)$$

where A_0 is the initial mole percent of cis-decalin, A_e is the equilibrium mole percent, A is the mole percent at time t , and k is the pseudo-first-order rate constant. Added radical sources will increase the pseudo-first-order rate constant and thus increase the rate of equilibration. Furthermore, if the added source provides over time a stable concentration of radicals of constant reactivity, the rate of equilibration should be well fit by Equation 1. To test this supposition, the extent of equilibration was measured after 15, 60, and 180 minutes without an additive and with either coal or petroleum residuum.

The time dependence of the decalin isomerizations is shown in Figure 1. The linear regression results are given in Table 2. The value of A_e was calculated by extrapolating the results of Schucker (7) to 425°C. The expected equilibrium ratio is 5.0, or about 83% trans-decalin. The large effect of added Illinois No. 6 coal is evident even at 15 minutes. The increase in the rate constant is striking; it becomes 50% larger when 10% coal is added. Both the ATB and the coal give good straight-line relationships. Thus, first-order reversible kinetics is a good approxima-

tion to the actual rate, and the efficiency of the hydrogen abstraction is not changing appreciably with time. This indicates that a steady-state radical activity is reached early in the reaction and maintained.

Of the benefits claimed for coprocessing, the synergism between the coal and residua leading to higher conversions for the mixtures than for either alone is especially intriguing (6). A chemical basis for this activity was sought in the total radical activity as measured by the cis-decalin isomerization. To accurately predict the expected activity of mixtures of coal and residua, the influences of coal concentration and ATB concentration on the extent of equilibration at 60 minutes were determined independently. These results, plotted as a function of the weight fraction squared, are shown in Figure 2. The dependence on concentration squared was determined empirically; considerable curvature was apparent when linear correlations with concentration were attempted. Linear regression analysis for the coal data gave

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.32 + 24.9 [\text{Coal}]^2 \quad (2)$$

where A_0 , A_e , and A are as defined in Equation 1. The regression analysis of the ATB data gives

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.30 + 13.1 [\text{ATB}]^2 \quad (3)$$

Both sets of data should, and do, share a common intercept.

Equations 2 and 3 define the dependence of the extent of decalin equilibration in the presence of only ATB or only coal. If there is no interaction between the coal and ATB, then the total isomerization will be given by the sum of the contributions of the coal, ATB, and background. Thus, Equation 4 should predict the extent of decalin isomerization after 60 minutes if no synergism or inhibition is present.

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.31 + 13.1 [\text{ATB}]^2 + 24.9 [\text{Coal}]^2 \quad (4)$$

The 0.31 in this equation is the average of the intercepts of Equations 2 and 3.

A parity plot of experimental data and the predicted results is shown in Figure 3. The open circles represent the data already presented in Figure 2 for the ATB and coal in the absence of one another, which were used to derive the Equation 4. The solid circles represent the data obtained from experiments using mixtures of coal and ATB. At low total concentrations, no difference between the experimental and the predicted extent of isomerization is seen. At moderate concentrations, a significant increase in the extent of isomerization above that predicted by the sum of individual effects becomes apparent. An enhanced steady-state activity is attained for these mixtures of Maya ATB and Illinois coal. The synergism observed in the conversion of the coal and ATB (6) may be related to the enhanced radical activity displayed by these mixtures.

The isomerization of decalin is a non-specific indicator of free radical activity, since any radical of sufficient energy can abstract the tertiary hydrogen. In contrast to this probe for overall activity, the demethylation of 1,3-dimethylnaphthalene is specific for hydrogen atom activity.

The free radical hydrocracking of 1,3-dimethylnaphthalene (DMN) proceeds via the attachment of a hydrogen atom to the position ipso to a methyl group. Subsequent loss of methyl radical leads to either 1- or 2-methylnaphthalene. The yield of the monomethylnaphthalenes is an indicator of the extent of hydrocracking activity. Additionally, the ratio of the products is a measure of the selectivity of the ipso substitution.

In the presence of added coal or ATB, the percent yield of methyl-naphthalenes increases. The change in the 1-methylnaphthalene (1-MN) yield with increasing additive is small at most, while the yield of 2-methylnaphthalene (2-MN) increases with added ATB or coal. The net effect on the selectivity of DMN hydrocracking is shown in Figure 4.

While the total yields of monomethylnaphthalenes provide an estimation of the hydrocracking activity, the ratio of the 2-MN to the 1-MN provides a sensitive measure of the selectivity of the hydrocracking reactions. Selectivity differences indicate a common intermediate does not predominate in all cases. McMillen et al. (5) have shown in studies of model compounds that the selectivity of attack at the 1- and 2-positions of naphthalene may vary according to the hydrogen atom donor responsible for the attack. The most reactive and least selective intermediate is the hydrogen atom itself. Hydrogen atoms are formed as the result of radical hydrogen abstraction from gas phase hydrogen (3). Hydrogen atoms react with suitable acceptors, such as aromatic hydrocarbons, to form sigma complexes. Hydrogen transfer from these complexes is less exothermic and hence more selective than direct attack by hydrogen atoms. In the present experiments, hydrogen atoms may form more selective hydrogen atom donors by attachment to aromatic species in the coal or ATB. In addition to providing hydrogen atom acceptors, the aromatic and hydroaromatic species in the coal and ATB could interact to form the intermediate sigma complexes directly. The disproportionation of dihydroanthracene and anthracene to form hydroanthracenyl radicals is an example of this type of reaction (8). Thus, the selectivity of the hydrocracking reactions can be altered by several means in the presence of coal or ATB.

The results in Figure 4 are particularly interesting for the case of mixtures of coal and ATB. The bottom two curves show the effect of each additive in the absence of the other. The top two curves show the effect of increasing either coal or ATB in the presence of a constant amount of the other. As the concentration of ATB is increased in the absence of coal (bottom curve), the selectivity increases in a nearly linear fashion. This effect is more pronounced in the presence of coal. The efficiency of the coal in altering the selectivity of the hydrocracking is much greater than that of the ATB. Only 5% coal is needed to achieve the same selectivity as 20% ATB.

Surprisingly, selectivities in the mixtures are higher than in either component separately. A limiting value around 7.5 is approached at the highest levels of addition. These preliminary data are insufficient to determine whether the selectivity produced by addition of still higher levels of coal by itself would approach the same limiting value. However, it now appears that the combination of the ATB with the coal enhances the approach of the selectivity to this value. Thus, as revealed by this probe, the nature of the hydrogen atom intermediates becomes more dominated by coal or coal products as ATB is mixed into the systems.

CONCLUSIONS

Selected organic compounds can be used to probe the types of reactions occurring during the coprocessing of coal with petroleum residua. By combining the results from both the decalin isomerization and the dimethylnaphthalene cracking, a fuller description of the nature of the free radical activity during coprocessing can be achieved. As measured by the equilibration of decalin, the total radical activity remains fairly constant with time. This total activity is increased with added coal or ATB, and thus these additives can be viewed as functioning as free radical initiators. Some portion of this total activity results in hydrocracking reactions. The selectivity of these hydrogen atom or mediated hydrogen atom reactions is strongly influenced by coal and to a lesser degree by ATB. The total radical activity is greater than expected from a simple additivity of effects, while the selectivity of the demethylation of dimethylnaphthalene is more strongly mediated by coal when ATB is also present. Work to determine if these effects can be seen for other coals and residua is under way.

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Table 1. Analyses of Coal and Residua

	<u>Illinois No. 6</u>	<u>Maya ATB</u>
<u>Proximate Analysis, wt%</u> (As Received)		
Moisture	11.52	<0.03
Volatile Matter	34.04	----
Fixed Carbon	44.78	----
Ash	9.66	0.06
<u>Ultimate Analysis, wt%</u> (As Received)		
Carbon	61.57	84.2
Hydrogen	5.53	11.9
Nitrogen	0.83	0.29
Sulfur	2.47	3.0
Oxygen (Indirect)	19.94	0.55
Ash	9.66	0.06

Table 2. Linear Regression Results for the Time Dependence of the Decalin Isomerization

<u>Additive</u>	<u>Slope x 1000</u> <u>(Min.⁻¹)</u>	<u>Y-Intercept</u>	<u>R²</u>
None	6.87	-0.09	0.991
10% Maya ATB	6.98	0.00	0.999
10% Illinois No. 6 Coal	10.66	0.01	0.990

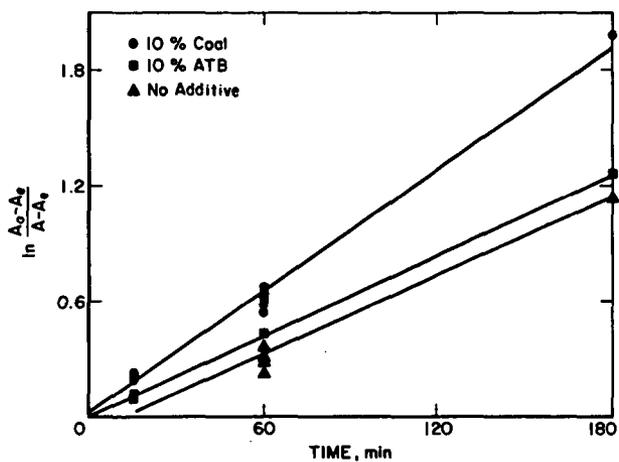


Figure 1. First Order Reversible Kinetics for the Decalin Isomerization.

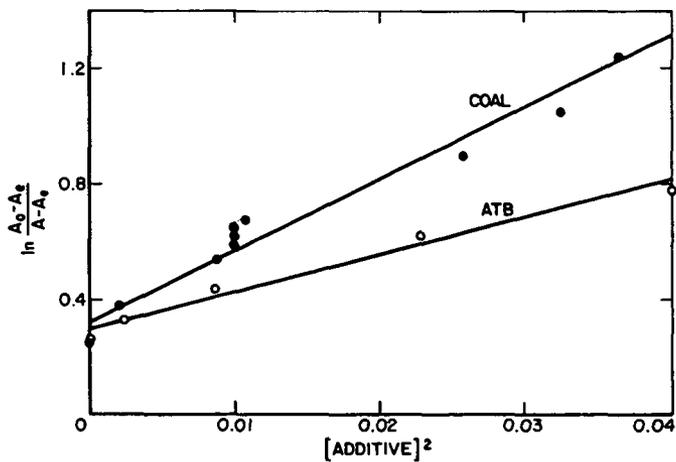


Figure 2. Effect of Coal and ATB on the Rate of the Isomerization of Decalin.

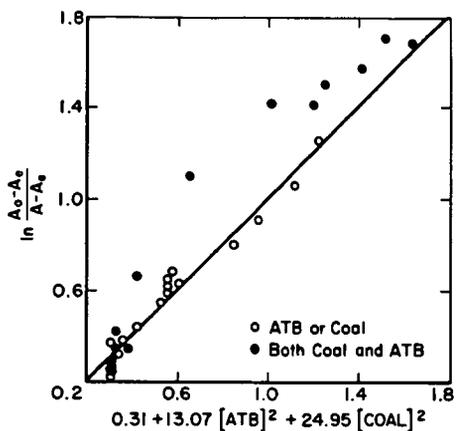


Figure 3. Parity Plot for the isomerization of Decalin.

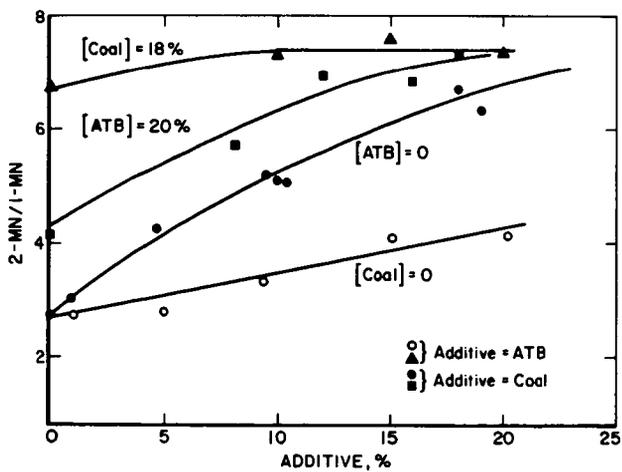


Figure 4. Effects of Coal and ATB on the Hydrocracking Selectivity.

Coal Liquefaction: Impact of Alkyl Substitution in Naphthalene Model Solvents

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ABSTRACT

The solvent 1-methylnaphthalene has a unique ability of being able to effect the use of gaseous hydrogen during coal conversion. This unique characteristic is not universal; rather it is exhibited only for about one-third of the eastern and western Kentucky coals examined in this study. With these exceptional coals, 1-methylnaphthalene may be as, and sometimes even more, effective than tetralin in converting coal to pyridine soluble products.

INTRODUCTION

One of the features of a process solvent that is believed to be important is the amount of donatable hydrogen that is present in the form of hydroaromatic compounds. Neavel (1), for example, shows that, in the initial stages of the liquefaction of an Illinois high-volatile C bituminous coal, the conversion to pyridine solubles is similar in tetralin, a good hydrogen donor solvent, and in naphthalene, a solvent without donatable hydroaromatic hydrogens. Only after a few minutes does one see a significant difference in the overall conversion. With tetralin, a conversion of greater than 90% is attained rapidly, and this remains constant during the next 100 minutes of residence time (Figure 1a). When naphthalene is the solvent, the early conversion reaches ca. 85% but rapidly declines during the next 40 minutes of residence time to a level below 40% conversion (Figure 1b). Neavel's data dramatically emphasize a concept that has developed over the years as it relates to the need for donatable hydrogen in a liquefaction solvent that inhibits retrograde reactions.

For studies in microreactors, a convenient way to vary the amount of hydrogen donor is to use a model solvent containing tetralin and naphthalene. 1-Methylnaphthalene, a liquid at room temperature, is frequently used instead of naphthalene, a solid at room temperature since this makes the experimental procedure for sample removal and analysis easier. Naphthalene and 1-methylnaphthalene could be interchanged, on a molar basis, without altering the amount donatable hydrogen and, presumably, without altering the conversion for a solvent with a particular donatable hydrogen content.

For example, Pina et al. (2) found that the conversion of a western Kentucky coal was essentially constant as the fraction of 1-methylnaphthalene was increased up to 0.8 to 0.9 range; as the amount of donatable hydrogen was further decreased by increasing the amount of 1-methylnaphthalene a dramatic, rapid decrease in coal conversion was observed. Derbyshire and Whitehurst (3) made a similar observation for the conversion of a Belle Ayr sub-bituminous coal in a mixture of tetralin with 2-methylnaphthalene or pyridine; in this case, a lower concentration of the nondonor methylnaphthalene was required to

cause a decrease in conversion. Chiba et al. (4) have obtained conversion data with 1-methylnaphthalene-tetralin and a Yallourn coal that are intermediate to that of the above two studies. Maa et al. (5) reported that EXXON Research & Engineering Company had developed a solvent-quality index (SQI) to characterize the ability of recycle solvents to effect coal conversion and that, for some coals, below a critical value of SQI, the liquid yields and coal conversions decreased sharply. Furthermore, for the three coals reported, two coals, an Illinois No. 6 bituminous and Wyodak sub-bituminous, showed a much stronger sensitivity to SQI than did a West Virginia Ireland Mine bituminous coal. The implication of the data presented in this study is that all coals do not respond in the same manner to a given SQI.

For some Kentucky coals, a higher conversion may be obtained in a pure 1-methylnaphthalene solvent than in a tetralin. These data indicate that the amount of donatable hydrogen required for a "good" solvent is dependent upon the coal. In view of the expanding use of 1-methylnaphthalene as a model solvent (e.g., Ref. 6) to provide solvents of varying amounts of donatable hydrogen, some of these results are described in this report.

EXPERIMENTAL

The coal samples were collected from the working face of the mine and stored under argon prior to analysis and liquefaction. Chemical and petrographic analyses of the coals are given in Table 1. The coals were ground to -100 mesh, stored under argon and dried prior to the liquefaction experiments.

The liquefaction experiments were conducted in a 50 ml microautoclave reactor. The reactor charge was typically 5 g of coal and 7.5 g of model solvent. The reactor was pressurized with the appropriate gas (H_2 or N_2) to 800 psig at ambient temperature. The reactor was immersed in a heated fluidized sand bath for the desired reaction time. Typically, the time required to reach a reaction temperature of $385^\circ C$ was two minutes, or less. Mixing of the reactor charge was facilitated by a 1/4" steel ball in the reactor. The reactor was vertically shaken (1" amplitude) at a rate of 400 cpm. At the end of the liquefaction experiment, the reactor was immersed in a cold fluidized sand bath to quickly cool to less than $100^\circ C$ in less than two minutes to quench the reactions.

Once the reactor has reached ambient temperature, the product gases were collected in a sample bomb for g.c. analysis. The remaining products were quantitatively washed from the reactor with benzene into a Soxhlet thimble. The sample was extracted with benzene until the solution was clear or a pale yellow. From the benzene solubles, the asphaltene fraction was separated from the oil fraction by precipitation of the asphaltenes with pentane. The preasphaltene fraction was obtained by a Soxhlet extraction of the benzene insolubles with pyridine. Conversions were obtained by subtracting the weight percent pyridine insolubles (maf basis) from 100%.

The extraction solvents were HPLC grade and obtained from Burdick and Jackson. The liquefaction model solvents were used as received from Aldrich Chemical Co.

RESULTS AND DISCUSSION

An eastern and western Kentucky coal were converted in tetralin or 1-methylnaphthalene solvent using a reaction time of 15 minutes, a temperature of 385°C and either a hydrogen or nitrogen atmosphere (Figure 2). The data clearly show that molecular hydrogen is utilized in the liquefaction of both coals when 1-methylnaphthalene is the solvent. When tetralin was employed as the solvent, similar conversions were obtained when the reactor vessel was pressurized with either hydrogen or nitrogen. However, when 1-methylnaphthalene was used as the solvent for either coal, the conversion in the hydrogen atmosphere was about double the conversion in a nitrogen atmosphere. Thus, the 1-methylnaphthalene is effecting the utilization of gaseous hydrogen to produce higher conversions. Even more surprising is the observation that, in a hydrogen atmosphere, the 1-methylnaphthalene is as effective as a solvent as tetralin for coal conversion.

The observation that equal conversions are obtained using 1-methylnaphthalene and tetralin as liquefaction solvents does not apply for all coals. Even when a hydrogen atmosphere is used, the expected lower conversions are obtained for ca. 60% of the eastern Kentucky coal samples in Figure 3 (see reference 7 for coal analysis); i.e., the conversion when tetralin is utilized is appreciably higher than when 1-methylnaphthalene is the solvent. The data in Figure 3 indicate that equivalent conversions are obtained for those special coals in both solvents (which span the entire range of conversions). Therefore, this phenomena is not restricted to a set of coals with high or low reactivities. From the data, it may be concluded that some unique coal property, or properties, are responsible for this observation. Similar results have been obtained with western Kentucky coals.

The time dependence of conversions in the two solvents are shown in Figure 4 for a western Kentucky #9 Alston coal. The same conversion is obtained for either nitrogen or hydrogen atmosphere at 15 and 30 minutes with the tetralin solvent. A very different result is obtained with the 1-methylnaphthalene solvent. With this latter solvent and a hydrogen atmosphere, the conversions up to 30 minutes are clearly greater than when tetralin was employed. In addition, the conversions, when a nitrogen atmosphere was used instead of hydrogen, were lower (ca. 30%) and did not increase with longer reaction times. With 1-methylnaphthalene and hydrogen, the conversion at 60 minutes was the same as when tetralin was used as the solvent. Therefore, in addition to the surprising fact that the conversion of the western Kentucky #9 coal is initially greater in the 1-methylnaphthalene solvent, it does not appear that the retrograde reactions, as shown in Figure 1b, have made a measurable contribution in lowering conversions, even after 60 minutes. Again, the data clearly show that 1-methylnaphthalene is able to effect gaseous hydrogen usage and, with this particular coal, appears to be able to provide the hydrogen needed for conversion to pyridine solubles even more effectively than tetralin.

The data in Figure 5 indicate the effect of alkyl substitutions in aromatic and hydroaromatic rings on the conversions obtained for a Western Kentucky #9 and Eastern Kentucky Peach Orchard coal. The conversions obtained by these two coals, using naphthalene as the solvent, are lower than those obtained when tetralin was employed as the liquefaction solvent; this is anticipated from previous reports. Liquefaction of the two coals using 2-methylnaphthalene as a solvent produce significantly lower conversions when

compared to those obtained in 1-methylnaphthalene. However, the conversions in 2-methylnaphthalene are essentially the same as those observed for the liquefaction of the coals in naphthalene. One explanation for the above data may be the physical state of the model solvents employed. Naphthalene and 2-methylnaphthalene are solids at room temperature while 1-methylnaphthalene is a liquid. Poor mixing during the initial stages of liquefaction using the solid model solvents could be a factor in the lower conversions observed using these compounds. However, this does not appear to be the case as shown by the data in Figure 6. With the two solid liquefaction solvents, 2-methylnaphthalene and 2,3-dimethylnaphthalene, the microautoclave was preheated to a temperature slightly above the melting point of the solvent and mixed prior to immersion in the sand bath to obtain the reaction temperature. As shown by the data in Figure 6, the conversions, within experimental error, are the same regardless of the physical state of the model solvent prior to heating to reaction temperature.

Dihydronaphthalene is a more effective solvent than tetralin, and this has been observed frequently (e.g. Ref. 8). In fact, Virk et al. (8) propose that Woodward-Hoffmann rules apply so that 1,2-dihydronaphthalene will be more effective for transferring hydrogen to phenanthrene type structures while 1,4-dihydronaphthalene will be more effective for hydrogen transfer to anthracene compounds. These authors present data to show that, at 400°C and 30 minutes reaction time, 1,2-dihydronaphthalene provides essentially the same conversion as tetralin, and the conversion of in these two solvents is about twice that obtained in naphthalene (ca 70 vs. 30%). However, the conversion in 1,4-dihydronaphthalene is greater than in tetralin (81 vs. 70%). Our data differ from since the conversion in 1,2-dihydronaphthalene is much greater than in tetralin (Figure 5).

It is surprising that both methyltetralins used in this study produce significantly higher conversions of these two coals when compared to the results obtained using tetralin. In fact, the two methyltetralin compounds produce as high a conversion as 1,2-dihydronaphthalene does. One could argue that in 1-methyltetralin the tertiary hydrogen provides a relatively weak C-H bond, and this could provide a lower activation energy reaction pathway for hydrogen transfer. However, this argument does not apply for 5-methyltetralin.

At this time, we have no ready explanation how the 1-methyl substituent promotes the use of gaseous hydrogen so much more effectively than does the 2-methyl substituted naphthalene during coal conversion. Likewise, the effect must be specific since 1-ethylnaphthalene does not appear to be a better solvent than the unsubstituted solvent, naphthalene (Figure 5). The coal properties in Table 1 do not provide a ready explanation as to why some coals have equivalent or better conversion, thorough utilization of gaseous hydrogen, in the 1-methylnaphthalene case when compared to the tetralin case.

These results clearly show that 1-methylnaphthalene is a unique liquefaction solvent for some coals and may produce results that are not typical of all nondonor solvents. At the same time, the results suggest that some coals have a unique property or properties which promote the utilization of gaseous hydrogen through nondonor solvents, and that it may be possible to take advantage of this property to improve hydrogen usage through coal selection. Finally, 1-methylnaphthalene, as a model solvent, may have utility

in identifying those coals, such as Ireland Mine coal, that appear to be able to be converted in a low SQI recycle solvent.

ACKNOWLEDGMENT

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TABLE 1. Coal Properties

	<u>W. Ky. #9</u>	<u>E. Ky. Peach Orchard</u>
ASH (dry)	11.71	5.29
VM (daf)	43.21	40.11
FC (daf)	56.79	59.89
C (daf)	76.80	83.24
H (daf)	5.41	5.54
N (daf)	1.90	1.70
S (daf)	8.41	.96
O (diff, daf)	7.48	8.56
Pyritic S (daf)	5.22	.08
Organic S (daf)	2.87	.87
Sulfate S (daf)	.32	.01
Vitrinitis	90.9	65.1
Intertinites	7.1	22.5
Liptinites	2.0	12.4

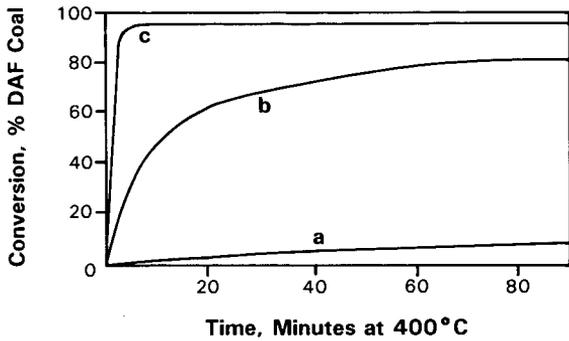


Figure 1a. Conversion of Coal reacted at 400°C in tetralin; (a) noncondensable gas; (b) benzene-soluble material + gas; (c) pyridine-soluble material + gas. DAF = dry ash-free (from Reference 1).

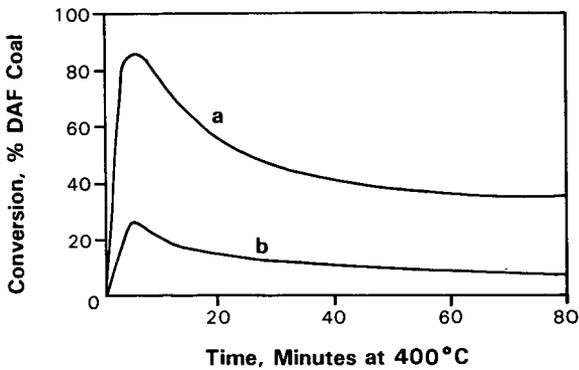


Figure 1b. Conversion of coal reacted at 400°C in naphthalene: (a) pyridine-soluble material; (b) benzene-soluble material. DAF = dry ash-free (from Reference 1).

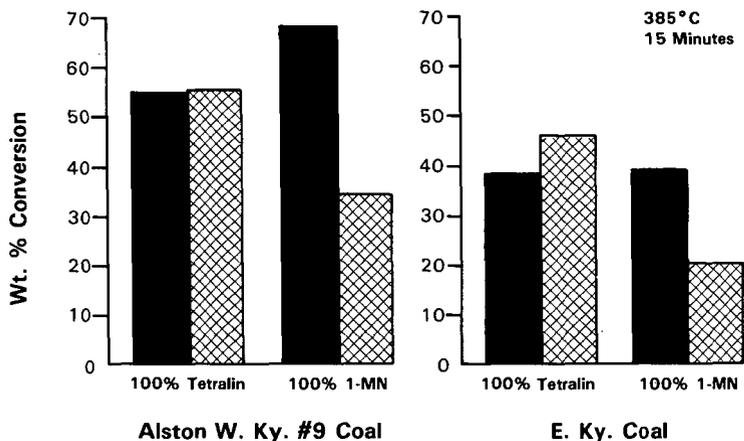


Figure 2. Conversion in a donor (tetralin) or nondonor (1-methylnaphthalene) solvent using hydrogen (■) or nitrogen (⊠) atmosphere.

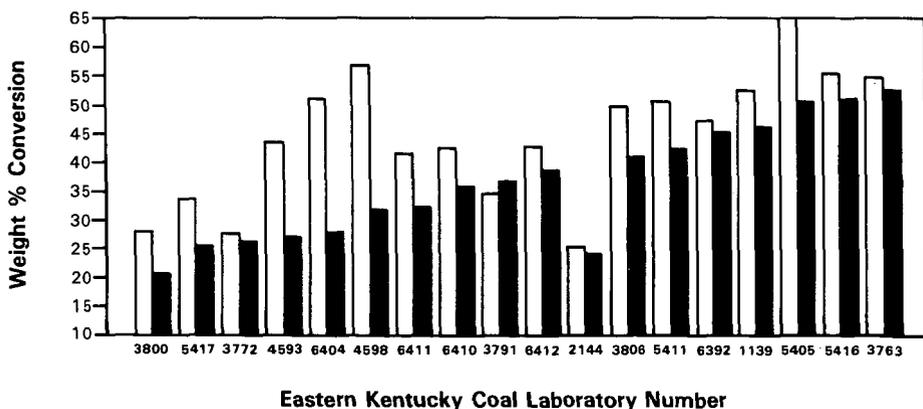


Figure 3. Comparison of conversions at 385°C and 15 minutes for eastern Kentucky channel samples in tetralin (□) and 1-methylnaphthalene (■) solvents.

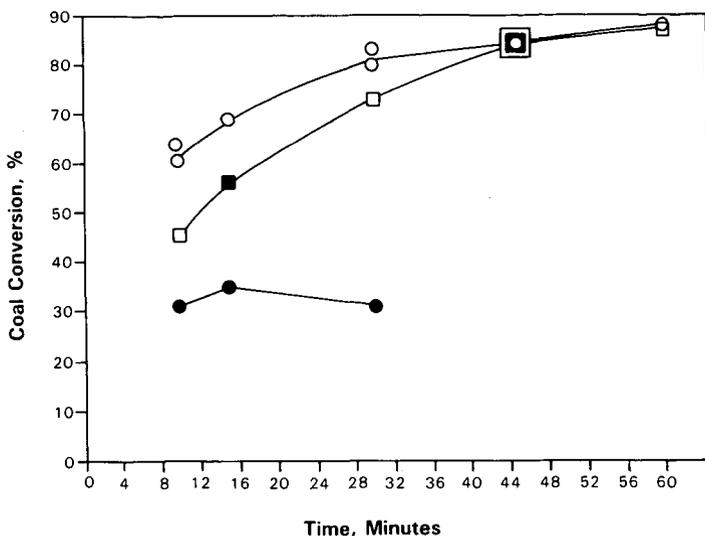


Figure 4. Time dependence of conversion of a Western Kentucky No. 9 Alston coal at 385°C utilizing (1) gaseous (□) hydrogen or (■) nitrogen with a tetralin solvent or (2) gaseous (○) hydrogen or (●) nitrogen with 1-methylnaphthalene solvent.

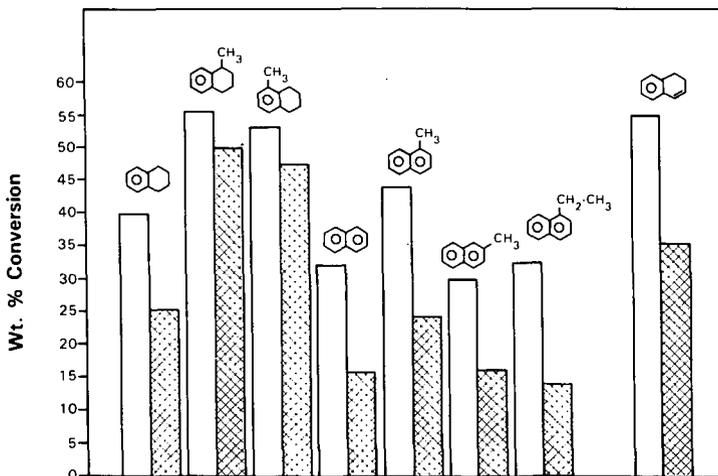


Figure 5. Coal conversion at 15 minutes at 385°C in the presence of gaseous hydrogen for a Western Kentucky No. 9 Alston coal (□) or Eastern Kentucky Peach Orchard coal (▨) and with the indicated solvent.

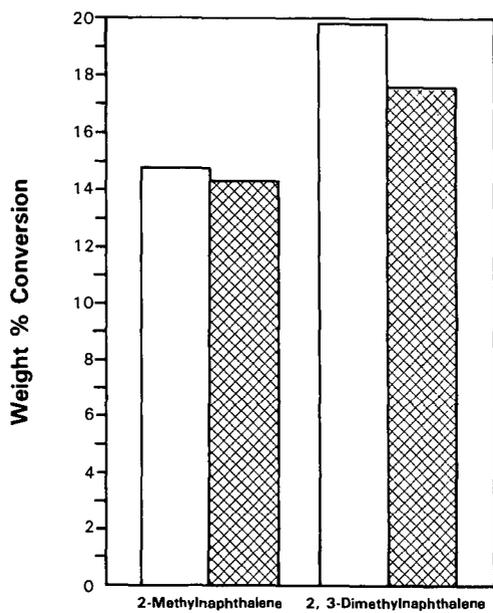


Figure 6. Comparison of the conversion of a Peach Orchard coal starting with a solid (□) or in liquid (▨) solvent.

Hydroliquefaction of Coal-Oil Agglomerates

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ABSTRACT

A novel coal hydroliquefaction process has been developed at PETC that employs a low-solvent-to-coal ($S/C = 0.35$) feed with a water-soluble dispersed catalyst. The effectiveness of liquefaction catalysts, iron and molybdenum, when loaded on the outside surface of coal-oil agglomerates is compared to that of aqueous impregnation. In the presence of 1 wt% iron and 5 vol% hydrogen sulfide, the iron-impregnated coal gave higher conversions than an agglomerated feed. Iron catalyst must be in intimate contact with individual coal particles for highest reactivity. Aqueous impregnation is, therefore, the best catalyst-loading method for dispersed iron. In the presence of 0.1 wt% molybdenum, higher conversions were, however, achieved with the coal-oil agglomerates than with molybdenum-impregnated coal. Oil agglomeration of feed coal eliminated the need for impregnation of molybdenum catalyst on the coal to achieve high conversions at low solvent-to-coal ratio of 0.35. In the absence of catalyst, higher conversions were also achieved with coal-oil agglomerates compared to a simple mixture of coal and oil at $S/C = 0.35$. The improved reactivity of agglomerates is thought to be due to the complete wetting of individual coal particles by binder oil, a hydrogen donor solvent, which was effected during the oil agglomeration step.

INTRODUCTION

During the development of novel approaches to direct liquefaction, organic solvent, water, and a water-soluble transition metal salt catalyst were found to be complementary aids to increase soluble yields of coal hydrogenation.¹ The dependence of tetrahydrofuran (THF) soluble yields on the organic solvent-to-coal (S/C) ratio of the feed described a plateau in the presence of equal masses of coal and water. Conversions reached a maximum with a small amount of solvent, $S/C = 0.5$, and additional organic solvent caused no change in soluble yields. The use of small concentrations of a water-soluble molybdenum salt effectively increased the plateau value of conversion and decreased the S/C ratio for the onset of the plateau compared to uncatalyzed systems.

Subsequently it was shown that in the presence of a dispersed molybdenum salt catalyst, conversions are independent of water partial pressure.² Yields of THF solubles in excess of 90 percent were achieved at S/C as low as 0.25 in the molybdenum-impregnated systems with no added water. The combination of 1 percent iron and 5 volume percent addition of hydrogen sulfide was found to be as effective as 0.1 percent molybdenum in low-solvent-to-coal ($S/C = 0.33$) systems.³

Low-solvent-to-coal liquefaction could potentially reduce the product recycle stream and increase throughput of the coal feed for a given size of equipment. Spherical agglomeration is considered for preparation of the low-solvent-to-coal feed because of ease of handling. Our previous work had, however, been involved with only iron- and molybdenum-impregnated coals.¹⁻³ Catalyst effectiveness by another loading method, deposition on the outside of the coal-oil agglomerates during agglomeration, has to be assessed. At a low solvent-to-coal ratio ($S/C = 0.35$), an effective liquefaction catalyst is required to prevent solvent starvation and high yields of undesired products, char and hydrocarbon gases.

Previous studies have indicated that the mode of catalyst addition is important in coal liquefaction.⁴⁻⁶ Both molybdenum and iron are effective during coal hydrogenation without organic solvent when loaded on the coal particles by an aqueous-impregnation procedure. The effectiveness of ferrous sulfate improved with prolonged mechanical mixing, but it was still less than when iron was aqueously impregnated onto the coal.^{4,5} However, Schlesinger et al.⁷ indicated that impregnation with molybdenum was not needed if the ammonium heptamolybdate was thoroughly mixed in the presence of a solvent ($S/C = 1.5$). The present research investigates the effects on conversions of the mode of catalyst addition and the form of the coal-oil feed in low-solvent-to-coal systems. Results are reported for uncatalyzed systems and with use of water-soluble salts of molybdenum and iron.

EXPERIMENTAL

MATERIAL

Minus-200-mesh grind of Illinois No. 6 (Burning Star mine) bituminous coal was used (dmmf analysis: 5.3% H, 75.4% C, 1.0% N, 3.4% S, 14.9% O). In the experiments with added catalysts, molybdenum or iron, the catalyst was loaded on the coal either by aqueous impregnation or by deposition on the external surface of coal-oil agglomerates.

In the aqueous impregnation procedure, the feed coal was prepared by mixing with water containing a dissolved transition metal salt, ammonium heptamolybdate or ferrous sulfate. The mixture was then dried in a vacuum oven at 110°C, and the catalyst deposited on the coal particles.

In the oil agglomeration procedure, a coal-derived binder oil was added to an agitated mixture of coal and water, and coal-oil agglomerates were formed into spherical particles of 2- to 3-mm-diameter size. In experiments with catalyst, the water contained the dissolved molybdenum or iron. The agglomerates were then drained by sieving. The catalyst was deposited on the agglomerates by evaporation of catalyst solution in a vacuum oven at 110°C. Previous work has shown that coal-oil agglomerates have negligible internal void, so any water adhering to agglomerates after draining was on their outer surface.⁸

For each method of catalyst addition, the catalyst concentration was either 0.10% molybdenum or 1.0% iron, reported as weight percent based on coal. The amount of catalyst deposited was calculated by measuring weight loss of water on drying. Hydrogen gas containing 5 volume percent of hydrogen sulfide was used in experiments with iron catalyst. The liquefaction solvent serving as the agglomeration binder oil was SRC II heavy distillate produced in Run 2406 at the Fort Lewis, Washington, pilot plant. The solvent-to-coal ratio was 0.35 for all experiments, i.e., those employing coal-oil agglomerates and those utilizing unagglomerated coal as feed.

PROCEDURE

Liquefaction experiments were carried out in a stirred one-liter batch reactor. The standard operating conditions for all experiments were either a 400°C or 427°C reaction temperature and a 60-minute reaction time at the desired temperature. Typically, the batch autoclave was charged with 144 gm of either a simple mixture of coal and organic solvent or a charge of coal-oil agglomerates, then pressurized (cold) to 1300 psig with hydrogen gas. The stirrer was operated at 1000 to 1100 rpm. It took from one to one and one-half hours to heat the reactor system electrically from ambient temperature to reaction temperature.

ANALYSIS

The gaseous products were metered and then analyzed by gas chromatography. The yield of C₁ through C₄ was determined as hydrocarbon gases. The hydrogen consumption was calculated from the difference between the initial hydrogen gas charged and the final hydrogen gas collected. The liquefaction residues were analyzed by solvent extraction for THF, benzene, and pentane insolubles. The conversions were calculated by

$$\% \text{ conversion} = \frac{\text{dmnf coal} - \text{organic insolubles}}{\text{dmnf coal}} \times 100\%$$

The conversions were corrected for the insolubles in the SRC II heavy distillate. It was arbitrarily assumed that the organic vehicle was inert in calculating conversions, since insolubles deriving from coal or solvent could not be distinguished.

RESULTS AND DISCUSSION

There was a concern that at the same concentration of catalyst, expressed as a weight percent of coal, agglomerates would show reactivity lower than that of feed coal for which the coal particles were individually impregnated with catalyst. Agglomerates are typically 2 - 3 mm in diameter, while individual coal particles have diameters on the order of 74 microns for minus-200-mesh grind. The catalyst deposited on the external surface of agglomerates will not be as highly dispersed as it is when impregnated on individual coal particles. Indeed, in systems containing 1.0 percent iron and 5 volume percent hydrogen sulfide, agglomerates showed liquefaction reactivity lower than

that of feed coal that was previously aqueously impregnated with iron catalyst (see Figure 1). At 400°C reaction temperature, the benzene-soluble yield was lowered by 9%, and the pentane-soluble yield by 25%. Catalytic activity of iron depends strongly on close contact of iron with coal.

In the presence of 0.10% molybdenum catalyst, oil agglomeration of feed coal, however, increased liquefaction yields (see Figure 2). At 400°C, agglomerated feed coal was more reactive than molybdenum-impregnated coal and increased substantially the liquefaction yields of soluble fractions. The benzene-soluble yield was improved by 12%, and pentane-soluble yield by 28%. At 427°C, the catalytic effect became prominent and masked the contributions of oil agglomeration. High conversions to THF and benzene solubles were obtained for both agglomerated and molybdenum-impregnated coal feeds. At low solvent-to-coal ratio of 0.35, oil agglomeration eliminated the need for impregnation of molybdenum catalyst into coal.

Since agglomerated feedstock with molybdenum catalyst showed an enhancement in liquefaction reactivity, experiments were performed to investigate the effect of the reactant form in uncatalyzed reactions. Figure 3 compares yields of soluble fractions for both agglomerated coal feed and a simple mixture of coal and solvent at the same composition without any catalysts. The liquefaction reactivity was improved dramatically with the oil-agglomerated coal compared to nonagglomerated feed. At 427°C, the enhancement in the liquefaction yields was 19% for all soluble fractions. However, conversions to solubility yields were significantly lower compared to the results obtained with catalyst-impregnated coal feed (see Figures 1 and 2).

Thus an increase in liquefaction reactivity was observed in non-catalyzed systems with oil-agglomerated coal. During coal-oil agglomeration, a water slurry of coal is first contacted with oil while being agitated. Through a series of transfer steps that occur between oil droplets and coal particles during agitation, coal particles become coated individually with oil. Subsequently, the coal particles coalesce and, with further time and agitation, form spherical agglomerates. The bridging oil in coal-oil agglomerates is thought to exist in a capillary state, giving the agglomerates a unique structure.⁸ The agglomerates are noteworthy for their compactness (absence of interior air space), sphericity, and strength. Each coal particle is completely wetted and in intimate contact with a binder oil, which is also a liquefaction donor solvent, within the agglomerate. During initial dissolution, donor solvent is readily available for donating and shuttling hydrogen. The enhanced hydrogen-transferring processes caused higher hydrogen consumption in agglomerated systems with or without any catalysts (Figures 4, 5, and 6), and improved the yields of solubles.

CONCLUSIONS

Molybdenum is effective during low-solvent-to-coal liquefaction when loaded on the outside surface of coal-oil agglomerates. However, iron catalyst must be in intimate contact with in-

dividual coal particles for highest reactivity. Aqueous impregnation is the best catalyst-loading method for dispersed iron. Oil agglomeration of feed coal increased liquefaction yields in systems with no catalyst. The unique structure of coal and binder oil, which is also a hydrogen donor solvent, in the agglomerated state enhances the hydrogen-transferring processes during initial dissolution.

ACKNOWLEDGMENT

The reactions were conducted by William Staymates.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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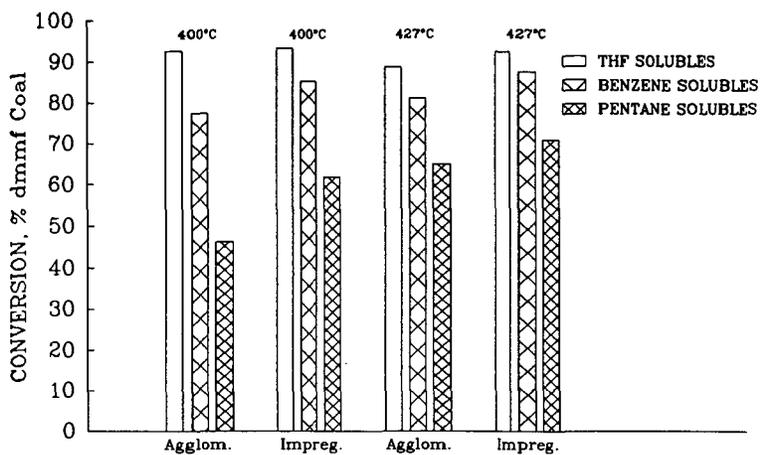


Figure 1. In Systems Containing 1.0% Iron and 5.0 Volume % Hydrogen Sulfide, Aqueous Impregnation Is a More Effective Catalyst-Loading Method than Agglomeration.

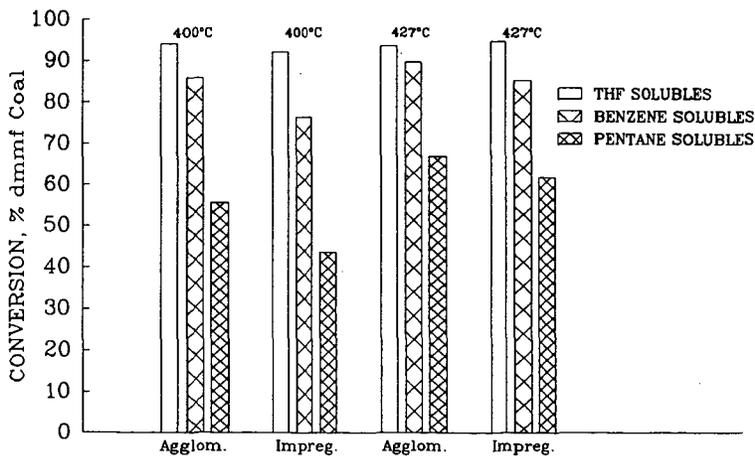


Figure 2. In Systems Containing 0.10% Molybdenum, Oil Agglomeration Improves Liquefaction Yields.

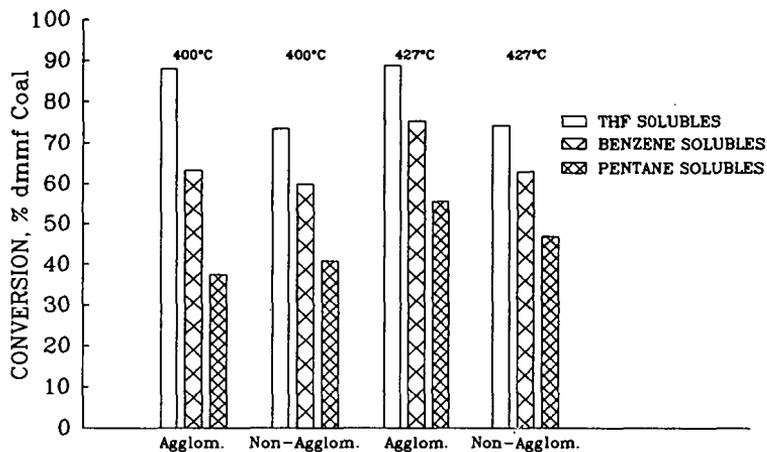


Figure 3. In Non-Catalyzed Systems, Oil Agglomeration Enhances Liquefaction Reactivity.

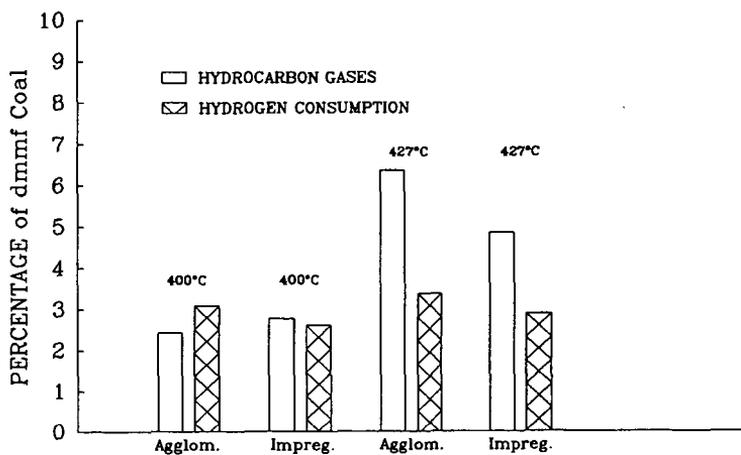


Figure 4. In Systems Containing 1.0% Iron and 5.0 Volume % Hydrogen Sulfide, Agglomerated Feed Consumes More Hydrogen.

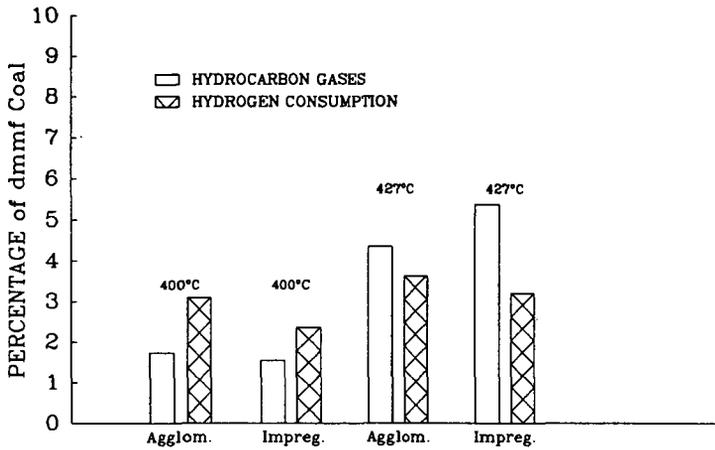


Figure 5. In Systems Containing 0.10% Molybdenum, Agglomerated Feed Consumes More Hydrogen and Produces Less Hydrocarbon Gases.

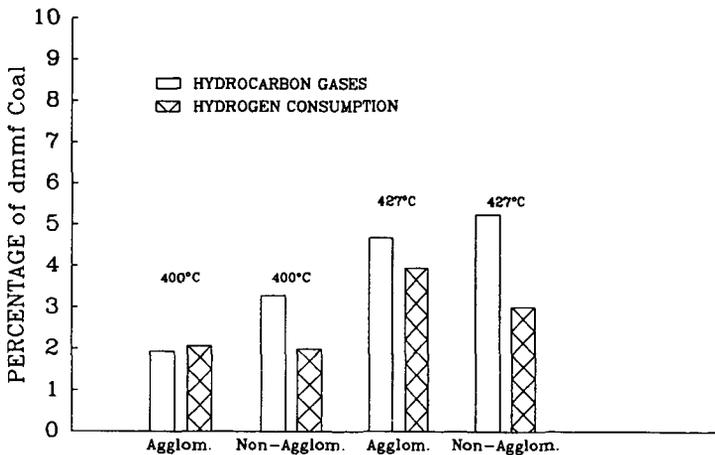


Figure 6. In Non-Catalyzed Systems, Agglomerated Feed Also Consumes More Hydrogen and Produces Less Hydrocarbon Gases.

HIGH LIQUID YIELDS FROM BITUMINOUS COAL VIA
HYDROPYROLYSIS WITH DISPERSED CATALYSTS

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INTRODUCTION

In some respects, coal hydroxyprolysis is potentially a more attractive route for the production of liquid fuels than direct liquefaction techniques utilizing solvents. It offers a process configuration that avoids the use of a recycle solvent, which constitutes up to two-thirds of the reactor feed stream. However, historically, pyrolysis processes have been associated with low conversions of coal to liquid products (1-3), making char the principal product for which some application, apart from providing process heat and hydrogen, must be found. Moreover, large quantities of methane are usually produced during hydroxyprolysis at temperatures above 600°C which are required to achieve substantial liquid yields. Consequently, hydrogen consumptions are high. Results of two-stage hydroxyprolysis studies, in which primary tar vapors are passed through a catalyst bed, previously reported by several of the authors (4-6) have shown that daf yields of 20-25% distillate along with only 3-4% methane can be achieved if non-catalytic hydroxyprolysis of bituminous coal, carried out at a pressure of about 150 atmospheres and a temperature of 500°C, is followed by catalytic upgrading of the tar at a temperature of 400°C.

Early work (7,8) established that coals could be catalytically hydrogenated in batch reactors in the absence of a solvent to give high conversions to pyridine soluble materials. Impregnated molybdenum catalysts were among the most active studied. More recent work (9) has demonstrated that dispersed sulfided Mo is effective under mild conditions; over 50% chloroform soluble material can be generated from bituminous and subbituminous coals by reaction at 400°C and a cold-charge hydrogen pressure of 70 atmospheres. Lewis acids, such as zinc and stannous chlorides, have been shown to enhance liquid yields (10,11), but relatively large concentrations of catalyst are required. Early work has shown that Mo could be used to achieve hydroxyprolysis yields exceeding the proximate volatiles content (12,13). However, sulfided Mo, which is thought to be the most active form for coal conversion, was not used. Moreover due to the high temperatures and pressures used, secondary reactions could not be controlled giving rise to a low selectivity to liquid products.

In this paper we report the results of catalytic hydroxyprolysis experiments in which greater than 60% daf coal basis yields of tar are produced with weight ratios of tar to gases up to 80% higher than observed in an uncatalyzed reaction. The work has also shown that dispersed sulfided molybdenum and hydrous titanium oxide (HTO) catalysts coated directly on the coal are superior to Lewis acids and alumina supported hydrogenation catalysts in terms of tar yields achieved and reduction of the amount of light hydrocarbon gases produced. In addition, we have performed two-stage hydroxyprolysis tests which demonstrate that the tar produced is readily upgraded.

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EXPERIMENTAL

Coal and Catalysts

A high volatile UK bituminous coal (Linby), ground to 75 to 150 micron particle size range, was used for these tests. Analysis of the coal has been reported elsewhere (4). Catalysts used for these tests were 1) zinc and stannous chloride Lewis acids, 2) a commercial Ni-Mo/alumina, 3) bulk HTO (14,15) formulations (Pd and Co-Ni-Mo), 4) coatings of Ni and Pd HTOs and 5) dispersed sulfided Mo. Lewis acid catalysts were impregnated into the coal from aqueous solution. Powdered (-200 mesh) alumina supported and bulk HTO catalysts were physically mixed with the coal, the catalyst weight being 20% daf coal. Ni and Pd HTO catalyst coatings were dispersed by coating the coal with sodium hydrous titanium oxide (Na HTO) followed by contact of the Na HTO-coated coal with aqueous solutions of either Ni or Pd. This resulted in the active metal being incorporated into the hydrous titanate coating via ion exchange for Na⁺. Finely divided MoS₂ was dispersed by wetting the coal with solutions of (NH₄)₂MoS₄ or (NH₄)₂MoO₂S₂. The amounts of active metals in all the materials are given in Table I.

Apparatus and Procedure

The hydropyrolysis reactor and procedures used for the tests have been described previously (4,5). Most of the tests were single-stage catalytic hydropyrolysis experiments, carried out at 150 atmospheres hydrogen pressure and 500°C. The hydropyrolysis zone was heated at a rate of 5°C/s from ambient and held at temperature for 10 min. Hydrogen was passed downward through the reactor at a flow rate equivalent to 5 l/min at standard temperature and pressure and tars were collected in an ice-cooled trap. For comparison with the catalytic experiments, a single-stage test was also performed without catalyst. In addition, two two-stage experiments were performed: the first with a non-catalytic hydropyrolysis stage followed by a presulfided Ni-Mo/alumina catalytic upgrading stage (5,6) operated at 400°C, and the second with dispersed MoS₂ catalyst (0.6% Mo, daf coal basis) in the hydropyrolysis stage followed again by presulfided Ni-Mo/alumina catalyst in the second stage.

Product Recovery and Analysis

Gas exiting the reactor was collected and analyzed for C₁-C₄ hydrocarbons, CO and CO₂. Following the completion of each experiment, the post-reaction contents of the reactor tube were removed and weighed to determine the char and ash remaining. Liquid products contained in the reactor product cold trap were first weighed, then recovered with dichloromethane (DCM). Water was removed using phase separating paper and weighed, and the DCM solutions were evaporated to give tar samples for analysis. The daf coal basis percentage yield of tar for each experiment was calculated as the weight of material recovered in the cold trap less the weight of water produced. The tars were subjected to a variety of analyses to determine the elemental composition--including oxygen concentration, phenolic OH, aromatic hydrogen content, and number average molecular weight. For the two-stage experiments, the liquid products exiting the second stage of the reactor were recovered neat in order to determine the fraction of light naphtha.

RESULTS AND DISCUSSION

Single-Stage Hydropyrolysis

The products resulting from the single-stage catalytic hydropyrolysis experiments, classified as tar, methane, C₂-C₄ hydrocarbons, and char, are listed in Table I. For comparison with the catalytic experiments, the distributions for a non-catalytic experiment are included. As can be seen in Table I, all of the catalyzed

experiments produced significantly more tar than the non-catalytic case. Examination of the results for the various catalysts indicates that tar yields and product selectivity are dependent on the catalyst or active metal employed and the technique used to disperse the catalyst with the coal. The greatest tar yields, 59-64%, were achieved with well-dispersed catalysts containing metals known to be active for coal conversion.

The effect of the active metal may be seen by comparison of the experiments with Ni and Pd HTO coatings and MoS₂. As anticipated, the Pd and Mo catalysts gave higher tar yields (~60%) than the Ni catalysts (~50%). With respect to dispersion, Pd HTO catalysts coated onto the coal and the MoS₂ dispersed from aqueous solution gave higher yields than the Pd HTO and Ni-Mo/alumina finely divided catalyst powders which were physically mixed with the coal, even though the coal basis amount of active metal was significantly greater for the powdered catalysts. The Lewis acid catalysts, ZnCl₂ and SnCl₂, dispersed onto the coal from aqueous solution, produced tar yields of 36% and 54%, respectively, despite the five-fold difference in catalyst weight. This result suggests that further experiments are also needed with Ni and Pd HTO catalyst coatings to determine the minimum amount of active metal required to achieve high yields. Indeed, we have performed experiments similar to those reported here that showing that concentrations of Mo as low as 0.1% can be used without sacrificing tar yield.

In general, C₁-C₄ hydrocarbon gas formation increased with the increase in tar yield. For most of the catalytic experiments, the amount of methane formed (2-4%) was nearly equal to that for the non-catalytic experiment (3%). However, the Lewis acid catalysts produced significantly more methane (6%). The yield of C₂-C₄ hydrocarbon gases produced by the non-catalyzed case was 4%; the catalyzed experiments produced yields from 4 to 9%. Because liquids are the desired hydropyrolysis products, and gaseous hydrocarbons are not only of low value but result in wasteful consumption of hydrogen, a useful figure of merit, shown in Table I, for comparison of the efficiency of conversion is the selectivity defined in terms of the weight ratio of tar to gas yield. Compared to the selectivity for the non-catalyzed experiment, 3.7, the selectivities for the Lewis acid catalysts, 2.8 and 4.1, at best offer little improvement. However, the other catalysts show relative improvement in selectivity ranging from 35 to 80%.

Two-Stage Hydropyrolysis

The two-stage experiments were performed to demonstrate that the tar produced in greater yields from catalyzed hydropyrolysis can be hydrotreated in a second stage to produce a high quality liquid product. Table II shows the compositions of the primary tars produced by non-catalytic and catalytic hydropyrolysis, along with the compositions of the products resulting from second-stage vapor-phase hydrotreatment of the primary tars with presulfided Ni-Mo/alumina catalyst. First-stage product distributions in terms of yields of tar, hydrocarbon gases, and char are given in Table I for similar non-catalyzed and MoS₂ catalyzed experiments. As can be seen from the two tables, tar yield for the catalyzed product was double that for the uncatalyzed product in the single-stage experiments, and although the H/C ratio, aromatic hydrogen and nitrogen contents for both primary tars were similar after the first stage of the two-stage experiments, the oxygen and sulfur contents of the catalyzed hydropyrolysis tar were significantly less than those for the uncatalyzed tar. In addition, the number average molecular weight of the tar produced by the catalyzed experiment was only slightly greater than that produced by uncatalyzed hydropyrolysis.

The composition and average molecular weights of the tars described above indicate that upon hydrotreatment they should yield liquids of similar composition.

Examination of the analyses for the hydrotreated products of the tars shows this to be an accurate assumption. However, two significant differences were noted: the product resulting from the catalytically produced hydroxyprolysis tar had a lower H/C ratio, but a greater daf coal basis yield of light naphtha.

CONCLUSION

Although hydroxyprolysis processes have been historically associated with high yields of methane and light hydrocarbon gases, and low yields of total liquid products, the experiments described in this paper demonstrate otherwise. We have shown that with the proper choice of catalysts and reaction conditions, two-stage catalytic hydroxyprolysis can achieve yields of high-quality liquids rivaling those for two-stage direct liquefaction processes which utilize a recycle solvent. In addition, the yield of low value hydrocarbon gases can be minimized. Use of catalytic hydroxyprolysis to convert coal to liquid fuels may offer advantages associated with elimination of the recycle solvent, which constitutes two-thirds of the mass of the reactor feed in traditional direct liquefaction processes. However, in order to be economically feasible, processing technology must be developed to use low catalyst concentrations or to permit addition, withdrawal, regeneration and recycle of the first-stage hydroxyprolysis catalyst. This, of course, is a task requiring a great deal of additional effort.

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TABLE I. Product Distributions Resulting from Single-Stage Hydropyrolysis Experiments¹

CATALYST (daf Coal Basis Wt % Active Metal)	TAR	METHANE	C ₂ -C ₄ HYDROCARBONS	CHAR	SELECTIVITY Prod. Wt. Ratio (tar/gas)
None	26	3	4	60	3.7
ZnCl ₂ (5%)	36	6	7	45	2.8
SnCl ₂ (1%)	54	6	7	30	4.1
Ni-Mo/Alumina (3.6%)	42	3	4	42	6.0
CoNiMo HTO-bulk (2.9%)	38	2	4	46	6.3
Pd HTO-bulk (2.0%)	47	3	4	35	6.7
Ni HTO coating (0.5%)	50	4	6	32	5.0
Ni HTO coating (1.0%)	53	4	6	29	5.3
Pd HTO coating (0.7%)	64	3	9	16	5.3
Pd HTO Coating (1.6%)	62	4	7	20	6.2
MoS ₂ (0.6%)	59	4	6	20	5.9

1. Products are given on a Wt.% daf coal basis and included -6% water and -2% CO + CO₂.

TABLE II. Composition of Primary Hydropyrolysis Tar and Second-Stage Product for Experiments With and Without a Catalyzed First Stage¹

<u>Primary Tar Composition</u>	<u>Uncatalyzed First Stage</u>	<u>Catalyzed First Stage²</u>
C	84.3	86.1
H	6.8	7.0
O Wt % of product	5.3	3.6
N	1.5	1.7
S	0.9	0.4
OH	4.3	3.0
H/C atomic ratio	0.97	0.98
% Aromatic H of total H	36	33.5
M _n -number ave. mol. wt.	250	270

Second-stage Product³

C	84.0	88.0
H Wt % of product	13.6	11.9
OH	0.01	0.05
ppm N	7	33
H/C atomic ratio	1.94	1.62
% Aromatic H of total H	4	7
Light Naphtha (Wt % daf coal)	8.3	11.2

1. First Stage Conditions - 500°C, 150 atm hydrogen pressure.
 Second Stage Conditions - 400°C, 150 atm hydrogen pressure.
2. First Stage Catalyst - 0.4%, coal basis, MoS₂.
3. Second Stage Catalyst - Ni-Mo/alumina.