

## EFFECT OF SOLVENT CHARACTERISTICS ON COAL LIQUEFACTION

He Huang, Shaojie Wang, Keyu Wang, Michael T. Klein and William H. Calkins\*

Department of Chemical Engineering  
University of Delaware, Newark, Delaware 19716

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### Introduction

It has been known for a long time that the characteristics of the liquefaction solvent has a profound effect on direct coal liquefaction. The amount of hydrogen consumed during the liquefaction process, the degree and quantity of retrograde reactions that occur, and the quality of the liquid products are all influenced by the process solvent (1). A number of analytical approaches have been developed to determine the important characteristics of the solvent for coal liquefaction (1). The hydrogen donor ability has clearly been important (2). However, such other characteristics of a liquefaction solvent as solubility parameter (1), content and type of higher aromatic hydrocarbons (3), and phenolic content have also been found to be significant (1). Finseth et al. (4) have shown that the bulk of the hydrogen consumed from an uncatalyzed donor solvent liquefaction above 400 °C is consumed in gas generation, heteroatom removal and hydrogenolysis of the coal matrix. Wilson et al. (5) have also shown that the major role of hydrogen in uncatalyzed liquefaction is consumed by alkyl fission and hydrogenolysis reactions and not with hydrogenating aromatic rings. McMillan et al. (6) have postulated that a radical hydrogen transfer process along with donor solvent capping of thermally produced radicals from the coal as possible processes involved with the hydroaromatic donor solvents in coal liquefaction.

With the development of a short contact time batch reactor (SCTBR) (7), determining the influence of the processing solvent on the liquefaction rates, conversion profiles and the quality of the liquid product at a particular time became possible. The influence of type of solvent, combined with other effects, such as gas atmosphere (i.e., in hydrogen and in nitrogen) and catalyst, on the coal liquefaction is reported in this paper.

### Experimental

**Apparatus.** A Short-Contact-Time Batch Reactor (SCTBR) was devised to carry out the coal liquefaction. It allows the heat up of the process stream to reaction temperature in about 0.3 seconds. The removal and quenching of the reaction products occurs in a similar time period. The design and operation of such a SCTBR reactor system have been described in detail elsewhere (7,8).

**Solvents Used.** Four solvents: 1,2,3,4-tetrahydroquinoline (98%), tetralin (99%), 1-methylnaphthalene (98%), and decahydronaphthalene (99+%) from Aldrich with different hydrogen donor abilities and solubility parameters have been used in the coal liquefaction experiments.

**Catalyst Used.** Molybdenum naphthenate (6.8 wt% molybdenum from Shepherd Chemical Co.) was the liquefaction catalyst used in this study. The catalyst was prepared by dissolving about 0.5 g molybdenum naphthenate (equivalent to about 0.9 wt% Mo based on the amount of the coal charged) in the processing solvent. The catalyst was then sulfided by reacting the solution with about 1 g of methyl disulfide during the transport into the reactor and liquefaction.

**Coal Liquefaction.** Illinois #6 bituminous and Wyodak-Anderson subbituminous coals from the Argonne Premium Coal Sample program were used in this study. Proximate and elemental analyses, together with other analytical data, of these coals are available in the User's Handbook for the Argonne Premium Coal Sample program (9). All liquefactions were run as mixtures of processing solvent (S) and coal (C) at a mass ratio of S/C = 8 to minimize the effect of changing processing solvent concentration during the reaction. About 4 grams of coal were used for each reactor run, together with the added processing solvent to make up the reactant slurry.

**Workup Procedures of Reaction Products.** After a liquefaction run, the product mixture was filtered and the solid residue washed with cold fresh tetralin thoroughly and dried in a vacuum oven with a nitrogen purge at about 105 °C for 48 hours. The filter cake was then rinsed with methylene chloride and dried in a vacuum oven with a nitrogen purge at 105 °C for 12 hours. The solid residue and the liquid filtrate were analyzed separately (10). The mineral matter of the coal was shown to accumulate in the coal residue and not in the coal liquids. Therefore, ash in the residue determined by thermogravimetric analysis was used to calculate the conversion (10).

### Results and Discussion

**Coal Liquefaction Processes.** The conversions of Illinois #6 liquefaction in tetralin

without added catalyst under 1000 psig nitrogen at four temperatures (358 °C, 390 °C, 408 °C and 422 °C) for short reaction times (10 s to 10 min) are shown in Figure 1. Three distinct phases in the process were observed: a very rapid conversion followed by an induction period and then a slower liquefaction of the coal structure. The initial rapid conversion in the first 30 to 60 s is due to the extraction of a soluble fraction of the coal into the hot tetralin. The slow conversion after 1 or 2 min is caused by the chemical breakdown of the coal structure to liquid products. The induction period observed is actually a transition interval which is due to the simultaneous occurrence of two processes: a very rapid extraction and a relatively slower liquefaction of the coal structure itself. The amount of extraction increases as the liquefaction temperature increases. The equilibrium extraction of the Illinois #6 coal at 358 °C, 390 °C, 408 °C and 422 °C were about 18.4 wt%, 22.0 wt%, 31.9, and 39.8 wt%, respectively. Similar behavior was also observed in Wyodak-Anderson subbituminous coal liquefaction. The equilibrium extraction of the Wyodak-Anderson coal in tetralin at 390 °C under 1000 psig nitrogen is about 14.1 wt%.

From these observations, a hypothesis of two processes of coal liquefaction was postulated (10). Based on this hypothesis, Wang et al. (11) have developed a model to evaluate the kinetic parameters for each stage. They have reported that the extraction stage is about two orders of magnitude faster than the structure breakdown stages and have correspondingly lower activation energies. The liquefaction of the coal structure itself also consists of multiple steps of different rate constants and activation energies. The rate constant of the extraction stage and the equilibrium extraction fraction are dependent on the solvent characteristics and coal structures as well as liquefaction conditions.

It is important to point out that the coal liquefaction kinetic studies reported in the literature are largely based on liquefaction to high conversions (2,12,13). Therefore, the kinetic measurements are actually combinations of the rapid extraction with the much slower liquefaction of the coal structure.

**Effect of Gas Atmosphere on the Coal Liquefaction.** Conversions of the liquefaction of Illinois #6 and Wyodak-Anderson coals in tetralin at 390 °C for 30 min under 1000 psig N<sub>2</sub> or 1000 psig H<sub>2</sub> is shown in Figure 2. For the Illinois #6 coal, the liquefaction conversion in hydrogen was higher than in nitrogen. However, there was no difference for the Wyodak-Anderson coal liquefied in hydrogen or in nitrogen. The contents of pyritic sulfur in Illinois #6 and Wyodak-Anderson are 2.81 wt% and 0.17 wt%, respectively. This is a strong indication that pyrite in the Illinois #6 provides some catalysis for the liquefaction in the presence of hydrogen.

**Catalysis of Molybdenum Naphthenate.** Conversion of the Illinois #6 coal with molybdenum naphthenate (equivalent to 0.9 wt% Mo) was studied in an effort to understand the role of a hydrogenation catalyst relative to the liquefaction solvent in coal liquefaction. Figure 3 summarizes the results of a series of experiments aimed at determining the active species when the molybdenum naphthenate is the added catalyst. The sulfiding agent used was methyl disulfide. Comparison of the conversions in different liquefaction conditions shown in Figure 3 indicates that: 1). sulfided molybdenum naphthenate in the absence of hydrogen is not active; 2). the sulfiding agent itself plays no direct role in coal liquefaction; and 3). only sulfided molybdenum naphthenate (presumable as Mo<sub>2</sub>S<sub>3</sub> or MoS<sub>2</sub>) in the presence of hydrogen is the active catalyst for coal liquefaction.

**Effects of Solvent, Catalyst, and Gas Atmosphere on the Coal Liquefaction.** Conversion vs. time curves of the thermal (without added catalyst) liquefaction of Illinois #6 coal in 1,2,3,4-tetrahydroquinoline (THQ), tetralin, and 1-methylnaphthalene, in decreasing order of hydrogen-donor ability, run under 1000 psig nitrogen at 408 °C are shown in Figures 4a and 4b for two different time intervals. The liquefaction conversions using 1-methylnaphthalene as a processing solvent shows distinct stages of liquefaction kinetics: a very rapid extraction and followed by an extremely slow liquefaction of the coal structure. The equilibrium extraction of the Illinois #6 coal using 1-methylnaphthalene was 30.7 wt%. This value is very close to that using tetralin as a processing solvent. The solubility parameters of 1-methylnaphthalene and tetralin are 20.3 and 19.4, respectively. This suggests that the extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent used. However, the rates of coal structure breakdown in tetralin and in 1-methylnaphthalene were 0.0458 wt%/min and 0.00168 wt%/min, about 27 times difference. For the very strong hydrogen donor solvent of 1,2,3,4-tetrahydroquinoline, the extraction stage becomes indistinguishable from the liquefaction of the coal structure. This is because the rate of coal structure breakdown in the very strong hydrogen donor solvent is close to the rate of extraction. The rate of coal structure breakdown measured in this solvent was 1.41 wt%/min. Comparison of the rates of the coal structure breakdown in 1,2,3,4-tetrahydroquinoline, tetralin, and 1-methylnaphthalene suggests that hydrogen transfer from the solvent is the rate-determining step in uncatalyzed coal liquefaction. This is consistent with the observations that the activation energies for coal structure breakdown is much less than carbon-carbon bond strength (2,11-13).

Effects of solvent on the thermal liquefaction of the Illinois #6 coal in nitrogen and in

hydrogen are illustrated in Figure 5. These data show that the very strong hydrogen donor solvent, such as 1,2,3,4-tetrahydroquinoline, gives much higher conversion than tetralin. More interestingly, the liquefaction conversion in this very strong donor solvent shows no sensitivity to gas atmosphere (i.e., in nitrogen or in hydrogen), indicating little if any hydrogen is derived from the molecular hydrogen in the case of a very strong hydrogen donor solvent used. On the other hand, the liquefaction in the poor hydrogen donor solvents, such as decahydronaphthalene and 1-methylnaphthalene, shows much lower conversion than in tetralin under nitrogen pressure. However, for these very poor hydrogen donor solvents, the liquefaction conversions of the Illinois #6 coal in hydrogen is much higher than that in nitrogen, showing strong sensitivity to gas atmosphere. These results suggest that, in a poor hydrogen donor solvent, the hydrogen needed in the liquefaction process must be mostly derived from molecular hydrogen when a hydrogenation catalyst is present in the parent coal (for example, the pyrite in the Illinois #6 coal) and/or is added (such as sulfided molybdenum naphthenate).

Effect of molybdenum naphthenate catalyst in different solvents on the Illinois #6 coal liquefaction is shown in Figure 6. Liquefaction conversions are always higher in tetralin than in 1-methylnaphthalene for both of the thermal and catalyzed liquefactions. However, with the added catalyst, the conversions in tetralin increased only by a factor of 53%, 31%, and 29% for 30 min liquefaction at 390 °C, 403 °C, and 420 °C, respectively, compared to those in 1-methylnaphthalene by a factor of 123% and 97% for 10 min at 397 °C and 30 min at 410 °C, respectively. These results indicate that the catalysis by an added hydrogenation catalyst in coal liquefaction is more responsive when a poor hydrogen donor solvent is used. It also suggested that a hydrogenation catalyst could be used to compensate for the lack of hydrogen donor ability of a processing solvent.

To quantitatively evaluate the effects of solvent, catalyst, and gas atmosphere for the coal liquefaction, specific liquefaction conversion ratios of  $\alpha$ ,  $\beta$ , and  $\gamma$  are defined using the coal liquefaction conversion in nitrogen as a reference, i.e.,

$$\begin{aligned}\alpha &= \frac{X_{H_2}}{X_{N_2}} \\ \beta &= \frac{X_{catalyst}}{X_{N_2}} \\ \gamma &= \frac{X_{catalyst}}{X_{H_2}}\end{aligned}\quad (1)$$

where  $X_{N_2}$  is the liquefaction conversion in nitrogen;  $X_{H_2}$  is the liquefaction conversion in hydrogen; and  $X_{catalyst}$  is the catalyzed liquefaction conversion in hydrogen. The  $\alpha$  is selected to evaluate the hydrogen gas effect. The larger the  $\alpha$ , the stronger the hydrogen gas effect. When  $\alpha = 1$ , it means there is no hydrogen gas effect in the coal liquefaction. The  $\beta$  is calculated to evaluate the catalyst reactivity and the  $\gamma$  is used to evaluate the net reactivity of the added catalyst. The data to show the combination of the effects of solvent, catalyst, and gas atmosphere on the Illinois #6 and Wyodak-Anderson coal liquefactions, together with the calculated specific ratios of  $\alpha$ ,  $\beta$ , and  $\gamma$ , are summarized in Table 1. Based on the  $\alpha$  values, the order of the hydrogen gas effect on the Illinois #6 coal liquefaction for different solvents was decahydronaphthalene ~ 1-methylnaphthalene > tetralin > 1,2,3,4-tetrahydroquinoline. The stronger the hydrogen donor solvent, the less will be the hydrogen gas effect. In fact, there is no hydrogen gas effect on the Illinois #6 coal liquefaction for the very strong donor solvent of 1,2,3,4-tetrahydroquinoline for which  $\alpha = 1$ . The Wyodak-Anderson coal shows no hydrogen gas effect ( $\alpha = 1$ ) during the liquefaction in tetralin. Based on the  $\beta$  values, the order of the catalyst influence on coal liquefaction in different hydrogen donor solvents was 1-methylnaphthalene > tetralin. Furthermore, the higher the liquefaction temperature, the lower the catalyst influence on liquefaction conversion. This may be because, as temperature increases, the selectivity to liquid products during the liquefaction decreases. This is also supported by the  $\gamma$  values for the liquefaction of the Illinois #6 in 1-methylnaphthalene.

### Summary and Conclusions

The extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent. The liquefaction of Illinois #6 using 1-methylnaphthalene shows distinct stages of liquefaction kinetics similar to tetralin. However, compared to tetralin, it has an extremely slow breakdown rate of the coal structure. The equilibrium extraction for 1-methylnaphthalene was 30.7 wt% at 408 °C, which is very close to that (31.9 wt%) in tetralin. The extraction and coal structure breakdown stages of the Illinois #6 coal liquefaction in 1,2,3,4-tetrahydroquinoline, however, were indistinguishable.

A hydrogen atmosphere increases the thermal (uncatalyzed) conversion of Illinois #6, but had no effect on Wyodak-Anderson subbituminous coal. This is apparently due to the catalytic

effect of pyrite (or pyrrhotite derived from the pyrite) in the Illinois #6 coal, since this coal contains substantial amounts of pyrite whereas the Wyodak-Anderson coal contains only trace amount of pyrite.

Liquefaction yields and rates of coal structure breakdown are greatly increased by the use of a strong hydrogen donor solvent in which most of the hydrogen is contributed by the solvent rather than molecular hydrogen, suggesting that hydrogen transfer from the solvent is the rate-determining step in uncatalyzed coal liquefaction.

The order of the hydrogen gas effect on the Illinois #6 coal liquefaction for different solvents was decahydronaphthalene ~ 1-methylnaphthalene > tetralin > 1,2,3,4-tetrahydroquinoline. The stronger the hydrogen donor solvent, the less the hydrogen gas effect. When a poor hydrogen donor solvent was used and a hydrogenation catalyst either was present in the coal itself (for example, pyrite in the Illinois #6 coal) or was added (such as sulfided molybdenum naphthenate catalyst), hydrogen is predominantly contributed by molecular hydrogen.

#### Acknowledgments

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Table 1 Effect of solvent on the thermal and catalytic liquefactions of the Illinois #6 and Wyodak-Anderson coals in 1000 psig N<sub>2</sub> or H<sub>2</sub>

Sample	Coal	Solvent	T C	t min	Gas	Catalyst	X wt% [Note 1] [Note 2]	$\alpha$	$\beta$	$\gamma$
DOE00	Illinois #6	Tetralin	390	30	N <sub>2</sub>	No	42.6	1.09	1.53	1.41
DOE07	Illinois #6	Tetralin	390	30	H <sub>2</sub>	No	46.3			
DOE14	Illinois #6	Tetralin	392	30	H <sub>2</sub>	Yes	65.3			
DOE09	Illinois #6	Tetralin	404	30	N <sub>2</sub>	No	54.4	N.A.	1.31	N.A.
DOE16	Illinois #6	Tetralin	402	30	H <sub>2</sub>	Yes	71.2			
DOE10	Illinois #6	Tetralin	422	30	N <sub>2</sub>	No	59.9	N.A.	1.29	N.A.
DOE17	Illinois #6	Tetralin	418	30	H <sub>2</sub>	Yes	77.1			
DOE14	Illinois #6	1-methylnaphthalene	398	10	N <sub>2</sub>	No	24.7	1.41	2.23	1.58
DOE15	Illinois #6	1-methylnaphthalene	396	10	H <sub>2</sub>	No	34.9			
DOE15	Illinois #6	1-methylnaphthalene	395	10	H <sub>2</sub>	Yes	55.1			
DOE18	Illinois #6	1-methylnaphthalene	409	30	N <sub>2</sub>	No	33.7	1.63	1.97	1.20
DOE18	Illinois #6	1-methylnaphthalene	412	30	H <sub>2</sub>	No	55.1			
DOE18	Illinois #6	1-methylnaphthalene	412	30	H <sub>2</sub>	Yes	66.4			
DOE18	Illinois #6	THQ [Note 3]	412	30	N <sub>2</sub>	No	85.6	1.00	N.A.	N.A.
DOE18	Illinois #6	THQ	415	30	H <sub>2</sub>	No	85.5			
DOE23	Illinois #6	Decahydronaphthalene	400	30	N <sub>2</sub>	No	22.2	1.49	N.A.	N.A.
DOE23	Illinois #6	Decahydronaphthalene	400	30	H <sub>2</sub>	No	33.0			
DOE08	Wyodak-Anderson	Tetralin	392	30	N <sub>2</sub>	No	39.6	1.01	N.A.	N.A.
DOE08	Wyodak-Anderson	Tetralin	390	30	H <sub>2</sub>	No	39.8			

#### Notes:

1. Catalyst: Molybdenum naphthenate (equivalent to 0.9 wt% Mo) sulfided in-situ by methyl disulfide.
2. X: Liquefaction conversion on the daf (dry-ash-free) basis.
3. THQ: 1,2,3,4 - Tetrahydroquinoline

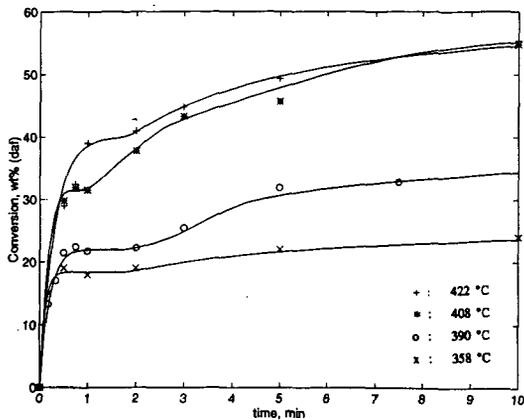


Figure 1 Conversion vs time for Illinois #6 coal liquefaction without added catalyst in tetralin (tetralin:coal = 8:1 mass ratio) under 1000 psig N<sub>2</sub> (for short contact times up to 10 min)

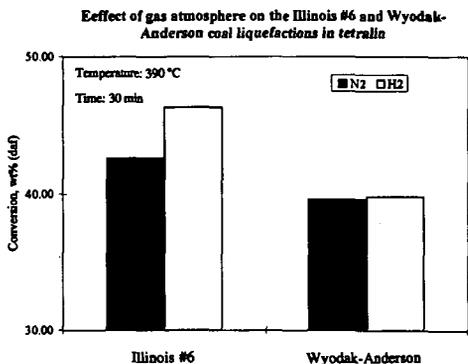


Figure 2

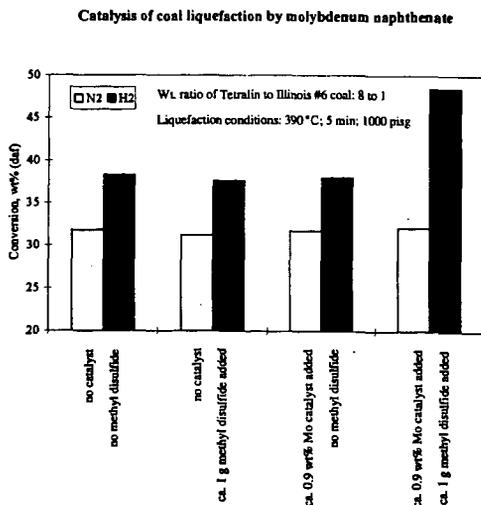


Figure 3

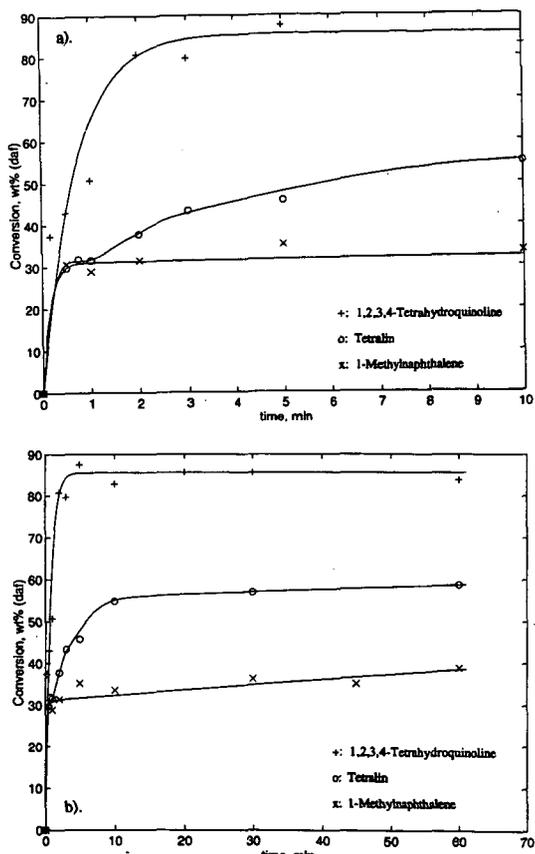


Figure 4 Conversion vs. time curves of the thermal liquefaction of Illinois #6 coal in 1,2,3,4-tetrahydroquinoline (THQ), tetralin, and 1-methylnaphthalene under 1000 psig nitrogen at 408 °C (Solvent:Coal = 8:1): a). for short contact times; b). for up to 60 min

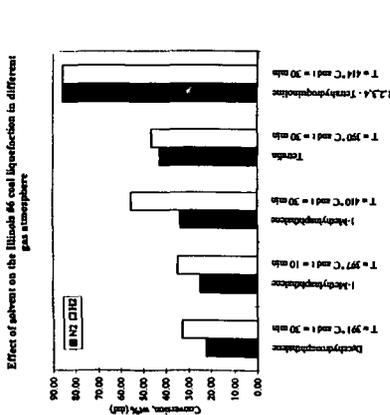


Figure 5

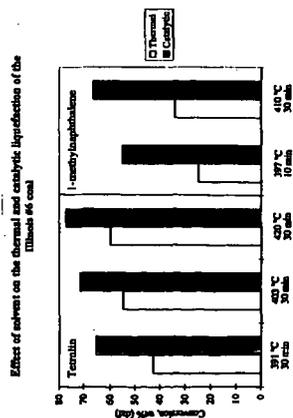


Figure 6