

Pretreatment for Coal Liquefaction

N. R. Pollack¹, G. D. Holder², and R. P. Warzinski

U.S. Department of Energy, Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

Keywords: coal liquefaction, pretreatment, mass transfer limitations

Abstract

Pretreatment of Illinois No. 6 coal using two different procedures at moderate temperatures, 100°C to 300°C, resulted in small (up to 8%) but consistent increases in subsequent liquefaction yields. In a hydrothermal pretreatment, coal and water were heated together and then separated. The increase in yields due to this pretreatment are probably due to a chemical change in the coal. A method of modelling chemically effective pretreatments is proposed. The other pretreatment that increased liquefaction yields involved soaking the coal at 300°C in a coal-derived solvent prior to liquefaction. Particle size experiments were also performed to determine if mass-transfer resistance was a factor. At short contact times, liquefaction yields were greater with smaller particles, whereas, at longer contact times, the yields approached the same limiting value regardless of the initial coal particle size.

Introduction

The use of pretreatments, including catalyst dispersion, to enhance the liquefaction of coal has recently drawn considerable interest. Such pretreatments are proposed to open up the pores of the coal, provide a more intimate contact of catalyst and coal, and possibly affect the ultimate reaction chemistry by chemically altering the nature of coal prior to the liquefaction step. In this paper, such pretreatments will be classified into two types: Type I, which are those primarily aimed at reducing mass-transfer limitations between the coal and liquefaction media; and Type II, which are those designed to affect the liquefaction chemistry.

Examples of Type I pretreatments include those which open the pores of the coal allowing the solvent and hydrogen to more easily penetrate the coal particle or those in which a catalyst or other chemical, such as a hydrogen donor, is placed within the pores of the coal so that it is at the reaction site when liquefaction begins. Note that the process of catalyst deposition may affect the morphology of the catalyst and would need to be distinguished from mass-transfer-related effects. With the exception of catalyst morphology effects, all of these pretreatments are designed to overcome mass-transfer limitations. Type I pretreatments would therefore be ineffective if such limitations do not exist in the particular liquefaction scheme under investigation.

Only those pretreatments that produce a change in the chemical structure, surface properties, or molecular arrangement of the coal prior to liquefaction can be classified as Type II pretreatments. If the same effect can be produced by just adding the reagent(s) to the liquefaction step, then a separate pretreatment would not be necessary.

¹ Calgon Carbon Corporation, Robinson Township PA 15205

² University of Pittsburgh, Pittsburgh, PA 15216

For example, in order for a hydrothermal pretreatment to be judged a Type II pretreatment, the water must produce an effect that is different than would be obtained by just adding water to the liquefaction solvent. This concept is fundamental in evaluating any Type II pretreatment.

Background

During the past several years, coal pretreatments have received increased attention as a means of improving the liquefaction process by either lowering the reaction severity or improving yields under conventional liquefaction conditions. Examples of Type I pretreatments include solvent swelling or presoaking in the liquefaction solvent, both of which have been previously reported to enhance liquefaction yields (1,2,3,4). The most straightforward Type I pretreatment would be a reduction in particle size. This subject has been reviewed by Whitehurst et al. (5). They concluded that, while some variations in conversion were observed for different particle sizes, there were no significant mass-transfer limitations in coal liquefaction, especially when good hydrogen-donor solvents were used in well-agitated systems. In other processes, however, such as high-temperature solvent extraction (5,6) and for chemical reactions at temperatures below those used for conventional liquefaction (7), the presence of significant intraparticle mass-transfer limitations was sometimes observed. Since the presence of mass-transfer limitations is dependent on the type of process and on the mechanics of the system being used, it is therefore judicious to investigate this matter in the development of a Type I pretreatment.

Common Type II pretreatments used for coal liquefaction are alkylation and hydrothermal processing. A recent example of an alkylation pretreatment is the work by Baldwin et al. (8). In this work, mild O-alkylation was shown to be a beneficial pretreatment for a subbituminous coal. The benefit was associated with the suppression of cross-linking reactions that take place during the initial stages of coal thermolysis. The effects were most pronounced at lower reaction severity. Concerning hydrothermal pretreatments, improvements in pyrolysis conversions resulting from steam and hot water pretreatments were originally reported by Brandes et al. (9), and Bienkowski et al. (10). Mochida also reported an improvement in liquefaction yields in a pyrene solvent system associated with a boiling-water pretreatment (11). Ross and coworkers report some improvement in product quality from donor-solvent liquefaction of a hydrothermally pretreated coal (12). Although these various systems have been studied, the mechanism and the actual benefit of hydrothermal pretreatments in liquefaction systems are still not fully understood.

Experimental

Two samples of Illinois No. 6 coal were used in the work reported here. Elemental analyses are contained in Table 1. One sample was ground to minus 48-mesh and minus 325-mesh top sizes. From a second sample of lump-size coal, a 10x48 mesh fraction was screened out after passing the coal through a delumper and a jaw mill. Part of the 10x48 fraction was further ground in a ball mill for 15 minutes under argon to produce a minus 230-mesh sample. The coal-derived liquefaction solvent was a hydrogenated heavy distillate obtained from the V1074 separator at the Advanced Coal Liquefaction Test Facility in Wilsonville, Alabama.

A 38 cm³ (2.54-cm o.d., 12.7-cm long) stainless-steel microautoclave was used to perform the high-temperature pretreatments and the liquefaction tests. During operation, the microautoclave is

horizontally positioned and agitated by a Burrell wrist-action shaker. The microautoclave is rapidly heated to reaction temperature by immersion in a hot sand bath and quenched after reaction in water. Zero-contact-time experiments involved quenching the microautoclave as soon as reaction temperature was attained. The internal temperature and pressure are continuously monitored.

The liquefaction tests were performed on 3 g of coal or treated coal that was mixed with 9 g of solvent in the microautoclave. A 1000 psig hydrogen or nitrogen cold charge was used in these tests. Liquefaction conversions are measured by methylene chloride and n-heptane solubility and are based on the dry, ash-free, insoluble residues. The standard error in the conversion determinations is less than 4% in both cases. Additional details are available elsewhere (13, 14).

The hydrothermal pretreatments were performed using 5 g of coal and 10 g of water under an initial nitrogen pressure of 500 psig. After 30 minutes at 300°C, the microautoclave was quenched and transferred to a nitrogen-filled glove box where it was vented and opened. The contents were removed with deionized water and filtered to remove the excess water. A portion of the sample was then placed back in the microautoclave for the liquefaction test. Another portion was analyzed to determine the moisture and ash content of the pretreated sample.

In the presoak pretreatments, the microautoclave was heated to 300°C for 10 minutes before being transferred to another sandbath that was preheated to liquefaction temperatures. In one case, the presoak pretreatment was performed by placing the microautoclave and its contents in a cold sandbath and gradually bringing it up to liquefaction temperature over a period of about 2 hours.

Results and Discussion

Results of a Type I pretreatment on the minus 48-mesh sample of Illinois No. 6 coal are shown in Figure 1. The pretreatment involved presoaking the coal in the Wilsonville V1074 recycle solvent prior to liquefaction. In one case, indicated by PS in Figure 1, the presoak was carried out at 300°C for 10 minutes prior to immersing the reactor in another sand bath at liquefaction temperature. In another case, indicated by SH in Figure 1, the microautoclave was slowly heated to reaction temperature over a period of about 2 hours. At 400°C, both presoaking and slow heating led to small increases in conversion to both methylene-chloride and n-heptane solubles. The increases were less for the longer experiment in which slower heating was used. The magnitudes of the observed increases were of the same order of magnitude as that observed by Narain (4) but less than those observed by others (1,3).

Figure 1 also shows that increasing the liquefaction temperature to 425°C results in the pretreatment effect being absent in the case of the n-heptane conversions and negative for the conversions measured with methylene chloride. These results represent part of a larger body of experimental data yet to be reported (13), but they serve to illustrate the sensitivity we observed for this type of pretreatment with respect to the actual liquefaction conditions used.

To further assess the role of mass transfer limitations in donor-solvent liquefaction, experiments with Illinois No. 6 coal of various mesh sizes were conducted. Results of using these fractions in the Wilsonville V1074 solvent system are shown in Figure 2. Any benefits of using the smaller particle sizes in this system are only observed at very short contact times and diminish as contact time increases. As

with the presoak results described above, liquefaction at 425°C diminishes any benefit observed at the lower temperature.

Another set of experiments on this subject was performed to isolate the effect of solvent/coal contact using the more carefully sized coal particles (see the Experimental section for details). The liquefaction tests in this case were conducted at 400°C in tetralin under an inert atmosphere. As before, the results, contained in Figure 3, show that a small but consistent increase in methylene-chloride and n-heptane conversions accompany the use of the smaller-sized particles. The magnitude of the increase diminishes with increasing contact time but is still evident at 20 minutes. Analysis of the methylene-chloride-insoluble product produced from the 10X48 mesh sample showed the presence of particles larger than 48 mesh for the 0 and 5 minute tests but no evidence of the original particles at 20 minutes.

In summary of the above, the small influence that initial particle size has on ultimate (longer contact time) yields indicates that the same asymptotic yields are reached although the initial conversion is moderately inhibited by the larger particles. The asymptotic behavior also implies that the reactions are delayed slightly but not significantly changed in nature. The results from these tests and the presoak experiments indicate that mass-transfer limitations may exist under certain conditions and that, in these cases, Type I pretreatments may be effective in reducing these limitations. However, under conventional liquefaction conditions, large benefits should not be expected from Type I pretreatments. Such pretreatments may have greater utility under lower-severity conditions where coal particles do not disintegrate rapidly and the rates of the liquefaction reactions are slower. The work described here indicates that the largest effect related to any mass-transfer limitations probably occurs during the initial heating to liquefaction temperatures, since only small improvements are observed even in zero-contact-time experiments.

The effect of using a hydrothermal (Type II) pretreatment on Illinois No. 6 coal is shown in Figure 4. The pretreatments resulted in a small but consistent improvement in the methylene-chloride solubles (2%) and the heptane solubles (6%) compared to the yields obtained for untreated coals. In other work, similar but less consistent results were obtained for a Wyodak coal (13). These results are consistent with those of Ross and coworkers (12), which show similar small improvements in the yields of toluene soluble material after a hydrothermal pretreatment at 250°C. They also noted an improvement in the product quality due to the pretreatment as determined from FIMS data. They postulate that the pretreatment disrupts chemical associations between the organic and mineral phases of the coal causing the release of organic matter. In other work, Mochida et al. (11) speculate that hydrothermal pretreatments remove divalent cations such as Ca^{2+} and Mg^{2+} , which link oxygen functionalities and thereby impede liquefaction. In the pyrolysis work of Brandes et al. (9), the proposed reason for increased yields is the chemical interaction of the steam used in the pretreatment with oxygen functional groups in the coal. Although the hypothesized mechanisms for hydrothermal pretreatment are varied, the consensus is that it is a chemical effect and therefore classified as a Type II pretreatment. Also, in previous work, the addition of water directly to the liquefaction reactor was not found to cause any benefit in the conversion results or product quality (12,14).

The primary way by which Type II pretreatments can affect the degree of conversion as measured by solvent solubility is to change the rate at which soluble and/or insoluble products are produced. To be effective, the pretreatment must accelerate the rate at which soluble products are

produced, in the same manner that a catalyst would, or decelerate the rate at which insoluble products are produced. A simple first-order model can be used to describe the production of soluble and insoluble products from coal:



where k_S and k_I represent the rate constants for the reactions indicated. Using the first-order models, it is possible to determine the relative rate constants, k_S/k_I , before and after pretreatment by solving the following equation.

$$k_S + k_I = -\ln[1 - x_S(1 + k_I/k_S)]/t$$

where x_S is the fractional conversion to solubles at time t . Since two unknowns are present, conversions must be available at more than one reaction time. It should be noted that the k_S/k_I ratio would remain the same if both rates changed by the same amount (if the pretreatment caused the same final state to be reached only at a different time). Also note that the model does not explicitly account for the production of gases.

For the hydrothermal pretreatments shown in Figure 4, the k_S/k_I ratio for the methylene-chloride-soluble products improves from 1.47 prior to pretreatment to 1.61 after pretreatment. This small increase could be due either to an increase in the rate of formation of soluble products or to a decrease in the rate of formation of insoluble products.

The ratio, k_S/k_I , has been calculated for other chemical pretreatments reported in the literature. For hydrothermal pretreatment of oxidized coal prior to liquefaction in an aqueous-KOH/CO system (14), k_S/k_I for methylene-chloride-soluble products increased from 0.37 to 1.82. Alkylation of Wyodak Coal prior to donor-solvent liquefaction (8) caused the ratio for tetrahydrofuran-soluble products to increase from 0.54 to 2.22. Comparing these values with the ratio calculated for the experiments in Figure 4 shows that hydrothermal pretreatment prior to donor-solvent liquefaction has a smaller effect than the other pretreatments and liquefaction systems mentioned. Note that the largest effect of pretreatment comes when the initial ratio of k_S/k_I is quite small (0.4 to 0.5) owing either to a low rate of formation of soluble products or a high rate of formation of insoluble products.

Conclusions

The results of the experiments reported in this paper show that presoaking (a Type I pretreatment) in the liquefaction solvent resulted in small but consistent increases in conversions in a donor-solvent liquefaction system at temperatures below 425°C. Additional tests with different particle sizes confirmed the existence of mass-transfer limitations in the early stages of liquefaction under similar conditions. Overall, the benefit of using a Type I pretreatment will depend on the mass-transfer limitations relative to liquefaction rates in the system of interest. The greatest utility of Type I pretreatments will likely be in the development of lower-severity processes in which mass-transfer limitations would be greater and liquefaction rates lower. The effect of Type I pretreatments in catalytic systems also needs further investigation.

A Type II, hydrothermal pretreatment, also resulted in small but consistent increases in conversion in a donor-solvent liquefaction system. Other Type II pretreatments reported in the literature, such as alkylation, provide a greater benefit. A simple first-order model was used to compare the relative effectiveness of these Type II pretreatments. It is also important to note that benefits from Type II pretreatments can be due to an increase in formation of soluble products and/or to a reduction in the formation of insoluble products. These considerations should be taken into account when investigating Type II pretreatments.

Disclaimer

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

References

1. Rincon, J.M., Cruz, S., and Jairo, R. Proceedings, Int. Conf. on Coal Science, Volume II October 23-27, 1989, 851.
2. Snape, C.E., Derbyshire, F.J., Stephens, H.P., Kottenstette, R.J., and Smith, N.W. Fuel Proc. Technol. 1990, 24, 119.
3. Wham, R. M. Fuel, 1987, 66, 283.
4. Narain, N.K., Appell, H.R., and Utz, B.R. Prepr. Pap., Amer. Chem. Soc., Div. Fuel Chem. 1983, 28(1), 161.
5. Whitehurst D.D., Mitchell T.O., and Farcasiu M. in "Coal Liquefaction: The Chemistry and Technology of Thermal Processes," Academic Press, New York, 1980 pp 91-112.
6. Woodfine, B., Steedman, W., and Kemp, W. Fuel, 1989, 68, 293.
7. Larsen, J.W. and Lee, D. Fuel, 1983, 62, 1351.
8. Baldwin, R.M., Nguanpraesert, O., Kennar, D.R., and Miller, R.L. Prepr. Pap., Amer. Chem. Soc., Div. Fuel Chem. 1990, 35(1), 70.
9. Brandes, S.D., Graff, R.A., Gorbaty, M.L., and Siskin, K. Energy & Fuels, 3, 494.
10. Bienkowski, P.R., Narayan, R., Greenkorn, R.A., and Chao, K. Ind. Eng. Chem. Research 1987, 26(2), 202 and 206.
11. Mochida, I., Moriguchi, Y., Iwamoto, K., Fujitsu, H., Korai, Y., and Takeshita, K. Proceedings, Japan/U.S. NSF Chemistry of Coal Liquefaction Meeting 1985, 25.
12. Ross, D.S. and Hirschon, A.S. Prepr. Pap., Amer. Chem. Soc., Div. of Fuel Chem. 1990, 35(1), 37.
13. Pollack, N.R. Ph.D. Thesis, Chemical Engineering Department, University of Pittsburgh, in preparation.
14. Pollack, N.R., Holder, G.D., and Warzinski, R.P. Proceedings, Seventh Annual Pittsburgh Coal Conference 1990, Pittsburgh, Pa., 689.

Table 1. Elemental Analyses of Illinois No. 6 Coals Used.

Sample Designation	Moisture	Ash	----moisture and ash free----				
			C	H	O	N	S
-48 mesh	7.2	23.1	78.0	5.3	9.0	1.5	6.2
-325 mesh	5.2	22.9	77.3	5.3	9.7	1.5	6.1
10X48 mesh	9.5	16.2	83.2	4.8	5.2	1.5	5.4
-230 mesh	5.8	16.6	81.0	4.5	7.6	1.5	5.4

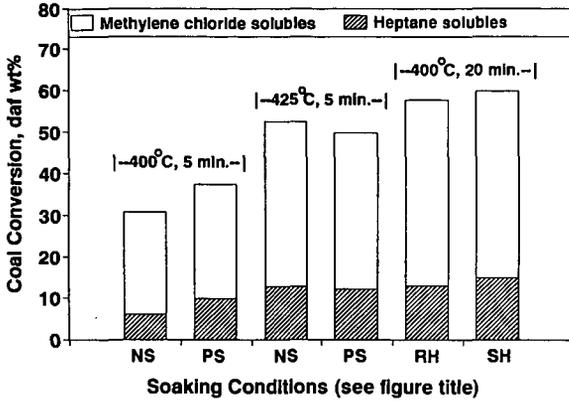


Figure 1. Effect of thermal soaking on the conversion of Illinois No. 6 coal in Wilsonville V1074 solvent. Liquefaction times and temperatures shown in the graph. All tests were under 1000 psig H₂ cold pressure. (NS - No Soaking, PS - Presoaked at 300°C for 10 min., RH - Rapid Heating, SH - Slow Heating)

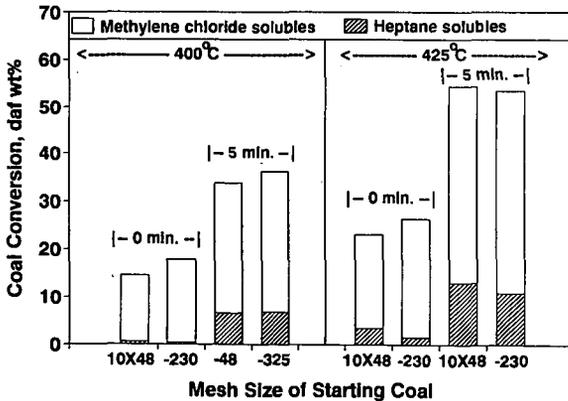


Figure 2. Effect of particle size on the conversion of Illinois No. 6 coal in Wilsonville V1074 solvent. Reaction times and temperatures shown in graph. All tests were under 1000 psig H₂ cold pressure.

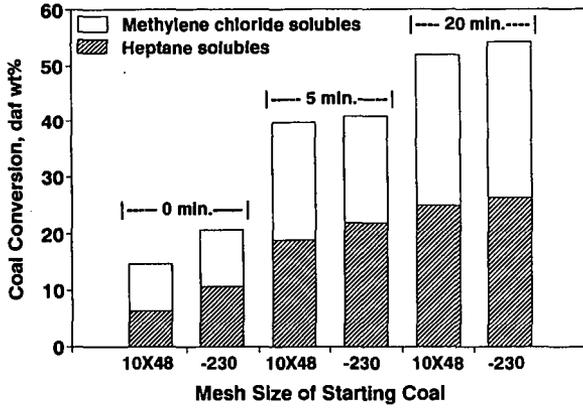


Figure 3. Effect of particle size on the conversion of Illinois No. 6 coal at 400°C for various times at reaction temperature. All tests were performed in tetralin under 1000 psig nitrogen cold pressure.

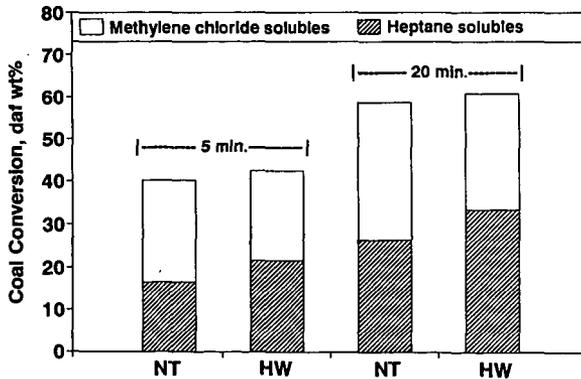


Figure 4. Effect of hydrothermal pretreatments on the conversion of Illinois No. 6 coal in tetralin at 400°C under 1000 psig (cold) H₂. NT - No treatment, HW - 15 minute pretreatment at 300°C under 500 psig (cold) N₂.