Morphology and Liquefaction Characteristics of Pyridine-Extracted Illinois No. 6 Coal

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Introduction

The primary goal of preconversion processing of coal prior to direct liquefaction is to alter the coal in some fashion so that hydrogenation reactions are favored and detrimental, regressive reactions are limited during the subsequent liquefaction. For example, catalytic hydrogenation at 300-350°C has been shown to favorably influence the yield and composition of products produced during catalytic liquefaction at 400°C (1). Other work has indicated that the glassy nature of coal itself may promote retrogressive pathways that would not exist if the coal structure had more mobility and flexibility (2). Altering the structure of coal by solvent swelling has also been shown to result in improved conversion in noncatalytic, donor-solvent liquefaction (3). As others have postulated, this may be due to the improved penetration and diffusion of reagents in the distorted structure of the swollen coal (4,5) and/or to the possible reduction in the glass transition temperature (used loosely for coal) of the swollen product (6,7).

When coal is swollen and extracted with pyridine, extensive morphological changes are known to occur (4,8,9). The magnitude of the changes in the surface area and porosity of the pyridine-insoluble product may be influenced by the manner in which the residual pyridine is removed. Work with highly porous, silica aerogels indicates that processes involving evaporative removal of a swelling solvent may result in partial collapse of the expanded structure owing to surface-tension effects on the walls of the pores generated by the leaving solvent (10). Maximum porosity is achieved in these systems if non-evaporative methods of solvent removal are used. One such method that avoids the formation of a liquid-vapor interface in the solvent removal process is the dissolution and removal of the swelling solvent by a supercritical fluid (SCF).

In the work reported here, three Illinois No. 6 coal samples were swollen and extracted with pyridine and then subjected to both vacuum drying and SCF extraction with CO_2 to remove the residual pyridine. Differences in morphological features and liquefaction behavior were observed depending on which technique was used. Tests were also performed to compare the liquefaction behavior of the pyridine-soluble fraction with the pyridine-insoluble portion of the coal.

Experimental

The work reported here was performed on three samples of minus 100-mesh Illinois No. 6 coal. Two were from the Burning Star mine and were prepared at the Pittsburgh Energy Technology Center. The third was from

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the Argonne Premium Coal Sample program. Elemental analyses of these coals are contained in Table 1.

Pyridine swelling and initial extraction were performed in an Erlenmeyer flask. The coal was added to an excess (approximately 6.5:1 on a weight basis) of reagent-grade pyridine and stirred for approximately two days with a magnetic stirrer. The slurry was then transferred to a cellulose Soxhlet thimble and exhaustively extracted with fresh pyridine until the extract was nearly colorless (pale yellow). The thimble was then removed and the excess pyridine allowed to drain away. The pyridine-insoluble product (PIP) recovered from the Soxhlet thimble contained about 2.5 times its original weight in pyridine. The pyridine-soluble product (PSP) was recovered by rotary evaporation.

Vacuum-dried samples of the PIP were prepared by placing a portion of the material recovered from the Soxhlet thimble in an oven at 110°C to 115°C under full vacuum supplied by a mechanical vacuum pump. The sample was dried in this fashion until the weight loss after a 1-hour interval was less than 0.5%.

Another portion of the PIP from the Soxhlet thimble was extracted with supercritical CO_2 (T_c - 31°C, P_c - 1056 psig) to remove the excess pyridine. The SCF extractions were performed in either a small (1.0 cm i.d. by 25.0 cm long) or large (2.2 cm i.d. by 50.0 cm long) empty HPLC column. The column was wrapped with heating tape, insulated, and connected to a high-pressure ISCO syringe pump filled with liquid CO_2 (375 cm^3 capacity). A back-pressure regulator was used after the column to control the pressure during the extraction. Thermocouples inserted into tee fittings at each end of the column were used to monitor the extraction temperature. With the larger column, another thermocouple was clamped to the surface at its midpoint. Auto-transformers were used to control the heating tapes on the column and on the inlet and exit lines. During the extraction, the column temperature was maintained at 40°C to 45°C and the back-pressure regulator was set at 2000 psig.

When using the small column approximately 12 g of the PIP was extracted. After heating the column, the extraction involved first pumping about 135 ml of CO_2 (as measured on the syringe pump scale) at 10 ml/hour and then 270 ml at 40 ml/hour. The unit was then slowly depressurized through a needle valve while maintaining the temperature at 40°C. The column was then removed and transferred to a nitrogen-filled glove box for sample recovery.

When using the large column, approximately 100 g of the PIP was extracted. The procedure was similar to that for the small column except that more CO_2 was used and at faster flow rates (525 ml at 40 ml/hour then 560 ml at 200 ml/hour). However, on a g-CO_2/g-coal basis, the amount of CO_2 used was less for the larger column, 11 g-CO_2/g-coal as compared to 34 g-CO_2/g-coal for the smaller column.

Surface area measurements, helium densities, and mercury densities were performed at the Center for Micro-Engineered Ceramics at the University of New Mexico by Dr. Douglas Smith. The surface area measurements included a five-point nitrogen analysis at 77 K and a four-point CO_2 analysis at 298 K. The nitrogen measurement provides an estimation of the surface area present in pores with diameters greater than 0.4 nm; whereas, the carbon dioxide measurement is believed to represent the total surface area of coal, including occluded pores (8,9).

Liquefaction tests were performed in a 38 cm^3 (2.54-cm o.d., 12.7-cm long) stainless-steel microautoclave, which was horizontally positioned in a fluidized sandbath and agitated at 360 cycles-per-minute by a Burrell wrist-action shaker. The microautoclave was rapidly heated to reaction temperature by immersion in the hot sand bath and quenched after reaction in water. The internal temperature and pressure were continuously monitored. The microautoclave was charged with approximately 3 g of coal or extraction product, 6 g of tetralin (if used), 1600 to 5000 ppm (based on metal) of a molybdenum-containing catalyst precursor (if used), 0.3 g of carbon disulfide, and 1000 psig hydrogen. When using a catalyst precursor, it was dissolved in only enough solvent to form a wet paste with the sample. The solvent was then removed, usually under vacuum at 60°C, before the liquefaction test. Liquefaction tests were carried out at 425°C for either 20 or 60 minutes. Liquefaction conversions were measured by sequential extraction with either of two sets of solvents -- methylene chloride/n-heptane or tetrahydrofuran/ cyclohexane -- using pressure filtration to separate the soluble products from the residues. Conversions were determined from the insoluble residues and are expressed on a dry, ash-free basis.

Results and Discussion

Sample 1 from the Burning Star mine was the first sample swollen and extracted in pyridine. Based on the as-received coal and the actual amount of solvent-free PIP recovered, 15% of this coal sample was extracted by pyridine. One portion of the PIP from the Soxhlet thimble was vacuum dried and another portion was extracted with supercritical CO_2 using the small column.

As previously mentioned, the objective of performing the SCF extraction was to remove the pyridine by a non-evaporative process that would avoid the formation of a vapor/liquid interface. A model based on the Peng-Robinson equation-of-state was used to estimate the vapor/liquid phase behavior for the CO_2/pyridine system (11). A binary interaction parameter of 0.080 was used in this calculation. Using this model, the mixture critical point at 40°C was estimated to be near 1160 psig. The operational conditions used, 2000 psig at 40°C, are well above this point. At these conditions, the CO_2 should initially dissolve in and expand the pyridine present in the sample, moving the interface out of the coal pores and quickly causing it to disappear without evaporation. The pyridine concentration in the pores would then be reduced by the continued addition of supercritical CO_2 until all of the physically entrapped pyridine was removed. As opposed to vacuum-drying, no surface-tension effects would be exerted on the walls of the pores by the leaving solvent. In fact, the SCF expansion of the pyridine phase may have the opposite effect in exerting a positive force, which would tend to maintain the porosity of the sample.

Both vacuum drying and SCF extraction should remove all of the physically entrapped, but not chemically associated, pyridine from the PIP. The elemental analyses in Table 1 show that the nitrogen contents of the vacuum-dried and SCF-extracted PIP are similar. Based upon elemental analyses and material balances, 6% to 10% pyridine is estimated to remain in the PIP after either procedure.

Table 2 contains the surface area and density results for both the vacuum-dried and SCF-extracted samples. Also shown in this table are the results from a CO_2-extraction experiment in which all of the conditions were the same as for the SCF extraction, except that the

temperature was maintained at 25°C. Under these subcritical conditions, the extraction would be performed with liquid CO_2. The results in Table 2 show that the vacuum-dried PIP has less nitrogen surface area and porosity than the starting coal, while the CO_2 surface area remains about the same. On the other hand, the end result after removal of the pyridine by SCF extraction is an increase in both the nitrogen and CO_2 surface areas and in the resulting porosity. Compared to vacuum drying, SCF extraction produces a PIP that has 6.5 times the nitrogen surface area, 1.9 times the CO_2 surface area, and 4.2 times the porosity.

The data in Table 2 also show that liquid-CO_2 extraction results in a product with nitrogen and CO_2 surface areas that are respectively equal to and greater than the untreated coal but less in both cases than the supercritical-CO_2 extracted sample. The porosity, however, appears to be more like the vacuum-dried sample than the one from supercritical-CO_2 extraction. This initial data supports the hypothesis that the SCF extraction not only eliminates surface-tension forces that would tend to collapse the expanded structure of the PIP but generates forces that help to maintain the expanded structure.

To further investigate this phenomenon, the Argonne Premium Coal sample was subjected to the same treatment described above, except the liquid-CO_2 extraction was not performed. The handling of the untreated coal and the Soxhlet extraction were performed under nitrogen to limit the exposure of this coal to air. This coal sample was found to be 33% soluble in pyridine (based on as-received coal and actual weights recovered). This is twice that of the Burning Star sample discussed above. Similar differences in pyridine extractability between premium and non-premium Illinois No. 6 coal samples have been reported (12,13). Surface area and density results for the vacuum-dried and SCF-extracted samples are also contained in Table 2. All of the trends noted previously for the Burning Star sample are observed in the results for the Argonne coal. The changes in the nitrogen surface areas are particularly noteworthy. The porosity achieved with the SCF extraction was nearly the same as for the Burning Star sample.

Analysis of the SCF-extracted PIP from the Burning Star sample over a period of time showed the increases in surface areas and porosity to be a transitory phenomenon. Surface area and porosity determinations made on fresh aliquots taken from the sample over a four-month period are shown in Figure 1. These results show that the nitrogen surface area, the carbon dioxide surface area, and the porosity decrease with time. The last reported nitrogen and porosity values are even less than for the starting coal and approach the values for the vacuum-dried sample, which are represented in Figure 1 by the open symbols.

Microautoclave liquefaction tests were performed on a second sample of the Burning Star coal which was swollen and extracted with pyridine as before. To prepare enough material, the large column was used for the SCF extraction. The pyridine solubility of this second sample was 23%, which is higher than the first sample of this coal but still less than the Argonne sample.

The vacuum-dried and SCF-extracted samples of the PIP from the second sample of Burning Star coal were used in both thermal and catalytic microautoclave liquefaction experiments to determine the effects of the different morphology on conversion. Ammonium heptamolybdate (AHM) was used as the catalyst precursor at about 5000 ppm (based on metal) in the catalytic tests. A summary of these results is contained in Figure 2. The first two pair of tests in this figure were made using tetralin,

both with and without AHM. The conversions to methylene chloride and heptane solubles were slightly higher in both cases for the SCF-extracted PIP than for the vacuum-dried sample, and the greatest difference occurred in the heptane conversion in the catalytic case. The last pair of tests was performed without added solvent, again with 5000 ppm AHM. In this case, the conversions were measured in tetrahydrofuran and cyclohexane. This particular liquefaction and solvent-analysis system accentuates the effects of the pretreatment procedures on the liquefaction conversions.

From these results, the morphological changes associated with the SCF-extracted samples appear to facilitate liquefaction of these samples, especially in the presence of a catalyst. A possible explanation is that the expanded structure caused by this treatment permits the catalyst precursor to better penetrate these samples during the impregnation procedure, resulting in the improved liquefaction conversions. Investigation in this area is continuing to further substantiate and understand these results.

Additional microautoclave tests on both the PSP and the PIP were performed to investigate the fate of these materials during liquefaction. Figure 3 shows the results of subjecting the PSP to liquefaction with and without solvent and catalyst. In these tests, the contact time at 425°C was 60 minutes and the catalyst precursor was ammonium tetrathiomolybdate (ATM) added from water. The first set of bars shows the pre-liquefaction solubilities of the PSP in tetrahydrofuran and cyclohexane. The next test shows that, in the absence of both catalyst and hydrogen-donor solvent, the solubility in tetrahydrofuran drops sharply while the cyclohexane solubility increases. The remaining data in Figure 3 show that the presence of either a hydrogen-donor solvent or catalyst prevents the retrogressive behavior observed in the absence of these compounds. In the data set shown, the presence of a catalyst provides higher conversions than when a hydrogen-donor solvent is used.

The liquefaction results for the SCF-extracted PIP are contained in Figure 4. No hydrogen-donor solvent was used in any of these tests. Adding ATM as previously described improved both the tetrahydrofuran and cyclohexane conversions. A further improvement in the conversions was also noted when the ATM was added from pyridine and then subjected to extraction with supercritical CO_2 to remove the pyridine. In this case, greater penetration of the ATM into the PIP is likely since the pyridine would re-swell the PIP and facilitate transport of the ATM into the particles. Removing the pyridine with supercritical CO_2 would prevent the ATM from being pulled back out of the particles with the leaving solvent, as might be the case if vacuum drying were used. This aspect of the work is under further investigation.

Summary

Our work has shown that a coal sample can be prepared with an expanded structure, that is, one in which the porosity is two to four times as great as the starting coal. This effect is due both to the removal of pyridine-soluble material and to the means of removing the residual pyridine from the insoluble portion. A non-evaporative procedure, such as SCF extraction, leaves the coal structure, at least temporarily, in an expanded state, whereas vacuum drying causes an immediate collapse of the extracted coal. Upon liquefaction, conversions were consistently

higher for samples subjected to SCF extraction compared to vacuum drying. The greatest benefit was observed in the catalytic tests.

Additional liquefaction tests were performed on both the PSP and PIP. The PSP formed a more refractory product when subjected to liquefaction in the absence of both a catalyst and a hydrogen-donor solvent. The presence of either the catalyst or the solvent reduced this retrogressive behavior. The benefit of a catalyst in this situation was marginally greater than the presence of a hydrogen-donor solvent. The importance of a catalyst was also noted in the liquefaction of the PIP. Dispersal of a catalyst precursor in a manner that may be superior to aqueous impregnation resulted in marginal improvements in liquefaction conversions of the PIP.

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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.

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Table 1. Elemental analyses.

Sample Designation	Moisture	Ash	C	H	O	N	S
		---------moisture free--------					
Burning Star Sample 1							
Untreated Coal	3.5	10.4	69.1	4.7	11.6	1.4	2.9
Pyridine-Insoluble Product							
Vacuum Dried	3.0	12.1	65.7	4.3	12.3	2.1	3.0
SC-CO_2 Extracted	3.4	11.1	67.0	4.3	11.9	2.3	2.9
Liquid CO_2 Extracted	4.5	11.4	66.8	4.2	12.9	2.5	3.0
Burning Star Sample 2							
Untreated Coal	2.1	8.6	70.6	5.0	12.0	1.5	2.4
Pyridine-Insoluble Product							
Vacuum Dried	1.0	9.8	69.6	4.7	13.4	2.5	2.5
SC-CO_2 Extracted	3.2	10.1	70.1	4.9	11.4	2.9	2.4
Pyridine-Soluble Product	10.5	0.6	80.7	6.0	8.8	2.4	1.2
Argonne Premium Sample							
Untreated Coal	4.5	14.8	65.6	4.5	9.4	1.2	4.9
Pyridine-Insoluble Product							
Vacuum Dried	2.4	17.4	63.0	4.1	10.5	2.2	4.8
SC-CO_2 Extracted	1.6	17.5	63.0	4.2	9.6	1.9	5.0

Table 2. Surface area and density results.

Sample Designation	Surface area, m^2/g		Density, g/cm^3		Porosity*
	N_2	CO_2	He	Hg	
Burning Star Sample 1					
Untreated Coal	12.3	93.4	1.47	1.33	0.10
Vacuum Dried	2.6	91.6	1.47	1.40	0.05
SC-CO_2 Extracted	17.0	170.7	1.46	1.16	0.21
Liquid CO_2 Extracted	12.6	143.9	1.47	1.38	0.06
Argonne Premium Sample					
Untreated Coal	25.8	76.8	1.46	1.38	0.05
Vacuum Dried	1.7	90.3	1.46	1.42	0.03
SC-CO_2 Extracted	36.0	111.2	1.47	1.19	0.19

*Porosity = Hg density(1/Hg density - 1/He density)

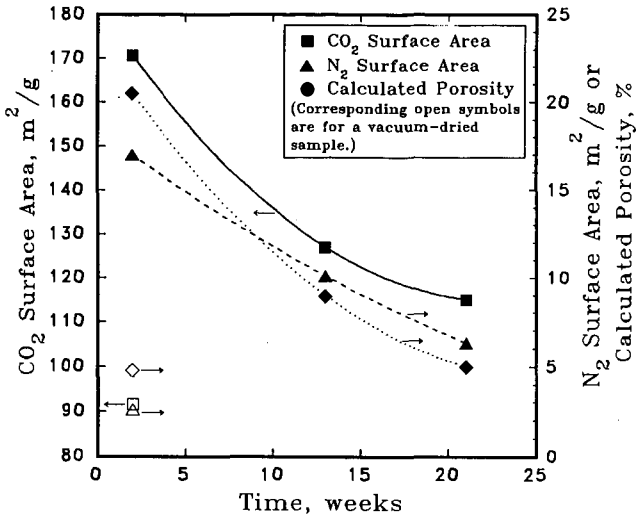

Figure 1. Morphological changes in the SCF-extracted pyridine-insoluble product with time.

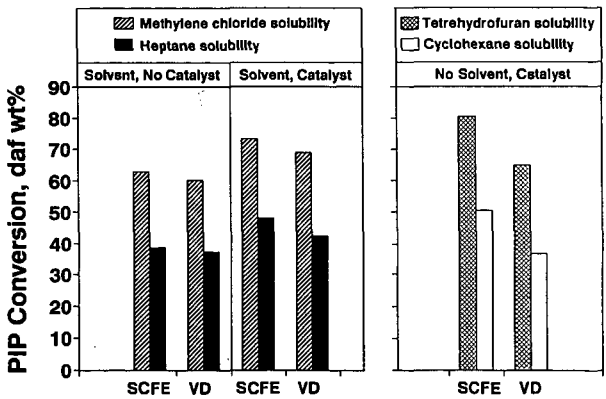

Figure 2. Thermal and catalytic liquefaction of SCF-extracted and vacuum-dried pyridine-insoluble product with and without tetralin and 5000 ppm AHM. SCFE - Supercritical Fluid Extracted. VD - Vacuum Dried. Micro-autoclave tests performed at 425°C, 20 min., 1000 psig hydrogen (cold).

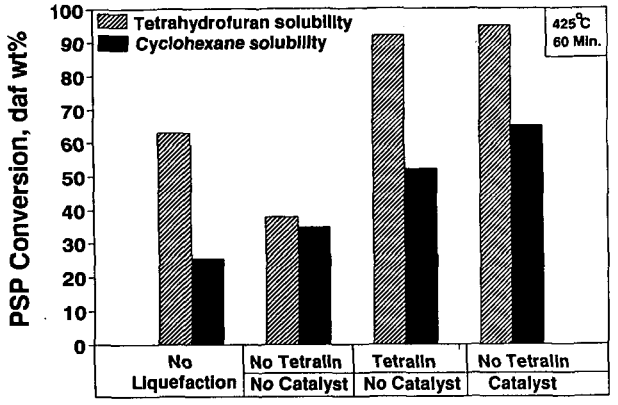

Figure 3. Conversion of pyridine-soluble product in thermal and catalytic liquefaction tests. 1600 ppm Mo added as ATM in the catalytic test. All tests were under 1000 psig hydrogen (cold).

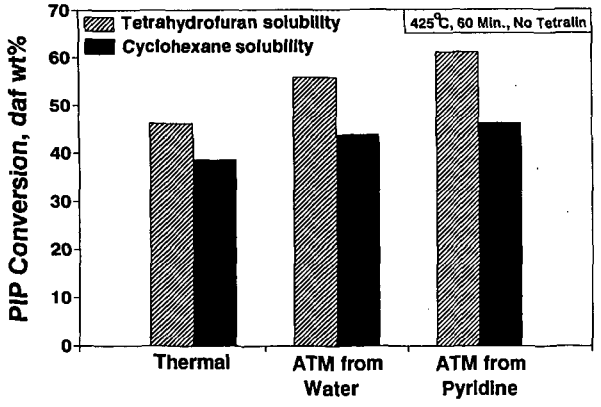

Figure 4. Thermal and catalytic liquefaction of SCF-extracted pyridine-insoluble product. 1600 ppm Mo as ATM applied by incipient wetness from water and by using a pyridine solution followed by SCF extraction. All tests were under 1000 psig hydrogen (cold).