

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/255559884>

# Low-Temperature Treatment of Illinois No. 6 Coal in Ionic Liquids

ARTICLE *in* ENERGY & FUELS · JUNE 2012

Impact Factor: 2.79 · DOI: 10.1021/ef3002923

---

CITATIONS

9

---

READS

15

4 AUTHORS, INCLUDING:



[Nuexida Pulati](#)

Pennsylvania State University

6 PUBLICATIONS 58 CITATIONS

SEE PROFILE



[Jonathan Paul Mathews](#)

Pennsylvania State University

104 PUBLICATIONS 941 CITATIONS

SEE PROFILE



[P. C. Painter](#)

Pennsylvania State University

161 PUBLICATIONS 3,214 CITATIONS

SEE PROFILE

# Low-Temperature Treatment of Illinois No. 6 Coal in Ionic Liquids

Nuerxida Pulati, Maria Sobkowiak, Jonathan P. Mathews, and Paul Painter\*

Earth and Mineral Sciences (EMS) Energy Institute, Department of Materials Science, and Engineering and the John and Willie Leone Department of Energy and Minerals Engineering, Penn State University, University Park, Pennsylvania 16802, United States

**ABSTRACT:** Certain ionic liquids can fragment coals to a remarkable degree at temperatures below 100 °C. Here, it is shown that when Illinois No. 6 coal is mixed with the ionic liquid 1-butyl-3-methylimidazolium tetrafluoromethanesulfonate and tetralin and held at temperatures of 300 °C or less under hydrogen, a dramatic increase in pyridine solubility is obtained. The highest yield of soluble material was in excess of 90% [dry and ash-free (daf) basis], but the results were very variable, partly as a result of the small sample sizes used.

## ■ INTRODUCTION

The solubility of coal in various solvents has been studied for many years, and the subject has a rich and deep literature. Essentially, the ability of a solvent to dissolve at least a portion of a particular coal depends upon the chemical structure of that coal and the ability of the solvent to interact favorably with polar functional groups, particularly those that hydrogen bond, while minimizing unfavorable contributions to the free energy of mixing from dispersion and weak polar forces. An additional but related factor involves the extent to which a solvent can disrupt or swell a coal sample, thus releasing any trapped molecules. This depends upon not only the same thermodynamic forces that are involved in dissolution but also the nature and degree of cross-linking between the “molecules” or organic components of the coal in question. If one makes the standard assumption that non-anthracitic coals are macromolecular networks, then cross-linking primarily involves covalent linkages. However, it has also become clear that inorganic cations form ionic domains involving carboxylate groups in low-rank coals and  $\pi$ -cation interactions in medium-rank coals. These ionic domains can be although of as reversible cross-links,<sup>1–3</sup> in that removing the cations can lead to enhanced swelling and solubility in certain solvents.

Both solvent extraction and demineralization have in recent years become the basis for important new coal technologies.<sup>4</sup> Using flow-type extractors, Miura et al.<sup>5</sup> reported extract yields of 65–80% for bituminous coals at a temperature of 350 °C in nonpolar solvents, while Yoshida et al.<sup>6</sup> reported similar yields using light cycle oil at 360 °C. This latter group coined the term “HyperCoal” for these very low ash content extracts. Much of the work on HyperCoal has been discussed in a recent, comprehensive review of coal demineralization.<sup>4</sup> This review also assesses the use of acid/alkali leaching/dissolution of mineral matter components to produce “ultraclean coal”. Demineralized coal allows for the use of technologies that increase coal combustion efficiency while reducing harmful emissions.

Although the temperatures used in thermal extraction studies are lower than those used in conventional liquefaction, they are still relatively high and it would clearly be advantageous if extractions could be conducted at lower temperatures. In recent work, we have shown that certain ionic liquids (ILs) fragment,

swell, partially solubilize, and disperse a Powder River basin coal and Illinois No. 6 coal as extremely fine particles to a remarkable extent.<sup>7</sup> This resulted in enhanced extraction yields in polar solvents. Imidazolium ILs based on 1-butyl-3-methylimidazolium ([bmim]) cations with various anions were evaluated in that work. It was observed that ILs with chlorine counterions broke up and dispersed the coals to a much greater extent than those with larger anions. Following the work by Hu and Guo<sup>8</sup> on the interaction of ILs with asphaltenes, it was proposed that this could be due to the larger charge density on  $\text{Cl}^-$  ions relative to other anions (e.g.,  $\text{BF}_4^-$  and  $\text{CF}_3\text{SO}_3^-$ ), enhancing its ability to engage in acid–base interactions and, hence, disrupt associations between polar entities in certain coals.

In this paper, we will report an extension of this work to a study of the effect of higher temperatures on the solubility of coal/IL mixtures. Unfortunately, ILs with halogen anions are only stable up to temperatures of about 150 °C. Accordingly, here, we consider imidazolium ILs that are stable at higher temperatures.

## ■ EXPERIMENTAL SECTION

The ILs used in this study were 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][ $\text{BF}_4$ ] (>98.5%), and 1-butyl-3-methylimidazolium tetrafluoromethanesulfonate, [bmim][ $\text{CF}_3\text{SO}_3$ ]. Both were purchased from Sigma-Aldrich and used as received. The Illinois No. 6 coal was obtained from the Penn State Coal Sample Bank and Database (DECS-24) and is reported to have a moisture content of 13.20% and an ash content of 13.39%. Pentane, pyridine, and tetrahydronaphthalene (tetralin) were also obtained from Sigma-Aldrich.

Low-temperature “soaking” experiments were conducted in a vertical microautoclave reactor of 10 mL capacity. The vertical microautoclave reactor was charged with coal (~2 g), IL, and tetralin in the proportions reported in the Results of this paper. The contents of the reactor were stirred for 1–2 min to obtain a well-dispersed mixture before the reaction, which was conducted under 6.9 MPa pressure of hydrogen.

Following the low-temperature “soaking” reactions, the products were removed from the reactor with pentane, dried, and transferred to

Received: February 18, 2012

Revised: May 14, 2012

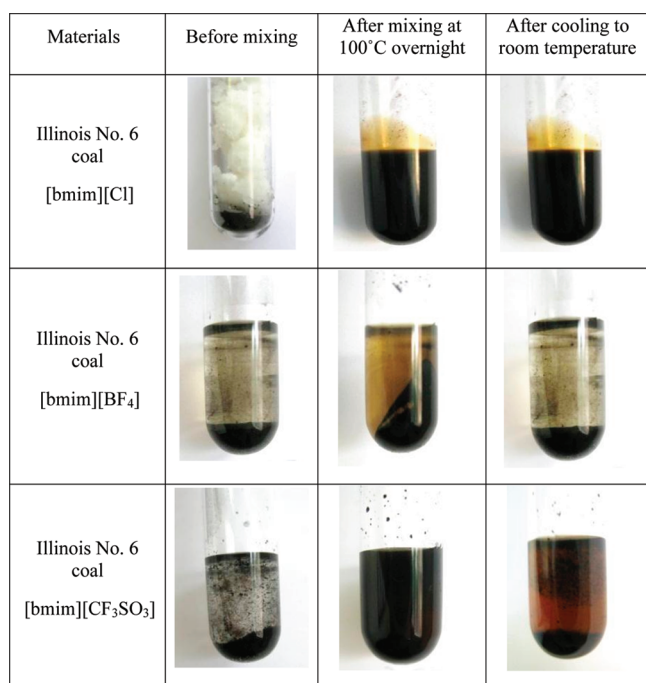
Published: May 15, 2012

a Soxhlet glass thimble. Liquid products, which included pentane with some oil, tetralin, and ILs, were allowed to filter through the thimble. The residual sample in the thimble was dried and extracted with pyridine. The pyridine residue was washed with water to remove residual solvent, and the extract put into water, filtered, and dried at room temperature under high vacuum until reaching a constant weight.

## RESULTS

In initial work, we demonstrated that Illinois No. 6 coal and two sub-bituminous coals are fractured and dispersed to a remarkable degree in certain ILs.<sup>7</sup> This fragmentation results in a large increase in the amount of soluble material that can be obtained using conventional solvents, such as *N*-methyl-2-pyrrolidone (NMP). It is useful to briefly review this earlier work and reproduce some of these results to allow for a facile comparison to the new material.

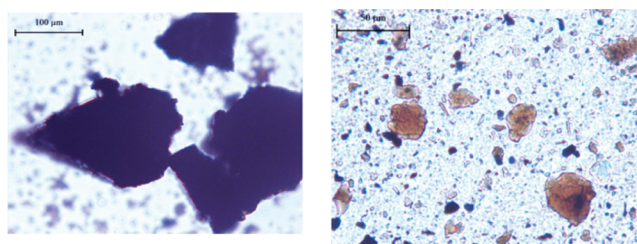
As mentioned above, the IL that gave the optimum degree of dispersion in previous work was [bmim][Cl]. Figure 1 shows



**Figure 1.** Appearance of Illinois No. 6 coal mixed with specific ILs (10% coal by weight) (from left to right): initial contact at room temperature, after heating to 100 °C overnight, and after cooling to room temperature.

Illinois No. 6 coal and this IL in initial contact at room temperature. This IL melts at about 80 °C, and upon heating to this temperature, a black dispersion is formed that appears unaltered upon cooling to room temperature. A micrograph of the original coal particles smeared between microscope slides is compared to that of a smear of the dispersed material in Figure 2. It can be seen that the coal particles have become highly fragmented.

Not all ILs result in this degree of dispersion at low temperatures. Also shown in Figure 1 are the results obtained using [bmim][BF<sub>4</sub>] and [bmim][CF<sub>3</sub>SO<sub>3</sub>]. The former does not result in any appreciable dispersion of the coal, even at 100 °C. However, in [bmim][CF<sub>3</sub>SO<sub>3</sub>], a black dispersion is formed at elevated temperatures, but upon cooling to room temperature, coal particles can be clearly seen, at both the bottom of



**Figure 2.** (Left) Optical micrograph of an Illinois No. 6 coal suspended in water and smeared between micrograph slides (100 μm scale). (Right) Micrograph of a smear of the same coal after heating to 100 °C for 2 h with the IL [bmim][Cl] and then cooled to room temperature (50 μm scale).

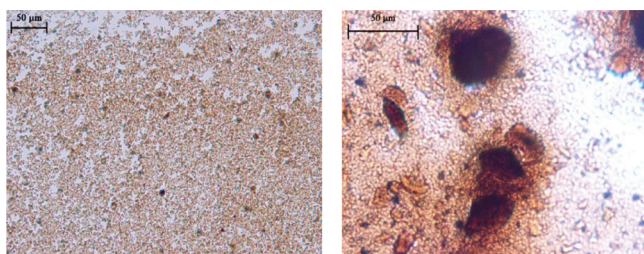
the tube and floating around in the slightly discolored solvent. They do not appear to be significantly fragmented, but this may be a result of aggregation upon cooling.

Although the ILs [bmim][BF<sub>4</sub>] and [bmim][CF<sub>3</sub>SO<sub>3</sub>] were not effective in terms of fragmenting coal at low temperatures, they were chosen for further study because they were reported to be stable at temperatures up to 400 °C.<sup>9</sup> Accordingly, we conducted initial experiments where Illinois No. 6 coal/IL mixtures were heated to temperatures of 250, 300, and 340 °C for various periods of time in tubing bombs under a pressure of 6.9 MPa of hydrogen. At temperatures of 300 °C or less, some fragmentation of the coal was observed, but there was little change in pyridine solubility relative to the untreated coal [~27% pyridine soluble, on a dry and ash-free (daf) basis]. At temperatures of 340 °C, there was a significant increase in the pyridine solubility of the product, but we will not consider these results in detail because we subsequently found that the experiments were flawed in a number of respects. First, the claims for the temperature stability of the ILs we used are based on thermogravimetric analysis (TGA) experiments, which were conducted by ramping the temperature at a chosen rate.<sup>10–12</sup> Subsequent work has shown that ILs slowly degrade lower temperatures over longer times.<sup>13,14</sup> This indeed seems to be the case, in that we observed that discoloration slowly developed over time upon holding [bmim][BF<sub>4</sub>] at 300 °C, even in a hydrogen atmosphere (however, even under these conditions, no change in the ILs infrared spectrum was observed). In addition, other recent work shows that the BF<sub>4</sub> anion slowly hydrolyses to give HF (among other products) in the presence of water.<sup>15</sup> We therefore focused subsequent work on the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>]. A second flaw in our initial experiments involved the apparent inability of hydrogen to contact any radicals that may have formed under these conditions, possibly because hydrogen is not very soluble in ILs. This became apparent when tetralin was used in some experiments and an immediate increase in the yields of soluble material was obtained.

At an 1:8:2 ratio (by weight) of coal/IL/tetralin, a yield of close to 50% pyridine-soluble material (on a daf basis) was obtained by heating to 300 °C (6.9 MPa of hydrogen) for only 10 min. This result is shown in Table 1, together with results obtained at other times and temperatures. Increasing the “soaking time” to 4 h (300 °C and 6.9 MPa of hydrogen) gave a dramatic increase in pyridine solubility, to about 77% by weight (on a daf basis). A micrograph of the slurry obtained under these conditions is shown in Figure 3. The resulting coal particles are now a very fine dispersion, consisting of mostly small particles (~1–2 μm), as shown in the micrograph on the

**Table 1. Pyridine-Soluble Extract Yields Obtained by Heating Illinois No. 6 Coal with IL and Tetralin under a Pressure of 6.7 MPa of Hydrogen**

IL	proportions (coal/IL/tetralin)	time	temperature (°C)	extract yield (% on a daf basis)
[bmim] CF <sub>3</sub> SO <sub>3</sub>	1:8:2	10 min	300	~50
	1:8:2	4 h		~77
	1:3.5:2	4 h		~54
[bmim] CF <sub>3</sub> SO <sub>3</sub>	1:8:2	10 min	250	~31
	1:3.5:2	4 h		~51
	1:3.5:2	8 h		~84
				~66
[bmim] CF <sub>3</sub> SO <sub>3</sub>	1:3.5:2	4 h	280	~95
				~97
				~47
				~75
				~78
				~83
				~69

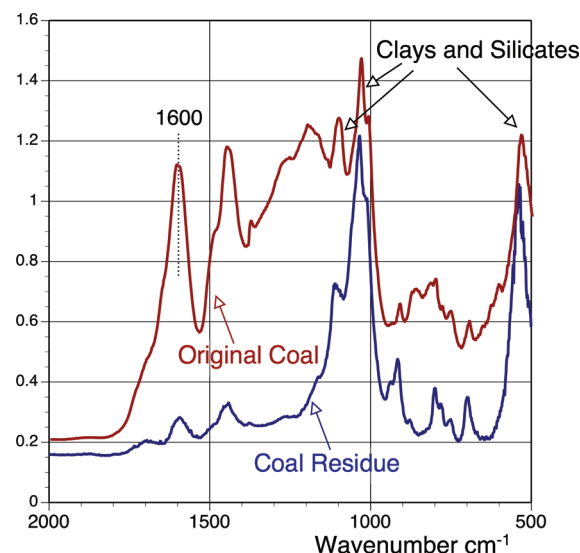
**Figure 3.** Optical micrograph of an Illinois No. 6 coal held at 300 °C under hydrogen at 6.9 MPa for 4 h in the presence of the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] and tetralin.

left, although certain regions of the sample showed the presence of larger particles (micrograph on the right). This observation suggests that ILs alone can be used to both disperse and solubilize coal in a liquid phase and at least partially catalyze its conversion to liquid fuels.

A repeat of the experiment resulted in a product with a pyridine solubility of only 54% (on a daf basis). However, we reduced the ratio of coal/IL/tetralin to 1:3.5:2 in this experiment. Nevertheless, one troubling aspect of this work that will reappear in other experiments is the inconsistency in the yields that we obtain. The micrographs shown in Figure 3 indicate that there may be some coal components (macerals?) that are more resistant to IL treatment at elevated temperatures than others, a point that we will return to later.

Although the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] appears to be more stable at high temperatures than [bmim][BF<sub>4</sub>], we were concerned about degradation of the IL affecting our results and decided to focus our attention on temperatures lower than 300 °C. An initial experiment at 250 °C with a “soaking time” of 10 min (6.9 MPa of hydrogen) gave a product with a pyridine solubility of 31% (on a daf basis), close to that of the untreated coal. However, holding at this temperature for 4 and 8 h gave yields of 51 and 84% pyridine-soluble material (on a daf basis), respectively, very promising results. However, a repeat of the 8 h experiment resulted in a product with a pyridine solubility of 66%, still good but maddeningly different from the initial result and outside what we anticipated would be the normal range of experimental error.

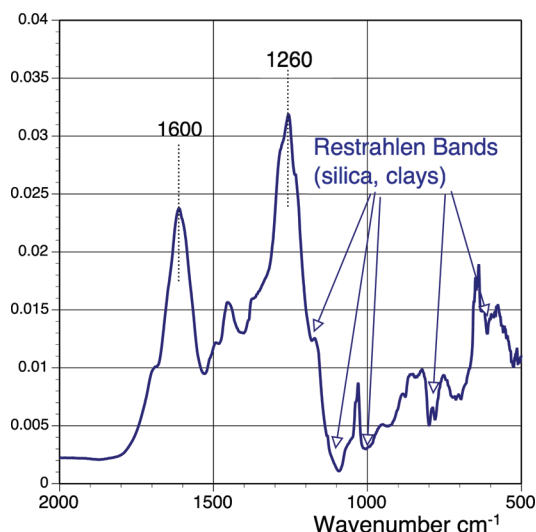
We conducted the largest number of experiments at a temperature of 280 °C with a “soaking time” of 4 h (6.9 MPa of hydrogen), in an attempt to shorten the time necessary to obtain large yields of soluble material, while minimizing any degradation of the IL. The results are also shown in Table 1. A very wide range of yields of pyridine-soluble material was obtained, with two on the order of 95% (on a daf basis) but one as low as 47% (on a daf basis). The infrared spectrum of the pyridine-insoluble residue obtained from one of the highly soluble products is compared to that of the original coal in Figure 4. It can be seen that the spectrum of the residue is

**Figure 4.** Comparison of the infrared spectrum of an Illinois No. 6 coal sample and the pyridine-insoluble residue obtained from heating the coal at 280 °C under 6.9 MPa of hydrogen for 4 h in the presence of the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] and tetralin.

dominated by bands because of minerals near 1000 cm<sup>-1</sup>, while the characteristic ring-stretching mode of the organic component near 1600 cm<sup>-1</sup> appears with only weak intensity. In the spectrum of the original coal, the 1600 cm<sup>-1</sup> band is much more intense. As might be expected, spectra of residues from runs that gave a lower yield of soluble material were intermediate between these extremes. This suggests that the range of results obtained is not entirely due to errors in removing samples from the tubing bombs (for example) but in some experiments that have other origins.

Nevertheless, some reactions resulted in the presence of dark, solid, agglomerated particles that were very difficult to remove from the tubing bombs and did contribute to weighing errors. Small amounts of the particles were dislodged from the bottom of the tubing bomb after an experiment where the coal was treated at 280 °C under 6.9 MPa of hydrogen for 4 h in the presence of the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] and tetralin. They were then washed to remove residual IL, and the infrared spectrum of this material is shown in Figure 5. At first sight, the spectrum makes no sense, because it is dominated by a band near 1260 cm<sup>-1</sup> that cannot be found in the spectra of the parent coal or the IL. However, careful examination reveals that this band is actually an artifact because of Restrahlen effects. Essentially, it appears that some of the mineral matter has probably fused, giving material that was more difficult to grind using standard procedures and, hence, particles of larger size. There are then significant contributions to the spectrum from reflected light,





**Figure 5.** Infrared spectrum of the solid particles scraped from the bottom of the tubing bomb after heating the coal at 280 °C under 6.9 MPa of hydrogen for 4 h in the presence of the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] and tetralin.

which leads to distorted band shapes and band inversion. Thus, normally intense absorption bands because of minerals between 1100 and 1000 cm<sup>-1</sup> and the characteristic silica doublet near 800 cm<sup>-1</sup> bands are now inverted, leaving a strong artifact band near 1250 cm<sup>-1</sup>. This suggests that this residual material is predominantly mineral matter, because the effect of band inversion still leaves a strong positive contribution to the spectrum near 1260 cm<sup>-1</sup>.

It has been recognized that Lewis acids (usually in large quantities) and strong acids (particularly super acids, such as the fluorosulfonic acids) can catalyze the depolymerization of coal at low temperatures and pressures (~100 °C in some experiments).<sup>16</sup> The mechanism by which this occurs is ionic rather than free radical, and hydrogen is still required to cap the products and prevent retrogressive reactions. Some of these acids are environmentally challenging; therefore, an industrially viable process that takes advantage of an acid-catalyzed reaction has not been developed.

However, Lewis acids, such as BI<sub>3</sub> and ZnCl<sub>2</sub>, are soluble in [bmim][CF<sub>3</sub>SO<sub>3</sub>]; therefore, some experiments were performed in the presence of these catalysts. It was mentioned that BI<sub>3</sub> did appear to have a minor effect, but because of its sensitivity to water, it is difficult to use. Attention was therefore focused on ZnCl<sub>2</sub>. Experiments were performed at 250 °C and 1000 psi of H<sub>2</sub> pressure in the presence of tetralin and ZnCl<sub>2</sub> for various times. The proportions of materials used and the amount of pyridine are reported in Table 2. It can be seen that the yield of soluble material increased from about 32% after 10 min to 89% (on a daf basis) after 8 h. However, the yield of soluble material is not substantially different from that which was obtained in the absence of ZnCl<sub>2</sub>.

In a similar fashion, including ZnCl<sub>2</sub> did not significantly change the yield of pyridine-soluble material at soaking temperatures of 280 °C, as also shown in Table 2. Two runs gave decent yields, 90 and 67% (on a daf basis), but a third run gave a yield of only 45% (on a daf basis). However, during the course of this experiment, it was observed that the hydrogen pressure dropped significantly, to 700 psi; therefore, this result was not included in Table 2. Infrared spectra of the pyridine-insoluble residues of these samples were similar to those

**Table 2.** Pyridine-Soluble Extract Yields Obtained by Heating Illinois No. 6 Coal with IL, ZnCl<sub>2</sub>, and Tetralin under a Pressure of 6.7 MPa of Hydrogen

IL	proportions (coal/ IL/ZnCl <sub>2</sub> /tetralin)	time	temperature (°C)	extract yield (% on a daf basis)
[bmim] CF <sub>3</sub> SO <sub>3</sub>	1:3.5:0.5:2	10 min	250	~32
		2 h		~60
		4 h		~49
		8 h		~89
[bmim] CF <sub>3</sub> SO <sub>3</sub>	1:3.5:0.5:2	4 h	280	~90
				~67

obtained in the absence of ZnCl<sub>2</sub>, with the residue from the 90% soluble sample being dominated by bands because of minerals.

## DISCUSSION

Although the results reported here are highly variable, there is clearly a significant yield of pyridine-soluble material as a result of soaking coals in ILs at elevated but still low temperatures, ≤300 °C. Most covalent bonds in coal cleave thermally at temperatures in excess of 375 °C. Cleavage and hydrogenation in imidazolium ILs occurs at much lower temperatures, as low as 250 °C (albeit at long times). Presumably, the mechanism is not thermal cleavage. One possibility is that the catalytic activity of these imidazolium ILs is related to the acidic nature (pK<sub>a</sub> = 21–23) of the hydrogen at the C<sub>2</sub> position.<sup>17</sup> (i.e., the carbon between the two nitrogens in the imidazolium ring). This could act to “shuttle” hydrogen from tetralin onto the coal.

The most disturbing aspects of these results are their variability. Although infrared spectroscopy confirmed that the residues from the runs that gave the highest yields of soluble material were largely mineral matter, indicating that the calculated yield was not a result of losses in transferring materials, the spectra of lower yield runs obviously contained unconverted organic material. One possible reason for the variability in these results is that we only used small sample mass; hence, the heterogeneity of coal could play a role. We observed that, in some experiments, dark, solid particles agglomerated at the bottom of the tube, and these were hard to remove, although several different methods were tried. They appeared to consist of agglomerated minerals together with some organic matter. Accordingly, there was some sample loss when transferring samples from vials to the reactor and then transferring the mixture from the tubing bomb to the Soxhlet thimble. Future work using larger sample mass should alleviate this problem.

## CONCLUSION

Heating Illinois No. 6 coal at relatively low temperatures (<300 °C) in the IL [bmim][CF<sub>3</sub>SO<sub>3</sub>] and in the presence of tetralin and hydrogen results in significant fragmentation and a large increase in its pyridine solubility. The highest yield of soluble material was in excess of 90% (on a daf basis). The infrared spectra of the residues were dominated by mineral bands, with weak absorptions because of organic groups being apparent. However, there was a great deal of variability in the results, and experiments on a larger scale need to be conducted.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: painter@matse.psu.edu.

## Notes

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) Painter, P. C.; Opaprakasit, P.; Scaroni, A. *Energy Fuels* **2000**, *14*, 1115–1118.
- (2) Opaprakasit, P.; Painter, P. C.; Coleman, M. M.; Scaroni, A. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2001**, *44* (3), 331–333.
- (3) Opaprakasit, P.; Painter, P. C.; Scaroni, A. *Energy Fuels* **2002**, *16*, 543–551.
- (4) Wijaya, N.; Zhang, L. *Energy Fuels* **2011**, *25*, 1–16.
- (5) Miura, K.; Shimada, M.; Mae, K.; Sock, H. Y. *Fuel* **2001**, *80*, 1573–1582.
- (6) Yoshida, T.; Takanohashi, T.; Sakanishi, K.; Saito, I. *Energy Fuels* **2002**, *16*, 1006–1007.
- (7) Painter, P.; Pulati, N.; Cetiner, R.; Sobkowiak, M.; Mitchell, G.; Mathews, J. *Energy Fuels* **2010**, *24*, 1848–1853.
- (8) Hu, Y.-F.; Guo, T.-M. *Langmuir* **2005**, *21*, 8168–8174.
- (9) Hunt, P. A. *J. Phys. Chem. B* **2007**, *111*, 4844–4853.
- (10) Muhammad, A.; Mutalib, A. M. I.; Wilfred, C. D.; Murugesen, T.; Shafeeq, A. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.
- (11) Awad, W. H.; Gilman, J. W.; Nyden, M.; Harris, R. H.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; De Long, H. C.; Fox, D. M. *Thermochim. Acta* **2004**, *412*, 47–53.
- (12) Ohtani, H.; Ishimura, S.; Kumai, M. *Anal. Sci.* **2008**, *24*, 1335–1340.
- (13) Del Sesto, R. E.; McCleskey, T. M.; Macomber, C.; Ott, K. C.; Toppisch, A. T.; Baker, G. A.; Burrell, A. K. *Thermochim. Acta* **2009**, *491*, 118–120.
- (14) Meine, N.; Benedito, F.; Rinaldi, R. *Green Chem.* **2010**, *12*, 1711–1714.
- (15) Freire, M. G.; Neves, C. M. S. S.; Marrucho, I. M.; Coutinho, J. A. P.; Fernanades, A. M. *J. Phys. Chem. A* **2010**, *114*, 3744–3749.
- (16) Derbyshire, F. *Energy Fuels* **1989**, *3*, 273–277.
- (17) Dupont, J.; Spencer, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5296–5297.