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EXAMINATION OF COAL SOLUBILITY AND FRAGMENTATION WITH VARIOUS IONIC LIQUIDS

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ABSTRACT

The organic component of coal is heterogeneous and often has a complicated network structure. When exposed to certain solvents, swelling and partial dissolution often occurs. However, due to the structural complexity of coal, an understanding of the interaction between solvents and coal remains challenging. In this thesis the effect of a new class of solvents, ionic liquids are investigated. It was reported that ionic liquids dissolve cellulose, previously considered insoluble in all solvents. In the work described in this thesis, ionic liquids were used as a "solvent" to contact coal under different condition to observe if enhanced solubility also occurs. Several ionic liquids were contacted with coals and ionic liquid mixtures were heated up to 100˚C overnight and cooled back to room temperature. Ionic liquid containing 1-butyl-3-methylimidazaolium cation with different types of anions were studied; Ionic liquids containing $[Cl]^-$ anions formed a black dispersion/gel upon heating up the mixture to 100˚C and a black slurry remained after cooled to room temperature. Long alkyl chain and benzyl chain substituted imidazolium ionic liquids produced, a viscous black slurry/ gel formed when coal/ionic liquid mixtures were heated up to 100˚C and the mixture remained a viscous gel upon cooling. Optical micrographs showed the coal had fractured to smaller size particles.

Other ionic liquids, such as $[bmim][CF_3SO_3]$, $[bmim][BF_4]$, were also found to disperse or fragment coal particles when heat up to 250˚C or 300˚C when combined with tetralin and hydrogen under pressure. Higher yields of pyridine soluble materials were obtained after coal was treated with $[bmim][CF_3SO_3]$. FTIR-DRIFT characterized the pyridine insoluble residue. With the spectra mainly contain mineral matter components, a good indication that extensive of hydrogenation of coal can take place under these lower temperatures by adding ionic liquid, $[bmim][CF_3SO_3]$. The coal/ionic liquid dispersion also showed enhanced solubility when simply stirred in NMP at room temperature compared to samples without ionic liquid additions.

The extent of swelling and dispersing of coal with certain ionic liquids is related to intermolecular interactions. Ionic liquids can engage in a wide range of intermolecular interactions, hydrogen bonding, ion-dipole and dipole-dipole interactions, π-cation interactions, etc. Under quantification of these contributions would aid elucidation of mechanics for this coal/ionic liquid dissolution/dispersion system.

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CHAPTER 1

INTRODUCTION

1.1 Coal Structure

Coal is a natural feedstock for carbon materials, one of the most important sources of fuel. It is relatively abundant and inexpensive compared to petroleum. Coals are “a brown to black sedimentary rock composed mainly of consolidated and chemically altered plant remains[1].”

Coal is composed of macerals, which are optically homogeneous, discrete organic entities, which can be identified using an optical microscope[2]. Macerals are divided into three categories: vitrinite, liptinite and inertinite that reflect their compositional and/or depositional differences[2]. The shiny, glass-like vitrinite, a major component in N. American coals, is oxygen-rich with moderate hydrogen and aromatic content[2]. Liptinite is hydrogen-rich and highly aliphatic[2]. The inertinite is more carbon-rich and is more aromatic[2]. Figure 1-1 shows photomicrographs of the main macerals groups in a bituminous coal. Table 1-1 gives some description of maceral origins and importance.

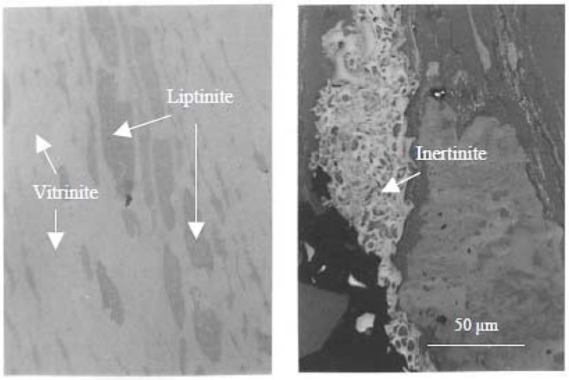

Figure **1-1** Photomicrographs of main macerals groups in a bituminous coal[3]

Table **1-1** Origin and importance of macerals and maceral groups[4]

Maceral Group	Maceral	Origin	Group Properties
Vitrinite	Collinite (telinite)	Wood or bark	Principal constituent of coal, readily hydrogenated, oxidized easily, relatively oxygen rich
Liptinite (exinite)	Resinite Cutinite	Plant Resins Needles and leaf cuticles	Yields greatest quantity of by-products when carbonized
	Sporinite Alginite	Spores Algae	Readily hydrogenated in coals with more than 25% volatile
Inertinite	Sclerotinite	Fungal Remains	
	Micrinite (macrinite)	Granular matter from protoplasm	Relatively inert, not easily hydrogentated or oxidized
	Semifusinite	Wood or bark severely oxidized before burial	An important additive in coke

The organic component of coal mainly consists of carbon, hydrogen and oxygen with lesser amounts of nitrogen and sulfur[5]. It has a wide range of composition, from 65% ~ 95% carbon, 2% ~ 6% hydrogen, 2% ~ 30% oxygen, 1% ~ 13% sulfur, and up to about 2% nitrogen[5]. Organic oxygen forms are rank dependent and may be phenolic, hydroxyl, carboxylic acid, carbonyl, ether linkages and in heterocyclic oxygen forms. Heteroatoms like nitrogen, sulfur and various metals are also present in mineral matter in coal[5]. The sulfur content of coal is variable: appearing as both inorganic and organic forms[6]. Minerals in coal usually include clays, quartz, carbonates, sulfide minerals, etc[5]. Clays are hydrated aluminosilicates having a general formula $Al_2O_3.4SiO_2.nH_2O$. These are a source of a wide variety of metals in coal[5]. Carbonate minerals include metal carbonates like $CaCO_3$, $FeCO_3$, $MgCO_3$, etc[5]. Metal pyrites like FeS_2 constitute sulfide minerals and are often the main source of inorganic sulfur in coal[5].

Coal is formed from various types of organic precursors, ranging from oxygen rich carbohydrates, lignin, glycosides, protein, and hydrogen rich compounds, lipids and resins[4]. The formation of coal usually involves two steps: diagenesis, the biochemical stage, and catagenesis, the geochemical stage[4]. In the biochemical stage, humic acids, products of the mild decomposition of lipids and lignin, mixed with other compounds, such as lipids and resins, undergo polymerization to form kerogen, an insoluble, high molecular weight material[4]. Due to the difference in the composition of deposits, kerogen can be divided into three different types[4]. Type I and II are hydrogen rich, straight chain compounds and are mostly the source of oil and natural gas[4]. Type III, derived mainly from the lignin of higher plants, is more oxygen rich and has a predominantly cyclic carbon structure and is the source of coal[4]. Type III kerogen mixed with various inorganic sediments, under different geological environments, temperature, pressure and time, undergoes different degrees of chemical change[4]. This catagenesis results in a loss of oxygen and an increase in carbon, which leads to the formation of coals of different composition and rank[4]. Brown coal has about 65% C, 6% H and 25% O (by mass)[4]. Loss of moisture and a reduction in oxygen results in the formation of lignite, which has about 72% C, 6% H and 20% O (by mass)[4]. Loss of carboxyl and methoxyl groups leads to the formation of subbituminous coal about 75% C, 5% H and 15% O composition (by mass)[4]. Due to the hydrogen redistribution process, the carbon content gradually increases to ~ 80% (by mass) in bituminous coal. With further loss of oxygen, the composition of coal can reach >91% carbon by mass, with the formation of highly condensed aromatic structures[4]. Therefore, from low to high carbon content, coal can be classified as low-rank to high-rank, from brown coal, lignite, subbituminous, high-volatile bituminous, medium-volatile bituminous, low-volatile bituminous and anthracite[2].

A knowledge of the structure of coal is important for its practical utilization[7]. Coal is generally thought to have a macromolecular structure[3], but it is not well defined. However, coal is considered to consist of primary macromolecules of polyaromatic polynuclear structure with some heteroatom groups and secondary interactions, such as hydrogen bonds, cation bridges and charge transfer interactions through oxygen functional groups, which can act as cross-links[7]. Most coal swells in organic solvents, and swollen coals shows elasticity like rubber, indicating that coal, has a network structure[6]. There are two kinds of postulated network models[6]. The covalent network model, widely accepted, assumes that coal has covalently bound giant networks that are insoluble in any solvents, and relatively small amounts of solvent-soluble, low molecular weight substances are trapped in the networks[6]. The non-covalent network model was proposed wherein coal consists of individual molecules that form huge associates[8].

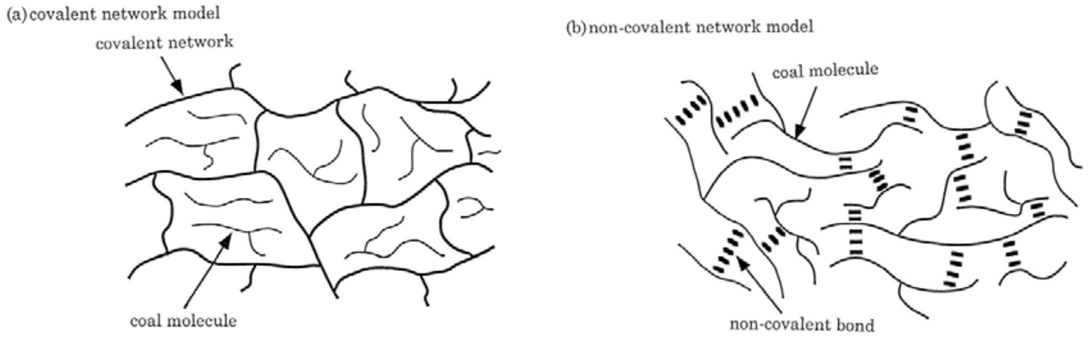

Figure **1-2** Coal covalent and non-covalent network models[6]

1.2 Coal Liquefaction

Coal liquefaction occurs at higher temperatures, coal liquefaction classified into two different processes, direct liquefaction and indirect liquefaction[5]. Indirect Coal liquefaction is the production of synthesis gas via the combination of gasification and the water-gas shift to produce hydrocarbons (including liquid fuels and chemicals) with the aid of Fischer-Tropsch catalyst.

Direct liquefaction is the conversion of coal to liquid without the intermediate formation of synthesis gas[4]. The fundamental stage of direct coal liquefaction is thermal decomposition of coal structure under a hydrogen atmosphere in the presence of a donor solvent. In direct liquefaction, coal is liquefied in the presence of a solvent medium at temperatures usually in the region of 400-500 ˚C commonly under hydrogen pressure 1000 psi (7 Mpa)[9.10] . Direct coal liquefaction is considered to take place into two consecutive steps: conversion to a soluble form (dissolution or depolymerization) and reduction in molecular weight and removal of heteroatoms, which is often called as upgrading process[9,11]. An important process is a breakup of the macromolecular structure of the coals into radicals, release of some trapped molecules and the disrupting of weak secondary bonds, hydrogenation to produce products[12]. A typical bituminous coal has an atomic H/C ratio of about 0.7, while for many petroleum products H/C ~1.2[1]. Thus the principal requirement for liquefaction is to increase the H/C content by adding hydrogen to the coal, while removing oxygen, sulfur and nitrogen atoms[4].

Coal liquefaction product generally includes three types: gases, composed mainly of CO and CO_2, light hydrocarbons; solids, composed of altered mineral matter and a largely organic component; and liquids, which contain a variety of aromatic and aliphatic hydrocarbons[13]. After liquefaction, the products obtain extracted with solvent, and the solvent extractable part subsequently separated by solvent fractionation: mainly the preasphlatenes, the asphatenes, and the oils. The oils are hexane-soluble and the most desirable product of liquefaction[13]. The solvent insoluble kept for further application. The solvent used to separate the products into preashaltenes is usually tetrahydrofuran (THF), if required toluene and/or pyridine to be used to determine an intermediate fraction.

Direct liquefaction usually operates at high temperates (400-500˚C), high pressures (up to 70 MPa), and with hydrogen donor solvents[14]. The solvent plays a main role in the transfer of hydrogen to carbon radicals after thermal cleavage of C-C bonds[13]. In addition to the hydrogen addition reaction, hydrogen redistribution and transfer reactions also occur, not only between coal molecules and the added hydrogen, but also between the liquid products, the solvent molecules, and gaseous hydrogen[14].

The role of solvent during liquefaction is to stabilize free-radicals by donating hydrogen, promote the cracking of coal macromolecules, and preventing condensation of the radicals. In addition, coal particles swell when exposed to solvents at elevated pressure and temperature[15], leading to a better mixture with solvent, which can initiate or improve liquefaction reactions.

1.3 Purpose

A problem in developing a technologically viable process for coal liquefaction involves the complex interplay between solvents and catalysts. Most commonly used solvents are derived from refinery processes and are relatively non-polar and are thus limited in their ability to interact with the coal. They aid in dispersion of the coal particles, but dispersion is not good. Heterogeneous solid catalysts and homogeneous soluble catalysts are expected to have better activity when coal particles have been fragmented and partially solubilized. Therefore, coal liquefaction is usually proposed to occur in two stages – one is to swell and disperse the coal so as to obtain a better contact with catalyst, while the second stage involves cracking and hydrogenation. Hydrogenation and hydrogenolysis in the early stages of coal liquefaction is similarly limited until coal particles have been fragmented and partially solubilized. A solvent or class of solvents that would simultaneously partially solubilize, fragment, disperse and provide good contact between catalysts and coal at relatively low temperatures without the use of precursors will be a desirable advance.

The purpose of this thesis was to investigate a novel class of solvents or additives that could enhance coal swelling and dissolution. In other work in this laboratory, Ruveyda Cetiner used ionic liquids to give a better enable catalyst contact[14]. Here the effect of systematic changes in IL structure will be investigated in terms of their ability to improve solvent extraction yields.

The ability of ILs to promote liquefaction directly at temperatures below 300˚C is also investigated.

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CHAPTER 2

DISSOLUTION AND DISPERSION OF COAL IN IONIC LIQUID

2.1 Swelling and Solubility of Coal in Conventional Solvents

Coal has a complicated structure[1]. Once coal is placed in a good solvent, much of the low molecular weight components of the coal will dissolve, but the cross-linked network absorbs solvents and commonly swells without dissolving[1]. The amount of soluble material, usually described as extractability, refers to the soluble and extractable content of a coal[2]. Solvent swelling is an important method for studying network systems as the cross-linked structure of coal and the interactions between solvent and coal can affect the swelling rate and extent and extract yield. Understanding the solvent swelling and solubility of coal is of both fundamental and practical importance.

Coal rank has a major influence on the nature and amount of material obtained by solvent extraction[3]. Low- and medium-rank coals are highly polar, interacting through hydrogen bonds involving phenolic OH, carboxylic acids, and other groups containing heteroatoms[4]. Therefore, non-polar hydrocarbon solvents, such as toluene or hexane, have a limited ability to swell these coals and extract only small amounts of soluble material[3]. Polar compounds containing nitrogen or oxygen, such as amine, phenol, carbonyl, etc., are effective in extracting 20-40% of coal below 200˚C[1]. In particular, solvents which have acceptor groups that can form strong hydrogen bonds, pyridine or N-methylpyrrolidinone (NMP), can swell and dissolve low-rank coal to a significant extent[1]. They are mostly nucleophilic in nature due to the presence of a lone pair of electrons on the nitrogen atom.

Solvents such as phenanthrene and diphenyl can extract up to 90% (by mass) of coal at 400˚C by thermal degradation of coal into smaller soluble molecules[1]. There are some hydroaromatic compounds, such as tetralin (1,2,3,4-tetrahydronaphthalene), that can act as good hydrogen-donor solvents and can stabilize smaller coal fragments formed by thermal disintegration. In addition to pure solvents, mixed solvents such as alcohol-benzene are often used to obtain better extraction yields[1]. The mechanism of the observed synergetic effect of the two solvents observed has been proposed to be related to the increase in the penetration of solvents into coals by swelling[1].

In what appears at first to be unusual, it was observed that simply soaking various coals in chlorobenzene (115˚C) for a few days resulted in a significant decrease in the amount of pyridine-extractable material[4]. Soaking in pyridine for just 1 day had the same effect. This decrease in swelling and extractability of coal was thought to be a consequence of an increase in cross-link density and it was suggested that the coal is a cross-linked structure in which clusters of aromatic and hydro-aromatic rings cross-link and undergo a rapid re-orientation motion[4]. It was subsequently proposed that the decrease in pyridine solubility of coals after soaking in solvent was due to an increase in cross-linking associated with the formation of ionic clusters[5].

For most of the Argonne Premium coals, the amount of pyridine-soluble material increased dramatically on acid treatment[5]. It was proposed that for low and to some extent medium rank coals this is mainly due to the presence of ionic clusters formed by carboxylate groups[5]. For high rank coals, it was proposed that the existence of π-cation interactions played as a major role[6]. It was suggested that cross-links in coal should be classified into two types, one is the “permanent” covalent linkages that cleave only at high temperatures or through chemical reaction; the other is, “reversible” cross-links, largely associated with ionic structures such as carboxylate salts and π-cation complexes[6].

It has also been found that a mixed solvent, CS_2 and 1-methyl-2-pyrrolidinone (NMP), is extremely effective in dissolving Upper Freeport Argonne Premium coal at room temperature [7-9]. On this basis, it was proposed that this coal is largely an associated structure held together by secondary interactions, such as hydrogen bonds, π-π interactions, and charge transfer complexes[7-9]. Upper Freeport Argonne Premium coal gives a very high extraction yield (60 wt% (daf)) in CS_2-NMP mixed solvent (1:1 by volume, 8:5 mole ratio), and the extraction yield is increased by the addition of small amounts of compounds such as tetracyanothylene (TCNE) and p-phenylenediamine. However, this coal may be unusual, in that the mixed solvent system does not give such high yields for many other coals.

Dissolution or swelling of coal is the first step in any process where coal is brought in contact with an organic solvent for which it has an affinity. As the solvent penetrates the coal matrix, the coal-coal interactions are replaced by more favorable coal-solvent interactions. This causes the coal to swell to accommodate the solvent. Ionic liquids should be able to interact with charged mineral species that form “reversible” or physical cross-links in coal, thus affecting swelling and solubility. In this chapter the dispersion and swelling of coals in ionic liquids will therefore be examined.

2.2 Background- Ionic Liquids (ILs)

Ionic liquids are formed by an organic cation with a delocalized charge and a weakly coordinating anion[10]. This weak interaction together with the asymmetry of (usually) the cation, causes a decrease of the melting point compared to the most common inorganic salts, providing a range of salts that are liquid below 100 °C[11]. Ionic liquids are electrically conductive and have extremely low vapor pressure[11]. Depending on the particular anion and the side chain length for cationically stabilized ionic liquids, the property of ionic liquids can be varied systematically.

A widely available group of ILs is based on imidazolium cations[13]. The imidazolium cation usually contains two alkyl groups, each attached to the nitrogen atoms on the imidazolium ring. In this thesis, the symbol [mim] refers to the methyl imidazolium cation, so that 1-butyl-3-methylimidazolium cation is represented as [bmim]. The electronic structure of the $[bmim]^+$ cation is illustrated below in figure 2-1 and is described by a C^4=C^5 double bond at the rear, a delocalized three-centre 4 e^- component across the front (N^1-C^2-N^3) of the imidazolium ring and a weak delocalization in the center region[14]. Experiments and calculations show that the hydrogen on the 2-position of the imidazolium ring is the most acidic and is chiefly responsible for forming hydrogen bonds with electronegative atoms in anions. According to Weigaertner[14], hydrogen bond formation is driven by Coulombic stabilization, which compensates for an associated destabilization of the electrostatic contribution to the system. Interactions are dominated by a large positive charge at C^2, owing to the electron deficit in the C=N bond.

The viscosity and melting points of ionic liquids with a [bmim] cation and a range of anions, $[Cl^-]$, $[BF_4^-]$ and $[N(Tf)_2^-]$ have been studied[15]. The IL 1-butyl-3-methylimidazolium chloride has a very high viscosity and is a solid at room temperature, while 1-butyl-3-

methylidazolium tetrafluoroborate is viscous liquid, and 1-butyl-3-methylidazolium trifluoromethansulfonate [bmim][CF_3SO_3] is a liquid with a moderate viscosity[16,17].

A strong attraction between a nitrogen-containing aromatic cation and a neutral π system has been reported in several papers[18,19]. The interactions of the aromatic cations with a π system are important for understanding the solvation of aromatic molecule in ILs. Ionic liquids are capable of engaging in different types of interactions, e.g., dispersive, π-π, hydrogen bonding, dipolar, ionic[20]. The wide range of interactions that ILs can engage in suggests they may prove useful solvents for coal. Because of the wide range of interactions, it was not completely understood which ionic liquid would interact most favorably with certain coal, but ILs based on imidazolium cations were chosen for this study. IL properties can be "tuned" by varying the substituent groups and by varying cations or anions. The solubility of different species in imidazolium ILs should depend on polarity, and the ability to form hydrogen bonds and engage in ionic interactions. The role of the chloride anion and its hydrogen bond basicity behavior is believed to be crucial in achieving dissolution of compounds capable of hydrogen bonding to the ILs. For example, it is reported that [bmim][Cl] can dissolve up to 25% cellulose[21]. Accordingly, in this chapter the effect of varying the structure of ILs on their ability to dissolve and disperse certain coals will be investigated.

In this chapter, several different types of ionic liquids use to disperse coals. The first of these ILs, the [bmim][Cl] ionic liquid is immisicible with non-polar solvents, but soluble in water, have a lower thermal stability1. The ionic liquids containing halogen anions degrade at low temperatures (150˚C)[22]. The other ionic liquid [bmim][BF_4] and [bmim][CF_3SO_3] used have higher thermal stability, and they are stable up to 400˚C.

2.3 Experimental

2.3.1 Materials

The Ionic liquids used in this study were imidazolium ILs, because they are chemically stable and easier to handle compared to other ionic liquids. The ILs: 1-butyl-3-methylimidazolium chloride, [bmim][Cl] (>99%), 1-butyl-3-methylidazolium tetrafluoroborate, [bmim][BF_4](>98.5%), 1-butyl-3-methylidazolium trifluoromethansulfonate [bmim][CF_3SO_3], 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-methyl-3-propylimidazolium iodide [pmim][I], 1-butyl-2,3-dimethylimidazolium chloride [bmmim][Cl], were all purchased from Sigma-Aldrich. Illinois No. 6 coal was obtained from the Penn State Coal Sample Bank and Database, and Wyodak coal was obtained from the Argonne Coal Sample Bank. Chevron USA Inc, an affiliate of the Chevron Corporation, provided an additional Powder River Basin (PRB) subbituminous coal (moisture 13.7% and mineral matter 8% by mass). Pyridine and N-methyl-2-pyrrolidone (NMP) were obtained from Aldrich.

Table 2-1: Elemental and proximate analysis coal samples

Illinois #6 Seam (Harrin Seam) hvCb rank Sample DECS-24
The Penn State Coal Sample Bank

Proximate Analysis	As rec'd	dry	daf	Dmmf (Parr)
% Moisture	13.20			
% Ash	11.62	13.39		
% Vol. Matter	35.44	40.83	47.14	45.51
% Fixed Carbon	39.74	45.78	52.86	54.49

Wyodak Anderson coal
The Argonne Coal Sample Bank

Proximate Analysis	As rec'd	dry	daf	Dmmf (Parr)
% Moisture	28.09			
% Ash	6.31	8.77		
% Vol. Matter	32.17	44.73		

% Fixed Carbon		68.43		76.04

Calculation of as-received, MAF, and dmmf values from dry data from Commercial Testing and Engineering Co. Parr Formula: MM (dry) = 1.08 Ash (dry) + 0.55 S (total dry),
Modified Parr Formula: MM (dry) = 1.13 Ash + 0.47 Pyritic S(dry) + 0.50 Cl(dry). Abbreviations: AS= As received; VM= volatile mater; MAF= moisture and ash-free; Dmmf= dry, mineral matter free.

2.3.2 Coal/Ionic Liquid Mixing and Extraction

Mixtures were obtained by adding 0.5 g of coals to centrifuge tubes. This is followed by 5 g of 1-butyl-3-methylimidazolium chloride, [bmim][Cl], which is a solid at room temperature. The samples were then heated in an oil bath to a temperature to 100°C. A liquid mixture was formed and remained as a gel on cooling. Samples were extracted and smeared between microscope slides and micrographs were obtained in transmitted light using a Leica DM 4000 (×200 magnification) research microscope.

After heating overnight, the sample was centrifuged. The liquid was separated from the aggregate using a pipette. It was difficult to determine what portion of the coal is dissolved in the ionic liquid and how much is present as finely dispersed particles, because the dispersion could not be filtered using conventional filter paper (cellulose dissolves in this IL and glass filters clogged). Therefore, both the liquid and solid were centrifuged, separated and put into water before filtering. The filter cake was dried in the oven, and the amount of soluble material estimated for the mass.

To evaluate the influence of the anion the following ionic liquids were evaluated; 1-butyl-3-methylidazolium tetrafluoroborate, [bmim][BF_4], 1-butyl-3-methylidazolium trifluoromethansulfonate [bmim][CF_3SO_3], 1-butyl-3-methylimidazolium hexafluorophosphate

[bmim][PF_6], 1-methyl-3-propylimidazolium iodide [pmim][I], 1-butyl-2,3-dimethylimidazolium chloride [bmmim][Cl], 1-benzyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride and 1-methyl-3-octyllimidazolium chloride.

2.3.3 Solvent Extraction of IL Treated Coals

Coal was pretreated with ionic liquid to determine if treatment changed its solubility in pyridine and NMP. 0.5 g coal was added to a test tube, then 2.5 g of ionic liquid was added and the mixture was heated to 100 ˚Cin an oil bath for 24 hours. Part of the sample was taken for characterization by optical microscopy. The remainder was washed with distilled water to remove ionic liquid, filtered and dried.

Pyridine extraction process: The dried sample soxhlet extracted with 200 ml pyridine. The glass thimble filter used in the soxhlet extraction has a pore size of 40-60 µm and was supplied by ChemGlass. The coal was placed in the glass thimble and extracted for one or two days until a clear solution above the coal was observed, indicating a complete extraction. The pyridine solvent was then removed from the extract by a rotary evaporator, followed by high vacuum at room temperature until it reached a constant weight. The extraction residue was washed with a large amount of water and finally with 2% THF in water to remove the remaining pyridine. Subsequently, the sample was placed under a high vacuum at room temperature for 2 days and its weight was recorded when cooled down to room temperature.

NMP extract process: The dried coal samples were added to 100 ml of NMP in a 250 mL ground glass flask. Mixing was accomplished with a magnetic stirrer. Samples were extracted under room temperature for 24hours, and filtered with Teflon filter paper. The filter cake was washed with water and then dried overnight in vacuum. The filtrate was isolated from the NMP by rotary evaporation before vacuum drying. The filter cake was washed and dried overnight in a vacuum oven at a temperature ≤50°C. The coal residue was weighed after cooling to room temperature.

The soxhlet equipment used in the experiment is showed as below in figure 2-1.

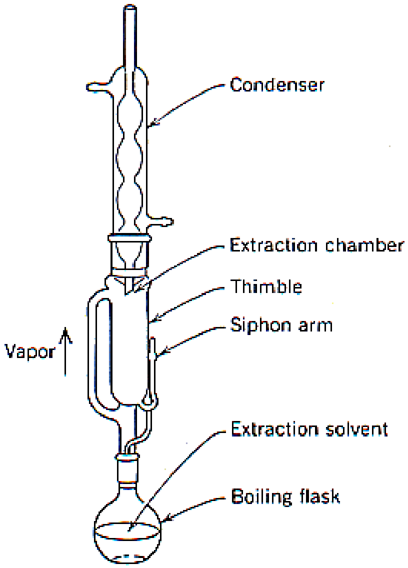


Figure **2-1** Soxhlet equipment[22]

For both the NMP and pyridine extractions, the extraction yield was calculated as:

Extraction yield (wt %) = Mass [(Original coal amount-residue)/ (Original coal amount)] ×100%

(Equation 2-1)

2.4 Results

2.4.1 Coal Mixed with Ionic Liquids

The initial results with the IL [bmim][Cl] were obtained in collaboration with Ruveyda Cetiner and Maria Sobkowiak. Initially, a 10% (mass) mixture of Illinois No. 6 coal and [bmim][Cl] was prepared. A dark black solution/dispersion was obtained when the sample was heated up to 100˚C in a test tube. Figure 2-2 below shows the IL/ coal mixture before and after heating. It can be seen that the initial solid mixture forms a liquid upon heating and the mixture stays in the liquid state upon cooling. The mixture is a viscous dispersion, as can be seen by its slow response upon tilting the tube (Figure 2.2c).

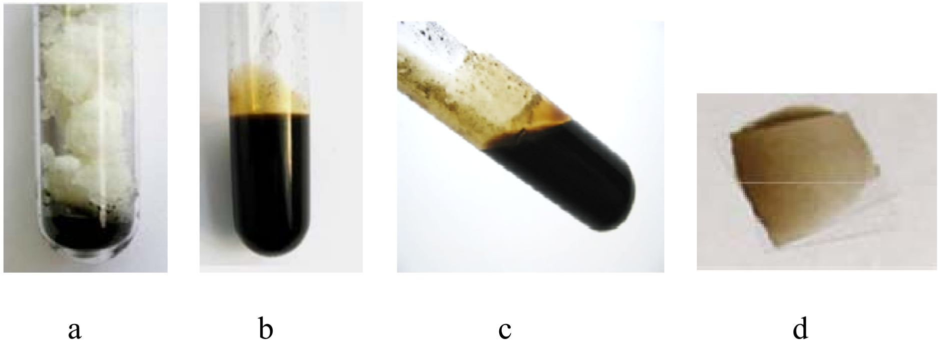
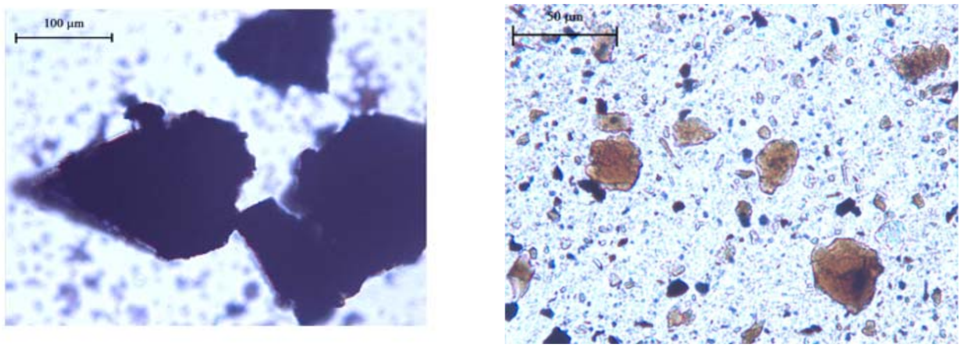


Figure **2-2** Heating 1: 10 ratio IL #6 coal with 1-butyl-3-methylimidazolium chloride [bmim][Cl] : a. Initial mixing, b. heated overnight at 100˚C, c. after cool down to room temperature, d. sample smear between two slides

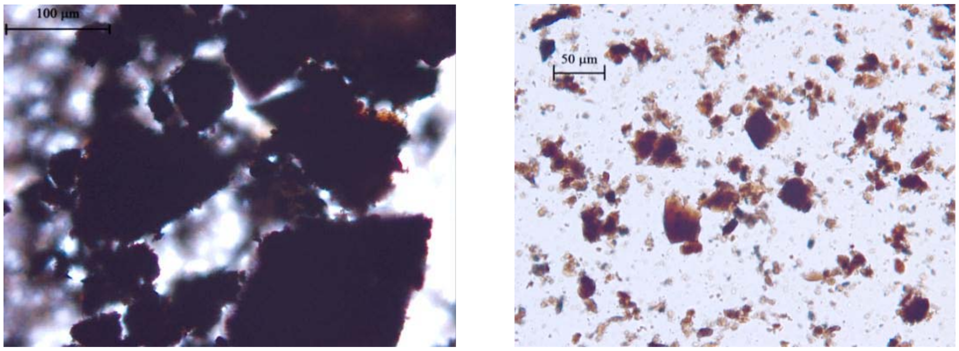
Optical microscopy was used to observe the dispersion of Illinois No. 6 coal in the IL, as shown in figure 2-3. The original coal (left micrograph) appeared as large, black, thick particles that were mostly of the order of 100 μm or larger. The right micrograph in figure 2-3 shows the ionic liquid treated sample. The particles appeared to be much smaller, thin (they are compressed between two slide covers) enough to be somewhat transparent. The ability to deform swollen coal is due to the solvent reducing the glass transition temperature in the solvent mixture to below room temperature[23].



a b

Figure **2-3** a, Optical micrograph of an Illinois No. 6 coal suspended in water and smeared between micrograph slides (100 µm scale); b, Micrograph of a smear of the same coal after heating to 100˚C for 2 hours with the [bmim][Cl] and then cooled to room temperature (50 µm scale)

Similar experiments were performed on a Power River Basin (PRB) coal. The micrographs (× 200) of the original PRB coal (left) and the broken and dispersed material obtained after contact overnight with [bmim][Cl] (right) are shown in figure 2-4. The larger particles dispersed in the ionic liquid are ≤ 50 µm in size, while the numerous smaller particles are 10 µm or smaller. The IL [bmim][Cl] has disintegrated the original coal particles. When the solvent phase was removed quickly using a small amount of water, it was observed that remaining particles are rubbery, showing that they are solvent-swollen gels[3]. Ionic liquids such as [bmim] [BF_4], [bmim][CF_3SO_3], [bmim][PF_6], [pmim][I] have also been tested. Table 2-1 shows what was observed when Illinois No. 6 coal was mixed with these ionic liquids. The appearance of the mixtures is described in table 2-2.



a b

Figure **2-4** a, Optical micrograph of PRB suspended in water and smeared between micrograph slides (100 µm scale) ;b, Micrograph of a smear of the same coal after heating to 100˚C for 2 hours with the IL [bmim][Cl] and then cooled to room temperature (50 µm scale)

Table **2-2** Appearance of Illinois No. 6 coal mixed with specific ionic liquids, two parts (ionic liquids and Illinois No. 6 coal) in contact at room temperature and after heating up to 100˚C overnight then cooled down to room temperature

Materials	Before mixing	After mixing at 100˚C overnight	Cool down to room temperature
Illinois No. 6 coal [bmim][Cl]			
Illinois No. 6 coal [bmmim][Cl]			

Illinois No. 6 coal [bmim][BF_4]			
Illinois No. 6 coal [bmim][CF_3SO_3]			
Illinois No. 6 coal [bmim][PF_6]			
Illinois No. 6 coal [pmim][I]			

Table **2-3** Description of Illinois No. 6 coal mixed with ionic liquids

Ionic liquid	Room temperature appearance	Appearance at 100˚C	Appearance when cooling to room temperature
[bmim][Cl]	two solids in contact	thick, black, solution dispersion	Thick viscous, black, solution dispersion
[bmmim][Cl]	two solids in contact	thick, black, solution dispersion	thick, black, solution dispersion
[bmim][BF_4]	clear liquid in contact with coal particles	Clear liquid in contact with coal particles	Clear liquid in contact with coal particles
[bmim][CF_3SO_3]	clear liquid in contact with coal particles	thick, black, solution dispersion	slightly discolored liquid in contact with coal particles
[bmim][PF_6]	clear liquid in contact with coal particles	Thick black gel covered with white	thick black gel covered with white
[pmim][I]	slightly discolored liquid in contact with coal particles	Black solid gel	Black solution

ILs such as [bmim][BF_4] do not fracture and disperse Illinois No. 6 coal samples at room temperature, or even when heated up to 100˚C (table 2-1). Upon initial contact at room temperature, the coal particles are apparently unaffected and the solvent appears clear (apart from suspended particles). Upon heating to 100˚C, a black dispersion is formed with some ILs, such as [bmim][CF_3SO_3], but upon cooling to room temperature, the coal particles can be clearly seen both at the bottom of the tube and floating around in the slightly discolored solvent. They were not broken up significantly, alternatively this is may be a result of aggregation of small particles upon cooling.

2.4.2 Different Coals Mixed with IL [bmim][Cl]

Due to the high dispersion of Illinois No. 6 coal and the PRB coal in [bmim][Cl], other coals or additional samples were also tested with this IL, following the same experimental procedure. Pictures before and after mixing are shown below in tables 2-3 and table 2-4.

Table **2-4** Appearance of other coals after mixing with specified ionic liquid

	Illinois No. 6 coal [bmim][Cl] Thick, black, solution/dispersion	
	PRB coal [bmim][Cl] Thick, black, solution/dispersion	
	Wyodak coal [bmim][Cl] Thick, black, solution/dispersion	

When PRB coal and Wyodak coal were mixed with [bmim][Cl], a viscous black solution/ dispersion was obtained, similar to the mixture obtained with Illinois No. 6 coal .

Table **2-5** Appearance of Upper Freeport coal after mixing with [bmim][Cl], [bmim][CF_sSO_3]

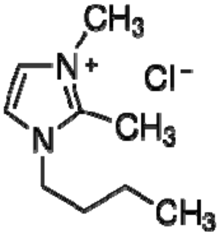
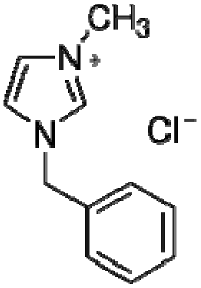
Materials	Before heating	After overnight heating at 100˚C	After heating for 4 days at 100˚C
Upper Freeport coal [bmim][Cl]			
Upper Freeport coal [bmim][CF_3SO_3]			

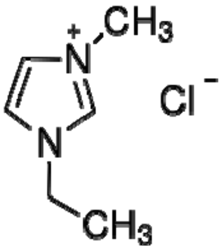
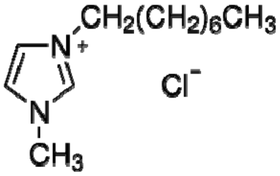
The Upper Freeport coal showed a different behavior. As can be seen from the table 2-4. Instead of dispersion, a simple suspension was observed when the coal/ionic liquid mixture were held at elevated temperature (near 100˚C) overnight. The interactions that promote swelling, fracture, dissolution and dispersion in the PRB coal, Wyodak coal and Illinois No. 6 coal in certain ILs were not favorable in Upper Freeport coal[3]. This is surprising, because this coal gives a large amount of soluble material in the mixed solvent NMP/CS_2.

2.4.3 Illinois No. 6 coal Mixtures with Long Chain Substituted [bmim] Cation Ionic Liquids

To determine the influence of cation structure, imidazolium chloride ionic liquids with various alkyl chain lengths were studied. 1-butyl-2, 3-dimethylimidazolium chloride, 1-benzyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride and 1-methyl-3-octylimidazolium chloride were mixed with Illinois No. 6 coal at about 100˚C overnight. The structures of these ILs are shown in table 2-5. All these ILs had the same anion ([Cl^-]) and the results obtained by mixing with Illinois No. 6 coal are also shown in table 2-5.

Table **2-6** Description of ionic liquids mixed with Illinois No. 6 coal

Ionic liquids	Structure	Phenomena
1-butyl-2,3-dimethylimidazolium chloride [bmmim][Cl]		mixing under temperature 100˚C, get particle slurry mixture, cool to room temperature it becomes solid
1-benzyl-3-methylimidazolium chloride [benzylmim][Cl]		Mixing under temperature 100˚C, get oily slurry state mixture, cool to room temperature becomes sticky solid

1-ethyl-3-methylimidazolium chloride [ethylmim][Cl]		Oily slurry state upon mixing to 100˚C, coal particles aggregate in the bottom of the tube at room temperature
1-methyl-3-octyllimidazolium chloride [octylmim][Cl]		Viscous slurry state upon mixing to 100˚C, stays as a slurry state at room temperature

Upon heating up to 100˚C, slurries were obtained. Due to the higher viscosity of 1-benzyl-3-methylimidazolium chloride and 1-methyl-3-octylimidazolium chloride, the solution obtained stayed in an oily slurry state. The 1-butyl-2, 3-dimethylimidazolium chloride, 1-benzyl-3-methylimidazolium chloride coal slurries formed a solid when cooled down to room temperature. When left for several days, the sticky solid disappeared and a slurry state of dispersion was formed. For 1-ethyl-3-methylimidazolium chloride, when mixed with Illinois No. 6 coal and heated up to 100˚C, the mixture formed a slurry state dispersion, but when cooled down to room temperature the coal particles aggregated in the bottom of the test tube.

To compare these results with those obtained with [bmim][Cl], pictures were taken right after heating the four mixtures and these are shown in figure 2-5. All samples appeared to be a dark suspension that had gel-like qualities right after heating to 100˚C overnight.

Figure **2-5** Comparing four different type of imidazolium ionic liquids when heated with Illinois No. 6 coal at 100 ˚C (from left to right: 1-methyl-3-octyllimidazolium chloride, 1-benzyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride)

Micrographs obtained from smears of these dispersions are shown below in figure 2-6 to 2-9. The ILs [bmmim][Cl], [emim][Cl], [omim][Cl], [benzylmim][Cl] fragment Illinois No. 6 coal to different degrees.

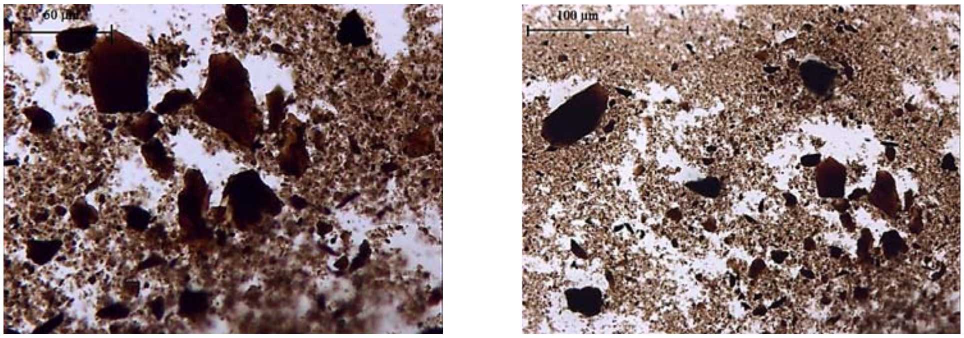


Figure **2-6** Illinois No. 6 coal treated with 1-butyl-2, 3-dimethylimidazolium chloride at 100˚C shown at different magnifications

For 1-butyl-2, 3-dimethylimidazolium chloride, the coal fragmented into very small particles, as showed in figure 2-6. Several particles of ~50μm in size can be seen, but most of the coal appears to have been fragmented into very small particles.

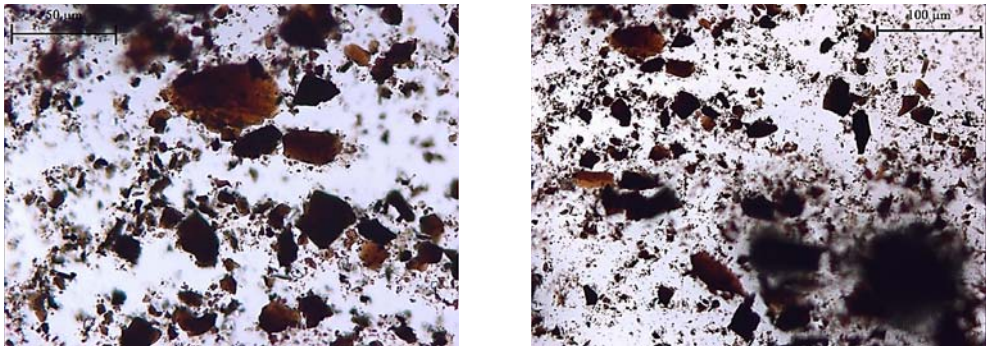


Figure **2-7** Illinois No. 6 coal treated with1-ethyl-3-methylimidazolium chloride at 100˚C shown at different magnifications

Compared to [bmmim][Cl], [emim][Cl] treated samples were less fragmented, as shown in figure 2-7. The particles size varies from ~5 µm to ~60 or 70 µm. Some coal particles appeared to be thin and transparent.

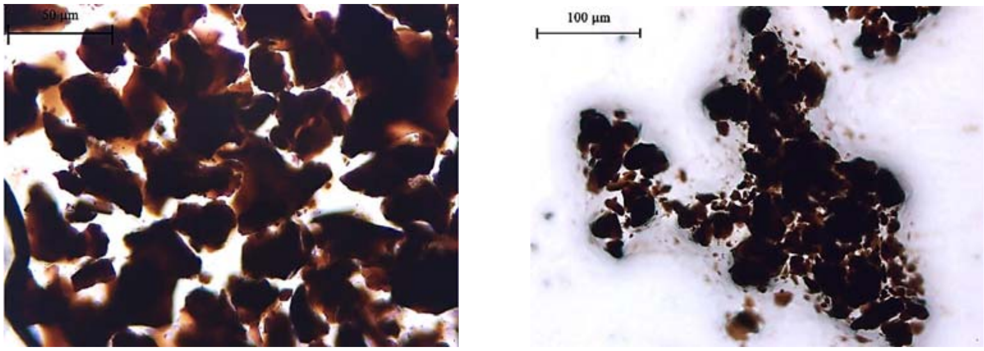


Figure **2-8** Illinois No. 6 coal treated with 1-methyl-3-octylimidazolium chloride at 100˚C shown at different magnifications

The 1-methyl-3-octylimidazlium chloride coal mixture was a viscous, brownish gel, containing of agglomerated particles. These particles appear to be mainly uniformly distributed, about ~50 µm in size with inter-dispersed smaller particles, as shown in figure 2-8.

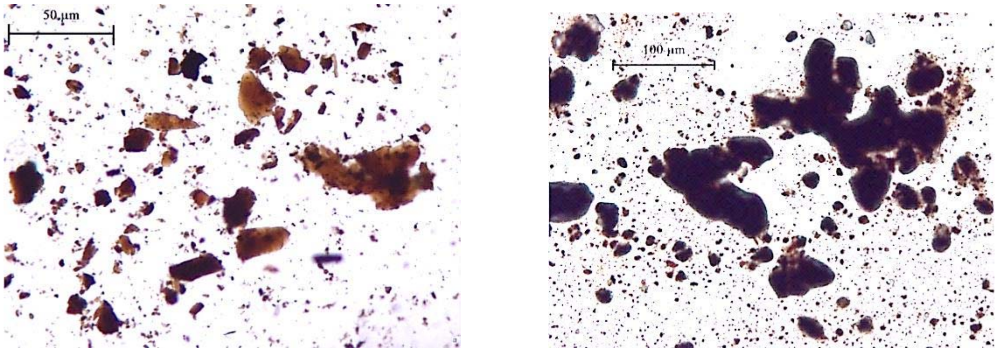


Figure **2-9** Illinois No. 6 coal treated with 1-benzyl-3-methylimidazolium chloride at 100˚C

A viscous solid gel was also formed when Illinois No. 6 coal was treated with 1-benzyl-3-methylimidazolium chloride. In the micrographs show in figure 2-9, the particles size varies with both large and small particles. Fragmentation has occurred, but to a lesser extent compared to the other ILs studied.

2.4.4 Coal/ IL Mixtures Extracted with NMP and Pyridine

As described in the previous sections, Illinois No. 6 coal and [bmim][Cl] will form a viscous gel-like suspension. Therefore, determining the solubility of Illinois No. 6 coal in [bmim][Cl] is a challenge. Centrifugation was used to partly separate the solution. The supernatant was removed and the residue was remixed with ionic liquid. The second supernatant was then poured off. It was estimated that nearly 23% by mass of Illinois No. 6 coal was soluble in this IL (after overnight heating). The results are listed in table 2-5.

Because of the difficulties encountered when filtering and centrifuging the viscous dispersion, the IL/coal suspension was diluted with NMP, and the mixture stirred at room temperature for 40 hours. The dispersion was filtered and the soluble coal extract precipitated in water. Both the residue and extract part were soxhlet extracted with water to remove residual

[bmim][Cl] and NMP. It was found that ≥ 40% (by mass) of the Illinois No. 6 coal dissolves in the IL/NMP mixture. Similar experiments on the PRB coal resulted in a 30% (by mass) NMP extraction yield.

The long chain alkyl imidazolium ionic liquids, 1-methyl-3-octylimidazolium chloride and the shorter chain [bmim][Cl] and [emim][Cl], were tested. The 1-methyl-3-octylimidazolium chloride treated sample gave 47% (by mass) soluble material. The yield obtained with 1-ethyl-3-methylimidazolium chloride is 13% (by mass) when stirred in NMP for 40 hours. This amount is smaller than Illinois No. 6 coal directly extracted with NMP. This is probably related to the particle size obtained after IL treatment; the [emim][Cl] did not break up the coal as much as the longer side chain ILs, [bmim][Cl] and [omim][Cl], and also may have resulted in aggregation.

Table **2-7** Coal samples treated with IL, NMP, and Pyridine (data reported here is on as received basis)

<table>
<tr><th>Coal</th><th>Ionic Liquid</th><th>Solubility in ionic liquid, heated up to 100˚C (by mass)</th><th colspan="2">NMP extraction yield, room temperature (by mass)</th></tr>
<tr><td>Illinois No. 6 coal</td><td>[bmim][Cl]</td><td>23%</td><td colspan="2"></td></tr>
<tr><td>Illinois No. 6 coal</td><td></td><td></td><td colspan="2">16%</td></tr>
<tr><td>Illinois No. 6 coal</td><td>[bmim][Cl]</td><td></td><td>46%</td><td>40 %</td></tr>
<tr><td>Illinois No. 6 coal</td><td>[omim][Cl]</td><td></td><td colspan="2">44%</td></tr>
<tr><td>Illinois No. 6 coal</td><td>[emim][Cl]</td><td></td><td colspan="2">13%</td></tr>
<tr><td>PRB coal</td><td>[bmim][Cl]</td><td>19%</td><td colspan="2"></td></tr>
</table>

PRB coal			15%
PRB coal	[bmim][Cl]		30%
Upper Freeport coal	[bmim][Cl]	14%	
Upper Freeport coal			21%
Upper Freeport coal	[bmim][Cl]		23%
Wyodak coal	[bmim][Cl]		24%
Blind Canyon coal	[bmim][Cl]		27%

When mixed with [bmim][Cl], Wyodak coal and Blind canyon coal formed black suspensions. When the mixture was then stirred with NMP, 24% and 27% of soluble material was obtained (by mass).

Figure 2-10 summarizes the extract yields obtained from three coal samples, Illinois No. 6, PRB coal and Upper Freeport coal. The Ionic liquid used was [bmim][Cl]. Ionic liquid treated samples gave higher extraction yields in NMP, with Illinois No.6 coal showing the largest increase in solubility relative to the untreated coal. Pyridine solubility also increased for Illinois No. 6 coal and the PRB coal, but the increase was not as significant as that obtained with NMP. However, Upper Freeport coal showed higher pyridine solubility than NMP solubility after IL treatment. As mentioned above, this coal is anomalous in its behavior with solvents.

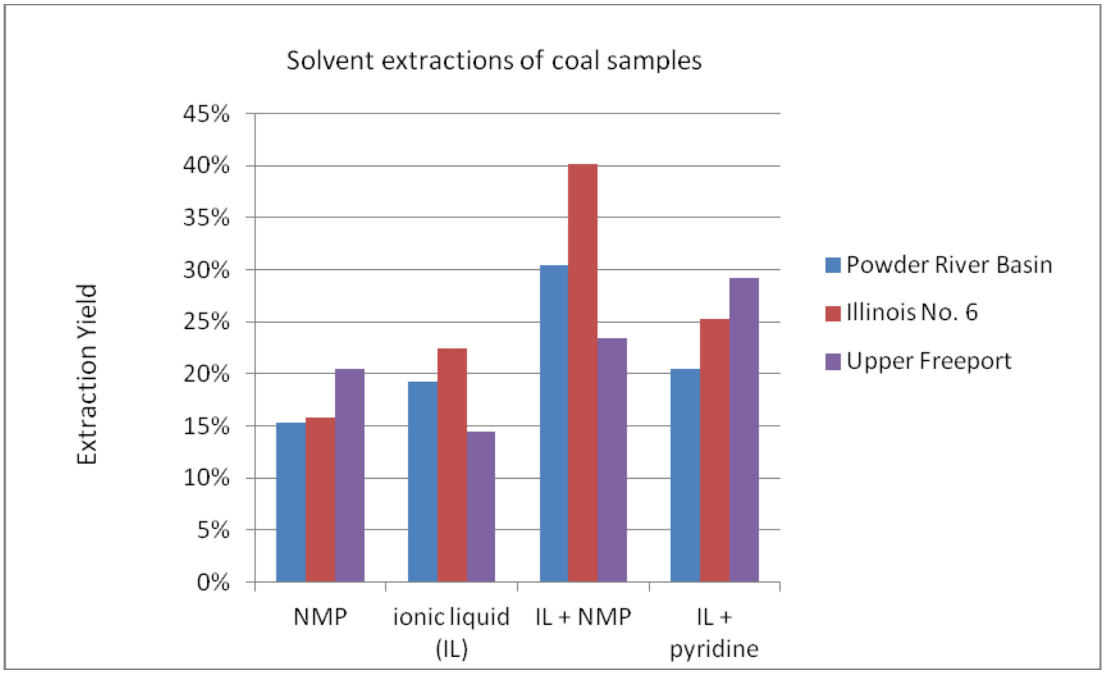


Figure **2-10** Extraction yields of coal samples (([bmim][Cl]+pyridine) extraction data is obtained from reference[3])

(NMP: the NMP extraction yield of coal samples extracted with NMP at room temperature; IL: the yield of coal samples mixed with ionic liquids and solubility obtained by centrifugation and separate the solution; IL+NMP: the NMP extraction yield of ionic liquid coal mixture stirred in NMP at room temperature; IL+ pyridine: the pyridine extraction yield of ionic liquid coal mixture stirred in pyridine at room temperature)

To summarize the data obtained:

Original coal NMP solubility: Illinois No. 6 coal ≈ PRB coal < Upper Freeport coal

Ionic liquid treated coal pyridine solubility: Upper Freeport coal > Illinois No. 6 coal > PRB coal

Ionic liquid treated coal NMP solubility: Illinois No. 6 coal > PRB coal > Upper Freeport coal

PRB coal solubility in solvent: IL+NMP > IL+ pyridine> IL > NMP

Illinois No. 6 coal solubility in solvent: IL+NMP> IL+ pyridine> IL> NMP

Upper Freeport coal solubility in solvent: IL + pyridine> IL+NMP> NMP > IL

2. 5 Discussion

It is well known that coal and other materials can spontaneously fracture in the presence of solvents. Keller and Smith[24] first commented on an earlier observations of Bangham et al.[25], that charcoal “virtually exploded” when added to methanol and went on to show that coal particles spontaneously fractured in the presence of certain solvents. However, the fractured particle sizes are typically large[25]. In a classic study of the fracture of cross-linked glassy-polymers, Alfrey et al.[26] noted that flat round discs of styrene - divinylbenzene copolymers would break apart with “an audible ping, splash” on being placed in contact with certain solvents. Again, the material was fractured into several large pieces. Brenner[27] also observed that coal particles expand, become cracked, and greatly distorted in the presence of good solvents, but they were not fractured or dispersed to the extent reported here. Van Niekerk et al.[28] also recently observed a similar fracturing of millimeter-sized particles of South African coals. However, the degree of fracturing and dispersion observed here with ILs is much more extensive than that observed in any previous studies.

Fracturing is a consequence of the high stresses that can be generated by the swelling process[3]. In synthetic polymers this was attributed to the large increase in stress that occurs when a glassy core that is diminishing in size is trying to hold a thick swollen shell in compression[26]. In coals, a mismatch in the swelling tendencies of different types of macerals, the presence of mineral inclusions and various other heterogeneities that lead to uneven swelling also play a role[28,29]. However, the extent of disintegration and subsequent dispersion of coals observed when mixed with certain ILs is unusual. This is probably a consequence of a rapid and large buildup of stresses when some of the coals studied here are immersed in [bmim][Cl] and certain other ILs[3].

The ability of certain ILs to disintegrate and disperse at least some coals is most likely related to the intermolecular interactions between the components of these mixtures, resulting in a rapid swelling of the coal. Ionic liquids can engage in a wide range of intermolecular interactions, which makes the identification of the specific forces involved in fracture and dispersion difficult[3]. There is probably some electrostatic interaction between ILs and mineral surfaces and any chelated ions in the coal. In addition, there are also ion-dipole and dipole-dipole interactions, together with hydrogen bonding[3]. It is also well-known that ILs can engage in π-cation interactions[28]. It is possible that the replacement of metal cations with bulky IL groups also plays a role in the fracturing and dispersion observed[3]. Furthermore, removal of π-cation cross-links would allow greater swelling, and probably more fracturing.

The strength and extent of the interactions between coals and ionic liquids will vary with the structure of the coal, the nature of the substitutes on the imidazolium ring and the nature and size of the anion[3]. In a study by Hu and Guo[30], it was noted that a disparity of cation and anion size in ILs could result in local difference in charge density, promoting the ability of chlorine anions, which have the largest charge density of the anions studied, to engage in acid-base interactions and hence disrupt interactions between asphaltene molecules. Consisted with this, the ionic liquids that broke up and dispersed two of the coals we studied to the greatest extent both had [Cl^-] counterions. The mixture stays as a black solution/ dispersion/gel even after cooling down to room temperature. This supports the proposal of Hu and Guo[30], that anion charge density is an important factor.

Different results were obtained when coals were mixed with other types of ionic liquids. Only a slightly discolored liquid was obtained when [bmim][BF_4] ionic liquid was contacted with coal particles at 100˚C. The [bmim][CF_3SO_3] ionic liquid formed a black solution gel when heated to 100˚C overnight. However, when cooled to room temperature, the particles aggregated in the bottom of the tube. The [pmim][I] ionic liquid forms a black solid aggregation, and a black suspension when cooled to room temperature. The [bmim][PF_6] ionic liquid formed a gel, but a white precipitate appeared upon cooled to room temperature. This was probably due to a crystallization of the phase-separated IL. Because the coal was not dispersed it was not investigate this gel further. All these ILs have an anion with a larger anion and a smaller charge density than Cl^- ions, supporting the proposal that charge density is an important factor.

Certain ionic liquid treated PRB and Illinois No. 6 coal s also showed enhanced solubility in NMP and pyridine. The solvent NMP was added to act as dispersant, but also worked as a solvent to increase the extract yield. About 47% soluble materials by mass was obtained in NMP when Illinois No. 6 coal was treated with [bmim][Cl]. But for PRB coal and Upper Freeport coal, the NMP soluble materials are lower, 30% and 24% (by mass, as received basis) respectively. Due to the difference in structure and rank, the coal solvent interactions probably differ, but at this early stage in the research the nature of the interactions that have the largest effect remains to be determined.

Taken as a whole, these results suggest that Illinois No. 6 coal and the PRB coal consist of entities that are indeed covalently cross-linked networks rather than purely associated structures[3]. In rubber-like (lightly cross-linked) networks made up of flexible chains, the “sol” fraction is usually readily extracted, the macromolecules being able to diffuse out by a reptation process. Aharoni and Edwards[31] point out that if both the network and sol are highly branched and rigid, the latter might be trapped, as illustrated schematically in figure 2-11. They experimentally determined that the solvent extraction of such networks failed to remove highly branched macromolecules. Cody also suggested that bituminous coal structure was “entangled”[32].

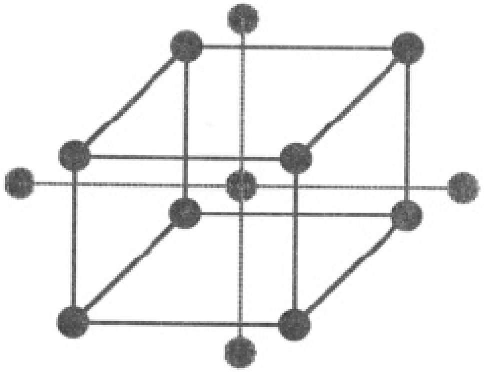


Figure **2-11** Schematic representation of a branched, rigid polymer trapped in a rigid network[33]

Many coals behave as if they are made up of such cross-linked, stiff chain entities. There are some classic studies that demonstrate that a proportion of soluble material is extracted from coal only with great difficulty, taking months in some cases[34], while shock heating of coal to 420-450˚C results in a large increase in the extractability[33]. Brown and Waters proposed that the trapped materials in the coal can be released by a breakdown in the network[33]. It is possible that by breaking just a few bonds, a significant amount of soluble materials can be obtained as a result of by releasing high molecular weight but soluble material. Here it was shown that under non-cracking conditions, 100˚C or lower temperatures, the disintegration and dispersion of certain coals in specific ILs indicate that there is an indeed significant amount of trapped soluble material in these coals, and these were released as a result of the ILs being able to fracture these coals into small particles.

The long chain alkyl imidazolium ionic liquid, 1-methyl-3-octylimidazolium chloride was also tested relative to shorter chain ILs. An oily slurry state mixture was obtained when Illinois No. 6 coal was mixed with 1-methyl-3-octylimidazolium chloride. For 1-ethyl-3-methylimidazolium, the mixture aggregated in the bottom of tube when cooled down to room temperature. The mixture treated with NMP, and the long chain IL [omim][Cl], gave the highest soluble yield in NMP, 44% (as received basis). For [emim][Cl] only 12% (as received basis) material was found to be soluble in NMP. The [emim][Cl] ionic liquid did not break up the coal as much as the longer side chain ILs, [bmim][Cl] and [omim][Cl].

Clearly, alkyl side chain length has an effect. Longer side chains would lower the overall solubility parameter of the IL, affecting dispersion forces. It would appear that a longer side chain minimizes solubility parameter differences between coal and solvent[35].

2.6 Conclusion

Ionic liquids were used as solvents with coal. It was observed that ILs such as [bmim][Cl] can disperse and dissolve coal particles when heated up to 100˚C. However, if the anion is changed from $[Cl]^-$ to $[CF_3SO_3]^-$, $[BF_4]^-$ or $[PF_6]^-$, there is little effect on coal under the same conditions. Changing the cation, the long chain ionic liquids [omim][Cl] and [benzyl][Cl] form viscous gels when contact with ionic liquids. Shorter chain ILs [emim][Cl] did not fracture and disperse the coal as much. The responsible contributions from the various interaction between ionic liquid and coal is not yet elucidated, but, hydrogen bonds formed between coal and the $[Cl]^-$ anion is a likely factor in the dissolution and fragmentation properties of certain ILs.

Different coals also show different behavior upon mixing with ionic liquids. Illinois No. 6 coal and PRB coal have a better dissolution ability in [bmim][Cl] compared to Upper Freeport coal. This is a surprise, in that Upper Freeport coal is very soluble in NMP/CS_2 mixtures. This coal appears to be anomalous and its structure different to other coals examined.

Mixing certain coal/IL mixtures with NMP or pyridine results in enhanced extraction yields. This correlates with the degree to which the coal is fractured into small particles. The better contact that is then obtained with solvent enhances the yield of soluble material. This suggests that a significant amount of soluble material is trapped in the coal network.

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CHAPTER 3

LOW TEMPERATURE “SOAKING” OF COALS WITH IONIC LIQUIDS

3.1 Introduction

Coal liquefaction is the conversion of solid coal to liquids or soluble materials[1]. The process of liquefaction produces compounds which have higher hydrogen content. Direct coal liquefaction is the most energetically efficient method of producing liquids from coal and it is possible to obtain the highest oil yields through this technique. Table 3-1, shows the composition range of hydrogen, oxygen, sulfur and nitrogen contents in fuel oils and hydrocarbons. It can be seen that in order to produce liquid fuels from coal, hydrogen must be introduced.

Table **3-1** Composition of Typical Fuel Oils and Hydrocarbons[2]

Fuel	Carbon	Element			
		hydrogen	oxygen	sulfur	Nitrogen
Typical crude oil	86.0	11.0	0.7	1.5	0.5
Fuel oil	86.0	13.4	02	0.3	0.1
Gasoline	85.0	15.0	0.0	0.1	0.0
Bituminous coal	78.0	5.7	11.6	3.3	1.0
Subbituminous coal	71.9	6.1	20.2	0.6	1.0
Benzene	92.3	7.7	0.0	0.0	0.0
Naphthalene	93.7	6.3	0.0	0.0	0.0

Direct coal liquefaction mechanisms are very complex. Generally, the liquefaction process involves two steps: one is the rupture of the macromolecular structure of coal into radical fragments at elevated temperature, followed by hydrogenation of those fragments to produce molecules with lower molecular weights. Temperature is very important, due to the necessity for thermal rupturing of carbon-carbon linkages during liquefaction. Free radical formation and subsequent free radical reactions during liquefaction normally do not occur at a low temperature (below 360˚C), while too high a temperature leads to coking reactions. During liquefaction, coal dissolves in a solvent or is partially solubilized in a solvent. Hydro-cracking and hydro-treating can then occur due to hydrogen transfer reaction between the coal and solvent and hydrogen and coal. Heat, pressure and catalysts all are essential factors. However, direct coal liquefaction at high temperatures and pressures remains marginal in terms of economics. Because of the cost of liquefaction, both solvent extraction at elevated temperature (about 360˚C) and demineralization at low temperatures have been investigated.

Although the temperatures used in thermal extraction studies are lower than those used in conventional liquefaction work, they are still relatively high and it would clearly be advantageous if extractions could be conducted at lower temperatures. In the preceding chapter it was shown that certain ionic liquids fragment, swell, partially solubilize, and disperse a Powder River basin coal and Illinois No. 6 coal to form extremely fine particles to a remarkable extent. It was observed that ILs with chlorine counterions broke up and dispersed the coals to a much greater extent than those with larger anions. However, ILs with halogen anions are only stable up to temperatures of about 150˚C. Other ionic liquids such as [bmim][CF_3SO_3] and [bmim][BF_4] are stable up to 400˚C[3-5]. Accordingly, to determine the effect of higher temperatures on the yield of soluble material, imidazolium ILs that are stable at higher temperatures were studied and the results are reported here. These types of experiments were referred to as temperature “soaking” in industry and that term is used here to describe heating at temperatures of 300˚C or less.

3.2 Experimental

3.2.1 Materials

The Ionic liquids used in this study were 1-butyl-3-methylidazolium tetrafluoroborate, [bmim][BF_4] (>98.5%) and 1-butyl-3-methylimidazolium tetrafluoromethanesulfonate, [bmim][CF_3SO_3]. Both were purchased from Sigma-Aldrich. The Illinois No. 6 coal is reported to have a moisture content of 7.97% and a mineral matter content of 15.8%, while the Wyodak coal has a moisture content of 28.09% and a mineral matter content of 8.7%. Chevron USA, Inc., an affiliate of the Chevron Corporation, provided a PRB sub-bituminous coal, which had been dried and had a moisture content of 13.7% and a mineral matter content of about 8%. Pentane, pyridine, tetrahydronaphthalene (tetralin) were obtained from Aldrich.
(Coal data listed as table 2-1)

3.2.2 Low temperature "Soaking" Experiments

Low temperature "soaking" experiments were conducted in a vertical micro-autoclave reactor of 10ml capacity. The vertical micro-autoclave reactor was charged with coal, ionic liquid and tetralin. The contents were stirred for 1~2 mins to get a well dispersed mixture before the reaction. The reactions were conducted at 6.9 Mpa pressure of hydrogen.

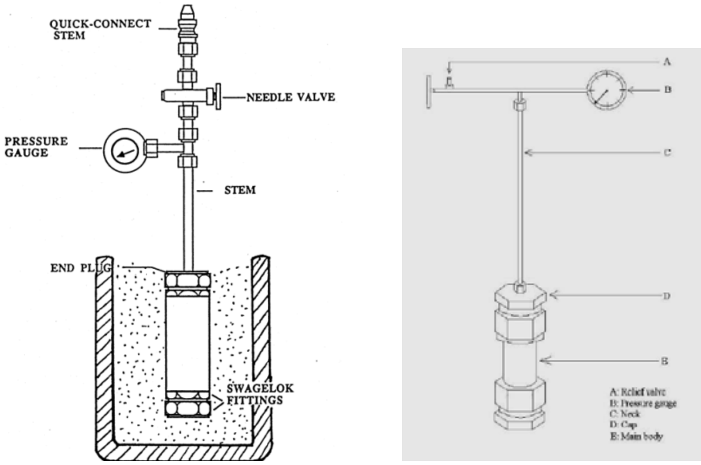

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Figure **3-1** Coal liquefaction reactor – sand bath (left) and tubing bomb (right)

The Ionic liquid [bmim][BF_4] and [bmim][CF_3SO_3] were used because of their thermal stability. Several different approaches were used in this work:

1) Initial studies used temperatures of 300˚C or greater.
2) Because of solvent instability, temperatures below 300˚C were also investigated.
3) Several residence times were explored, 10min, 30 mins, 2 hours, 4 hours and up to 8hours.
4) Catalyst influence was quantified, such as zinc chloride ($ZnCl_2$) and boron triiodide (BI_3).

3.2.3 Soxhlet Extraction

Following a low temperature "soaking", the reaction products were washed, dried and transferred to a soxhlet glass thimble. Liquid products, which included pentane with some oil, tetralin and ionic liquids, 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 pyridine, and the extract put into water, filtered and dried at room temperature under high vacuum until reaching a constant weight.

3.2.4 Determination of the Pyridine-Extraction Yields

Two types of calculation have been used for calculation of pyridine extract yield of samples. Experimental data corrected based on dry ash free basis (daf), related data are listed in table 2-1 in chapter 2.

1) Extraction yields were based on the amount of soluble material, removed from the liquefaction vessel. The extractability in pyridine calculated is based on

Extraction yield (wt. %) =

(daf) Mass [(The dried sample-Residue)/ (The dried sample)] ×100 %

Equation (3-1)

2) In later experiments, the extraction yield was based on the amount of coal initially used for liquefaction.

Extraction yield (wt. %) =

(daf) Mass [(Original coal amount-Residue)/ (Original coal amount)] ×100%

Equation (3-2)

The calculation method was changed because of the possibility that the amount of unconverted residue in the initial work was potentially underestimated.

3.2.5 Using FTIR – DRIFT to Characterize Coal Samples

Drift spectra were recorded on a Nicolet spectrometer at a resolution of 2 cm^{-1} with 400 scans. Drift samples were prepared with 3~5 mg sample diluted with 200 mg KBr.

3.3 Results

3.3.1 Initial Studies

As shown in the previous chapter, [bmim][BF_4] and [bmim][CF_3SO_3] do not disperse a PRB coal or an Illinois No. 6 coal samples at room temperature. However, these ILs were reported to be stable up to temperatures of about 400˚C, compared to temperatures of about 150˚C for [bmim][Cl][6,7,8,9]. Therefore, the [bmim][CF_3SO_3] and [bmim][BF_4] were chosen for initial higher temperature soaking experiments.

Illinois No. 6 coal was mixed with [bmim][BF_4] ionic liquid both with and without tetralin and catalyst to conduct temperature “soaking” experiments. The mixtures were heated in tubing bomb reactors in a sand bath at temperatures of 250˚C, 300˚C and 340˚C. In early experiments, after the coal/IL samples were heated under 1000psi hydrogen pressure, the samples were washed out from the reactor using warm water, then filtered and dried in a vacuum oven at 50˚C. Samples were weighed and soxhlet extracted with pyridine. Initially, it was thought that warm water might aid samples removing from the reactor. While concurrently the water would also remove the ILs from the coal. However, samples removal from the reactor remained challenging resulting in the loss of sample during transfer. Due to this sample loss, the pyridine extractability of samples was based on the amount of sample obtained after drying, not on the initial starting coal amount. The results are reported in table 3-2.

Table **3-2** Illinois No. 6 coal treated with [bmim][BF_4] ionic liquid

	Illinois No. 6 coal	Condition	Extract yields (daf basis)
1	[bmim][BF_4] (1:5)	250˚C 1000psi H_2 4hours	32%
2	[bmim][BF_4] (1:5)	300˚C 1000psi H_2 10mins	29%
3	[bmim][BF_4] BI_3 (1:5)	300˚C 1000psi H_2 10mins	27%
4	[bmim][BF_4] (1:5)	300˚C 1000psi H_2 4hours	52%
5	[bmim][BF_4] (1:5)	340˚C 1000psi H_2 4hours	56%
6	[bmim][BF_4] BI_3 (1:5)	340˚C 1000psi H_2 4hours	74%
7	[bmim][BF_4] Tetralin (1:8:2)	300˚C 1000psi H_2 10mins	46%
8	[bmim][BF_4] Tetralin (1:8:2)	300˚C 1000psi H_2 4hours	57%
9	[bmim][BF_4] Tetralin (1:5:5)	340˚C 1000psi H_2 10mins	62%

These initial experiments relied on direct hydrogenation of fragments radicals from hydrogen as mediated by IL, and at temperatures of 300˚C or less did not result in significant amounts of soluble products. For example, about 29% of pyridine soluble materials was obtained when soaking in [bmim][BF_4] at 300˚C for 10 minutes (listed in table 3-2 as No. 2). Optical microscopy was used to observe the mixture after "soaking". As can be seen from the micrographs in figure 3-2, short time contact with ionic liquid resulted in some fragmentation. The left micrograph shows the products obtained at 300˚C for 10mins, while the right micrograph is the product obtained with BI_3 added as a catalyst. The product particle size is non-uniform in shape, with larger particles of ≈50μm or even larger, together with some smaller particles (10μm). With catalyst added, the particles were smaller and with greater transparency. Most particles are ≤ 50μm. However, the yield of pyridine soluble material was not very different and it can be concluded that soaking for short times under these conditions does not result in significant amounts of soluble products. It is interesting that the size of particles obtained and the solubility in pyridine are close to those obtained by treating with the IL [bmim][Cl] at 100˚C.

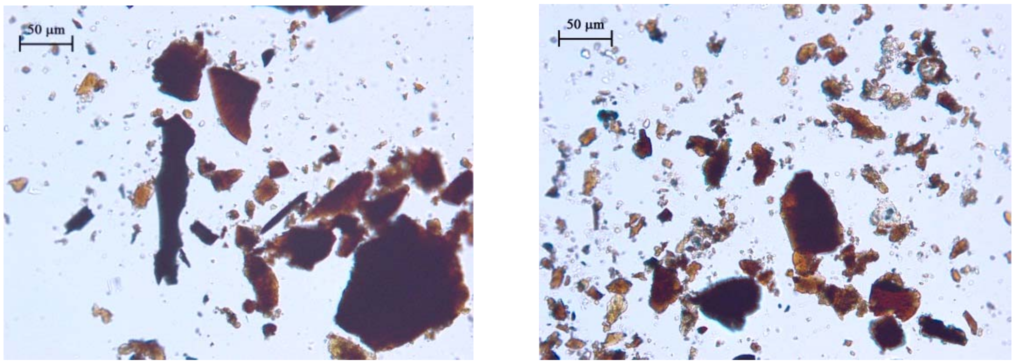

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Figure **3-2** Illinois No. 6 coal / [bmim][BF_4] at 300˚C 1000 psi H_2 pressure 10 minutes (a); b:Illinois No. 6 coal / [bmim][BF_4]/ BI_3 at 300˚C 1000 psi H_2 pressure 10 minutes (b)

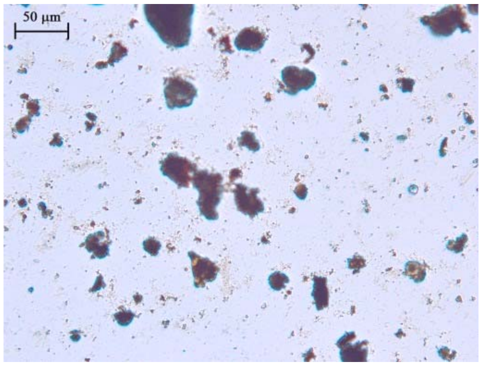

Figure **3-3** Illinois No. 6 coal / [bmim][BF_4] at 340˚C 1000 psi H_2 pressure 10 minutes

At longer times, 4 hours at 300˚C (run 4 in table 3-2), the yield of pyridine soluble material increased somewhat, to 52% by mass (daf), but this is still not a significant yield of soluble material. However, the yield of soluble material increased significantly when the temperature was raised to 340˚C. Treatment at this temperature for 4 hours resulted in a yield of about 56% pyridine soluble material (run 5). This yield increased to about 74% if the catalyst BI_3 was added to the mixture (run 6).

One possible reason for the low yield of soluble products could be the inability of hydrogen to contact any radicals formed under these conditions. Hydrogen for example may not be very soluble in ILs. Tetralin was therefore used in some subsequent experiments. An immediate increase in the yields of soluble material was obtained. At an 8:2 ratio (by weight) of IL to tetralin, a yield of close to 46% soluble material was obtained at 300˚C after treatment for only 10 minutes (run 7 in table 3-2). This increased modestly to about 57% when the coal was soaked for 4 hours (run 8). However, at a temperature of 340˚C for only 10 minutes with a 1/1 ratio of IL to tetralin a yield of 62% pyridine soluble material was obtained.

The highest pyridine extractability obtained in this series of experiments was 74% by mass (daf), when the Illinois No. 6 coal was mixed with [bmim][BF_4] using BI_3 as catalyst and treated at 340˚C (1000 psi hydrogen pressure) for 4 hours. The product was a slurry. Samples were taken from the lighter (more liquid/oil) part (figure 3-4 micrograph a) and dense (more particles) part (figure 3-4 micrograph b), then examined under microscope. It can be seen that the resulting coal particles are finely dispersed, the size of particles being on the order of 1~2 µm.

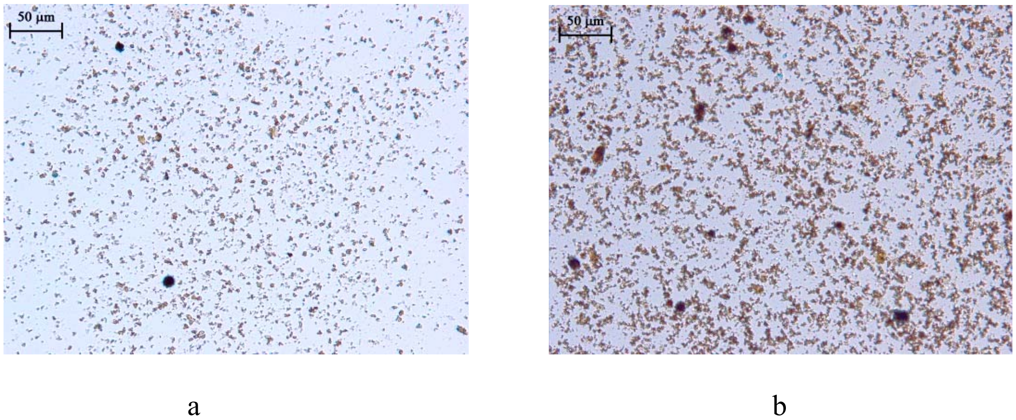

Figure **3-4** Illinois No. 6 coal /[bmim][BF$_4$]/BI$_3$ 340˚C 1000 psi H$_2$ pressure 4 hours treatment liquid part (a) and residue part (b) (74%) (×200)

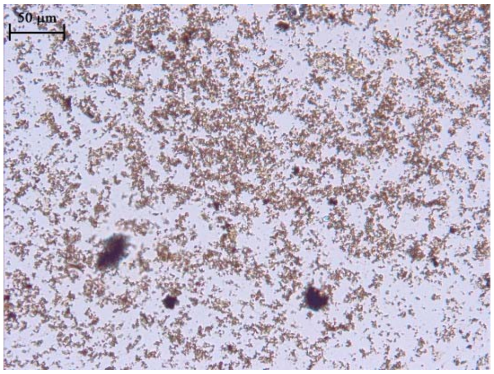

Figure **3-5** Illinois No. 6 coal /[bmim][BF$_4$] 340˚C 1000 psi H$_2$ pressure 4 hours treatment (54%) (×200)

Under the same conditions, without adding catalyst, the particles were again dispersed, but as discussed above, the yield of pyridine soluble material was not as large.

3.3.2. Using A More Stable Ionic Liquid

At temperatures lower than used in conventional liquefaction experiments or those used to produce “hyper coal”[10] (usually 350-360˚C) significant qualities of soluble material were apparently obtained. However, this work was flawed in two ways. First, the failure to remove all of the materials from the tubing bombs could have resulted in a poor mass balance. In addition, the highest yields were obtained at temperatures of about 340˚C. This temperature is only slightly lower than that used to produce hypercoal and therefore not a significant advance.

After commencing this work, a paper was published showing that [bmim][BF_4] ionic liquids slowly degrade at longer times at temperatures above 300˚C[11]. In addition, other new work showed that the BF_4 anion slowly hydrolyses to give HF in the presence of water[12]. The IL [bmim][BF_4] is therefore a poor choice for this work. Attention was therefore focused on [bmim][CF_3SO_3] a more stable ionic liquid. At temperatures less than 300˚C, several different ranks of coal were tested.

3.3.3 Illinois No. 6 coal

As with the work using the IL [bmim][BF_4], described above, soaking Illinois No. 6 coal with [bmim][CF_3SO_3] under 1000 psi hydrogen but in the absence of a hydrogen donor solvent such as tetralin does not result in significant yields of pyridine soluble material. As shown in table 3-4, soaking for 10 minutes at 300˚C yields 14% soluble materials (run 1), while including the catalyst BI_3 (very small amount, ~0.5 g) raises the amount of soluble material slightly to about 21% (by mass, daf)(run 2). As will be shown below, because of the large variability in the results, this difference is not significant.

Table **3-3** Illinois No. 6 coal /IL/tetralin heating at 1000 psi hydrogen pressure

	Illinois No. 6 coal	Condition	Pyridine Extract Yield (daf basis)
1	[bmim][CF_3SO_3]	300˚C 1000psi H_2 10mins	14%
2	[bmim][CF_3SO_3] BI_3	300˚C 1000psi H_2 10mins	21%
3	[bmim][CF_3SO_3] Tetralin (1:8:2)	300˚C 1000psi H_2 10mins	50%
4	[bmim][CF_3SO_3] Tetralin (1:8:2)	300˚C 1000psi H_2 4hours	77%
5	[bmim][CF_3SO_3] Tetralin (1:3.5:2)	300˚C 1000psi H_2 4hours	54%
6	[bmim][CF_3SO_3] Tetralin (1:3.5:2) BI_3	300˚C 1000psi H_2 4hours	56%
7	[bmim][CF_3SO_3] Tetralin (1:8:2)	250˚C 1000psi H_2 10mins	31%
8	[bmim][CF_3SO_3] Tetralin (1:3.5:2)	250˚C 1000psi H_2 8hours	84%

Although the yields of soluble material are not large, this treatment did break up the coal particles extensively. Micrographs of the slurries obtained in these two experiments (run 1 and run 2) are shown in below figure 3-6. Most of the particles are ≥50 μm in size, and are mostly transparent. Although the IL [bmim][CF_3SO_3] did not break up the coal significantly at lower temperatures (100˚C). At higher temperatures, even with a short time, this IL fragments and disperses the coal particles. Although high yields of soluble material were not obtained, this fragmentation should help provide good contact with catalysts or solvent during liquefaction.

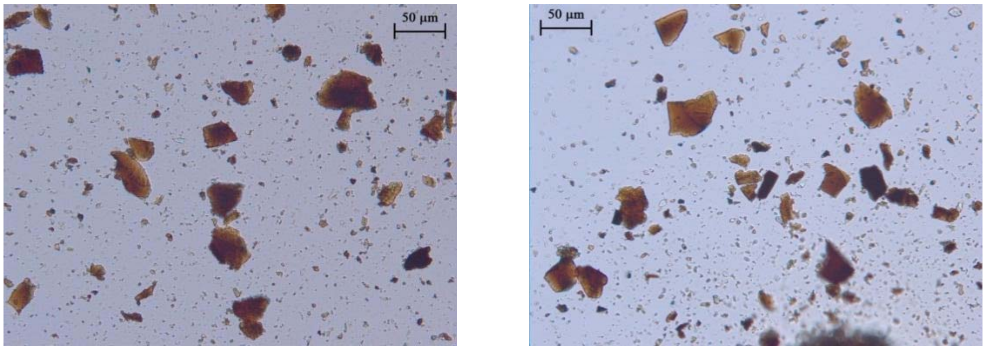

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Figure **3-6** Illinois No. 6 coal / [bmim][CF_3SO_3] 300˚C 1000 psi H_2 pressure 10 minutes (×200) (a); Illinois No. 6 coal / [bmim][CF_3SO_3] / BI_3 300˚C 1000 psi H_2 pressure 10 minutes (×200) (b)

If tetralin was now included in the mixture placed in the tubing bomb and the experiment repeated under the same conditions of time, temperature and pressure, the yield of pyridine soluble material increased significantly to about 50% (daf). Increasing the soaking time to 4 hours gave a dramatic increase in pyridine solubility, to about 84% by mass daf. A micrograph of the slurry obtained under these conditions is shown in figure 3-7. The resulting coal particles are now a very fine dispersion, consisting of mostly small particles (~1-2 µm). 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.

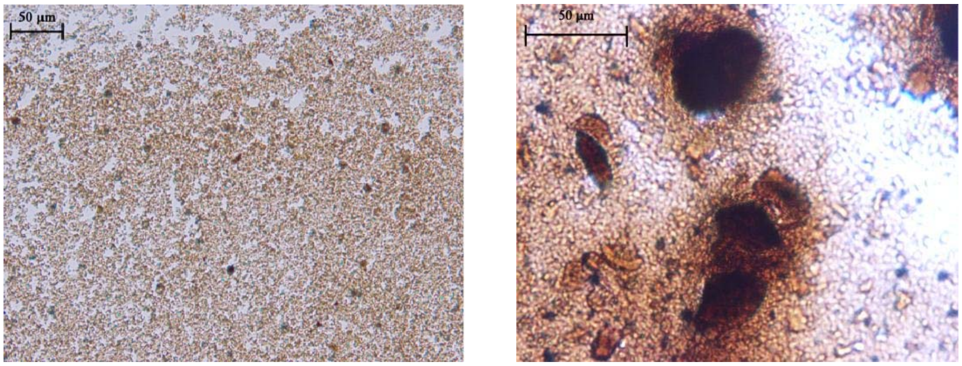


Figure **3-7** Illinois No. 6 coal /[bmim][CF_3SO_3]/tetralin dispersion at 300˚C under hydrogen at 1000 psi for 4 hours

Run 3 and 4 were performed at a high ratio of IL to coal, 8:2 by weight, with 2 parts tetralin by weight. This high concentration of IL might be impractical on an industrial scale, so experiments were performed at lower ratios of IL to coal, 3.5:2 (again with 2 parts tetralin). The yields of pyridine soluble material now decreases to about 54% (run 5). Including a catalyst (BI_3) did not change this yield significantly (run 6).

It was observed that even at 300˚C some slight discoloration of the IL occurred at longer times. So two experiments were performed at a lower temperature of 250˚C. A ten minute treatment resulted in a yield of about 31% pyridine soluble material, while an 8 hour treatment (with a lower IL to coal ratio, 3.5: 2 instead of 8:2) resulted in a very high yield of pyridine soluble material, almost 84 % on an ash free basis. Because very long treatment times would also raise practical concerns, experiments at an intermediate temperature, 280˚C, were also performed. The results of this work were also highly variable. Table 3-4 shows the results of these soaking experiments performed for 4 hours at this temperature, with a 3:2 ratio of IL to coal.

Two runs gave a pyridine soluble yield of near 95% and 97%, while a third run gave a yield of only 47%. Other experiments, described below, also gave a wide range of yields for reasons that will be considered in the discussion section.

Table **3-4** Pyridine extraction yield of low temperature soaking coal

Illinois No. 6 coal	Condition	Extraction yield (Mineral matter free basis)		
[bmim][CF_3SO_3] /Tetralin (3:2)	1000 psi H_2, 280˚C, 4hours	95%	97%	47%

Infrared spectroscopy was used to study the insoluble pyridine extraction from the highest yield sample. Figure 3-8 shows the spectrum. The strong bands between 1100~ 1000 cm^{-1} and near 500 cm $^{-1}$ are due to clays and silicates. It can be seen that there are weak bands near 1600 cm^{-1} due to aromatic groups and near 1700 cm^{-1} because of carbonyl, but these absorptions are very weak. The insoluble residue was largely mineral matter.

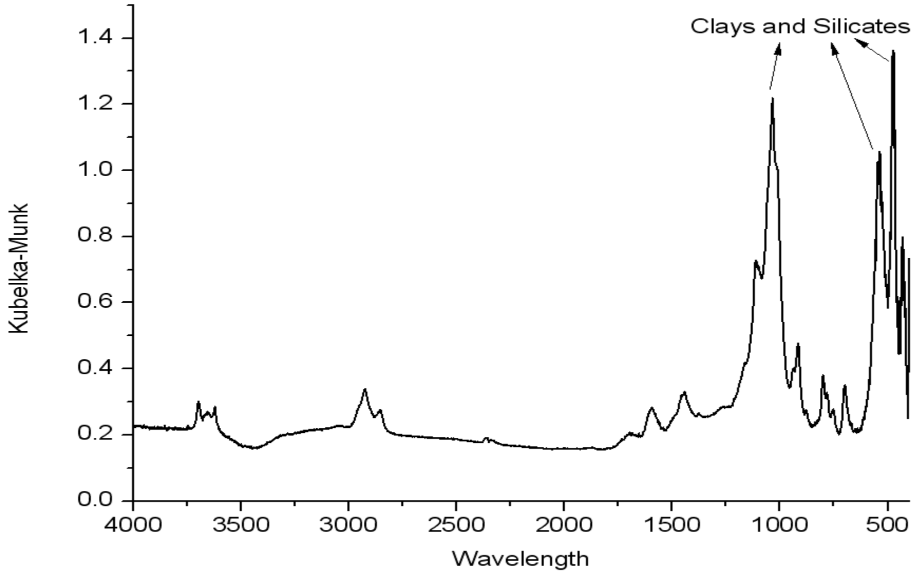


Figure **3-8** Infrared spectra of the pyridine residues obtained after "soaking" of Illinois No. 6 coal with [bmim][CF_3SO_3]/tetralin (~100% soluble in pyridine, daf basis)

3.3.4 Power River Basin (PRB) Coal

The micrographs in figure 3-9 show products obtained from the PRB coal samples treated with [bmim][CF_3SO_3] at 250°C under hydrogen at 1000 psi for 2, 4 and 8 hours in the presence of tetralin as a hydrogen donor. Compared to the untreated coal (figure 3-9 a), a 2 hours (figure 3-9 b) soaking treatment reduces the coal to a particle size less than 50µm, for the most part. The coal particles appeared to be uniformly distributed and the dispersed particles were agglomerated. The 4 hour treatment (figure 3-9 c) appeared to fragment the particles into very small pieces, many as small as 10µm, with even smaller particles also being present. After 8 hours treatment (figure 3-9 d), the sample consists of a smear of liquid like materials together with some agglomerated particles.

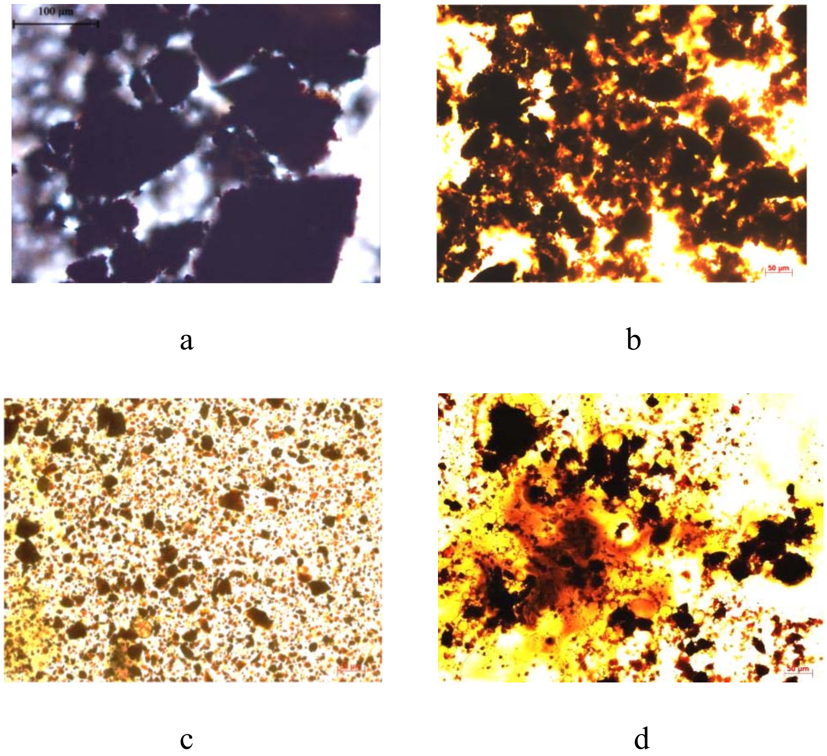


Figure **3-9** PRB original coal (a); PRB coal treated with [bmim][CF_3SO_3] at 250˚C under hydrogen at 1000 psi for 2 hours(b), 4 hours(c) and 8 hours(d) soaking experiment

The sample removal process from tubing bombs remained challenging. Instead of using warm water, pentane was used to wash and remove the samples. There was still some material left at the bottom of reactors, which was hard to remove. The pentane slurry mixture were directly transferred into a thimble, and dried at room temperature. The product was then soxhlet extracted with pyridine.

The pyridine extractability of the PRB coal for two runs under the same conditions (250˚C, 4 hours) is shown in table 3-5. In one run a very high yield of 80% (mineral matter free basis) pyridine soluble material was obtained (listed as No.1 in table 3-5). This result is helpful, because it indicates that heating with [bmim][CF_3SO_3] at a lower temperature (250˚C) is capable of fragmenting and solubilizing the coal. It means the dispersion and dissolution role of this type of IL works better with PRB coal at a lower temperature, such as 250˚C. However, the variability in the yield of soluble material is a concern.

Table **3-5** PRB coals/IL/tetralin heating at 250˚C under 1000 psi hydrogen pressure

	PRB coal	Condition	Extraction yield (Mineral matter free basis)
1	[bmim][CF_3SO_3] Tetralin (1:3:2)	1000 psi H_2 250˚C 4hours	80%
2	[bmim][CF_3SO_3] Tetralin (1:3:2)	1000 psi H_2 250˚C 4hours	43%

3.3.5 Adding $ZnCl_2$ as Catalyst

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)[13] . 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, so an industrially viable process that takes advantage of an acid catalyzed reaction has not been developed.

However, Lewis acids such as BI_3 and $ZnCl_2$ are soluble in [bmim][CF_3SO_3], so some experiments were performed in the presence of these catalysts. It was mentioned that BI_3 did appear to have a minor effect, but because of its sensitivity to water it is difficult to work with. Attention was therefore focused on $ZnCl_2$.

Experiments were performed at 250˚C, 1000 psi H_2 pressure in the presence of tetralin and $ZnCl_2$ for various times. The proportions of materials used and the amount of pyridine are reported in table 3-6. It can be seen that the yield of soluble material increased from about 32% after 10 minutes to 89% after 8 hours.

Table **3-6** Illinois No. 6 coal / [bmim][CF_3SO_3]/tetralin heated at 250˚C with zinc chloride as catalyst

Materials	Condition	Pyridine extraction yield(daf basis)
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3.5:0.5:2)	250˚C, 1000psi H_2, 10mins	32%
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3.5:0.5:2)	250˚C, 1000psi H_2, 2hours	60%
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3.5:0.5:2)	250˚C, 1000psi H_2, 4hours	49%
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3.5:0.5:2)	250˚C, 1000psi H_2, 8hours	89%

Increasing the soaking temperature to 280˚C did not change the yields of pyridine soluble material significantly, as can be seen from table 3-7. Two runs gave decent yields, 90% and 67% (by mass, daf), but a third run gave a yield of only 45% by mass (daf). However, during the course of this experiment it was observed that the hydrogen pressure dropped significantly, to 700 psi and this probably have certain influence on the yield.

Table **3-7** Illinois No. 6 coal / [bmim][CF_3SO_3]/tetralin heated at 250˚C with zinc chloride as catalyst

Materials	Condition	Pyridine extraction yield(daf basis)
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:2.5:0.5:2)	280˚C, 1000psi H_2, 4hours	90%
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3:0.1:2)	280˚C, 1000psi H_2, 4hours, Pressure drop to 700psi	45%
[bmim][CF_3SO_3], $ZnCl_2$, Tetralin (1:3:0.5:2)	280˚C, 1000psi H_2, 4hours	67%

Infrared spectra of the pyridine extraction residues were obtained, as show in figure 3-10 and figure 3-11. The spectrum of the (90 %) yield sample displays only weak bands near 1600 cm^{-1} due to aromatic groups and near 1700 cm^{-1} because of carbonyl groups. Bands between 1100 ~1000 cm^{-1} and bands between 600~500 cm^{-1} are due to clays and silicates. The spectra of both residues displays a weak band near 700 cm^{-1}, assigned to residual pyridine. Pyridine is very difficult to completely remove from residues and their extracts[15]. As might be expected, the spectrum of the residue from the highest yield sample is dominated by mineral bands, with only weak bands due to organic material. The bands due to organic material (e.g. 1600 cm^{-1}) are much more prominent in the spectrum of the lowest yield sample.

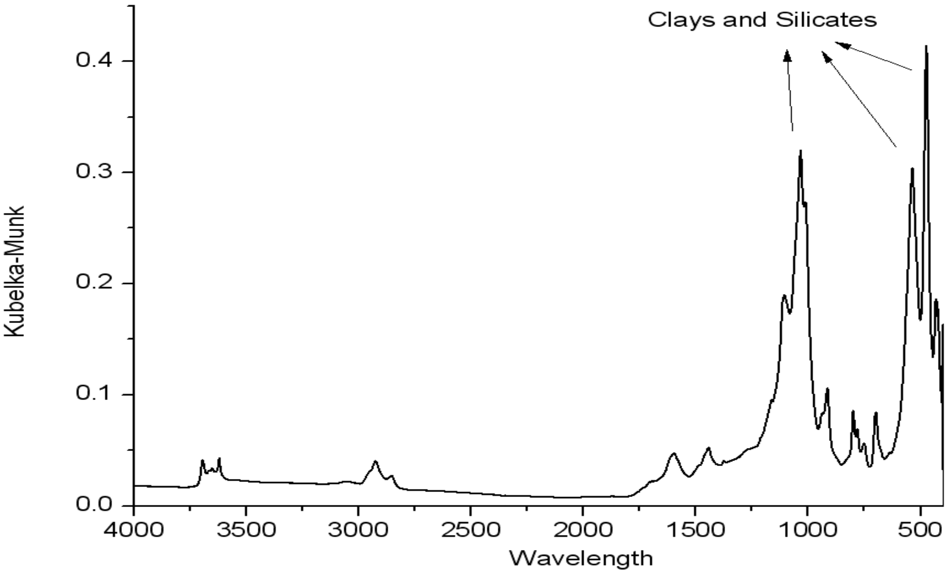


Figure **3-10** Spectra of pyridine residue of Illinois No. 6 coal / [bmim][CF_3SO_3]/ tetralin/ zinc chloride at 250°C (90% pyridine soluble, daf basis)

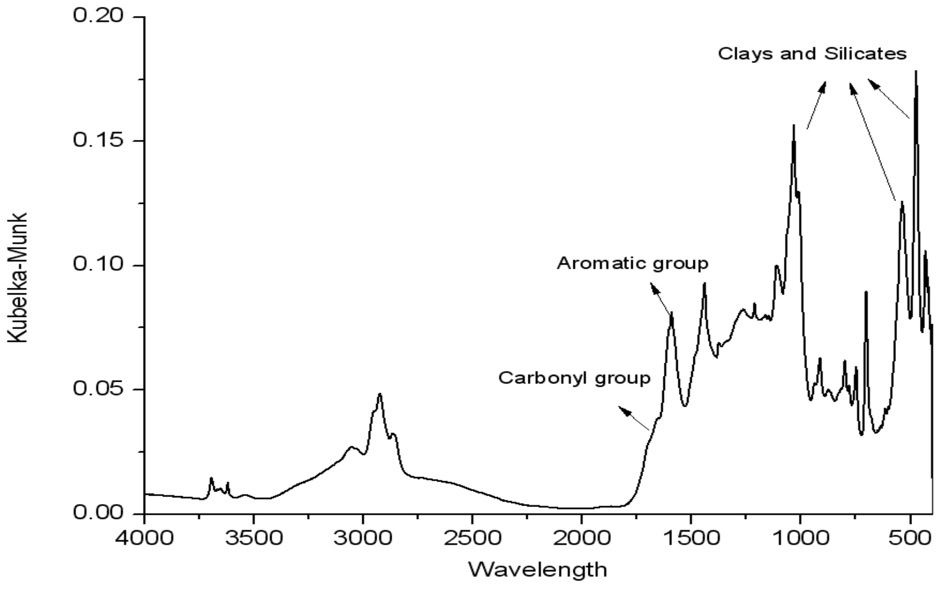
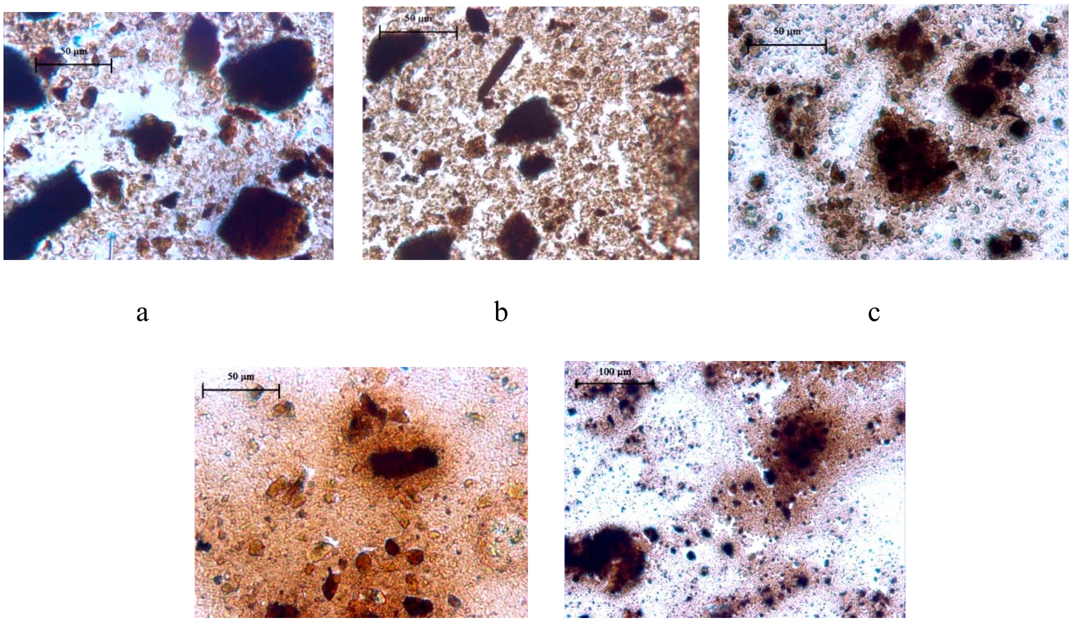


Figure **3-11** Spectra of pyridine residue of Illinois No. 6 coal / [bmim][CF_3SO_3]/ tetralin/ Zinc chloride at 250°C (67% pyridine soluble, daf basis)

Optical microscopy was used to study the dispersion or fragmentation degree in the ionic liquids treated products. The fragmentation varies with the heating time. The coal particles remain as large particles with short heating time. As seen from the micrographs in figure 3-12, with increasing time, the coal is dispersed into thinner and smaller particles. However, agglomeration also happens with fine dispersed particles.



a b c

d e

Figure **3-12** Illinois No. 6 coal , [bmim][CF$_3$SO$_3$], ZnCl$_2$, tetralin, heated at 250˚C for 10 minutes (a), 30 minutes (b), 1 hour (c), 2 hour (d), 8 hour (e)

3.4 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_a = 21-23) of the hydrogen at the C2 position. (i.e. the carbon between the two nitrogens). This could act to "shuttle" hydrogen from tetralin onto the coal. However, much more work will be needed to establish a mechanism. 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 was 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.

Because funding was stopped and ILs was expensive, we could only use small samples, hence the heterogeneity of coal could play a role. After the tubing bomb reaction, a slurry state mixture was usually obtained. However, in some cases, dark solid particles agglomerated in the bottom of the tube, which are hard to remove, although several different methods were tried. There was some sample loss when transferring samples from vials to reactor, then transferring the mixture from tubing bomb to thimble. Problems with tubing bombs were also one reason for the reaction variability. The bombs were old and to some degree unreliable. On one occasion, pressure drop was observed. In addition, ionic liquids are viscous liquids. When coal particles, tetralin and ILs are mixed together, the mixing of components may have been imperfect. The inconsistent distribution of components in the mixture during reaction may lead to different degree of reaction.

The highest yield obtained was close to ~100% (mineral matter free basis) when Illinois No. 6 coal mixed with [bmim][CF_3SO_3] and tetralin at 280˚C for 4 hour. The spectra of the residue were dominated by mineral bands with only weak aromatic bands. This result shows us that the hydrogenation and fragmentation of coal can occur at lower temperature with the aid of an ionic liquid. By adding zinc chloride as a catalyst to the system, and reducing the reaction temperature to 250˚C, 90% extract yield was obtained. The spectra of the residue also show strong mineral bands, which means the insoluble pyridine residue after reaction are mostly mineral matter.

3.5 Conclusion

Certain ILs can be used to disperse, fragment and partially dissolve coals as small fragments or particles. Heating coal at relatively low temperatures (< 300˚C) in Ionic liquids such as [bmim][CF_3SO_3] and [bmim][BF_4] in the presence of tetralin and hydrogen results in significant fragmentation. However, the results varied significantly. The FTIR results show that, the spectrum of the residue from the highest yield sample is dominated by mineral bands, with only weak bands due to organic material. The bands due to organic material (e.g. 1600 cm^{-1}) are much more prominent in the spectrum of the lowest yield sample. This indicates that with the aid of ionic liquid, hydrogenation of coal can occur at relatively low temperatures, but more work is needed to both understand the mechanism and obtain consistent results.

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CHAPTER 4

Summary and Conclusions

Coal is heterogeneous material. When exposed to certain solvents, swelling of coal or dissolving of coal may occur. Certain Ionic liquid can disperse, fragment and partially dissolve coals as small fragments or particles (on the order of microns in some cases). The Ionic liquid [bmim][Cl] has a significant effect on Illinois No. 6 when contact at 100˚C, a black slurry was obtained and it was also observed that certain amount of coal dissolves in this ionic liquid. Optical micrographs showed the coal had fractured into smaller size particles. However, this type coal dispersion and solubilizing in ionic liquid have not been observed, so further studies were carried on for different ionic liquids and coals (Illinois No.6 coal, PRB coal and Upper Freeport coal). Coal mixture with ionic liquids containing 1-butyl-3-methylimidazolium $[bmim]^+$cation with different types of anions, and also ionic liquids containing $[Cl]^-$ anion with different substituent length cation were studied. What is interesting, is the ionic liquids that broke up and dispersed the coals (Illinois No. 6 coal and PRB coal) at 100˚C to the greatest amount both had chloride $[Cl]^-$ counterions. The micrograph of coal ionic liquids mixture also different because of the degree of dispersion, fragmentation and viscosity of ionic liquids differs, but basically show the dispersion and fragmentation of ionic-liquid treated coal comparing to original coal particles.

Imidazolium with larger anions did not disperse and fragment coals to the same extent. Upper Freeport coal was anomalous, the coal/ionic liquid suspension obtained when mixing with [bmim][Cl] when heated at 100˚C, was different to what was observed with Illinois No. 6 coal , Wyodak coal and PRB coal, significant fragmentation and dispersion was not observed. When

Illinois No. 6 coal mixed with long alkyl chain and benzyl chain substituted imidazolium ionic liquids, a viscous black/ slurry gel obtained when coal/ionic liquid mixtures were heated up to 100˚C, the mixture remained as a viscous gel upon cooling to room temperature. NMP was added to the coal ionic liquids mixture, and different extract yields were obtained. The Illinois No. 6 coal / [bmim][Cl], and Illinois No. 6 coal / [octylmim][Cl] mixture, gave very large yields in NMP, more than 40% of extractable materials. For 1-ethyl-3-methylimidazolium chloride ionic liquid/coal mixture, the lowest yield of NMP soluble materials was obtained about 12%, which is smaller than the original Illinois No. 6 coal when directly treated with NMP, about 15%. The increase in solubility was suggested as the ability of certain ILs to break coal into small particles, releasing trapped materials. Hydrogenation also took place, higher yields of pyridine soluble materials were obtained after coal was treated with [bmim][CF_3SO_3].

For the highest yield product, the pyridine residue spectra were mostly dominated by mineral bands. This indicates that it is possible to solubilize coal at relatively low temperatures (280˚C) with the aid of ionic liquids. By adding zinc chloride as a catalyst, at 250˚C, large amount of soluble materials were obtained with corresponding spectra showing mainly mineral bands in the pyridine residue. Ionic liquid may facilitate the hydrogen transfer reaction rate during liquefaction by reducing coal particle size.

Optical microscopy used to observe the particle dispersion and fragmentation. It was observed that certain ILs can fragment Illinois No. 6 coal as very fine dispersed particles. The degree of fragmentation or dispersion varies based on the ionic liquids used, the treatment time and temperature. This may be the result of ionic liquid disrupt the original coal network interaction.

The interaction between coal with ionic liquids and other components in the system remains difficult to explain. Ionic liquids can engage in a wide range of intermolecular interactions, which makes the identification of the forces involved in fracture and dispersion difficult. There may be some electrostatic interaction between ILs and mineral surfaces and any chelated ions in the coal and also ion-dipole and dipole-dipole interactions, together with hydrogen bonding. It is also well-known that ILs can engage in π-cation interactions, disrupting π-cation interactions also appear as cross-links in various coals. It is possible that the replacement of metal cations with bulky IL groups plays a role in the fracturing and dispersion.

The fine contact between coal and ionic liquid is required. There is one possible explanation toward the mixing process that, when the mixing is highly effective, which means each particle in mixture contact well with each other, and then we possibly can get more fragmented coal particles which dispersed in ionic liquid. Moreover, for coal, ionic liquid, and tetralin mixture, a well-contact mixture may result in more dispersed fractured coal particles. Therefore, the possibility and ability of obtain well mixed reactants are important for the further processing.

Suggestion for Future Work

When coals are mixed with various types of ionic liquid, different phenomenon are observed. The temperature, heating hours and plus pressure, catalyst are all factors that affect the dissolution and fragmentation of coal in ionic liquids. However, the interaction between ionic liquid and coal is remains unclear. A further investigation of the mechanism of interaction between ionic liquids and coal are necessary to understand and control the process of fragmentation and dissolution.

Due to the viscosity of ionic liquids, the filtering process is a major problem determining solubility. Several different types of filtration were tried. NMP or pyridine was used to dilute the coal/ionic liquid mixture, and it was found that soluble materials can be obtained in NMP or pyridine. Most of the work reported here involved the IL, Illinois No. 6 coal and PRB coal. A much wider range of coals and ILs need to be systematically studied.

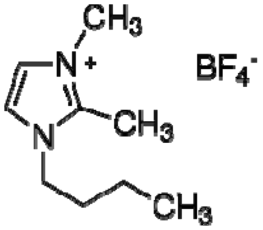
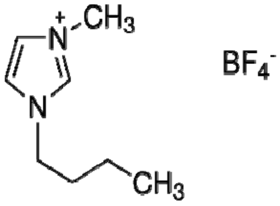
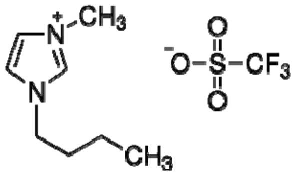
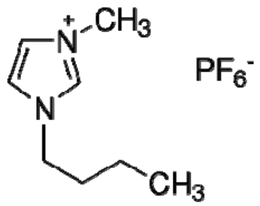
"Soaking" at elevated temperatures, but less than 300˚C, breaks down coal particles significantly. However, the mechanism which leads to fragmentation of coal and fragmentation kinetics under these conditions is not understood yet. Even though the results varied, it was demonstrated that a high proportion of pyridine soluble materials could be obtained. These need to be confirmed on a larger scale with better liquefaction equipment. Optical microscopy was used here to observe coal particles, and better technique need to be used to characterize and quantify coal particle size and distribution. The products after liquefaction probably need further handling. More research is need on strategies to reduce temperature and reaction duration, and pressure requirement to minimize operating cost while obtain desirable product. Better techniques which can optimize the mixing of reactants are also required. A sequence of valuable data on time and temperature may provide insights into the time-temperature relationship of the mixing system.

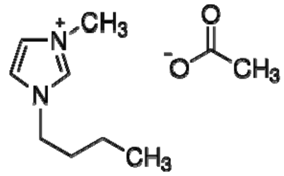
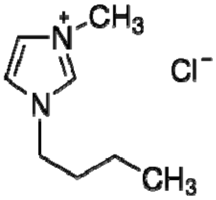
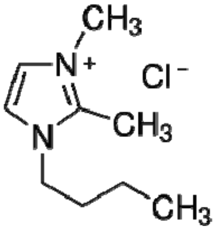
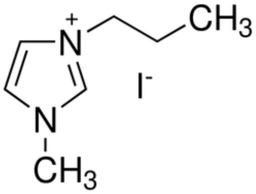
Higher pyridine soluble materials were obtained by adding zinc chloride as catalyst. The effect of combining ILs with Lewis acid catalysts would also be an important area for future work.

In summary, ionic liquids can engage in a wide range of intermolecular interactions with coals and can be used in dispersion, fragmentation and liquefaction of coals. However, this process needs more practical optimization to achieve better control over reaction process and for further coal applications.

APPENDIX

Ionic Liquid Category

Ionic liquid name		Empirical Formula		Company and catalog No.
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[BDiMIM] [BF_4] $C_9H_{17}BF_4N_2$ $[C_9H_{17}N_2]^+BF_4^-$		Mr: 240.05 pale yellow liq.	Fluka Cat. 04383
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM] [BF_4] $C_8H_{15}BF_4N_2$ $[C_8H_{15}N_2]^+BF_4^-$		Mr: 226.03 yellow liq.	Fluka Cat. 39931
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[BMIM] Otf $C_9H_{15}F_3N_2O_3S$ $[C_8H_{15}N_2]^+CF_3SO_3$		Mr: 288.29 d. 1.292	Aldrich Cat. 76420
1-Butyl-3-methylimidazolium hexafluorophosphate	BMIM-PF_6 $C_8H_{15}F_6N_2P$ $[C_8H_{15}N_2]^+ PF_6^-$		Mr: 284.1 d. 1.38 Light	Aldrich Cat. 70956

			Yellow, Liquid	
1-Butyl-3-methylimidazolium acetate	$C_{10}H_{18}N_2O_2$ $[C_8H_{15}N_2]^+CH_3O_2^-$		Mr: 170.21 d. 1.055	Aldrich Cat. 39952
1-Butyl-3-methylimidazolium chloride	$C_8H_{15}ClN_2$ $[C_8H_{15}N_2]^+Cl^-$		Mr: 174.67 white to off-white solid	Fluka Cat. 04129
1-Butyl-2,3-dimethylimidazolium chloride	$C_9H_{17}ClN_2$		Mr. 188.70	Fluka Cat. 78194
1-methyl-3-propylimidazolium iodide	$C_7H_{13}IN_2$		Mr: 252.10	Fluka Cat. 49637