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The Graduate School
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**FRAGMENTATION OF COAL AND IMPROVED
DISPERSION OF LIQUEFACTION CATALYSTS
USING IONIC LIQUIDS**

A Thesis in
Energy and Mineral Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

August 2011

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ABSTRACT

Coal has been utilized for coal-to-liquid fuels and coal-to-chemical industries both historically in South Africa and recently in China. Abundant bituminous and low-rank coal reserves in the US make them potential sources of an alternative to the oil derived petrochemical industry. Consequently, it is desirable to evaluate new processes for conversion of solid coal-to-clean liquid fuels. One such approach may utilize ionic liquids, a relatively new addition to industrial processing. Ionic liquids can engage in a wide range of intermolecular interactions with coal that may result in alternative approaches to fragment, disperse, and dissolve coal. They have negligible vapor pressure, are non-flammable, and would be easier to handle than traditional solvent approaches.

The goal of this work was to explore the ability of certain ionic liquids (ILs) to fragment, disperse and partially dissolve coals in order to allow a better contact with micron size catalyst particles prior to direct coal liquefaction. Attention was focused primarily on the ionic liquid 1-butyl-3-methylimidazolium chloride [bmim][Cl] and the coals studied were Illinois No.6 bituminous coal and Power River Basin subbituminous coal. Coal was mixed with ILs in a ratio of 10% by weight at 100 °C in an oil bath without agitation. Fragmentation was evaluated by optical microscopy.

It was found that the IL [bmim][Cl] fragmented and dispersed Illinois No. 6 coal to a remarkable extent. Optical microscopy demonstrated that the -100 mesh particles were reduced in size to <10 microns. Other solvents are also known to fragment coal but none are capable of such a large particle size reduction. PRB subbituminous coal tested also fragmented extensively, but to a lesser degree than Illinois No. 6 coal. Fragmentation was probably a result of ability of ILs to fragment, dissolve and disrupt intermolecular interactions in these coals. Such dispersion is likely beneficial for liquefaction where coal and catalyst interactions are important for both yield and quality.

The ability of [bmim][Cl] to fragment the coal was then used to obtain good contact with commercially obtained 2 μm MoS_2 catalyst. Single-staged liquefaction was performed at 425 (or 400) $^{\circ}\text{C}$ for 30 min. and tetralin was used as hydrogen-donor solvent. As a result of close contact, a subsequent liquefaction under standard conditions resulted in a product that was almost completely soluble (99%, dmmf) in pyridine. The yields of soluble material obtained for two subbituminous coals were less, but were comparable to those obtained in work reported in the literature that used soluble catalyst precursors. Surprisingly, in some experiments, oil yields were very high (50%). The oils are most desirable products in liquefaction. Thus use of ILs can improve the yield and or the quality of liquefaction products. Also it was shown that IL recovery is possible and it was concluded that this approach should be explored as a direct coal liquefaction method.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1. Goals of this Research and Organization of Thesis

Energy security is an important issue for the sustainable development of the global community. Advanced-coal technologies will increasingly play a significant role in addressing national energy challenges. For example, China has recently adopted advanced-coal gasification, direct coal liquefaction, indirect coal liquefaction, and Integrated Gasification Combined Cycle and co-production systems. In western China, seven coal-to-liquids (CTL) demonstration plants are being developed and total budget of these plants is \$12 billion US dollars [1]. Also SASOL in South Africa operates the world's largest commercial Fischer Tropsch coal-to-liquids facility at Secunda, with a capacity of 150,000 barrels per day [2]. Coal resources are more widely dispersed than oil reserves. Also, the U.S. has large coal reserves [3-4]. North American coal reserves account for around 26% of total world coal reserves [5] about 96% of which were located in the U.S. Therefore, coal has the potential to be a significant player in CTL and coal-to-chemicals. It is thus desirable to evaluate new processes for conversion of coal to clean liquid fuels [4, 6].

The dramatically lower prices which currently are available for low-rank coals compared to bituminous coals suggest that their use as feedstock for coal liquefaction may be attractive. However, the issue is complicated by low-rank coals producing lower yields of saleable products

per ton material processed [7]. The positive characteristics of low-rank coals are their relatively low cost, high reactivity, and natural (mineral matter and ion-exchanged) catalytic activity. Unfortunately, processing of low-rank coals results in higher gas yield partially due to high moisture content, lower liquid yields, and possibly a requirement for higher process pressure [7].

One of the most important differences between coal and petroleum is that coal has a lower H/C ratio. A typical bituminous coal has an atomic H/C ratio of 0.7, while petroleum products have values around 1.2 [3]. Therefore, to produce liquid fuels it is necessary to add hydrogen directly (liquefaction) or indirectly (gasification). The first process that added hydrogen via direct liquefaction was the Bergius method in 1911 [4]. In this method, pulverized coal or coal-oil slurries were reacted with gaseous hydrogen at high pressures and high temperatures. Operating liquefaction at such a high pressure and temperature is not economically desirable. Since more severe operating conditions require more stringent equipment requirements, this results in higher initial costs and, often, higher maintenance costs. Because of these reasons coal-derived liquid fuels were not economically competitive with petroleum-based products in 1960's [8]. Today, even though China only has half of the U.S. coal reserves, Chinese government refuses to be dependent upon imported crude oil and is building coal-to-liquids (CTL) plants to provide electricity, diesel, gasoline, jet fuel, substitute natural gas, fertilizer, hydrogen and other chemicals [9]. Total investment of four CTL and two chemical plants is 10 billion USD in China [1].

Most coal liquefaction research in the past 70 years has been focused on strategies to reduce temperature and pressure requirements. Capital costs could be reduced by lowering process

requirements such as reduced temperature, and pressure. Operating cost could be reduced by reducing gas formation, reducing high hydrogen consumption and minimizing retrogressive reactions that form undesirable high molecular weight materials. However pulverizing coal is energy intensive and generally inefficient with regard to energy consumption. The goal here is ionic liquids (ILs) were used to fragment and disperse coal. Well-fragmented and dispersed coal is likely to have improved contact with dispersing MoS_2 catalyst and this enhances production of soluble material and reduces retrogressive reactions. Optical microscopy, traditional coal liquefaction and traditional Soxhlet extractions are the proper approaches towards the purpose. Molybdenum-sulfur catalysts have been widely used in coal liquefaction but they need to be well dispersed using several treatments to function effectively. Within direct liquefaction approach pre-treating coal with IL $[\text{bmim}][\text{Cl}]$ in the presence of an off-the-shelf MoS_2 liquefaction catalysts reduces the number of process steps. ILs may this improve liquefaction yields without these additional steps. Thus IL $[\text{bmim}][\text{Cl}]$ were evaluated to determine fragmentation of bituminous and subbituminous coals. Solubility yields determined after liquefaction and product distribution determined by sequential Soxhlet extraction with pentane, toluene, THF and pyridine, respectively.

The work presented in the following text covers a brief literature review of coal structure, liquefaction methods and catalysts in chapter 2. The ability of ILs to fragment and dissolve coals will be examined in chapter 3. Chapter 4 shows that certain ionic liquids can be used to fragment, disperse and partially dissolve coal to such an extent that good contact can be made with commercially obtained micrometer-size molybdenum disulfide particles by simply mixing these particles with ionic liquid/coal dispersion. Good liquefaction yields under standard

conditions are obtained using this approach. Also it is reported that recovery and reuse of ILs can be readily accomplished.

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CHAPTER 2

LITERATURE SURVEY

2.1. The Classification of Coal by Rank

2.1.1. What is Coal?

Coal is formed from accumulation of plant materials, organic precursors, ranging from proteins to carbohydrates, lipids, glycosides, resins, and lignin, that were preserved from complete decay and later altered by various chemical and physical processes in an anaerobic environment [1-2]. Because of the variety in these organic precursors and depositional and maturation differences, coal is a highly heterogeneous material. Coal formation occurs in two processes; diagenesis and catagenesis. First, during diagenesis, organic precursors decompose; proteins undergo hydrolysis to smaller polypeptides, and on extensive hydrolysis, decompose all the way to the constituent amino acids, carbohydrates and glycosides also undergo hydrolysis to smaller polysaccharides and eventually to simple sugars [3-4]. The hydrolysis products form compounds called humic acids. After, putrefaction processes components of this mixture react generating an insoluble high molecular-weight material called kerogen, which can be classified into three types based on the nature of the original organic source material. These three types of kerogens have different chemical compositions; types I and II kerogen are hydrogen-rich and predominantly straight chain compounds [4]. In contrast, type III is oxygen-rich and contains high amounts of aromatic compounds [3-4]. Subsequently, kerogen undergo catagenesis process under anaerobic

conditions at higher temperatures and high pressure. At the end of the catagenesis process type I and II kerogen is transformed into natural gas and petroleum, while type III kerogen is converted primarily to coal [3].

Coal maturation is represented by the van Krevelen diagram during the catagenesis which essentially classifies coal by atomic H/C ratio versus atomic O/C ratio [5]. Because of oxygen and hydrogen removal, the ratios start to decrease during the catagenesis progresses. Peat, brown coal, lignite, subbituminous, bituminous, and anthracite have increasing carbon content and decreasing hydrogen and oxygen content. Compared to lignites, bituminous coals have higher carbon content, lower oxygen content, and higher values of aromaticity, (f_a) and ring condensation, (R). The progression of changes accompanying the increase in coal rank is an evolution of the structure toward graphite. The structure of graphite being 100% C with and $f_a=1$, $R=\infty$ [3].

The ASTM rank classification of coals, is based on the basis of either volatile matter or fixed carbon reported on a dry-and mineral-matter-free basis, and on the calorific value (values lower than 14,000 Btu/lb) reported also on a moist, mineral-matter-free basis [3, 6]. With increasing rank from lignite to bituminous coals, the number of oxygen groups decreases and the ring system generally become slightly more condensed [7-9]. Low-rank to bituminous coals are of interest to liquefaction, the subject of this thesis. Anthracite coals do not respond favorably, even to catalytic hydrogenation [10].

The coals that produce the best yields for liquefaction are the high-volatile bituminous and subbituminous ranks, but the best yields produced can be optimized within this rank range by

changing the pressure, temperature, and reaction time [11-14]. Lignites can also be liquefied, but produce more CO_2 and H_2O because this coal contains higher percentages of oxygen than bituminous and subbituminous coals, and liquid yields are typically smaller as a result [12-13]. Another challenge in the liquefaction of lignites is that expensive H_2 used in removing the oxygen as H_2O . There has been no real success in the liquefaction of anthracite either [11-14]. Generally, it is known that anthracites are very hard to liquefy [11]. Hirsch's [15] structures for high-volatile bituminous and low-rank coals are "open" and "liquid-like" and have more reactive sites (cross-links made of carbon, hydrogen, and oxygen groups attached to aromatic cluster) to generate radicals and are more accessible to liquefaction reagents [15]. Figure 2.1 shows Hirsch's models of coal ranks [15].

With increasing rank, the number of oxygen groups decreases and the ring systems generally become more condensed and therefore have fewer reactive sites [7-8, 16]. Anthracites and medium-volatile and low-volatile bituminous coals have larger sized aromatic clusters because of less hydrogen and oxygen content, and accessibility to reactive sites is limited [16].

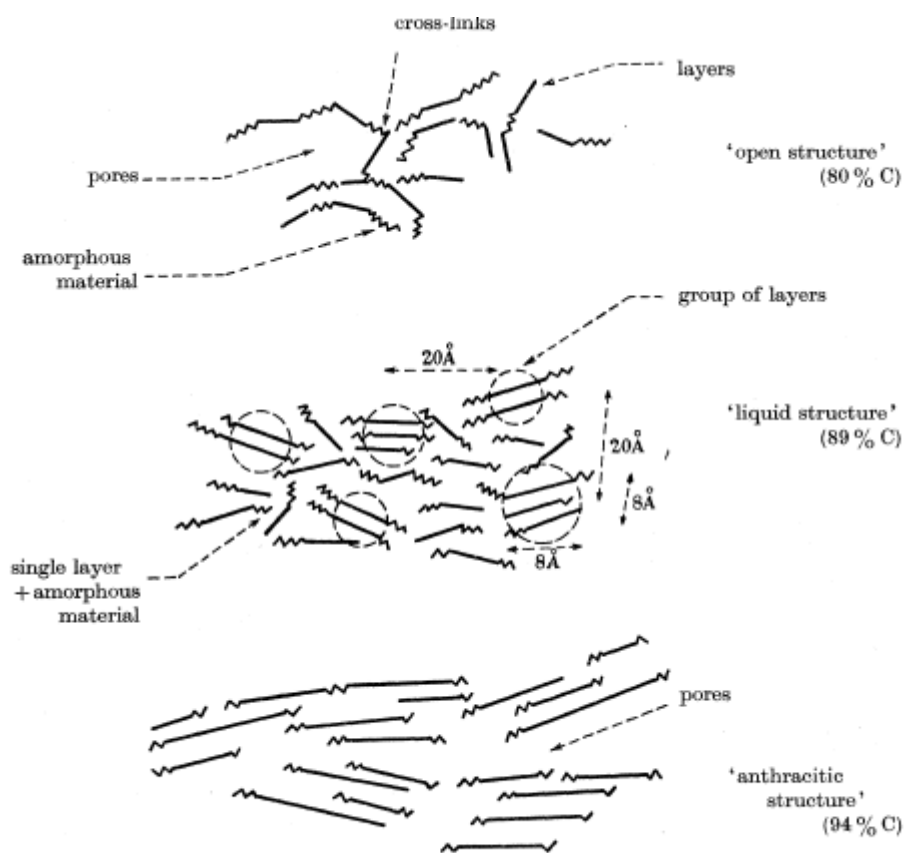


Figure 2.1: Hirsh's model of coal ranks

Source: Hirsch, P.B., Mathematical and Physical Sciences, 1954. 226(1165): p. 143-169.

2.1.2. Coal Petrography:

Coal is made up of inorganic (minerals) and organic (macerals) constituents. The organic part, which has components that can be identified microscopically, is macerals. Macerals are described and classified on the basis of optical appearance, morphology, size and their apparent origin from different botanical structures in the original plants that formed coal [3]. The study of macerals is coal petrography. Other sources explain how the different macerals have a different

chemical reaction based on their origin [3, 17]. The most reactive maceral group for coal liquefaction are vitrinite, with liptinite somewhat reactive and inertinite is generally the least reactive maceral group [3]. According to Joseph et al. removing of inertinite prior to liquefaction can improve process efficiency [18].

Using density gradient centrifugation the three major maceral groups, were separated from Kentucky coal [19]. The parent coal had 36.7% vitrinites, 32.9% inertinites and 30.4% liptinites. Liptinite concentrate was 88.6% liptinites, vitrinite concentrate was 75.4% vitrinite and inertinite concentrate 92.0% inertinite. The liquefaction of parent coal and three maceral concentrates was determined under 5.5 MPa H_2 , 15 min residence time, and three different reaction temperatures, 658, 700 and 718 K (385, 425, and 450 °C). Liquefaction conversion data obtained show that each of the three maceral groups has a lower conversion than parent coal at 658 K (385 °C). While all maceral conversions were low; vitrinite group achieved the highest conversion of the three maceral groups. Inertinite and liptinite reached almost the same conversion. With increasing temperature (700 and 718 K) liptinites concentrate samples have the highest conversion. In the parent coal residues, the inertinites slightly altered inertinites and granular residue. Also in the parent coal residue obtained from liquefaction at 658 K, liptinites were major components and authors proposed that this indicates liptinites were only slightly reactive at this temperature. Furthermore, the majority of the vitrinites in the parent coal converted to soluble products and granular residue. The vitrinite concentrate residue analysis indicates that the major component at 658 and 700 K was vitroplast and granular residue contribution was minimal in the residue. However, at 718 K, vitroplast residue amount decreased and granular residue amount increased. These data explained that parent coal conversion should decrease with increasing

reaction temperature. The oil yield derived from the liquefaction of the maceral concentrates was almost the same at 658 K, but at higher temperatures at 700 and 718 K, liptinites produced the highest oil yield and also the highest yield of polar material in the oil fraction. As a result, the conversion of the three maceral groups concentrate sample was similar at low temperature. When the reaction temperature increases, the conversion of the macerals shows the following trend: liptinites > vitrinites > inertinites [19].

2.1.3. Minerals in Coal:

More than 125 minerals have been identified in coal [3, 20]. This inorganic matter includes clays, carbonates, silica, sulfide, and pyrite, and the inorganic content is reported in two different ways; as ash values or mineral matter content. The ash value is measured by proximate analysis, where the coal is subjected to combustion and the remaining ash mass is determined.

There are effects of mineral matter on the progress of coal liquefaction. Mineral matter catalyzed hydrogen gas consumption and other reactions of coal and its products [21]. Low-rank coals contain significant amounts of oxygen [21]. Some of this oxygen is present as carboxyl groups that can act as ion-exchange sites [22-23]. Thus, low-rank coals often contain significant amounts of calcium, sodium, magnesium and some potassium cations on carboxyl ion-exchangeable sites [22-23]. According to Joseph et al., these cations, especially calcium, can inhibit hydrogen transfer from the hydrogen donor solvent or H₂ gas to the coal free radicals, thus promoting the retrogressive reactions [22]. Acid demineralization, removal of cations in low-rank coals, especially for subbituminous coal, increases coal reactivity, liquid yield in

liquefaction [24] and pyridine extraction yield [23, 25], also decreases conversion at long conversion times because of increases in both regressive and forward reactions [21]. Demineralization has different effects on the liquefaction of coal depending on the coal type and rank [21-23]. Commonly found coal minerals can be grouped into six families; Clay, carbonates, silica, sulfide, salt and sulfates [3].

Clay minerals (aluminosilicates) are usually the predominant inorganic constituents associated with coal, often accounting for 50% of the total mineral matter [17]. Kaolinite, montmorillonite, illite and mixed layer illite-montmorillonite are the mostly common clays in coal [3, 17, 26-27]. Clays are hydrous oxides of aluminum and silicon, which contain a variety of other cations in the structure. The hydrous clay minerals are built up of tetrahedrally (Si, Al, Fe^{3+}) and octahedrally (Al, Fe^{3+} , Fe^{2+} , Mg) coordinated cations organized to form either sheets or chains [28]. Clays supply aluminum and silicon to the coal and to the ash along with lesser quantities of other elements such as potassium [3, 17].

Carbonates are salts of iron, magnesium, and calcium, or mixtures of these elements. Carbonates form by precipitation caused by direct reaction or by pH change [3, 17].

Silica in coal is in the form of quartz and usually can account for up to 20% of the total mineral matter in coal [3, 17].

Sulfide minerals of particular importance here are the pyrite group, FeS_2 , which is essentially composed of metal disulfides that occur in different crystalline forms [29]. Sulfides generally amount to less than 5% of the total mineral matter in most coals. Sulfide minerals in coal are

considered to be good catalysts in the hydrogenation of coal to produce liquid fuels [3]. The most significant effect is the acceleration of pentane-soluble oils formation during liquefaction [30].

Salt is fortunately rare in United States coals [17]. Salt can cause enhanced corrosion of metals [3].

Sulfates are often present in low concentration in most U.S. coals [3, 17]. The principle sulfates are those of iron and calcium [3].

2.2. Coal Structure and Coal Liquefaction:

Direct liquefaction is the conversion of coals to liquid and gaseous products without the intermediate formation of synthesis gas. In solvent liquefaction, coal is liquefied in the presence of a solvent medium at temperatures usually in the region of 400-450 °C and commonly under hydrogen pressure 1000 psi (7MPa) [10, 31]. Liquefaction takes place in two steps; solubilization (dissolution and depolymerisation) and reduction in molecular weight and heteroatom removal (upgrading) [10, 32]. 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, and hydrogenation to produce products [33]. During dissolution, considerable amounts of oxygen and sulfur are removed as gases. Remaining nitrogen, oxygen and sulfur containing groups are eliminated with catalytic upgrading [10].

Generally, catalysts need to be added to obtain significant liquid yields for many coals [34]. “Catalysts” aid “depolymerized” coal and liquids formation through addition of hydrogen to cap thermally produced coal radicals. They can also help improve the quality of liquids via

generating lower molecular weight compounds, for example asphaltenes to oils and gas, with the addition of hydrogen from a hydrogen donor solvent such as a tetralin (THN) or H₂ gas [10, 34-36].

When coal is liquefied, three main products are produced: gases, composed mainly of CO and CO₂, light hydrocarbons; solids, composed of altered mineral matter and a largely organic component; and liquids, which contain a variety of aromatic and aliphatic hydrocarbons [11, 21]. In most instances, the products are removed from the reactor (a tubing bomb for laboratory batch analyses) with a solvent and extracted with that solvent to produce a residue and a liquid product. The liquid is subsequently separated by solvent fractionation: mainly the preasphaltenes, the asphaltenes, and the oils. The oils are hexane-soluble and the most desirable products [11, 21]. The solvent used to separate the products into preasphaltenes is usually tetrahydrofuran (THF) [11], and, if required toluene and/or pyridine to be used to determine an intermediate fraction (asphaltenes).

2.3. Catalyst in Coal Liquefaction:

Coal liquefaction catalysts can be divided into two groups: dissolution catalysts and supported catalysts. The latter are used to upgrade primary coal liquids to increase the yield and quality of distillates and liquid products [10, 36]. Catalysts are used to activate molecular hydrogen or otherwise transfer hydrogen to cap these highly reactive radicals. If a catalyst is present, progressive and orderly molecular weight reduction predominates at temperatures where kinetics

favors hydrogenation. If catalyst is not present, formation of coke-like products and gases tends to be favored; also catalysts must be in an active form [10, 36-37]

Dissolution catalysts offer an advantage in that their more complete contact with the coal surface and the initial dissolution products makes them better suited to activating and transferring hydrogen. They are used to promote the breakdown of the coal structure to liquid product. Such catalysts are therefore used in a form where they impregnate the coal and normally these catalysts are used at concentrations up to a few mass percent [10, 36].

Because of the required intimate contact between dissolution catalysts and coal, unlike supported catalysts, they are difficult to separate and recover for reuse [36]. For this reason, such catalysts typically low cost or used at low concentrations. As the catalysts are dispersed through the liquefaction products, they may be partially recycled with the recycle solvent stream. Thus, the net catalyst consumption might be reduced, provided that the recycled catalyst retains some activity [10]. Dissolution catalysts are also known as dispersed, slurry, homogeneous, disposable and once-through catalysts [10].

Supported (heterogeneous) catalysts have been used for upgrading to dissolution products (primary coal liquids) to increase distillate yields and achieve some further level of heteroatom removal. These catalysts are applied to coal liquids with a combination of the Co, Ni, Mo and W, together with promotional additives. They are distributed over a porous support of alumina or silica-alumina. These catalysts must be converted to their sulfide form to achieve an active form [36].

The original developments in liquefaction catalysis in Germany during the earlier part of this century have been described in some detail by Wu and Storch [14] and Donath and Hoering [38]. The reader is also referred to the review by Weller [39] which traces the development of liquefaction catalysts, with a particular focus on molybdenum [10, 14, 38-40]. Molybdenum was first used in commercial-scale plants in Germany for the hydrogenation of brown coal tar and brown coal [38]. Initially, finely ground molybdenum oxide was used for brown coal tar hydrogenation. Later, it was found that supported Mo catalyst, formed by impregnating brown coal char with a solution of ammonium molybdate, was an effective catalyst at Mo concentrations below 1% [38]. The char was first treated with dilute sulfuric acid to remove calcium compounds in char. Most of the calcium in low-rank coals is in the form of salts of humic acids [41]. These calcium humates decompose in the liquefaction reactor to form calcium carbonate [41]. The calcium is ionically bonded to carboxylic acid and sometimes phenolic groups in coal [41]. These groups are weak acids and calcium can be ion-exchanged by washing with dilute acid treatment. Brown coal was liquefied using 2 wt% of Mo introduced as ammonium molybdate [38]. Subsequently, the Mo concentration was reduced to levels as low as 0.05 wt% by treating the coal with sulfuric acid. Catalyst and acid were sprayed on the coal before drying [10, 38].

Sulfiding the catalyst by the addition of sulfur as CS_2 greatly improved the yield of hexane-solubles when processing low-sulfur subbituminous coal [10]. The effect of Mo sulfiding is quite dramatic and stresses the need to convert the catalyst precursor to its active form. The $\text{Mo}+\text{CS}_2$ system is evidently superior to pyrite [10, 42-43].

Bituminous coal liquefaction is considered to be more difficult, due to the higher proportion of asphaltenes generated [10]. High concentrations of asphaltenes in the recycled oils increase the viscosity of the coal-oil slurry and contribute to regressive reactions during liquefaction.

2.3.1. Dispersed Hydrogenation Catalysts:

Dispersed catalysts offer an advantage, in that their more complete contact with the coal surface and the initial dissolution products make them better suited to activating and transferring hydrogen to the sites where it is needed [10, 37]. Sulfide catalysts have been dispersed directly on the coal surface [44]. Impregnated or ion-exchanged onto the coal surface may occur through their interaction with oxygen functional groups [44]. The use of highly dispersed catalysts reducing the amount of catalyst required. Molybdenum catalysts have been the focus of much of this work [44]. Derbyshire et al. pointed out that for high liquefaction activity, molybdenum must be present as MoS_2 and that the conditions used for impregnation can strongly influence catalyst dispersion and activity [43]. This approach therefore required additional steps to generate the active form.

In solvent-free liquefaction, there is a distinct benefit to impregnating the catalyst precursor on the coal over its addition as a powder [45]. Also Mo activity is increased with H_2SO_4 addition [45]. This is apparently not a result of a removal of the alkaline content of the coal or coal char [45]. Other acids such as hydrochloric, acetic and phosphoric acids do not give the same result. Work described by Given and Derbyshire, [46] has shown that the co-addition of H_2SO_4 with ammonium heptamolybdate has no effect when there is a quantity of available sulfur in the

reaction system [46]. It was suggested that sulfuric acid aids in the conversion of Mo to a sulfided form via the formation and reduction of molybdenum sulfate [10].

2.3.1.1. Effect of Added Catalysts:

Adding “catalysts” to coal alters the following liquid product properties [47]:

- 1- Improves product quality (lower viscosity of liquids, increased H content, reduced heteroatom content)
- 2- Improves net conversion
- 3- Improves selectivity (reduction in yield of hydrocarbon gases, asphaltenes and preasphaltenes, increase distillate yield)
- 4- Reduces hydrogen consumption

The decrease in liquid viscosity is probably due both to the distribution of lower boiling point components and to the elimination of functional groups [10, 36, 43]. Also, adding catalyst improves the performance at short reaction times [43]. Consequently, catalysts can reduce constraints on solvent quality, which can lead to process simplification [10, 36, 43].

Bituminous coals, “having reflectance values in range 0.65-0.72 and pyritic sulfur contents of 1.5 wt% daf coal, can be used for direct liquefaction without added catalyst” but subbituminous coals cannot be processed without the added catalyst for reasonable yields [48]. Native pyrite in these bituminous coals provides a suitable level of native catalytic activity [48]. Upon pyrite addition, low-rank coals generally produced higher oil yields than bituminous coals [10, 48-49]. It has been shown that adding pyrite can reduce reaction temperatures without significant loss of

liquefaction yields [10]. Alternatively, adding 5% finely dispersed pyrite increases the amount of liquid fuel that can be recovered from bituminous coals about 10 to 15% at constant reactions [12].

Historically, low-rank coals have been regarded as “poor” liquefaction feedstocks. Subbituminous coal can form cross-links more readily than bituminous coals [50], so the retrogressive reactions of low-rank coals are expected to be more significant. Derbyshire et al. proposed that this is the reason low-rank coals are more difficult to liquefy than bituminous coals [47, 49, 51-52]. Cross-linking reactions can be thermally initiated at low temperatures and render the coal less amenable to liquefaction. However, in the presence of an active catalyst, lower rank coals maybe more suitable for distillate production than higher rank coals [10, 14, 49, 53].

2.3.1.2. Catalyst Activity:

Catalytic activity is determined by the degree of dispersion and the composition of the catalyst under a given set of reaction conditions [53]. There are several ways of expressing the catalyst activity; the unit masses of catalyst under similar reaction conditions, or the activity per unit area of the support surface. High oxygen functional groups concentration improves metal dispersion and so enhances the catalyst activity [53]. Dispersion describes how the catalyst is distributed over the coal or in the coal-solvent mixture. The catalyst particles can only effect reactions within their vicinity, so the degree of coal-catalyst contact is essentially related to catalyst activity. In studies the level of dispersion is described qualitatively and is almost always inferred from the experimental liquefaction data. The catalyst is usually described as the precursor

compound and steps are rarely taken to investigate the form of the catalyst in the reaction products [10, 53].

For most metals, a sulfide is the thermodynamically stable form under liquefaction conditions and will be formed by reaction with the sulfur in the coal if no other sulfur-containing species are present. Fortunately, in some cases, the metal sulfide is active for coal liquefaction [10]. When processing low-sulfur coals, it is necessary to add sulfur with iron and molybdenum catalyst. It was found that molybdenum and tungsten metals became very active when presulfided by reaction with a mixture of H_2S and H_2 [10, 14, 38].

The bulk of the available evidence indicates that pyrrhotite is the active form of the iron catalyst under liquefaction conditions [54]. Iron introduced in oxide form is converted to the sulfide by reaction with sulfur in the coal or with added sulfur. In the presence of sulfur and water, iron oxides will react to form FeSO_4 as well as iron sulfides [54]. When H_2 was used instead of N_2 and Fe_2O_3 was the oxide, less FeSO_4 and more H_2S were produced and FeS was detected as well as FeS_2 [54]. These results agree with observations that pyrite and FeSO_4 are reduced to pyrrhotite during liquefaction. The formation of sulfate ion increased the cracking activity of Fe_2O_3 [55]. This was attributed to an increase in the acid strength of the oxide [55]. Pyrrhotite is a non-stoichiometric sulfide whose composition can be represented as Fe_{1-x}S , where $x=0-0.2$. Thus it is a defect structure with a variable number of metal vacancies. A high concentration of H_2S , originating for example with coals containing high content of pyrite and organic sulfur, produces pyrrhotites with a high concentration of metal vacancies, which tend to promote coal liquefaction [10, 54]. It is well known that the thermally initiated reactions of coal can occur very

rapidly [21, 56] and, especially for low-rank coals, can occur at low temperatures [57]. Increased liquefaction activity observed with decreasing particle size of added pyrite is due to the smaller particles facilitating the pyrite-pyrrhotite conversion [10, 54, 58].

It is not necessary for the active catalyst phase to possess long-term stability [10]. It needs only to persist for a relatively short time to be useful in coal liquefaction. Hydrogen sulfide can promote the cracking of diphenyl ether, diphenylmethane and bibenzyl [59]. Hydrogen sulfide, H_2S , also promotes coal conversion to a greater or lesser extent [58]. In this case the influence of H_2S may be related to the content of iron or other metals in the coal with which it could interact. The combination of pyrrhotite and H_2S was more effective than H_2S alone for hydrocracking diphenyl ether and diphenylmethane [10, 58-59].

The existence of two types of catalyst site has been proposed to explain the results obtained with supported catalysts [60-61]. Site I is a sulfur vacancy associated with a molybdenum atom and site II is a Bronsted acid site. Sulfur vacancies are responsible for hydrogenation and hydrogenolysis while the acid sites are responsible only for hydrogenolysis. The adsorption and dissociation of H_2S can convert a sulfur vacancy to a Bronsted site (H^+) by a reversible reaction [10, 60-61].

The presence of H_2S reduces the number of sulfur vacancies and increase the number of acid sites, which could account for the observed reduction in hydrogenation and the increase in hydrogenolysis. This interpretation is in terms of an anion and modified anion sites while, for pyrrhotite, metal vacancies have been proposed as the active sites [10] in the presence of H_2S .

The active form of Mo is often cited as MoS_2 the thermodynamically stable form at low partial pressures of H_2S . The hydrosulfurisation activity of a sulfide $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst has been found to be dependent upon the S/Mo ratio and increases as this value is reduced below 2.0 [10].

2.3.1.3. Nature of MoS_2 Catalyst:

The MoS_2 structure is layered and can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions in a trigonal prismatic arrangement. The active centers of MoS_2 -based catalysts are located on the edges of the layers, where sulfur vacancies are formed [62]. Therefore, catalytic activity of bulk or supported MoS_2 depends strongly on its dispersion. The syntheses of dispersed MoS_2 usually involves thermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$ (ATM) salt, the sulfidation of molybdenum oxide, metathesis reactions, or gas-phase decomposition of $\text{Mo}(\text{CO})_6$ in the presence of H_2S [62].

The catalysts used in this work, MoS_2 , have great potential to promote hydrogenation and coal depolymerization at temperatures of 350-450 °C [34, 37, 63-68]. Catalysts can help to accelerate the rate of hydrogenation with hydrogen donor solvent and match the rate of free-radical formation, preventing retrogressive reactions [63]. Molybdenum-sulfur catalysts have been widely used in coal liquefaction but they need to be well dispersed using several treatments to function effectively. ILs should significantly promote liquefaction yields with appropriate catalysts without these additional steps.

2.3.1.4. Recovery and Repeated Use:

Recycling catalyst reduces cost. Because of the intimate contact between dissolution catalysts and coal, it is difficult to separate the solid catalyst from the minerals present in the coal and from the cations bound to the organic part of coal. Deposition of carbon and minerals often deactivates the catalyst [44]. There are two ways to separate the catalyst. One is to eliminate or reduce the minerals in the coal because the major difficulty for the catalyst recovery comes from the separation of the solid catalyst from the minerals in the coal and the cations bound to the coal [44]. The second is to use a catalyst that has an ultrafine particle size and low specific gravity and both approaches allow for catalyst recovery and regeneration [44].

- 1- ***Reduction of minerals:*** Coal washing is a general procedure used to remove a part of the mineral matter. Acid-washing removes ion-exchangeable cations in low-rank coals. Removal of ion-exchangeable cations inhibits the deposition of minerals in transfer lines and reduces plugging problems [44]. The removal of cations also eliminates some linkages among the coal macromolecules, to enhance the solubility and depolymerization [44].
- 2- ***Catalyst designs:*** Very fine MoS₂ particles recovery is possible using a hydroclone [69]. However, the size distribution of minerals and the variation of MoS₂ particle size reduced the recovery rate [69]. Sakanishi et al. [69] proposed using nano-scale particles of hollow carbon to reduce the density of the catalyst, allowing it to be gravimetrically separable.

The liquefaction solvent, especially hydrogen donors, can reduce carbon formation on the catalyst, dissolution of the carbon precursors strongly adsorbed on the catalyst being a key to the suppress catalyst deactivation [44].

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CHAPTER 3

USE OF IONIC LIQUIDS TO PARTIALLY DISINTEGRATE AND DISSOLVE COALS

3.1. Introduction:

Ionic liquids have attracted increased interest in recent year as a result of their unique properties. Most ionic liquids have an organic cation and inorganic polyatomic anion [1]. Ionic liquids are organic salts and, in contrast to inorganic salts such as NaCl, their melting points are low, allowing the ability to work with more moderate temperatures. These organic salts are liquid at, or near, room temperature. The first report about room temperature molten salt, ethylammonium nitrate was in 1914 [2] but until 1990s these salts were not popular solvents, however it then became evident that many of the ion combinations form air- and water-soluble ILs [3-4]. Since then these salts were of interest to academia and industry. The ions have unique variability, such as hydrophobic or hydrophilic properties and ILs may not even mix with one another [5]. It is possible to control their physical and chemical properties by adjusting to structure of ILs via selecting either anion or cation for the desirable properties [5].

Ionic liquids can potentially engage in a wide range of intermolecular interactions with coal. Ionic interactions play an important role in low- and medium-rank coal chemistry [6]. This chapter shows how certain ionic liquids (ILs) can be used to fragment, disperse, and partially

dissolve certain coals as very fine particles to a remarkable extent. Such fragmentation will allow a better contact with similar sized catalysts, as described in the next chapter. First, the ILs used in this work will be described, together with a discussion of their intermolecular interactions.

3.1.1. Ionic Liquids:

Ionic liquids are organic salts and consist of large organic cations associated with various anions that are liquid below 100 °C, or even at room temperature [1, 7]. Simple inorganic salts, such as NaCl, melt at very high temperatures (801 °C) [1], unsuitable for routine use as solvents. Ionic liquids due to potential interactions with coal during liquefaction may facilitate higher reaction rates, reaction selectivity and yields. Also ILs are non-flammable so all these features make the process safer than traditional liquefaction approaches [1, 7]. Green chemistry strategies that avoid using hazardous solvents have demonstrated that ILs can replace conventional organic solvents in a number of industrial-scale applications [8]. Potential catalytic enhancements are stable at temperatures up to 300 °C or more [8]. The availability of a great variety of different cations and anions give ionic liquids their numerous unique properties that make them favorable for very different applications in diverse fields, such as synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry, and nanotechnology [7]. The chemical structures of some widely used ILs are illustrated in Figure 3.1 [9].

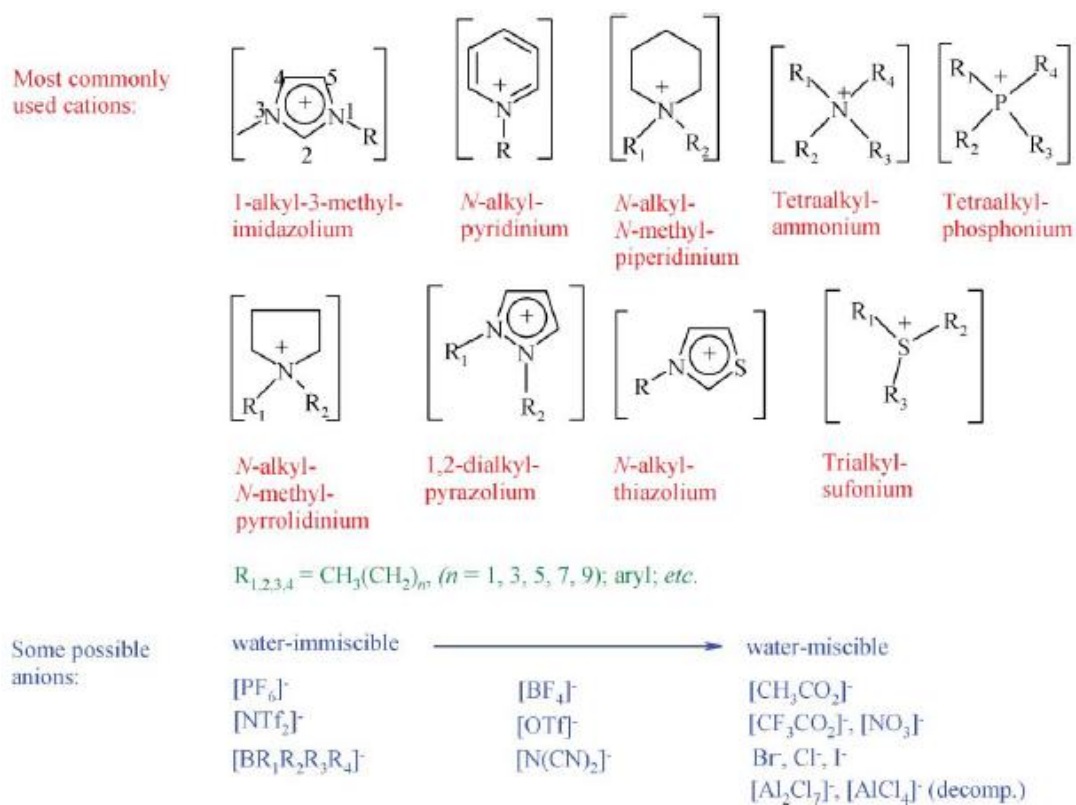


Figure 3.1: Some commonly used ionic liquid systems

Source: Plechkova, N. and K. Seddon, Chemical Society Reviews, 2008. **37**(1): p. 123-150.

Figure 3.2 shows electronic structure of 1-butyl-3-methylimidazolium cation [7, 10]. It shows the charge is localized to a partial the molecule it interesting properties and the potential to interact with coal. One area that has not yet received any attention is the use of ionic liquids in the direct liquefaction of coal.

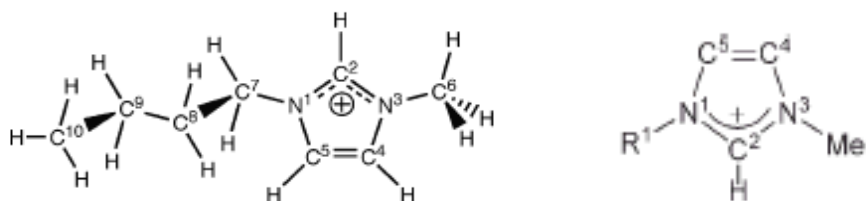


Figure 3.2: Electronic structure of 1-butyl-3-methylimidazolium cation (left) and 1-alkyl-3-methylimidazolium cation.

Sources: Weingaertner, H., *Angewandte Chemie International Edition*, 2008. 47(4): p. 654-670.
Hunt P. and Gould, I., *J. Phys. Chem. A*, 2006. 110(6): p. 2269-228

In this research, imidazolium ILs were chosen because they are more chemically stable, cheaper and easier to work with than other types of ILs [1]. Here the symbol [amim] represents the 1-alkyl-3-methyl imidazolium cation, so that 1-butyl-3-methyl imidazolium is [bmim]. The 1-alkyl-3-methylimidazolium salts exhibit unique properties in the electronic structure of the aromatic cations. The electronic structure of the [bmim]⁺ cation is best described by a C⁴=C⁵ double bond at the rear, a delocalised three-centre 4 e⁻ component across the front (N¹-C²-N³) of the imidazolium ring and a weak delocalization in the central region; delocalization between these regions is also significant [7, 10]. Weingaertner proposed that hydrogen-bond formation is driven by Coulombic stabilization, which compensates for an associated destabilization of the electrostatic contribution to the system. The hydrogen atoms C²-H, C⁴-H and C⁵-H carry almost the same charge, but carbon C² is positively charged owing to the electron deficit in the C=N bond [7]. On the other hand, C⁴ and C⁵ are partially neutral. Interactions are dominated by a large positive charge at C² and the build up of π -electron density above and below the ring, particularly in the region associated with the double bond between C⁴ and C⁵ [7,

10]. Schematic representation of the positions of the Cl^- ions in $[\text{bmim}][\text{Cl}]$ and $[\text{mmim}][\text{Cl}]$ are illustrated in Figure 3.3.

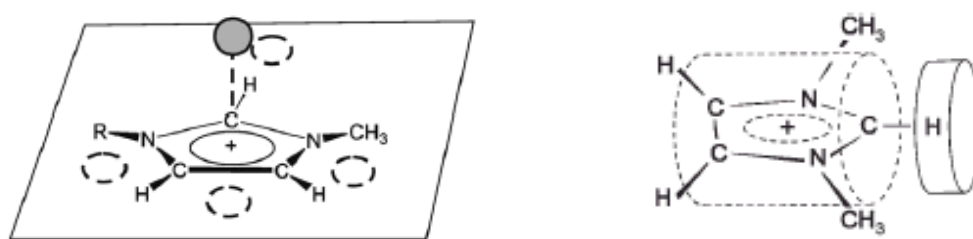


Figure 3.3: Schematic representation of the positions of the Cl^- ions in $[\text{bmim}][\text{Cl}]$ ($[\text{C}_4\text{mim}][\text{Cl}]$) (left) and liquid $[\text{mmim}][\text{Cl}]$ ($[\text{C}_1\text{mim}][\text{Cl}]$) (right)

Sources: Weingaertner, H., *Angewandte Chemie International Edition*, 2008. 47(4): p. 654-670.
Hunt P. and Gould, I., *J. Phys. Chem. A*, 2006. 110(6): p. 2269-228

Quantum-chemical computations for the $[\text{bmim}][\text{Cl}]$ pair indicate several stable positions of the Cl^- ion. Conformers with the Cl^- ion in front of the $\text{C}^2\text{-H}$ bond and top of C^2 of the imidazolium ring are energetically preferred [10-11]. The in-plane positions near $\text{C}^4\text{-H}$ and $\text{C}^5\text{-H}$ are markedly less stable. The $\text{C-H}\cdots\text{Cl}$ bridges are essentially ionic, although they have also been described as hydrogen bonds [10]. The cation-anion configurations in liquid $[\text{C}_1\text{mim}][\text{Cl}]$ were derived by Hunt et al. [10-11] from scattering data. The position of highest probability for the Cl^- ion is in a band around $\text{C}^2\text{-H}$. There is a lower probability of finding the Cl^- ion in the cylinder around the imidazolium ring. The methyl groups exclude some positions within this cylinder. Hydrogen-bond formation is favored by the acidic nature of the hydrogen atoms of the imidazolium salts and depends on the nature of the anion. [7, 10-11].

The [bmim] cation and a range of anions Cl^- , BF_4^- and $\text{N}(\text{Tf})_2^-$ were shown by Hunt et al. [12] to exhibit a range of viscosities and melting points. 1-Butyl-3-methyl-imidazolium chloride, [bmim][Cl] has a very high viscosity and is essentially a solid at room temperature, [bmim][BF₄] is viscous (168 cP), while [bmim][N(Tf)₂] (53 cP) is relatively fluid [12-13]. The viscosity differences were explained in terms of a complex index. There are nine possible sites for the Cl anion around the cation, however linear H-bonds at the rear of the ring are unlikely [10, 13]. The remaining seven sites can all be occupied over time, however the top and front, or the two front sides, cannot be occupied at the same time (due to Coulomb repulsion), and thus any given time the cation is likely have only five sites occupied. These are all internal interactions of ion pairs in the liquid state, but external connections are also important. The number of external connections each anion makes with other cations will impact the physical properties of the liquid [13]. Crystal structures indicate that each Cl anion interacts with approximately four distinct cations [13]. Thus each of the five interaction sites around the cation is filled by a Cl anion, and then each cation is connected to $5 \times 4 = 20$ other cations. The connectivity index for [bmim][Cl] is 20. In [bmim][BF₄], there are four internal interactions and only one fluorine atom is available to form an external link. The connectivity index for [bmim][BF₄] is therefore $4 \times 1 = 4$. Two N(Tf)₂ anions can essentially encapsulate a single cation and three of the four oxygen atoms are involved in coordinating to the cation, leaving a single atom that is available to interact with other cations. Thus a minimum first solvation shell of only two anions each with a single external connection giving a connectivity index $2 \times 1 = 2$ for [bmim][N(Tf)₂] [13]. Hence the relatively strong interactions, high connectivity, the high symmetry and charge density of the anion and low configurational variation allow the rationalization of the high viscosity and high melting point of [bmim][Cl]. In contrast, [bmim][N(Tf)₂] forms a low connectivity network of weakly linked

ions. [bmim][BF₄] lies midway between these two extremes, forming a weak but more regular network [12]. Atomic numbering of the 1-butyl-2,3-dimethyl-imidazolium cation is shown in Figure 3.4 [12].

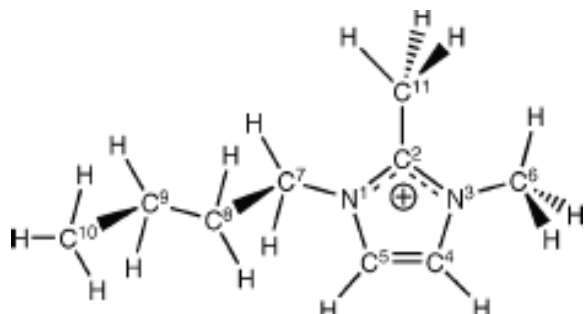


Figure 3.4: Atomic numbering of the 1-butyl-2,3-dimethyl-imidazolium cation.

Source: Hunt, P., J. Phys. Chem. B, 2007. 111(18): p. 4844-4853.

1-Butyl-3-methyl-imidazolium chloride ([bmim][Cl]) has one methyl group at the 3-position of the cation. Substitution for a methyl group at the 2-position of the cation to form 1-butyl-2,3-dimethyl-imidazolium, ([bmmim]⁺), eliminates the main hydrogen-bonding interaction between the Cl anion and the imidazolium cation. Loss of this hydrogen bonding interaction could be expected to lead to a reduction in melting point and a decrease in viscosity; however the opposite is observed experimentally; melting points and viscosity increase [12]. In [bmmim]⁺ based ionic liquids, cation-anion interactions are reduced because the free rotation of the butyl chain is restricted due to the steric bulk of the methyl group and the energetic preference of the anion to lie above or below the imidazolium ring rather than in front [12].

Recently, [C_nmim][X] ILs, where n is the carbon number in the alkyl group, with short alkyl chain lengths have been used to substitute for traditional organic solvents or water [8]. The long alkyl chain ILs have amphiphilicity, because of their hydrophobic chains and polar imidazolium

group, and have been called “surface active” [8, 14]. These salts have been used to form ordered molecular assemblies such as micelles, microemulsion vesicles and liquid crystals [14]. The positively charged imidazolium cation of $[C_n\text{mim}][X]$ plays an important role in constructing these novel microemulsions. Li et al. [8] investigated the effect of chain length of $[C_n\text{mim}][\text{Br}]$ on phase behavior, structural parameters and rheological properties with p-xylene and water. It was found that $[C_n\text{mim}][\text{Br}]$ can be substituted for surfactants and formed isotropic liquid crystalline phases. The properties of $[C_n\text{mim}][\text{Br}]$ such as “ π - π stacking” and “ π -cation” interactions play an important role in determining internal structural parameters, which are different from conventional cationic surfactants. Li et al. found that for the samples with the same component molar content, both the rheological steady and dynamic moduli are increased with an increase in the size of the carbon chain of $[C_n\text{mim}][\text{Br}]$ [8]. These results allow tailoring of the ILs for use as liquid crystals, solvent systems, or within microreactors in the preparation and processing of semiconductors, nanomaterials enzyme-catalyzed reactions, and extraction applications [8].

A strong interaction between a nitrogen-containing aromatic cation and a neutral π system has been reported by Dougherty et al. [15]. The interactions of the nitrogen-containing aromatic cations, such as imidazolium and pyridinium, with a π system are important for understanding the solvation of an aromatic molecule in room temperature ionic liquids (RTILs). This interaction has often been explained as a cation- π interaction [16], while the same interactions sometimes been called a donor-acceptor, charge-transfer, π/π , or CH- π interaction [17-18].

The interactions in benzene complexes with the ILs pyridinium and N-methyl pyridinium should be categorized as a cation- π interaction [19]. The ab initio calculations of Tasuzuki et al. [19] show that the interactions in pyridinium and N-methylpyridinium complexes are significantly larger than those in the benzene-pyridine complex and the benzene dimer. The pyridinium and N-methylpyridinium complexes are stabilized by large electrostatic and induction interactions (cation- π). On the other hand, the interaction in the benzene-pyridine complex is a π - π interaction. The dispersion interaction is mainly responsible for the attraction in the benzene-pyridine complex as in the case of the benzene dimer. Short-range interactions such as charge transfer or orbital-orbital interactions, are not important for the attraction in these complexes [19]. However, the size of the interaction energy depends strongly on the orientation of benzene dissolved in pyridinium- or imidazolium-based RTILs and has a large activation energy [19]. The most stable benzene-pyridinium complex is where the N-H bond of pyridinium points toward the benzene [19]. This structure is favored by the attraction between the positive charged N-H and the negative charge on the benzene molecule [19].

These wide ranges of interactions that ILs can engage in suggest that they may prove useful solvents for coal. Specifically, potential for significant and aggressive interaction between some ionic liquids and coal may aid in its dissolution (and thus catalyst dispersion potential). Also, ILs that would simultaneously partially solubilize, fragment, disperse, and directly mediate good contact between catalysts and coal at relatively low temperatures, without the use of precursors, might prove to be a useful advance for direct coal liquefaction. In this chapter, the use of three ionic liquids, [bmim][Cl], [bmim][CF₃SO₃] and [bmim][BF₄] to disperse coals is described. The first of these ILs, [bmim][Cl] is immiscible with non-polar solvents, but soluble in water;

however its thermal stability is low [1, 20]. ILs containing halogen anions degrade at fairly low temperatures for these materials (about 150 °C) and are therefore not suitable as solvents in hydrogenation and hydrogenolysis reactions [1]. The other two ILs were chosen for their higher thermal stability. It has been proposed that they are stable up to 400 °C, likely temperatures for coal liquefaction experiments. Because of the low thermal stability, if [bmim][Cl] is used to disperse the coal it needs to be removed (washed) prior to the harsher temperature of liquefaction.

3.1.2. Interactions in Coal:

Clearly, ILs can potentially engage in a wide range of intermolecular interactions with coal. Low-rank coals are highly oxygenated and are much more polar than bituminous coals [21]. The presence of a variety of highly polar oxygen functional groups also raises the possibilities for more specific interactions as well as more self-association of the coal through internal hydrogen bonding and ionic interactions [21]. Ionic interactions play an important role in low- and medium-rank coal chemistry [6]. Non-covalent interactions contribute to coal structure. These interactions are, in order of decreasing bond strength, ionic bonds, hydrogen bonding, and aromatic-aromatic interactions [22]. Low-rank coals cross-link through ionic bonds between carboxylic groups and di- and trivalent metals, e.g. calcium, magnesium, and iron ions. However, it should be possible to destroy such an ionic bond by acid washing [22]. Cross-linked coals are expected to swell to a lesser degree [23-24]. In addition, if the cross-link density of the network is high and chains are relatively stiff, a significant portion of any soluble fraction can be trapped [6, 25].

Several researchers believe that macromolecular coal generally has two different proton forms that have different degrees of rotational mobility [26-27]. These are immobile phase, involving in insoluble part of the coal and mobile phase, consisting of trapped molecules which are extractable using organic solvents [28]. In mobile phase smaller aliphatic groups are not cross-linked to the larger macromolecular structure [26-27]. The type and characteristic of the mobile phase of coal is not well identified [26-27]. The percentage of mobile phase can be estimated by using ^1H NMR [26-27] and field ionization mass spectrometry (FIMS) [26-27] and structure of the mobile phase determined by using pyrolysis/gas chromatography/mass spectrometry (PY-GCMS) [26-27]. Two views are presented about mobile protons observed by ^1H NMR spectroscopy in coal [27]. The first is that protons can be attributed to molecules that are free to rotate in cages of the macromolecular network and the second is that the mobile protons are associated with fragments of the macromolecular network that can be rotated due to single C-C or C-O bond linking such fragments to the network [29]. The understanding of the mobile phase is important to optimizing coal conversion processes. Coal radical reactivity is important for the liquefaction process, but mobility of the reactive sites is also critical [26-28].

Ionic clusters, which act like cross-links, are formed by carboxyl groups in low-rank coals. They are responsible for the decrease in the extraction yield and the swelling ratio of coal [30]. These ion/coal interactions act as “reversible” cross-links [30]. The coal loses ionic clusters upon acid treatment as a result of conversion to carboxylic acid groups. The removal of the ionic clusters results in an increase in the pyridine-extraction yield [23, 30]. If a solvent forms complex with cations, extraction yields may be enhanced [31]. This suggests that a study of the ability of ionic liquids to swell and solubilize coals would be useful.

It is well known that there are electrostatic interactions between ILs and mineral surfaces and chelated ions [6]. Because of the importance of ionic interactions in low- and medium-rank coals [6], it is possible that the replacement of metal cations with bulky IL groups could play a role in fracturing, dispersion, and dissolution of coal. The interaction would depend on the structure of the coal, substituents on the imidazolium ring and the size of the anion. Also, significant difference in the size of cations and anions (Cl^-) could result in local differences in charge density. In the study of Hu and Guo [32] it was shown that an increase in the ability to inhibit asphaltene precipitation correlates with decreasing the anion size and increasing the effective anion charge density, promoting the ability of Cl^- anions to engage in acid-base interactions and hence disrupt interactions between asphaltene molecules [32]. The goal of this study is to investigate ILs capability of solubilizing, disintegrating, and dispersing coals as very fine particles for consideration for a coal-to-liquids process. Fragmented and dispersed coal particles allow a better contact with micron size catalyst particles.

3.1.3. Application of Ionic Liquids:

The development of a cost-effective technology to produce liquids fuels from this nation's abundant supplies of coal will reduce our dependence on foreign oil, thus enhancing domestic economic and energy security. China has recently expanded into coal-to-fuels and a coal-to-chemicals market with traditional direct liquefaction approaches [9]. However, the application of ILs to the processing of fossil fuels is a new area with considerable technological promise. Much of this technology is presently being developed and deployed in Europe and China. Petrochina has also announced the implementation of ionic liquid-based process "Ionikylation" [9]. It has

been tested at the pilot plant scale, and retrofitted into an existing 65,000 tons per year sulfuric acid alkylation unit in China [9]. The retrofit not only increased the process yield, but also increased the unit capacity of the process by 40% [9]. This is certainly a forerunner of other IL commercial petrochemical processes.

Current industrial usage of ionic liquid technologies are listed below according to the company profiles [9].

1. **BASF** has done most publicly to implement ionic liquid technology. They have the broadest range of applications: The BASILTM process, breaking azeotropes, replacing phosgene, cellulose dissolution and aluminium plating.
2. **Eastman Chemical Company** had been running a process for the isomerisation of 3,4-epoxybut-1-ene to 2,5 dihydrofuran and the epoxidation of butadiene to 3,4-epoxybut-1-ene and its isomerisation to 2,5-dihydrofuran.
3. **IFP (Institut Français du Pétrole) – Axens** was the first to operate an ionic liquid pilot plant, whereas Eastman Chemical Company and BASF commercialized the first ionic liquid process. The Dimersol process consist of dimerisation of alkenes, typically propene (Dimersol-G) and butenes (Dimersol-X) to the more valuable branched hexanes and octenes. This is an important industrial process with total annual production of 3,500,000 tonnes dimer.
4. **Degussa** are developing ionic liquids on several distinguishable fronts like BASF. Ionic liquids applications are hydrosilylation, paint additives and lithium-ion batteries.

Other companies are working IL technologies: Air products, Central Glass Co., Ltd., Japan, IoLitec, SASOL, BP, Exxon Mobil, Chevron and Chevron Phillips, PetroChina, Eli Lilly, Pionics, Scionix, Linde. Potential applications are shown in Figure 3.5.

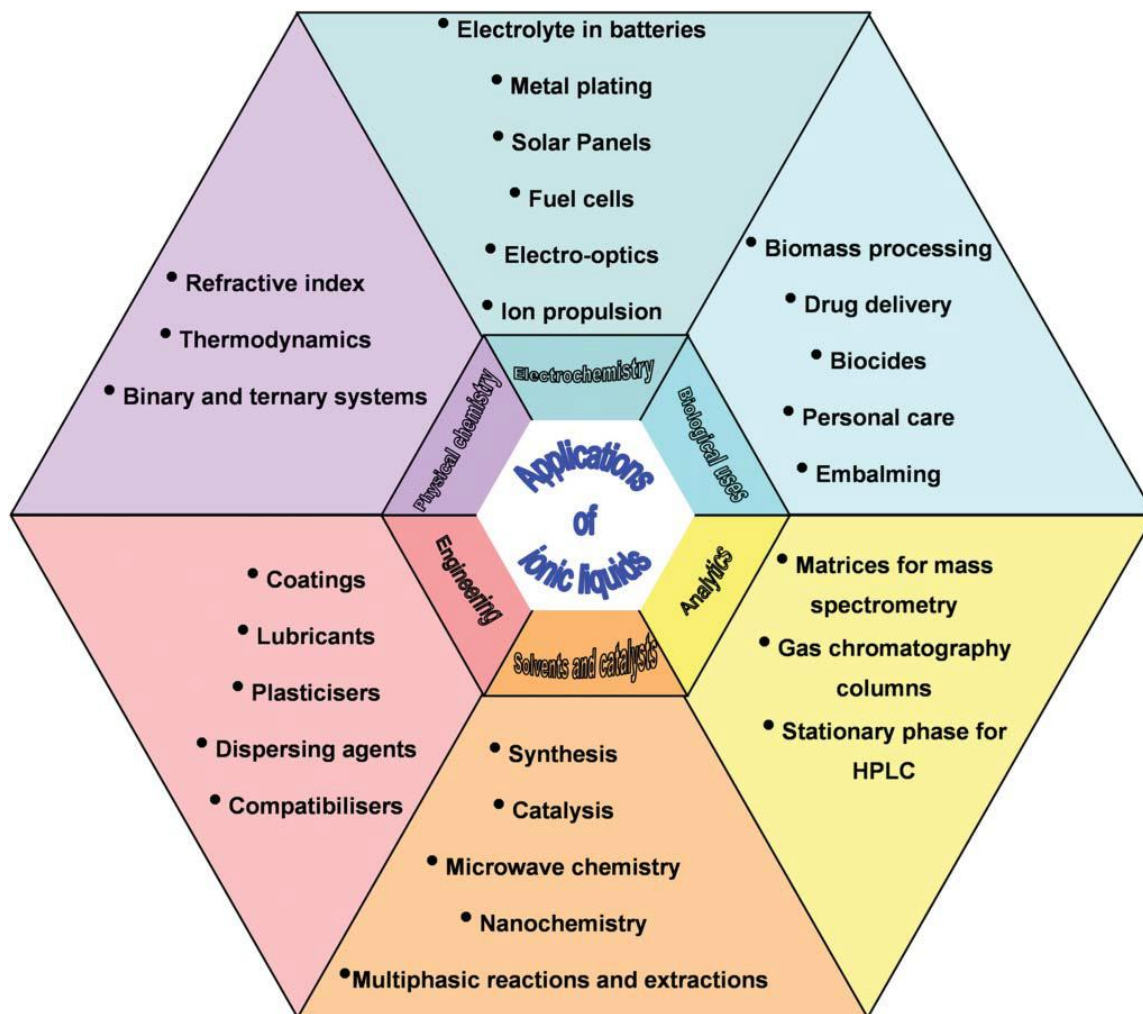


Figure 3.5 Applications of ionic liquids.

Source: Plechkova, N. and K. Seddon, Chemical Society Reviews, 2008. **37**(1): p. 123-150.

At the present time, ILs are expensive, although the price will come down as plants for production of these liquids come on-line in Europe and China. Nevertheless, even at today's prices an economically viable IL implementation at the industrial scale, such as the BASILTM process, can be built if the Ionic liquid can be effectively recycled. The ILs used in this study are likely to be effectively recyclable also because they are immiscible with hydrocarbon solvents such as alkanes and toluene but soluble in water. Essentially, coal can be broken up and partially hydrogenated in an IL/coal/solvent/catalyst mixture with the IL's (and some catalyst) being recovered for reuse with water. As IL's has essentially a zero vapor pressure, water is readily distilled from the IL at 100 °C for easy recycling.

3.2. Materials and Methods:

The ionic liquids were all purchased from Sigma-Aldrich and used as-received. The 1-butyl-3-methylimidazolium chloride was assayed at $\geq 99\%$ by HPLC. The other ILs used in this study were somewhat less pure, but all were assayed at $\geq 95\%$. The Illinois No. 6 coal (high-volatile bituminous coal) used in this study was an Argonne Premium Coal sample [33] Chevron USA Inc., an affiliate of Chevron Corporation, provided a Powder River Basin (PRB) subbituminous coal. The Illinois No. 6 coal has a moisture content of 8% and a mineral matter content of 18% (as-received). Chevron USA, Inc., an affiliate of the Chevron Corporation, provided a Powder River Basin (PRB) subbituminous coal, which had been partially dried and had a moisture content of 13.7% and a mineral matter content of about 8% by mass. The initial coal particles of both were mostly of the order of 100 μm or larger.

Coals (10% by weight) were mixed with ionic liquids in centrifuge tubes held at 100 °C overnight in an oil bath. Samples for microscopic observation were simply smeared onto glass slides at room temperature. Micrographs were obtained in transmitted light using a Leica DM 4000 (x200 magnification) research microscope.

Coals were used as-received. The ILs are hydrophilic and will likely pull moisture from the coal. Because ILs have a negligible vapor pressure at low temperatures, this moisture is readily removed by heating to 100 °C. It would obviously save on energy if coals used for liquefaction do not have to be dried, at least in the primary liquefaction step. For low-rank U.S. coals moisture content is often as high as 20-35 wt% [34-35]. Many researchers have evaluated low-rank coal moisture content and their drying behavior [34]. Miknis et al. [36] showed that thermal drying resulted in changes in the physical structure and cross-linking density of coals and a subsequent decrease in liquefaction yields. Also Gronhovd et al. [37] suggests that drying may deactivate coal because of the surface oxidation and collapse of the pore structure. Song et al., [34] found that vacuum or air drying at 100-150 °C can change Wyodak subbituminous coal physical and chemical properties and affects its conversion and oil yields and CO₂ yield both in catalytic and noncatalytic liquefaction at 350 °C. Their data show that drying in air causes oxidation and formation of the oxygen functional groups. Also oxidation of coal in air at 100-150 °C results in change of the phenolic and catechol into other related structures. In thermal (noncatalytic) liquefaction, raw coal gave higher conversion and higher oil yield than the dried coal [34]. The air dried coal gave better result than vacuum-dried coal in the presence of H-donor or non-donor solvent. For catalytic liquefaction using ammonium tetrathiomolybdate (ATTM) impregnated coal, again fresh raw coal gave better conversion and oil yield than either air or

vacuum dried coal [34]. However, pre-drying coal in air prior to ATTM impregnation and presence of either H-donor or nondonor solvent at 350 °C liquefaction run has little beneficial effect [34].

Iino et al. [38] investigated that the effect of water treatment at 227 °C and 327 °C on solvent extraction of selected coals. They were dried under vacuum at 80 °C. Water treatment at 327 °C increased the extraction (at room temperature) yield in the (1:1 by volume) with NMP/CS₂ mixed solvent. However, water treatment at 227 °C and heat treatments at 327 °C without water gave a slight increase in the extraction yields. They suggest that cross-links become relaxed by water treatment at 327 °C and this increases the swelling degree. Also, a decrease in the OH groups supply to the yield enhancement, because of the decrease in the amount of hydrogen bonds. Loss of functional groups via decrease in oxygen content also may enhance extraction yield [38].

3.3. Results:

The [bmim][Cl] is a solid at room temperature but it melts near 80 °C. Figure 3.6 shows two powders (IL and Illinois No. 6 coal) in contact at room temperature and after heating to 100 °C overnight, a dark black solution/dispersion was immediately obtained and the mixture remained a liquid on cooling to room temperature. It is difficult to determine what portion of the coal is dissolved in this IL and how much is present as finely dispersed particles. The dispersion could not be filtered using conventional filter paper because cellulose also dissolves in this IL. Also, Teflon and glass fiber filters filtration stopped at an early stage in the process, due to gel formation.

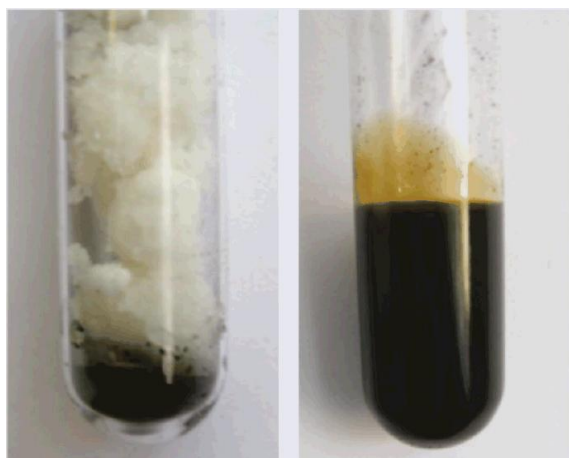


Figure 3.6: An Illinois No. 6 coal and the IL [bmim][Cl] (white material) (left) before and after heating to 100 °C.

There are very fine presumably swollen coal particles in the mixtures (by optical microscopy). Centrifugation at ordinary speeds was also ineffective at separation. However, by centrifuging hot tubes, pouring off the supernatant solution, remixing with IL and pouring off the second extraction after centrifugation, it is estimated that more than 19% of this coal (by weight) had “dissolved” in the IL. Figure 3.7 compares micrographs of the original PRB coal suspended in water and the same coal after heating to 100 °C with the IL [bmim][Cl] at the same magnification.

The larger particles of the coal are broken up and dispersed in the IL and are less than 50 μm in size, while the smaller particles are 10 μm or smaller. The initial coal particles were mostly of the order of 100 μm in size (microscopy observations) and the IL has disintegrated the original coal particles to a remarkable degree. Original Illinois No. 6 coal and a smear of the dispersion obtained after 2 h in contact with [bmim][Cl] micrographs are illustrated in Figure 3.8.

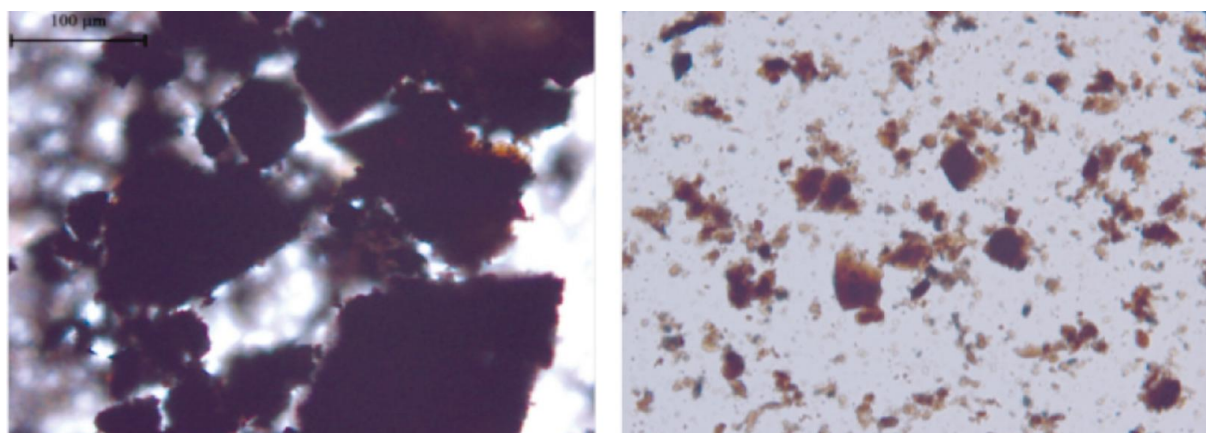


Figure 3.7: Optical micrograph (x200) of a PRB subbituminous coal suspended in water and smeared between micrograph slides (left) and a micrograph (x200) of a smear of the same coal after heating to 100 °C with the IL [bmim][Cl] then cooled to room temperature (right).

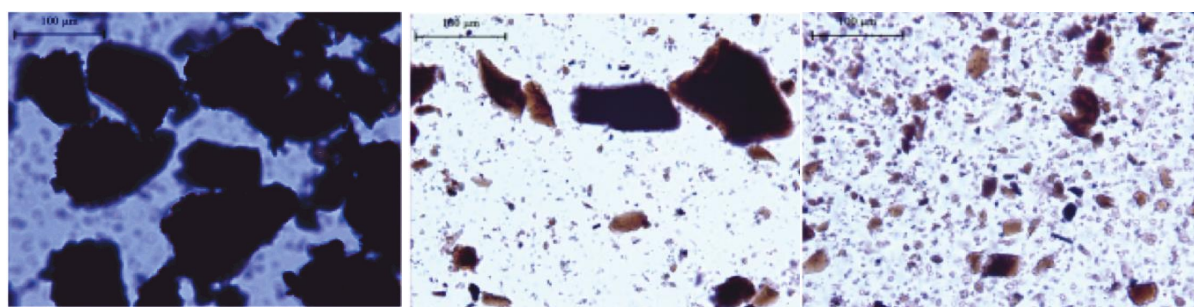


Figure 3.8: Optical micrograph (x200) of a Illinois No. 6 coal suspended in water and smeared between micrograph slides (left) and a micrograph (x200) of a smear of the same coal after heating to 100 °C with the IL [bmim][Cl] then cooled to room temperature (middle and right).

Illinois No. 6 coal was more fragmented and dispersed to an even greater extent than the PRB coal. Figure 3.8 compares micrographs of the original coal and a smear of the dispersion obtained after 2 h in contact with [bmim][Cl]. There are a few residual particles (middle micrograph), but the bulk of the sample has been dispersed as small particles, many of them 10 μm or less (right micrograph). A 2 h contact time is a short period so exposure with a longer contact time (72 h) was used to investigate fragmentation process. However shorter contact

periods may be preferred to reduce energy consumption. After 72 h at 100 °C there has been an increase in dispersion but this is challenging to quantify using this approach. Particles are less opaque, presumably because they are thinner (Figure 3.9).

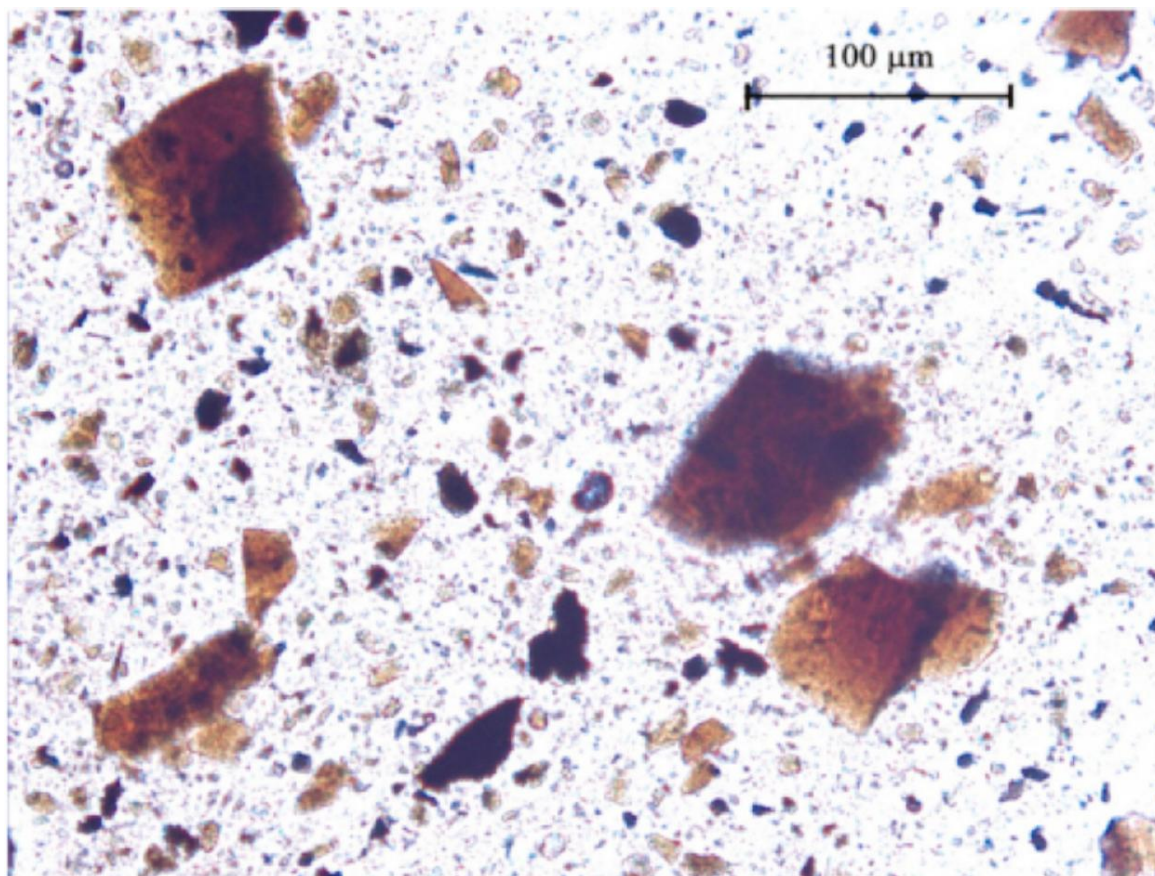


Figure 3.9: Optical micrograph (x200) of a smear of an Illinois No 6 coal after heating to 100 °C with the IL, [bmim][Cl] for 72 h and then cooled to room temperature.

Multiple experiments were investigated to compare the smears of the dispersion of Illinois No. 6 coals and PRB coals micrographs to ensure repeatability. All showed similar and <10 microns sized coal.

Figure 3.10 shows Illinois No 6 coal mixed with the IL, [bmim][CF₃SO₃]. It can be clearly seen that not all ILs will form this type of dispersion with the PRB (not shown) and Illinois No 6 coals.

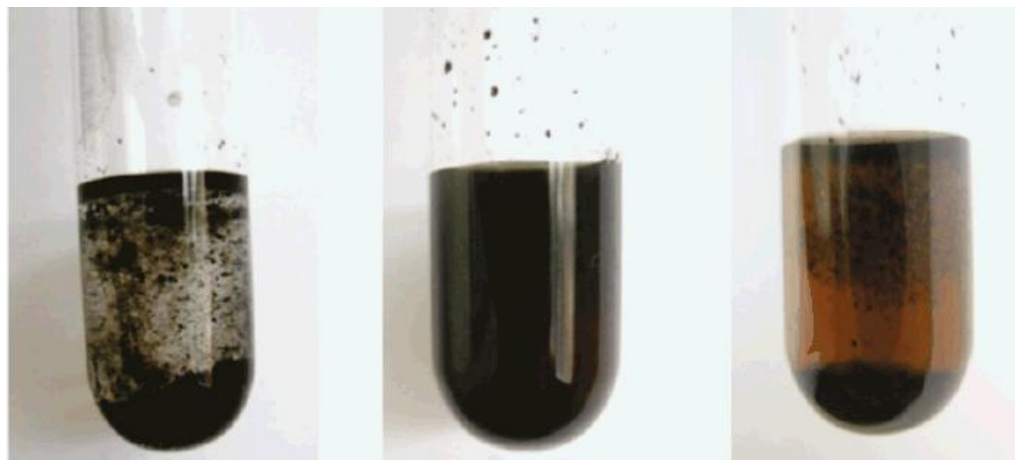


Figure 3.10: Illinois No. 6 coal and IL (white material) before mixed with the IL, [bmim][CF₃SO₃] at room temperature (left), at 100 °C (middle), and after cooling to room temperature (right).

The solvent was clear and the coal particles were unaffected upon initial contact at room temperature. When heated to 100 °C, a viscous black dispersion is formed. This is similar to that shown in Figure 3.6, using the IL [bmim][Cl]. But after cooling to room temperature the coal particles can clearly be seen both at the bottom of the tube and suspended in the discolored solvent. It appears that any smaller particles, that were formed, collected after cooling at the bottom of the tube. They were not fragmented significantly.

As discussed earlier, ILs can be tailored to have specific solvent properties by a choice of substituent and anion. Here, the IL [bmim][BF₄], does not immediately disperse a PRB coal and

Illinois No 6 coal sample at room temperature, unlike [bmim][CF₃SO₃]. Most ILs examined in this study, gave similar results to shown in Figure 3.10, only imidazolium salts with chlorine anions formed a fine dispersion of coal particles in a coal/IL solution with the Illinois No.6 and PRB coal samples.

Both ILs, [bmim][CF₃SO₃] and [bmim][BF₄] are described as being stable up to temperatures of about 400 °C, compared to temperatures of about 150 °C for [bmim][Cl]. That is why these two higher temperature stable ILs were chosen for study. Because the IL [bmim][Cl] gave the best results in terms of low-temperature dispersion, it was decided to use this IL to determine if a greater contact with catalysts was enabled and if this improved liquefaction (see Chapter 4).

3.4. Discussion:

It is well known that coals and other materials can spontaneously fracture in the presence of solvent [39]. Charcoal “virtually exploded” when added to methanol and coal particles spontaneously fractured in the presence of certain solvents [39]. Most of the original coal particles were larger than 250 µm in size and were reduced 60 µm or larger in size [40]. Alfery et al. [40] examined the fracturing of cross-linked glassy polymers. They noticed that flat round discs of styrene-divinylbenzene copolymers would break apart with “an audible ping, splash” on being placed in contact with certain solvents. Brenner et al. [41] observed that coals (polished coal surfaces) expand, become cracked, and greatly distorted in the presence of good solvents. Similarly thin-sections of coal also show this behavior [42]. Niekerk et al. [43] performed a structural analysis of a vitrinite-rich and inertinite-rich South African coal and also they observed

fracturing of millimeter-sized particles of South African coals using time lapse videography [44]. Removal of water is also known to fracture low-rank coals [45]. However, the fracturing here by ILs is far more spectacular and produces far smaller particles. To our knowledge no prior coal-solvent work has resulted in the fracturing or dispersion to the extent reported here at these low temperatures. This may also offer alternative approaches for cleaning coal.

The ability of certain ILs to fragment and disperse coals is most probably related to intermolecular interactions between the IL and the coal. As discussed earlier, ILs can engage in a wide range of intermolecular interactions. There are 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 [8, 19, 46]. These latter interactions appear to act as “reversible” cross-links in various coals [30-31]. It is possible that the replacement of metal cations with bulky ILs groups plays a role in the fracturing and dispersion.

Coal/IL interactions strength depends on the structure of coal, substituent on the imidazolium ring and size of the anion. It is observed that ILs broke up and dispersed Illinois No. 6 and PRB coals to a remarkable extent. The ionic liquids are based on an anion with high charge density, in connection with cations with sufficiently low charge densities. This significant difference in the size of cations and anions (Cl^-) could result in local differences in charge density. In the studies of Hu and Guo [32] it has been shown that an increase in the ability to inhibit asphaltene precipitation correlates with decreasing the anion size and increasing the effective anion charge

density, promoting the ability of Cl^- anions to engage in acid-base interactions and hence disrupt interactions between asphaltene molecules [32].

A great deal of work has been involved in HyperCoal or removing the coal from the minerals or by removing the minerals from the coal. Steel et al. [47-50] investigated removing mineral matter from -1 mm coal using acid and alkalis under hydrothermal conditions to obtain ultra-clean coal. However the treated coal contained 1000-5000 ppm ash yields. Yoshida et al. and Okuyama et al. [51-53] obtained HyperCoal, (“ashless”) by thermal extraction of various ranks of coals, including low-rank coals by using industrial solvents. The target for this study is an extraction yield exceeding 60% and ash yield lower than 200 ppm which allowed for the direct injection of coal into gas turbines [53-54]. The production of HyperCoal from low-quality coals such as high-ash yields, -sulfur, or -nitrogen coals would be important from the view of cost effectiveness and the variety of coal resources. HyperCoal were also characterized using structural and thermal analyses [55]. This study showed that all HyperCoal from bituminous coals and a subbituminous coal had high thermal reactivity and also high thermoplasticity during heating [55]. NMR measurements showed that the ratio of aromatic carbon increased with increasing extraction temperature, so some modification reactions occurred during the thermal extraction process. Ionic liquids thus may better enable HyperCoal production.

3.5. Conclusions:

Specifically, the dispersion and fragmentation potential of ionic liquids was explored with a Illinois No. 6 bituminous coal and a PRB subbituminous coal. It was found that the IL [bmim][Cl] fragments and disperses –100 mesh PRB and Illinois No. 6 coals as extremely fine particles (<10 microns) to a remarkable extent. This is probably a result of the ability of ILs to interact strongly with coal and coal/coal hydrogen bonds and coal/ion interactions with corresponding coal/IL and IL/mineral interactions.

The initial coal particles were mostly of the order of 100 μm or larger in size (optical microscopy observations). The [bmim][Cl] broke up -100 mesh coal particles at low temperatures upon heating to 100 $^{\circ}\text{C}$, which allowed the IL to melt and mix with coal. Coal samples after several hours contact with the IL, [bmim][Cl] at 100 $^{\circ}\text{C}$ become dispersed as small particles, majority of <10 μm . Many of the coal particles formed upon mixing appear to be partly transparent, most probably because they are very thin. It is estimated that more than 19% of this coal (by weight) had “dissolved” in the IL. But not all the ILs disperse these coals. The IL [bmim][BF₄] did initially appear to disperse the coals at 100 $^{\circ}\text{C}$, but the particles can clearly be seen both at the bottom of the tube and floating in the slightly discolored solvent upon cooling to room temperature. However, the other two ILs ([bmim][BF₄] and [bmim][CF₃SO₃]) did not disperse the coals by mixing at room temperature. The precise nature of these interactions is not known at this point and should be studied in future work.

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CHAPTER 4

FRAGMENTATION OF COAL AND IMPROVED DISPERSION OF LIQUEFACTION CATALYSTS USING IONIC LIQUIDS

4.1. Introduction:

Direct coal liquefaction is used to convert coal-to-liquids without the production of synthesis gas, (carbon monoxide and hydrogen gases) as an intermediate step. Accordingly, direct coal liquefaction should be the most efficient method to produce liquid fuels [1]. The direct liquefaction of coal generally occurs in two steps; conversion to a soluble form (both dissolution and depolymerisation) and reduction in molecular weight and heteroatom removal (upgrading). During the thermolysis, covalent linkages are thermally cleaved, and the resulting radicals are capped with hydrogen. According to Curran et al. [2] there is a significance relationship between conversion of coal molecules to soluble products and the amount of hydrogen transferred to the liquid coal products. They proposed a five step reaction mechanism;



During radical reactions, carbon-carbon bond homolyses occur and the radicals produced in the initial reaction, $\bullet\text{R}_i$, react with other coal molecules or with H-donor solvent molecules (DH_2), to form other radicals. Hydrogen-donor solvents play an important role in this stage, limiting retrogressive reactions [1]. Atomic or molecular hydrogen in the reactor can hydrogenate reactive sites [1]. (Depolymerisation occurs in this step and coal particles are fragmented and are reduced in size [1, 3].) As a result, coal liquids are produced by reaction of the solvent and hydrogen radicals with the coal radicals. The solvent/hydrogen carrier is being continually regenerated by the H_2 gas. However, the mechanism is simplified by assumptions to reduce the complexity of the system. The reaction path is not sufficient to explain all observations, as described by McMillen et al. [4-7]; the relative effectiveness of hydrogen donors does not correspond to their ability to scavenge radicals and three and four rings polycyclic aromatics are better liquefaction solvents overall than two ring aromatics. The radical scavenging by larger aromatics is less effective than smaller aromatic systems. McMillen et al. [4-5] proposed that in polycyclic aromatic solvent molecules these radicals can attack coal in the ipso position to help

break apart the coal in a bimolecular form, called radical hydrogen transfer (RHT). Radical species of coal or solvent origin transfer H-atoms in a bimolecular step shown in Figure 4.1.

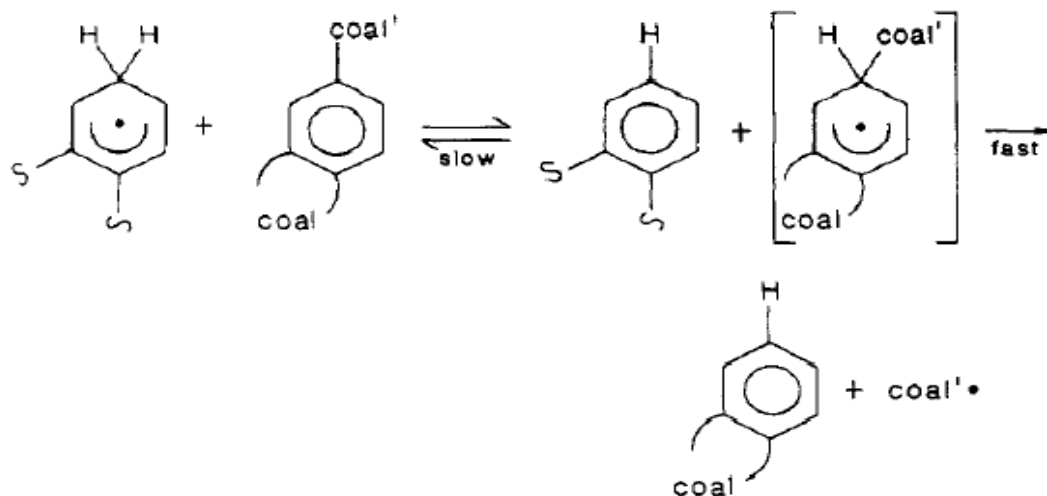


Figure 4.1: Radical hydrogen transfer mechanism, S are substituents

Source: McMillen, D.F., Malhotra, R., Hum, G.P., and Chang, S.J. *Energy & Fuels*, 1987. 1(2): p. 193-198.

A related mechanism was proposed by Hei and others [8] to explain their experimental data for the H_2S promoted cracking of model compounds. The radical species $\bullet\text{S}_x\text{H}$ is attached to the ipso position to effect cleavage. Derbyshire [3] suggests that RHT will tend to be a cleavage process, if a high concentration of solvent is present. At low concentrations, cleavage by the addition of free H-atoms will control the process.

Strong cross-links can be broken at liquefaction temperatures by a mechanism which involves the addition of the H-atoms or sulfur containing radicals to the ipso position of linkages to an aromatic system [3]. The hydrogen atom source is the free H-atoms from the solvent, coal or molecular hydrogen; RHT from solvent or coal species. A dissolution catalyst (presence of

catalyst dispersed through the dissolution) effect can be observed during thermal processes in that it increases hydrogen addition.

Aromatic rings are very stable unless they are hydrogenated to naphthenic rings, which may be thermally or catalytically cracked [9]. Radicals recombine or react with other molecules to form thermally stable bonds and the reactions continue until they are stabilized. Recombination reactions produce larger molecules that have more resistance toward further depolymerization. A variety of recombination reactions terminate the chain reactions. Neavel [10] suggested that such free radical reactions control coal chemistry and the dominant structures in coal are susceptible toward free radical attack. Methyl and hydroxyl substituents serve to increase the free radical reactivity of molecules [1, 11]

The amount of hydrogen released from the solvent is related to the heating rate. A slow heating rate allows more solvent dehydrogenation [12]. According to Derbyshire et al. [12], retrogressive reactions are more prevalent at high temperature in contrast to thermal or catalytic hydrogenation reactions. Retrogressive reactions can result in a lowering of the net distillate yield and in increasing the high boiling point liquid yield and solid residue. If the temperature is high (>450 °C), conditions become increasingly less favorable towards hydrogenation [12]. Also the population of free radicals will be reduced under these conditions, retrogressive reactions occur readily in low-rank coals, which can form cross-links more easily than bituminous coals [13]. Because of this, low-rank coals require more severe conditions to produce maximum oil yields. [14-15]. At temperatures of 400 °C and lower, however, subbituminous coals are more readily converted to liquid products and gases than bituminous coal [16]. Low-rank coal liquefaction

products have a higher oil to asphaltene ratio, are richer in hydrogen, and are more aliphatic than bituminous coals [16]. The occurrence of retrogressive reactions (termination reactions between coal radicals) forms high-molecular-weight products that are undesirable. “Catalysts” can help to minimize the extent of retrogressive reactions and maximize the production of soluble materials.

The second step in liquefaction is an upgrading of the products formed in the “primary liquefaction” step to form useful fuels through a further reduction in the molecular weight and heteroatom removal. Also in this step, nitrogen and remaining oxygen and sulfur are commonly removed. The focus of this study is the primary, depolymerization step, so upgrading will not be discussed further.

The primary liquefaction of coal can occur with or without solvent [3, 17-21]. Various catalysts have been studied, to maximize the production of soluble material and its quality, while minimizing retrogressive reactions [3, 12, 16, 19, 22]. Most of the solvents used in large-scale liquefaction processes are derived from crude oil refinery operations and they are relatively non-polar. However, non-polar solvents do not swell or disperse coal significantly [23]. Low-rank coals that are more suitable for liquefaction are more polar than bituminous coals and because of this reason their solubility in non-polar solvent is limited [23]. Consequently, contact with catalyst and hydrogenation and hydrogenolysis reactions are typically low in the early stages of liquefaction [3, 24]. Low-rank coals need to have more severe conditions, temperature or residence time, to get acceptable product yields and quality [24]. As a result, many laboratory liquefaction studies have focused on highly dispersed catalysts or soluble precursors that can be used to directly impregnate coal or can be dispersed as part of a coal/solvent mixture [25-32].

Sulfide catalysts have been dispersed directly on the coal surface. This may allow direct interactions between the catalyst and solid coal [1]. Highly dispersed and active catalysts also reduce the amount of catalyst required for recovery and regeneration [33-34]. Garcia and Schobert [27] compared three different sulfided catalysts, ammonium tetrathiomolybdate (ATM), sulfided ammonium molybdate and crystalline MoS_2 . They showed that MoS_2 provided the best liquid yield and hydrosulfurization performance at temperatures below 300 °C. MoS_2 is a very effective catalyst, even at low loadings, and catalyst distribution is essential, especially at low concentrations of catalyst [31]. Using higher concentrations of sulfided molybdenum improves liquefaction yields, but there is a limit. According to Derbyshire et al. [35-36], desulfurization was not improved at a loading more than 3% Mo as ammonium tetrathiomolybdate. The main role of the catalyst in coal liquefaction is to promote hydrogenation of the coal. Hydrogen transfer could also be accelerated by catalyst [3], capping coal radicals before they result in retrogressive reactions. Molybdenum disulfide catalyst first facilitates the depolymerization of the coal. When the coal reaches a certain extent of depolymerization, the catalyst acts to hydrogenate the heavier liquids to a lighter oil fraction [3, 37-38].

A solvent or class of solvents that would simultaneously partially solubilize, fragment, disperse, and directly mediate good contact between catalysts and coal at relatively low temperatures without the use of precursors, is expected to be an advance in this field. In previous chapters it has been shown that certain ionic liquids (ILs) fragment, swell (presumably), partially solubilize, and disperse a Powder River Basin (PRB) subbituminous and Illinois No. 6 bituminous coal as extremely fine particles to a remarkable extent [39]. This process also significantly enhances the

solubility yield of these two coals. In this chapter, this dispersion and solubilization effect is used to pretreat coals in the presence of a commercially available molybdenum disulfide catalyst ($<2\text{ }\mu\text{m}$ sized) to produce high liquefaction yields, under standard conditions, for these coals.

4.2. Materials and Methods:

The ILs used in this study were 1-butyl-3-methylimidazolium chloride, [bmim][Cl] ($>99\%$), and 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄] ($>98.5\%$), purchased from Sigma-Aldrich. Molybdenum disulfide, MoS₂, in the form of micrometer-sized particles ($<2\text{ }\mu\text{m}$), was also purchased from Sigma-Aldrich. Illinois No. 6 and Wyodak coals were obtained from the Argonne Premium Coal sample bank [40]. Chevron USA, Inc., an affiliate of the Chevron Corporation, also provided an additional PRB subbituminous coal.

The Illinois No. 6 coal has a moisture content of 8% and a mineral matter content of 18.1%, while the Wyodak coal has a moisture content of 28% and a mineral matter content of 8.7% (Table 4.1). PRB subbituminous coal, which had been partially-dried and had a moisture content of 13.7% and a mineral matter content about 8%. From Table 4.2 both coals had particle size less than $150\text{ }\mu\text{m}$ and also majority of their particle size were $50\text{-}100\text{ }\mu\text{m}$. Table 4.1 shows elemental and proximate analysis of these Illinois No 6 coal and Wyodak coal and also particle size measurements of these two coals shown in Table 4.2.

Table 4.1: Elemental and Proximate Analysis ^a

Coal	Illinois No. 6	Woyadak-Anderson
AR H ₂ O	7.97	28.09
AR Ash	14.25	6.31
AR VM	36.86	32.17
AR S	4.45	0.45
AR Btu	10999	8426
Dry Ash	15.48	8.77
Dry VM	40.05	44.73
Dry S	4.83	0.63
Dry Btu	11951	11717
Dry C	65.65	68.43
Dry H	4.23	4.88
Dry N	1.16	1.02
Dry Cl	0.05	0.03
Dry F ^b	0	0
Pyritic S	2.81	0.17
Sulfate S	0.01	0.03
Organic S	2.01	0.43
MAF C	77.67	75.01
MAF H	5	5.35
MAF N	1.37	1.12
MAF Org S	2.38	0.47
MAF Cl	0.06	0.03
MAF F	0	0
MAF O	13.51	18.02
MAF Btu	14140	12843
Dmmf C	80.73	76.04
Dmmf H	5.2	5.42
Dmmf N	1.43	1.13
Dmmf Org	2.47	0.48
Dmmf Cl	0.06	0.03
Dmmf F	0	0
Dmmf O	10.11	16.9
Dmmf Btu	14696	13020

^a Calculation of as-received, MAF, and dmmf values from dry data from Commercial Testing and Engineering Co. Modified Parr Formula (used): $MM(dry) = 1.13 \text{ Ash} + 0.47 \text{ Pyritic S(dry)} + 0.50 \text{ Cl (dry)}$. Parr Formula (not used): $MM(dry) = 1.08 \text{ Ash(dry)} + 0.55 \text{ S (total dry)}$. Abbreviations: IL, Illinois No. 6 seam; WY, Woyadak-Anderson seam; AR= as-received; VM = volatile matter; MAF = moisture and ash-free; dmmf = dry, mineral matter free; ^b Below detection levels for samples.

Source: <http://www.anl.gov/PCS/report/part2.html>

Table 4.2: Particle size measurements of Illinois No. 6 and Wyodak coals (-100 mesh)

Size (micron)	Wyodak-Anderson	Illinois No. 6
500+	0.00E+00	1.80E-01
500-425	0.00E+00	1.29E-01
425-355	6.40E-03	2.27E-01
355-300	7.73E-03	3.64E-01
300-250	8.26E-03	4.21E-01
250-212	6.45E-02	5.61E-01
212-180	5.01E-02	5.43E-01
180-150	5.29E-01	7.29E-01
150-125	1.96E+00	4.08E+00
125-106	5.01E+00	6.09E+00
106-90	1.00E+01	1.02E+01
90-75	1.18E+01	9.36E+00
75-63	8.00E+00	6.22E+00
63-53	1.55E+01	1.21E+01
53-45	1.05E+01	7.25E+00
45-38	6.28E+00	1.04E+01
-38	3.03E+01	3.12E+01
TOTAL	100	100

Source: <http://www.anl.gov/PCS/report/part2.html>

These coals were mixed with 3% MoS₂ particles in ILs (coal to IL ratio is 1 to 2 by mass) at 100 °C overnight and agitated a magnetic stirrer bar. Either [bmim][Cl] and [bmim][BF₄] were used; [bmim][Cl] dispersed the coal well but [bmim][BF₄] did not (chapter 3). The Argonne coals were not dried prior to mixing because it was expected that the ILs pull moisture from the coal. Also having a certain amount of moisture is likely to improve the liquefaction yield [41]. ILs have negligible vapor pressure at low temperatures, thus moisture is readily removed during the treatment at 100 °C. After treatment, the IL/coal dispersion was cooled to room temperature and IL was washed from the coal using 500 ml. hot distilled water via vacuum filtration. The ILs used here have very strong absorption bands in the infrared spectrum. However, in the spectrum of the washed coal samples, these bands were not detectable. The catalyst-impregnated coals were then dried in a vacuum oven (25" Hg= 0.084 MPa= 0.84 atm) overnight at low temperatures (~50 °C), to prevent additional transformations.

The final weight of the catalyst used is unknown, because MoS₂ catalyst is less than 2 µm in size, during washing and filtration some detached catalyst may have passed through the 2.5 µm filter paper. Filter paper with a smaller pore size could not be used because it clogged. The amount of catalyst had a maximum value of 3% of the weight of the coal, but is probably somewhat less.

In liquefaction experiments, catalyst impregnated coal-to-tetralin mass ratio was 1 to 2, and cold hydrogen pressure in the reactor was 6.9 MPa. Weighed catalyst-impregnated coal (about 1 g in initial experiments and 2 g subsequently) were placed in a 20 ml vertical microautoclave reactors (tubing bomb) with tetralin. The reactors were made of type 316 stainless steel. Prior to reaction,

the reactors were tested for possible leakage by pressurizing to 6.9 MPa with nitrogen and immersing in water. The reactors were purged by pressurizing one time with nitrogen and three times with hydrogen before the final pressurization with hydrogen. The reactors were heated in a fluidized temperature-controlled sand bath.

Liquefaction was carried out at 425 °C for 30 min. In some later experiments, a temperature of 400 °C was also used. Agitation was provided by vertical shaking. The liquid and solid contents of the reactor were transferred into a weighed glass thimble (40-60 micron pore size). The reactor was washed with pentane, and the washings were also filtered through the thimble. In some initial work, the pyridine solubility of the product was determined by using Soxhlet extraction. Extractions were also separated into oil, asphaltene and preasphaltene by sequential Soxhlet extraction with pentane, toluene, THF and pyridine, respectively, followed by rotary-evaporation and drying in a vacuum oven. The pyridine-soluble extract and final residue were then washed with water containing 1% tetrahydrofuran (THF) to remove as much of the pyridine as possible. These samples were then dried under vacuum (0.084 MPa) at 50 °C overnight. The experiments were repeated at least in triplicate. However, there was the occasional outlier in the data in which case additional runs were performed. Schematic for product work-up for liquefaction reactivity is illustrated in Figure 4.2.

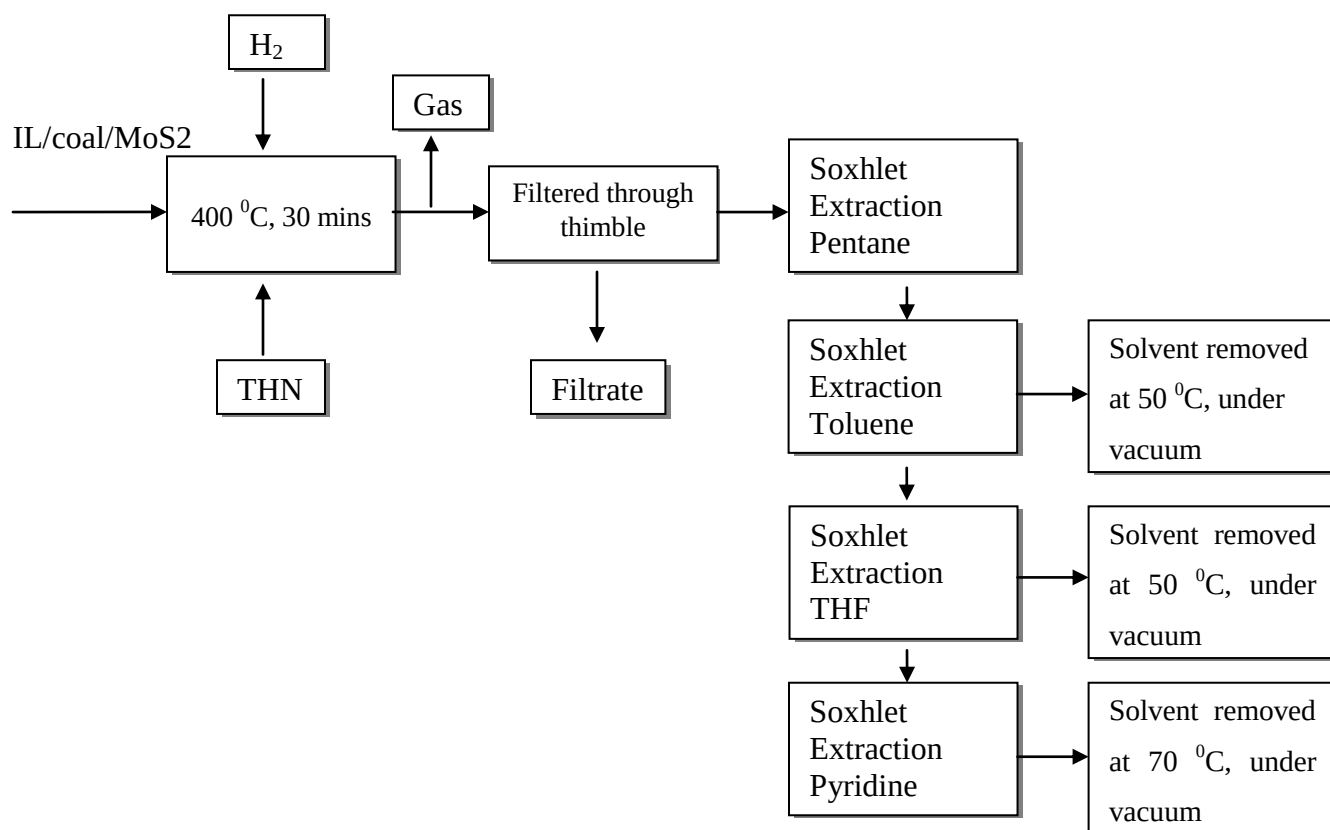


Figure 4.2: Schematic for Product Work-up for Liquefaction Reactivity

For subbituminous coals (both PRB and Wyodak) the tetralin/pentane mixture that passed through the thimble was dark brown. This indicates that this portion of the liquefaction product was soluble in these hydrocarbons. The tetralin/pentane soluble materials were collected for all coal samples for column separation analysis, discussed later. The residue was dried under vacuum (0.084 MPa) prior to Soxhlet extractions, with either pyridine alone, sequentially pentane, toluene, and pyridine, or sequentially pentane, toluene, THF, and pyridine, as described in the results. Solvent was removed from the residue after each Soxhlet extraction step by heating under vacuum (0.084 MPa) at about 50 °C, except for the final, pyridine-insoluble

residue, which was washed with water containing 1% THF to remove as much of the pyridine as possible. This washed residue then dried under vacuum at (0.084 MPa) 50 °C overnight.

FTIR spectra were obtained using a Thermo Scientific Nicolet 6700 Fourier transform infrared (FTIR) spectrometer or a BioRad FTS 3000 FTIR spectrometer. A wave number resolution of 2 cm^{-1} was used, and 200 scans were signal-averaged. Spectra were obtained using a diffuse reflectance accessory or for soluble samples as cast films on KBr windows. Solid samples were prepared by grinding with KBr in Wig-L-Bug, and spectra were referenced against pure KBr.

Experiments involving the reuse of the IL removed by washing also showed that a significant portion of the MoS_2 catalyst passed through the filter paper (because of the yield increase) and was present in the IL/water solution. After the IL was washed from the coal, water was evaporated and the residue used in new experiments to investigate how much catalyst is present in the recycled IL part, and if it is possible to use recycled IL/catalyst mixture. Recycling aids the economics of the process. The water is being easily removed from ILs via evaporation.

4.3. Results:

It was shown earlier in this thesis (chapter 3) that certain ILs fragment, disperse, and partially dissolve PRB and Illinois No. 6 coals as extremely fine particles to a remarkable extent. The initial coal particles were mostly of the order of 100 μm or larger in size (optical microscopy observations) also the particle size distribution in Table 4.2. Coal samples after several hours contact with the IL, [bmim][Cl] at 100 °C become dispersed as small particles, majority <10 μm

or less. Many particles also appear to be partly transparent, most probably because they are thin (see Figure 3.9). But not all the ILs disperse these coals to this degree. The IL [bmim][BF₄] did initially appear to disperse the coals at 100 °C, but the particles can clearly be seen both at the bottom of the tube and suspended in the slightly discolored solvent upon cooling to room temperature.

In initial studies, molybdenum disulfide particles dispersed in coal/IL mixture have a significant effect on liquefaction yields. These experiments simply involved standard liquefaction conditions of 30 min. at 425 °C under 6.9 MPa of hydrogen with a 2:1 mass ratio of tetralin/coal. The yield were constant around 80%, ar (95%, dmmf) soluble material for the Illinois No. 6 coal and 66%, ar (70%, dmmf) soluble material for the PRB coal comparable to published yields for the latter but higher than previous work for the former. Subbituminous coals gave lower yields of soluble material, comparable to the yields obtained by Sasaki et al. [42] and Song et al. (83.6%, dmmf for Wyodak coal) [29] for such coals. In work reported in the literature, Bockrath et al. [26] by using exfoliated MoS₂ catalyst and Miknis et al. [43] by using chemically dried coal have obtained 87% and 80% soluble material for the bituminous coal, respectively. These results were very promising. Also, these yields were calculated on the basis of the weight of soluble product relative to the weight of catalyst-impregnated coal obtained after contact with IL and subsequent washing with water to remove solvent, followed by drying under vacuum (0.084 MPa) at 50 °C. During washing the ILs from the coals, coal can re-absorb some moisture and water may not have been removed in this drying step, because of the hydrophilic structure of ILs. It was assumed that coals are dry after the vacuum drying step. After a simple mineral matter correction calculation, soluble yields of 95% and 70%, for Illinois No. 6 coal and PRB coal, respectively,

were calculated. This is a very high yield in comparison to Illinois No. 6 coal without catalyst and IL treatment yield (77%) and with catalyst without IL treatments yield (84%). The infrared spectra of the insoluble residues are compared in Figure 4.3 to determine organic contributions.

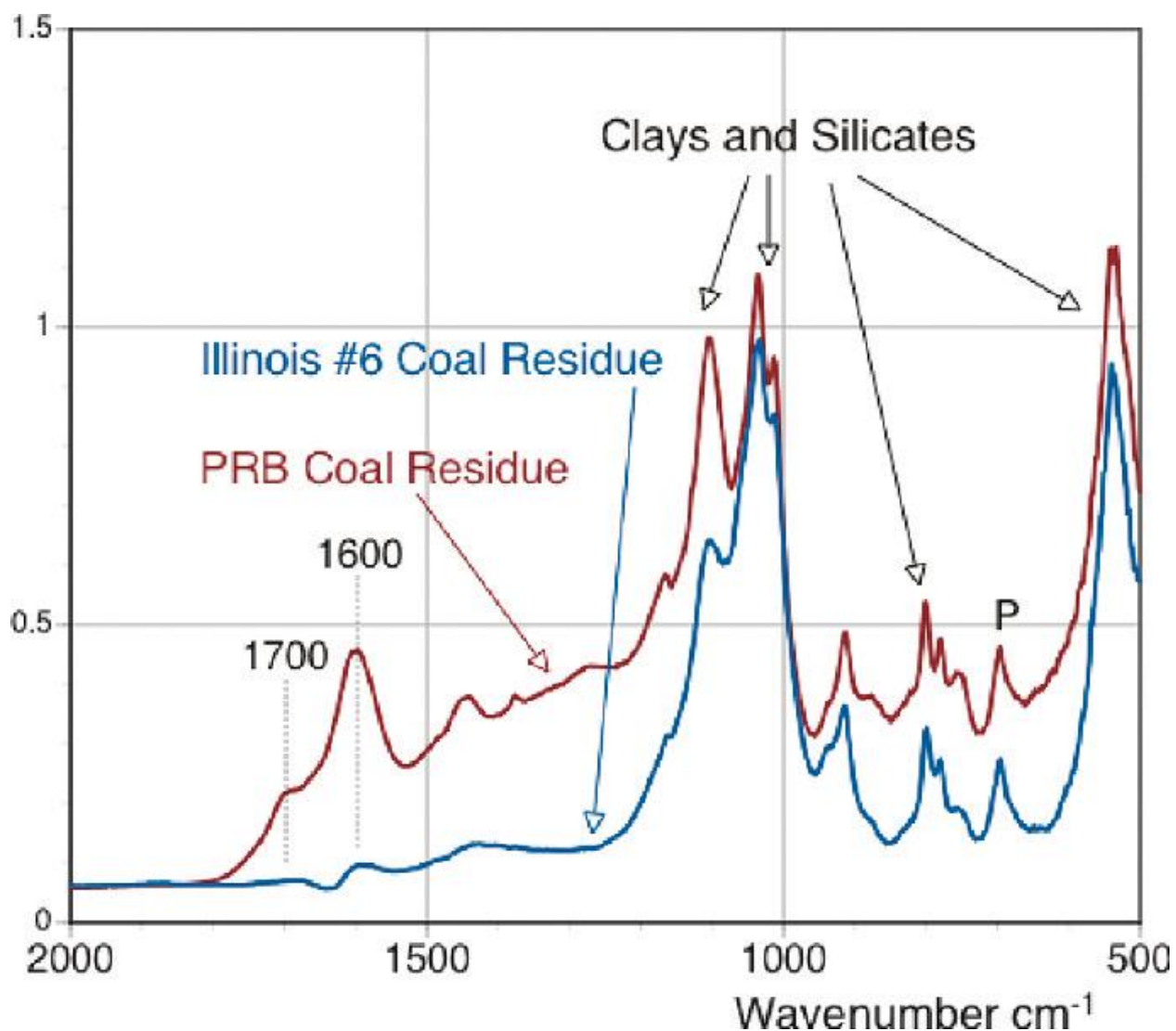


Figure 4.3: Infrared spectra of the residues obtained after liquefaction of an Illinois No. 6 coal after mixing with MoS_2 particles in the IL $[\text{bmim}][\text{Cl}]$. The letter P indicates a band due to residual pyridine.

There is a very small peak in the aromatic ring mode region near 1600 cm^{-1} in the Illinois No. 6 coal residue. This peak indicates that there is very little organic matter left in the Illinois No. 6 coal residue. The bulk of the residual material appears to be mineral matter, predominantly clays and silicates. In contrast, the PRB coal residue has clearly visible bands in the aromatic region, thus the PRB coal residue has more organic material than the Illinois No. 6 coal residue, consistent with lower liquefaction yield. Both coal residues have a weak band, labeled P in the spectra, near 700 cm^{-1} assigned to residual pyridine. Pyridine is very hard to completely remove from residues and their extracts. To remove as much of the pyridine as possible, residues were washed with water containing 1% THF. The relative weakness of this band indicates that there are only small amounts of this solvent remaining, but this is a source of error in yield determination.

In liquefaction experiments, it is conventional to do a sequential set of Soxhlet extractions using n-hexane, toluene, and THF to separate the products into oils, asphaltenes and pre-asphaltenes, respectively. Whitehurst et al. [17] used pyridine instead of THF and this approach was applied to some set of extraction experiments here. Liquefactions were carried out on an Illinois No. 6 coal, using the standard conditions, 30 min at $425\text{ }^{\circ}\text{C}$, under 6.9 MPa of hydrogen and 2:1 ratio of tetralin/coal. Five sets of experiments were performed with and without catalyst and with different ILs, the results are displayed in Table 4.3.

Table 4.3: Coal liquefaction results (425 °C) comparing IL pretreatment to conventinal catalyst impregnation (dmmf)

Illinois No. 6 Bituminous coal	Pentane soluble (%)	Toluene soluble (%)	Pyridine soluble (%)	Total soluble (%)	Total yield calculated from the weight of the residue (%)
(1) No IL treatment, no catalyst	~14.3	17.0	45.1	~76.4	77.2
No IL treatment, no catalyst Pyridine only			68.4	68.4	76.1
(2) [bmim][Cl] treatment, no catalyst			82.9	82.9	86.5
(3) Physically mixed with MoS ₂			74.4	74.4	84.3
(4) Mixed with MoS ₂ in [bmim][BF ₄]	~17.0	23.2	18.6	~59.4	69.3
(5) Mixed with MoS ₂ in [bmim][Cl]	~21.9	19.2	48.4	~89.5	~99
Mixed w/MoS ₂ in [bmim][Cl] Pyridine only			91.6	91.6	99

Some experiments used pyridine extraction only. First, a coal sample was simply reacted in the presence of tetralin with no added catalyst. The sample was not fragmented/dispersed in an IL prior to liquefaction. A total yield of about 77% soluble material on a mineral-matter-free and (presumed) dry basis was obtained. The yield was calculated two different ways, from the weight of extracted material and on the basis of the weight of the final residue, both relative to the weight of the treated sample after washing and drying. Predominantly, yields were calculated on the basis of the weight of the residue.

Both pentane-soluble and toluene-soluble extracts obtained in this experiment were dried under very high vacuum to remove any residual tetralin. The pyridine extracts and final residue were washed with water containing 1% THF to aid pyridine removal then dried under vacuum (0.084 MPa) at 50 °C overnight. In a duplicate experiment, where just the pyridine solubility was determined, a yield of about 76% soluble material was achieved, in good agreement with the first liquefaction run.

In the second experiment, the coal was first fragmented, dispersed and partially solubilized in [bmim][Cl] in the absence of the catalyst and the resulting material was liquefied in the presence of tetralin. The pyridine solubility of the second experiment with this treatment increased to about 87% (dmmf). This indicates that an IL treatment allows a better contact of the fractured and dispersed coal with solvent.

In the third liquefaction experiment, the coal was physically mixed with 3 weight% of catalyst prior to liquefaction. There was no IL treatment before liquefaction and a yield of about 84% (dmmf) pyridine-soluble material was obtained. This result is comparable to the second experiment; IL dispersed and fragmented coal in the absence of the catalyst. The fourth sample was first contacted with the IL [bmim][BF₄] and MoS₂ at 100 °C overnight. The IL and some catalyst particles were then removed with water prior to liquefaction. The total yield of soluble material decreased to about 69%, since [bmim][BF₄] cause agglomeration, this limiting contact between coal particles, solvent and catalyst.

The fifth liquefaction experiment was first conducted with the IL [bmim][Cl] and catalyst particles. The solubility yield increased to 99%. This number also includes some gaseous products and small amounts of difficult to remove pyridine. Successive extractions with pentane, toluene, and pyridine and a rerun of the experiment where just pyridine solubility was determined gave equivalent total yields. It is difficult to remove tetralin from the tetralin/pentane fraction that initially filtered through the extraction thimble. For some experiments; high vacuum system was used, but it also removed low-molecular-weight liquefaction products. As a result of these problems and any losses in each extraction step, the total yield calculated from summing the amount of soluble material in each fraction is less than that calculated from the weight of the insoluble residue. In addition, the total yield calculated on the basis of the weight of the final residue will also include gaseous products. On the other hand, the results clearly indicate that pre-treating the coal with IL [bmim][Cl] in the presence of an off-the-shelf catalyst significantly increases yields of soluble material relative to other processes. Essentially, all of the Illinois No. 6 coal becomes soluble after this treatment. However, the IL [bmim][BF₄] treatment decreases yields, because of agglomeration. These stacked infrared spectra of the insoluble residues of these experiments are compared in Figure 4.4.

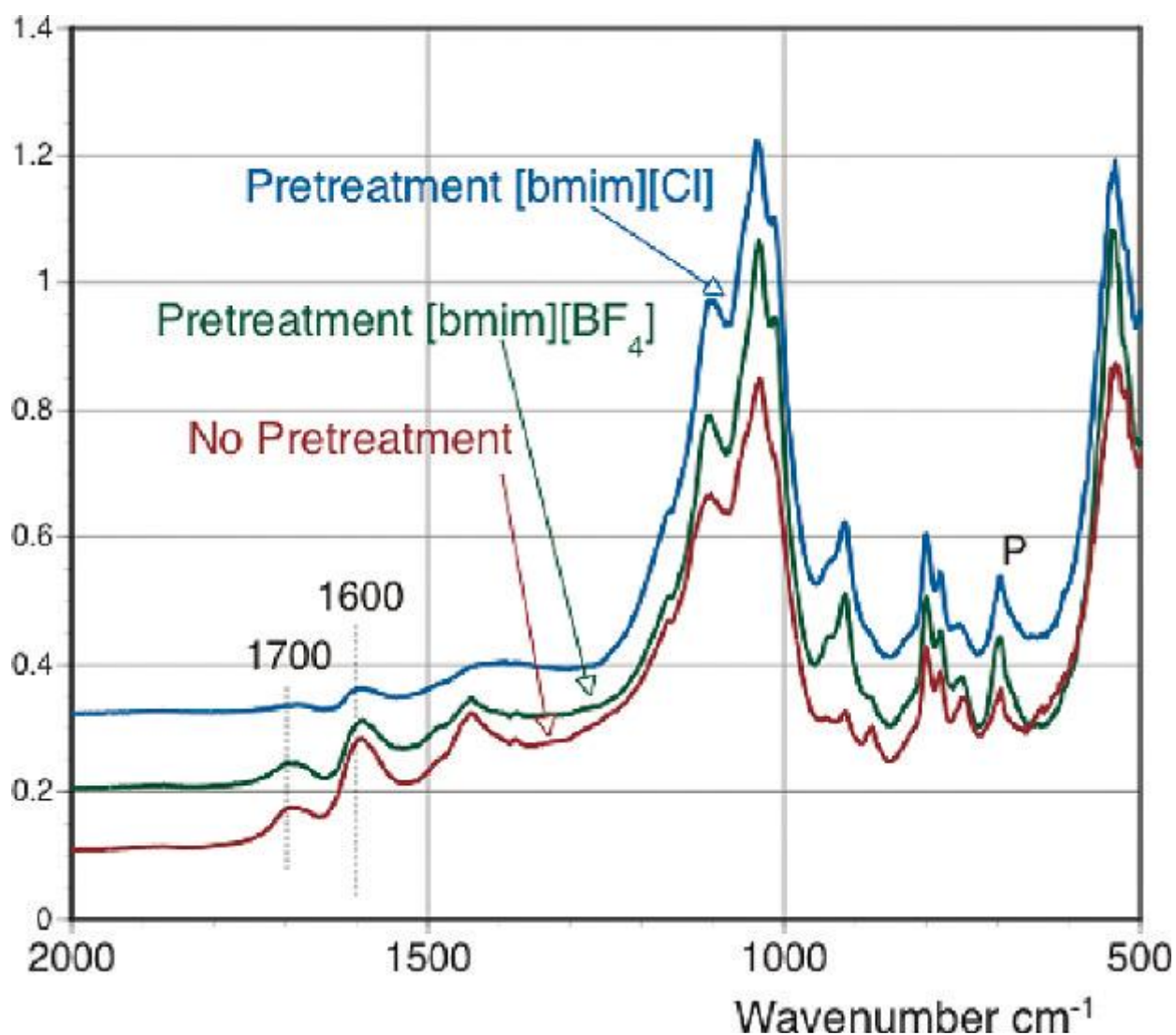


Figure 4.4: Infrared spectra of the residues obtained after liquefaction of an Illinois No. 6 coal after mixing with MoS_2 particles in the ILs [bmim][Cl] and [bmim][BF₄] and in the absence of IL. The letter P indicates a band due to residual pyridine.

There are weak bands near 1600 cm^{-1} due to aromatic groups and near 1700 cm^{-1} because of carbonyls in the spectra of samples. No pretreatment and [bmim][BF₄] pretreatment samples have a more intensive aromatic band and this is a reflection of their lower liquefaction yield.

Illinois No. 6 coal gave much greater yield of pyridine-soluble product than PRB subbituminous coal in Table 4.4. PRB coal was supplied in a partly dried manner. Miknis et al. [43] showed that thermal drying resulted in changes in the physical structure and cross-linking density of coals and a subsequent decrease in liquefaction yields. Also Gronhovd et al. [24] suggests that drying may deactivate low-rank coal because of surface oxidation and a collapse of the pore structure. Another subbituminous coal was therefore also studied. As-received Wyodak subbituminous coal samples from Argonne Premium Coal sample were used for the later liquefaction experiments. This coal was chosen since it is well studied in the literature so it would be easy to compare the results to previous work. All coal samples were first contacted with IL [bmim][Cl] and catalyst particles, before the liquefaction step. Liquefactions were performed for 30 min at 425 °C under 6.9 MPa of hydrogen with a 2:1 ratio of tetralin/coal. After liquefaction, all samples were filtered through the soxhlet thimble, tetralin/pentane soluble materials were not evaporated to remove tetralin but were kept for subsequent column separations. Tetralin/pentane insoluble materials were then subjected to successive extractions with pentane, toluene, THF, and finally pyridine. The THF extraction step was included so that the results could be compared to other reports in the literature that also used this solvent. These yields for two subbituminous coals and Illinois No. 6 coal are compared in Table 4.4.

Table 4.4: Coal liquefaction results (425 °C) using IL pretreatment on three coals (yields calculated on a dmmf basis)

	tetralin+ pentane soluble (%)	Pentane soluble (%)	toluene soluble (%)	THF soluble (%)	Pyridine soluble (%)	Total yield calculated from the weight of the residue(%)
Illinois No. 6 Bituminous coal	~45.4	7.6	17.4	10.1	6.6	87
PRB Subbituminous coal	~43.8	5.5	9.4	8.3	5.8	72.9
Wyodak Subbituminous coal	~50.0	7.3	9.5	4.1	5.2	76.6

Illinois No. 6 coal gave a surprising lower yield (87%, dmmf) of total soluble material when the yields were compared to initial results described above (99%), while the two subbituminous coals gave yields of about 73% and 77% for the PRB and Wyodak coals, respectively. Infrared spectra of the insoluble residues obtained from the liquefaction of the PRB coal and Illinois No. 6 coal are compared in Figure 4.5

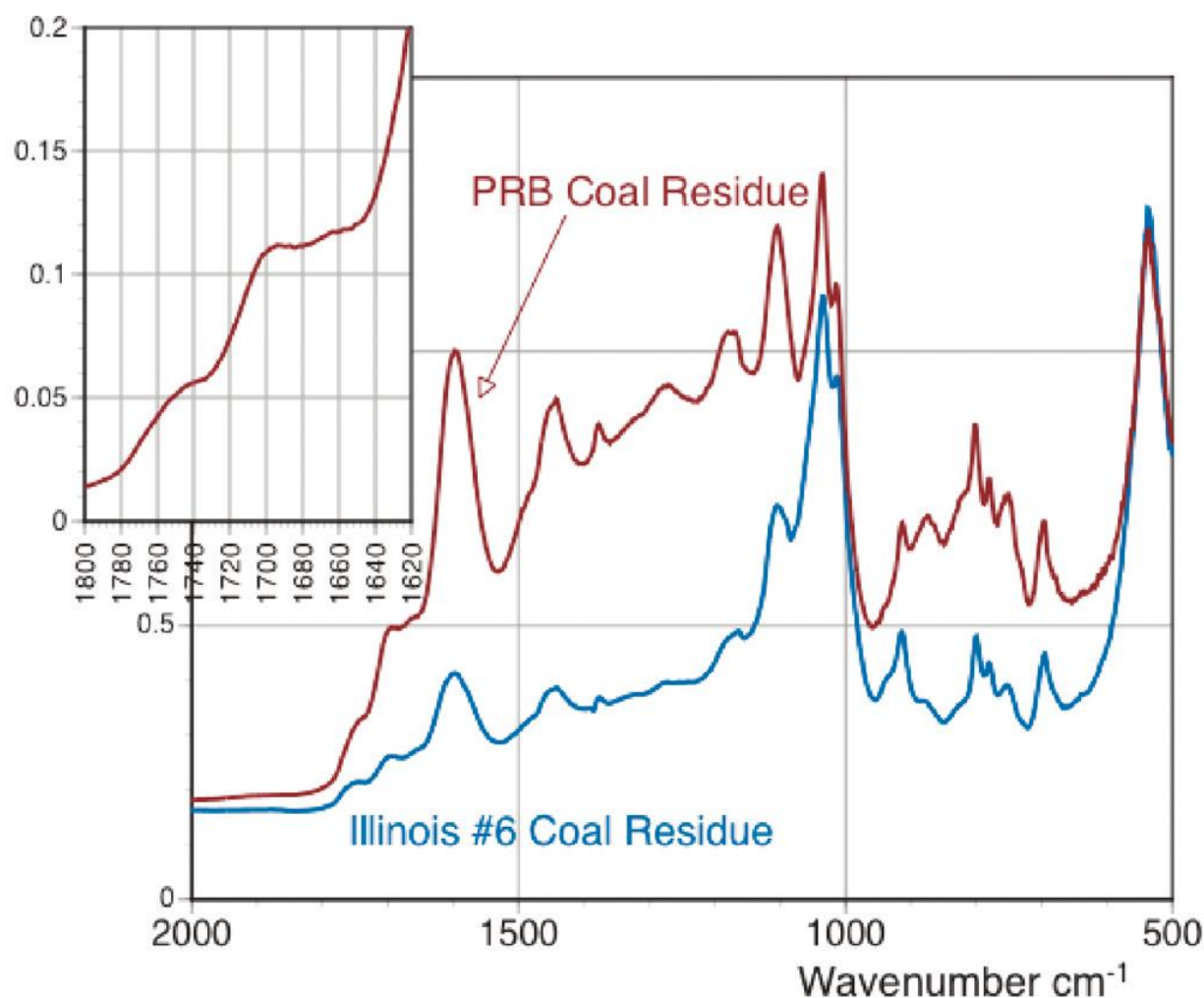


Figure 4.5: Infrared spectra of the residues obtained after liquefaction of an Illinois No. 6 and a PRB coal after mixing with MoS_2 particles in the IL $[\text{bmim}][\text{Cl}]$. The samples were sequentially extracted with pentane, toluene, THF, and pyridine. The inset shows the absorbance-scale-expanded region of the carbonyl-stretching region of the PRB coal

It can be seen that, in addition to the 1600 cm^{-1} band characteristic of aromatic rings, there are a number of bands between 1660 and 1800 cm^{-1} that can be assigned to carbonyl groups of various types. An inset in this figure shows an absorbance-scale-expanded plot of this region of the spectrum. Shoulders near 1740 and 1770 cm^{-1} can be assigned to anhydride groups. They are absent in the spectra of the same samples subsequently hydrolyzed by 0.1 N HCl . The formation

of such groups would be expected to cross-link the units present and thus decrease solubility. If the THF extraction step was skipped, these bands could not be seen in the spectra of residues. Such linkages form at temperatures above 100 °C and in this study THF was removed at 50 °C or less under vacuum (0.084 MPa), so the origin of these cross-links remains unknown. The experiments in Table 4.4 indicate that the tetralin/pentane soluble material is very large fraction of the product, 50% or more for the Wyodak coal. Some of the calculated yields would include gases, but there did not appear to be any unusually large amounts of volatile material produced in these experiments.

In a subsequent set of liquefaction experiments, where the THF extraction step was eliminated and the temperature of liquefaction was lowered to 400 °C, the production of significant amounts of tetralin/pentane soluble material was confirmed. Liquefaction experiments were performed for both subbituminous coals, PRB and Wyodak and also the Illinois No. 6 coal and the results are shown in Table 4.5.

The yields of total soluble material for Illinois No. 6 coal were close to 100% (dmmf). The PRB coal gave a yield of about 68% soluble material, comparable to the previous run (73% at 425 °C), but the Wyodak coal gave liquefaction yield of about 84%, higher than liquefactions performed at higher temperature of 425 °C (77%).

Table 4.5: Coal liquefaction results (400 °C) using IL pretreatment on three coals (yields calculated on a dmmf basis)

	tetralin+ pentane soluble (%)	Pentane soluble (%)	toluene soluble (%)	Pyridine soluble (%)	Total yield calculated from the weight of the residue(%)
Illinois No. 6 Bituminous coal	~46.9	7.7	10.2	34.9	~99
PRB Subbituminous coal	~30.7	12.6	1.6	22.3	67.3
Wyodak Subbituminous coal	~59.5	6.6	8.4	9.1	83.6

These repeat liquefaction experiments show good agreement with the previous result of Miknis et al. [43]. Experiments were performed in triplicate unless data outliers were obtained. Average data values are shown in Table 4.4 and Table 4.5. Drying coals thermally decreased the conversion for low-rank coals. They obtained 18% lower liquefaction yield for a Wyoming subbituminous coal (73% to 55%, dmmf). Because the PRB coal was thermally-dried there were apparently changes in the physical structure and cross-linking density of coals that lowered liquefaction yields. As a result, both Wyodak subbituminous and Illinois No. 6 high volatile bituminous coal gave better extraction yields at a lower temperature of 400 °C.

To confirm that oil-like material dissolved in the tetralin/pentane solvent mixture, the soluble material from the Illinois No. 6 liquefaction was loaded onto a silica gel column and eluted

sequentially with pentane, benzene and methanol. Fractions were collected in vials, as shown in Figure 4.6.

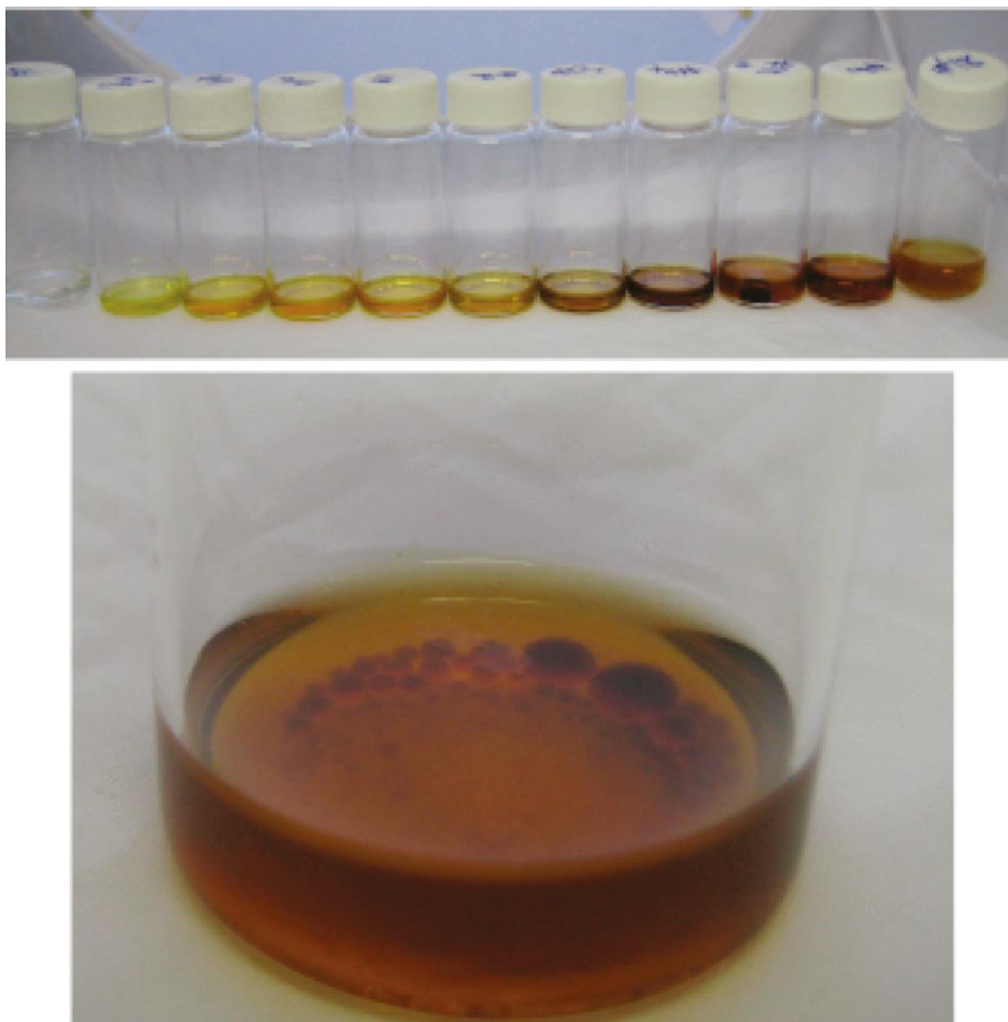


Figure 4.6: Photographs of the fractions collected after loading the tetralin/pentane soluble coal liquefaction products on a silica gel column and eluting sequentially with pentane, benzene, and methanol (upper).

Films were cast from the lighter colored material, but the parent solutions proved too dilute to provide sufficient material for the recording of good-quality infrared spectra. However, the darker fractions came off the column as single-phase solutions, but upon standing for a few hours, an oil phase separated, as can be seen in the picture of these vials, also shown in Figure 4.6. Infrared spectra of two of these oil fractions, eluted with benzene and benzene/methanol, obtained after evaporation of the solvent, are compared in Figure 4.7.

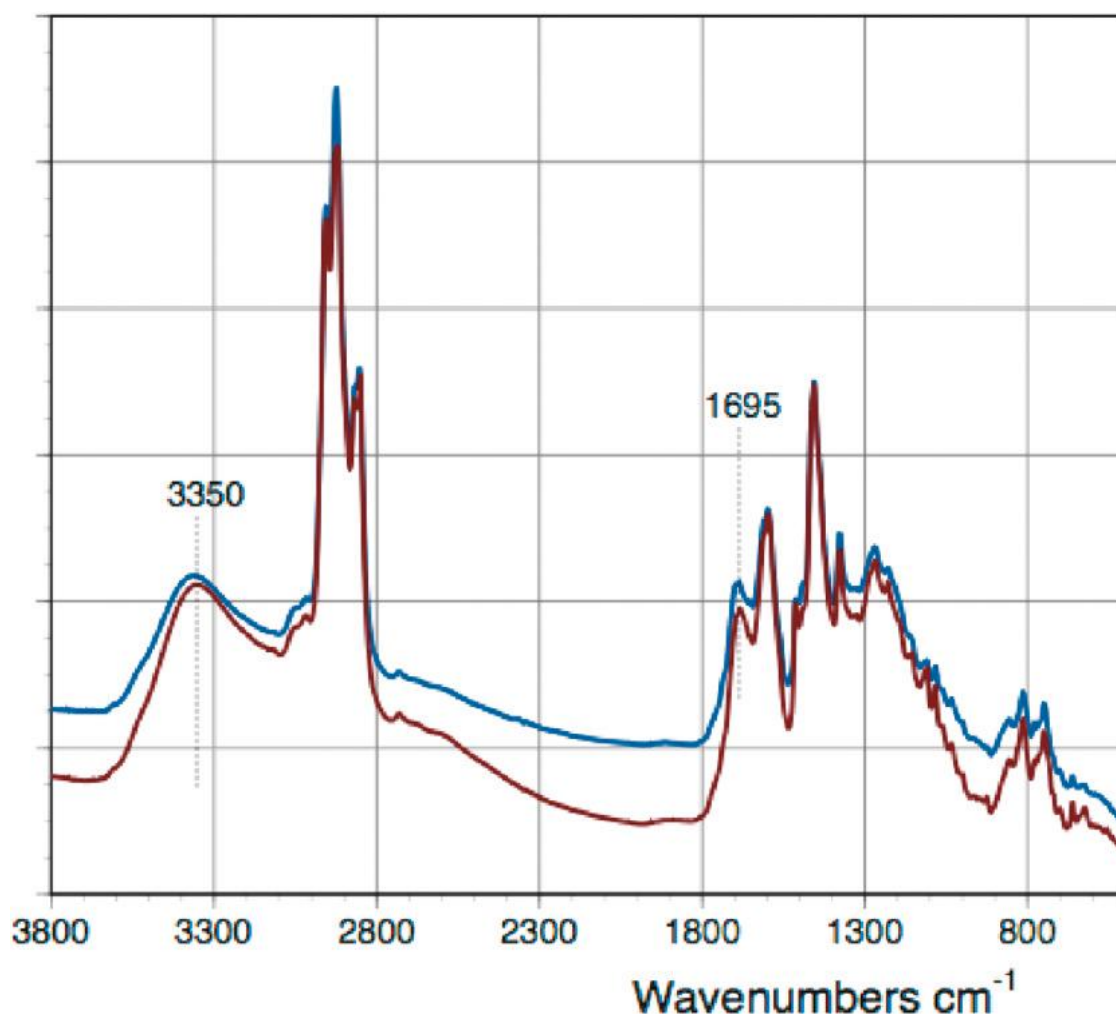


Figure 4.7: Infrared spectra of two of the fractions eluted from the silica gel column after evaporation of the solvent. The fractions are those contained in the vials that are third and fourth from the right-hand end of the collection shown in Figure 4.6.

The most intense bands in the spectrum are due to aliphatic CH groups, whose stretching modes can be observed between 2800 and 3000 cm^{-1} . These are much more intense than the equivalent bands in the spectrum of the parent coal, demonstrating that these fractions are much more aliphatic. However, bands due to carboxylic acids and phenolic OH groups can also be observed in the spectra, near 1700 and 3350 cm^{-1} , respectively, demonstrating that these fractions still have significant heteroatom contents. This extract was free of mineral matter/ash (based on lack of mineral matter functionality). Thus ILs may be an approach to hypercoal.

It is desirable to use ILs several times for new liquefaction runs via evaporation of the water from IL/water mixture. Table 4.6 shows that coal liquefaction results from using recovered IL pretreatment on Illinois No. 6 coal and also results were compared with original IL pretreatment on Illinois No. 6 coal.

The recovery of ILs was also investigated. Illinois No. 6 coal was mixed with the IL removed by washing in experiment (1). Also 1 weight % of the MoS_2 was added and the mixture treated at 100 °C overnight. After treatment, the IL/coal dispersion was cooled to room temperature and IL was washed from the coal using hot water, as in the other liquefaction experiment in this chapter. Then the catalyst-impregnated coal was dried in a vacuum oven overnight at 50 °C. The dried coal and tetralin was then placed in a tubing bomb reactor. Experiment utilized standard liquefaction conditions. The yield in the initial experiment was 87% (dmmf) soluble material. Reusing the IL gave an extraction yield of near 100% (dmmf). The same procedure was repeated with the washed IL from experiment (2) to run experiment (3). This is the second use of the IL, and the yield was 98%. The effect of not adding additional catalyst on liquefaction yield was also

studied. The washed IL from experiment (3) was used to run experiment (4). The yield was 90.2%. Experiment (2) and (3) gave better solubility than experiment (1). This is probably because the washed and recycled IL already has suspended catalyst, because of filter paper pore size is bigger than the catalyst particles, 2.5 μm and 2 μm in size, respectively. Experiment (4) also shows that the IL/water part has enough catalyst to perform liquefaction with good yields.

Table 4.6: Coal liquefaction results 425 °C comparing reusing IL pretreatment on Illinois No. 6 coal.

Illinois No. 6 Bituminous coal	tetralin+ pentane soluble (%)	Pentane soluble (%)	toluene soluble (%)	Pyridine soluble (%)	Total yield calculated from the weight of the residue(%)
(1) Mixed with MoS ₂ in [bmim][Cl]	~45.4	7.6	17.4	16.6	87
(2) Reuse of (1), added 1 wt% MoS ₂	~53.4	4.4	22.2	21.7	100
(3) Reuse of (2), added 1 wt% MoS ₂	~40.6	6.5	32.7	18	98
(4) Reuse of (3), no added catalyst	~38.1	9.3	29.3	13.2	90

4.4. Discussion:

Molybdenum catalysts, especially, MoS_2 , promote hydrogenation and coal depolymerization at temperatures of 350-450 °C [25-32]. These catalysts accelerate the rate of hydrogenation with hydrogen donor solvent better matching the rate of free-radical formation, reducing retrogressive reactions [28]. In previous work by Bockrath et al., MoS_2 was intercalated with lithium, then exfoliated in a mixture of THF/ water in the presence of coal to improve catalyst performance [26]. This technique enhanced the catalyst activity and gave “good” liquefaction performance. The purpose of work reported here was to demonstrate the ability of certain ILs to partially solubilize, fragment, and disperse coal as small particles enhancing contact with “off-the-shelf” MoS_2 to improve liquefaction yields. Dispersed and fragmented Illinois No. 6 coal was converted to a form to a remarkable soluble (99%, dmmf) in a series of solvent extractions. Two subbituminous coals gave lower yields (80%), comparable to those obtained by Sasaki et al. [42] and Song et al. [29].

Whitehurst et al. [17] reported that subbituminous coals gave lower liquefaction yields relative to bituminous coals. However, low-rank coals are comparatively rich in hydrogen, they produce higher oil to asphaltene ratios, also products that are more aliphatic than bituminous coal liquids [16]. However, if a lower liquefaction temperature was used, 400 instead of 425 °C, the yield of soluble material of Wyodak subbituminous coal increased. This suggests that the yield of soluble material could probably be improved using temperature-staged or temperature-programmed liquefaction [28]. Temperature-staged liquefaction (TSL) involves a rapid heat-up between the low and high temperature, while temperature-programmed liquefaction (TPL) involves a slower

transition. These techniques slow free radical formation, provide additional time for conversion of the catalyst precursor into an active form, enhance solvent-coal interactions, and help match the rate of hydrogenation, reducing radicals recombination [28]. These strategies are beneficial particularly for the lower yield coals. Temperature-staged liquefaction and temperature-programmed liquefaction are most effective in the presence of a catalyst and low-temperature pretreatment has a good impact on the performance of the catalyst, solvent or both. These techniques are not effective in solvent-free, noncatalytic reactions [28].

It was observed that a significant amount of liquefaction material is soluble in tetralin/pentane mixtures, more than 50% in some experiments in Table 4.5. This result is unexpected because pentane is non-polar and low-rank coals have polar characters. This study suggests that these polar products have a low-molecular weight.

4.5. Conclusions:

Certain ILs can be used to fragment, disperse and partially dissolve coals as small particles and this enhances contact with an “off-the-shelf” micrometer-size molybdenum disulfide catalyst. This, in turn, improves the yield of liquefaction. Also, using ILs and catalyst enhanced the oil yield. The IL [bmim][Cl] was very effective in dispersing Illinois No. 6 and two subbituminous coals. Essentially, dispersed and fragmented Illinois No. 6 coal is converted to a form that is almost completely soluble (99%, dmmf) after a subsequent standard liquefaction conditions. This is a very promising, high yield, typically in the literature are around 80% for this coal. The yields of soluble material obtained for two subbituminous coals were less, but were comparable to

those obtained in work reported in the literature using soluble catalyst precursors. Surprisingly, in some experiments, more than 50% of the liquefaction products were found to be soluble in tetralin and pentane, this beneficial oil yield was very high. The oils are most desirable liquefaction product. Also it was shown that IL recovery is possible, reducing the liquefaction cost for this approach.

The experiments were repeated at least in triplicate. However, there was the occasional outlier in the data, in which case additional runs were performed. Here small amounts (1g) of coal were utilized since the ILs are expensive (coal to IL ratio 1:2). However, using small amounts of coal may produce variations, as coals are heterogeneous. Using larger amounts of coal may reduce experimental variations. It is recommended to increase the amount of coal used to 5g in future studies.

Current technologies suffer from the inability of catalysts to contact the coal efficiently until a stage in the process where the coal has been fragmented and at least partially solubilized. This study has shown that certain ILs solubilize and disperse coal quickly under fairly mild reaction conditions. Coals dispersed and solubilized in this manner by a simple solvent have not been observed previously and it suggests that an exploration of the IL solvents may have a significant impact in coal research, processing, and use.

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CHAPTER 5

SUMMARY AND FUTURE WORK

5.1. Summary:

In general, the main objective of this work was to evaluate ILs use for conversion of coal-to-liquid fuels by direct liquefaction, to enhance liquefaction yields, reduce the number of process steps (catalyst activation), improve liquid yield, and quality

To achieve this goal ILs were used to fragment, disperse, and partially dissolve coals to allow a better contact with micron size catalyst particles during direct coal liquefaction. Ionic liquids may facilitate higher reaction rates, reaction selectivity, and yields, also ILs are non-flammable improving process safely [1-2]. Ionic liquids can engage in a wide range of intermolecular interactions particularly with certain ranks of coal. Ionic interactions play an important role in low- and medium-rank coal chemistry. ILs that would simultaneously partially solubilize, fragment, disperse, and directly mediate good contact between micron-sized catalysts and coal, at relatively low temperatures, without the use of precursors might prove to be a useful advance in this field. It could then be determined if this maximized the production of soluble material with a higher oil fraction, while minimizing the extent of retrogressive reactions during a subsequent liquefaction. Ionic liquids have shown promise in other industrial applications, but their application to coal processing is new. Selected ionic liquids were explored for use in direct

coal liquefaction. Specifically, the dispersion and fragmentation potential of ionic liquids was explored with an Illinois No. 6 bituminous coal and subbituminous coals.

ILs can also disperse many inorganic materials as fine particles and have also been used to stabilize catalysts as nanoparticles [1]. Molybdenum sulfide catalysts have been widely used in coal liquefaction, but they need to be well dispersed usually requiring several treatments to function effectively. ILs can significantly promote liquefaction yields with appropriate catalysts without these additional steps. Thus there are two goals pursued in here. The first was an evaluation of the ability of selected ILs to fragment and disperse coal as small particles, at mild temperatures, to allow good contact with micron sized catalyst particles. The second was to determine the liquefaction yields of the catalyst impregnated coal in a traditional direct-liquefaction experiment using tubing-bombs.

The ILs used in this study were 1-butyl-3-methylimidazolium chloride, [bmim][Cl] (>99%) and 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄] (>98.5%). Imidazolium ILs were chosen for study because they are more chemically stable, relatively cheaper, and easier to work with than other types of ILs [2]. The catalyst used, molybdenum disulfide, MoS₂, was obtained in the form of micrometer-sized particles (~2µm). Coal samples were mixed with 3% MoS₂ particles in ILs at 100 °C overnight. Microautoclave reactors (tubing bombs) were heated in a fluidized temperature-controlled sand bath and single-staged liquefaction conditions were used at a temperature of 425 °C for 30 min. In some experiments a temperature of 400 °C was also used. Tetralin was used as hydrogen-donor solvent. In addition, some experiments were performed without added catalyst and without ILs treatment to obtain a basis for comparison of yields. To

investigate the recovery of ILs, IL removed by washing was used several times in new liquefaction experiments with or without added catalyst. Relatively expensive ILs need to be recycled a large number of times in process if it is to be economic.

It was found that certain ILs fragment and disperse a PRB and Illinois No. 6 coal as extremely fine particles to a remarkable extent ($<10\text{ }\mu\text{m}$ from $\approx 100\mu\text{m}$ particles). This is probably a result of ability of ILs to disrupt intermolecular interactions in these coals. The IL [bmim][Cl] broke up -100 mesh coal particles at low temperatures upon heating to $100\text{ }^{\circ}\text{C}$, which allowed the IL to melt and mix with the coal. The other two ILs studied did not disperse the coals by mixing at room temperature, however. The nature and extent of these interactions is not well understood at this point and should be studied in future work.

The ability to fragment, disperse and partially dissolve coals as small particles was used to enhance contact with “off-the-shelf” micrometer-size molybdenum disulfide catalyst. This, in turn, improved the liquefaction yield. Also, using ILs and catalyst enhance the oil yield. The IL [bmim][Cl] was highly effective in dispersing Illinois No. 6 and two subbituminous coals. Essentially, the dispersed and fragmented Illinois No. 6 coal is converted to a form that is almost completely soluble (99%, dmmf) in pyridine after liquefaction was performed under standard conditions. The yields of soluble material obtained for two subbituminous coals were less, but were comparable to those obtained in work reported in the literature that used soluble catalyst precursors. In some experiments, more than 50% of the liquefaction products were found to be soluble in tetralin and pentane, so the desirable oil yield was very high. Also it was shown that IL recovery is possible and this could reduce the overall cost of liquefaction using this approach.

5.2. Future Work:

One possibility for future work is investigating how ionic liquids could be used to produce “clean” coal. In one of the previous experiments with the IL [bmim][Cl] and Illinois No. 6 coal, it is appeared possible to separate mineral matter via treatment with IL at 100 °C, overnight. These initial results need to be investigated further.

In addition, organic components in coal are extracted with certain solvents, but the extraction yield is usually fairly low at room temperature [3]. However, Renganathan et al. [4] reported that N-methyl-2-pyrrolidone (NMP) dissolved more than 60% of certain coals at its boiling temperature (202 °C). Also, Iino reported [5] that a CS₂/NMP mixed solvent (1:1 by volume) gave more than 60% extraction yield for some bituminous coals, even at room temperature. They examined 49 bituminous coals (C% 76.9-90.6 daf) and 29 of the coals gave high yields range of 30-66%. This suggest that combining ILs with other solvents might significantly increase the amount of soluble material that can be obtained, given the ability of certain ILs to fragment and disperse coals as fine particles.

Also there are other applications of ionic liquids to coal processing that could be investigated. For example, thermal extraction using 1-MN(or tetralin or LCO (cost effective) could be tried to obtain “ashless coal” [3, 6]. IL treated coal ([bmim][Cl]/coal 1:2 at 100 °C, overnight) could be used with this process to obtain HyperCoal. Yoshida et al. [6] showed that the extraction of coals at 360 °C with a flowing stream of 1-MN and LCO provided a smaller content of “ash” than

DMN and crude methylnaphthalene oil (CMNO). After the IL is removed from the treated coal, the product could be used for thermal extraction at 360 °C.

In summary, there are many opportunities to be pursued with the application of ionic liquids to coal. Specifically, direct coal liquefaction optimization and also coal cleaning/extraction in order to obtain chemicals.

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