



Trade Science Inc.

ISSN : 0974 - 7443

Volume 6 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Review

CTAIJ 6(2) 2011 [114-122]

Applications of ionic liquids in industry

Natasha Ramroop Singh^{*1}, James G. Speight²

¹The University of Trinidad and Tobago, Pt. Lisas Campus, Brechin Castle, Couva, (TRINIDAD AND TOBAGO)

²CD&W Inc., PO Box 1722, Laramie, WY 82073-1722, (USA)

E-mail: natasha.ramroopsingh@utt.edu.tt

Received: 24th June, 2011 ; Accepted: 24th Junly, 2011

ABSTRACT

The potential uses for ionic liquids and supercritical fluids are increasingly piquing the interest of researchers and scientists. As the physical and chemical properties of these neoteric solvent systems become understood there is a willingness to explore the possibilities of their use within academic communities the world over. Critical assessment of future energy production must take into consideration viable alternatives in conjunction with cutting edge technology. Explorative approaches aimed at substituting conventional solvents by ionic liquids to circumvent practically relevant disadvantages, such as in the extraction and processing of heavy oil and tar sand should also be of interest. There have been a few notable investigations available in the literature, which looks at the use of ionic liquids in oil shale and kerogen processing, methanol production, cellulose dissolution and desulphurization of refinery streams. These findings will be assessed herein, with the goal of finding a way forward, with respect to cheap, "green" energy production in the years to come.

© 2011 Trade Science Inc. - INDIA

KEYWORDS

Ionic liquids;
Heavy oil;
Kerogen;
Tar sand;
Green chemistry.

INTRODUCTION

An "ionic liquid" (also called *liquid electrolyte*, *ionic melt*, *ionic fluid*) is a salt in the liquid state in which the ions are poorly coordinated and which have melting points below an arbitrary temperature, such as 100°C or even at room temperature. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. A salt that melts without decomposing or vaporizing will usually yield an ionic liquid.

In addition, the liquid should only contain ions with lesser numbers of ion pairs or parent molecules. Ionic liquids tend to have low dielectric constants, which indicate that they are not ionizing solvents.

Ionic liquids with melting points below or near room temperature are especially interesting. For example, reactions and extractions may be performed under mild conditions, promoting lower likelihood of product thermal degradation and reducing energy costs. The types of organic cations include:

1. Mono-, di-, and trisubstituted imidazoliums, and substituted pyridiniums and pyrrolidiniums [the free electron pairs of one of the two nitrogen atoms in the five-membered imidazoline ring and of the sole nitrogen atom in the five-membered pyrrolidine or six-membered pyridine ring have been donated to univalent alkyl groups to produce an N⁺ cation]
2. Tetraalkylammoniums (R₄N⁺)
3. Guanidiniums [(NH₂)₃C⁺ and derivatives]

4. Isouroniums and thioisuroniums [urea and thio-urea derivatives of general formula $(\text{NH}_2)_2(\text{RX})\text{C}^+$ where $\text{X} = \text{O}$ or S and $\text{R} = \text{alkyl}$], and
5. Tetraalkylphosphoniums (R_4P^+)

The nitrogen cation with four organic substituents in Types 1 and 2 is called a quaternary ammonium ion. In types 3 and 4, the positively charged carbon atoms are electron-deficient.

The anions used in ionic liquids include alkyl sulfates and sulfonates, halides, amides, imides, tosylates [toluenesulfonates], borates (e.g. tetrafluoroborate, BF_4^-), phosphates (e.g. hexafluorophosphate, PF_6^-), antimonates and carboxylates. Ionic liquids are non-volatile and nonflammable, have high thermal stability, and show remarkable dissolution capabilities for both organic and inorganic compounds. They are being increasingly examined as replacements for volatile organic solvents in a wide range of industrial and laboratory chemical processes such as synthesis, catalysis and enzymatic biocatalysis, electrolysis and extraction.

Ionic liquids can improve industrial processes by minimizing wastes and allowing efficient product extraction. Because of their negligible vapour pressure, products may often be readily separated from the extraction media simply by distillation. Solubility and other physicochemical properties suitable for a particular application can be designed by appropriate combinations of the cations and anions.

For example, in general, chlorides are water-soluble while hexafluorophosphates are water-insoluble. As reaction solvents, ionic liquids have been shown to increase reaction rate, selectivity, and yield. By changing substitution patterns on the organic cation and changing anions, researchers can fine-tune reaction rates and selectivities for a particular catalyzed synthetic reaction. Because of their resistance to oxidation and reduction, they are suitable for electrochemical applications such as batteries, capacitors, electrochemical sensors, and photovoltaic devices.

Ionic liquids are suitable for replacing organic solvents in two-phase system separation processes because partitioning of organic molecules in ionic liquid/water systems follow traditional octanol/water distributions. Ionic liquid mixtures with secondary solvents are not simple combinations. An appropriate co-solvent can solubilize hydrophobic ionic liquids. Another

unique feature of ionic liquids is that they generally form liquid clathrates (inclusion compounds) in combinations with aromatic compounds.

Ionic liquids combine a unique, almost unprecedented set of properties such as non-volatility, non-flammability, electrical conductivity and highly selective solubility characteristics. Because of these distinctive properties (TABLE 1), ionic liquids are attracting increasing attention since many classes of chemical reactions can be performed using ionic liquids as solvents and/or as catalysts. Particularly significant are the low vapor pressure in most instances which contrast the environmental problems of volatile organic solvents. The miscibility of ionic liquids with water or organic solvents varies with side chain lengths on the cation and with choice of anion and they can be functionalized to act as acids, bases, or ligands.

TABLE 1 : General properties of ionic liquids.

Property	Comment
A salt	Cation is usually large
A salt	Anion is usually small
Melting point	Preferably below 100°C
Freezing point	Preferably below 100°C
Liquidus range	>200°C
Thermal stability	High
Viscosity	<100 cP
Dielectric constant	<30
Polarity	Moderate
Solvent properties	Good
Catalytic properties	Good
Vapor pressure	Low-to-negligible

Ionic liquids have many useful chemical applications. They have been used as novel solvents for organic synthesis, in liquid extraction, in electrochemical studies and in some cases as catalysts. The unique combination of properties such as extremely low vapor pressures and unusual and adjustable solvent characteristics present the possibility of developing *designer solvents* for particular applications. Furthermore, many synthetic processes which use transition metal catalysts and the metal nanoparticles play an important role as the actual catalyst or as a catalyst reservoir and ionic liquids are active in the formation and stabilization of catalytically active transition metal nanoparticles.

This review provides a brief assessment of the po-

Review

tential use of ionic liquids in current and future energy production, which must take into consideration viable alternatives in conjunction with cutting edge technology. Explorative approaches aimed at substituting conventional solvents by ionic liquids to circumvent practically relevant disadvantages, such as in the extraction and processing of heavy oil and tar sand are of interest, especially when the environmental issues associated with the production of synthetic crude oil from tar sand are considered.

DESULPHURIZATION OF PETROLEUM

The hydrodesulphurization of petroleum is a catalytic chemical process used to remove sulphur from petroleum products. The purpose of removing the sulphur is to reduce the sulphur dioxide (SO_2) emissions that result from using those fuels in automobiles, aircraft, locomotives, oil burning power plants, residential and industrial furnaces as well as other forms of fuel combustion.

Refiners are also interested in processes for removing mercaptans (RSH) from hydrocarbon streams from petroleum and natural gas. For example, a gaseous or liquid mercaptan-containing hydrocarbon stream may be passed over the ionic liquid by countercurrent or other extraction procedure. Basic metal salts dissolved in the ionic liquids form mercaptides that are separated from the hydrocarbon stream and oxidized to disulfides, which are insoluble in the ionic liquids.

In upgrading the products from the distillation and conversion of crude oil, the removal of sulphur atoms is a priority, as these are corrosive and harmful to the environment. The desulphurization of diesel normally occurs at 370°C , under a pressure of 60 bars, in the presence of hydrogen^[1]. The sulphur atoms are stripped from the hydrocarbons and are transformed into H_2S , by combination with H_2 , which is then treated to isolate the sulphur. As the consequences of sulphur emission into the atmosphere are severe, refiners are under increasing pressure to rethink and redesign their desulphurization units to lower even further, the sulphur content of fuels.

Ionic liquids as selective extraction agents of sulphur compounds are novel and of increasing interest^[2]. In fact, within the last few years, ionic liquids have been

used as an extraction solvent for the deep desulphurization of oil refinery streams. Jochen and co-workers^[3] have shown that Ionic liquids demonstrate selective extraction properties, especially with sulphur compounds that are difficult to remove using common hydrodesulphurization (HDS), such as dibenzothiophene derivatives. Added advantages of using Ionic liquids are the application of mild process conditions such as ambient pressures and temperatures and also, no hydrogen is required. Ionic liquids, $[\text{bmim}][\text{OCSO}_4]$ and $[\text{emim}][\text{EtSO}_4]$, both of which are halogen free and readily available at a reasonable price were shown to be promising candidates.

In another study performed by Lo *et al.*^[4] sulphur-containing compounds were extracted from light ionic liquids by a combination of both chemical oxidation and solvent extraction using room temperature ionic liquids $[\text{bmim}][\text{PF}_6]$ and $[\text{bmim}][\text{BF}_4]$. The ionic liquids were also able to be recycled and reused without any loss in activity.

In a paper by Shuguang and Zhang^[5], the use of Ionic liquids in the desulphurization process is discussed – sulphur containing compounds with a C-5 aromatic ring are favourably absorbed over C-6 aromatics, while sulphur-containing non-aromatics are poorly absorbed. It was shown that the absorption capacity of the Ionic liquids for sulphur containing compounds is sensitive to the structure of both the anion and cation of the IL. Adjustable hydrophobicity, polarity and selectivity prove to be favourable properties over organic solvents used for extraction.

The use of ionic liquids for selective extraction of sulphur compounds from diesel fuel was described for the first time by Bösman *et al.*^[6] Provisionally the best results were obtained with AlCl_3 -1-butyl-3-methylimidazolium chloride ($\text{bmimCl}/\text{AlCl}_3$) however, the desulphurization rate was not high (85%). The same authors have also obtained better results with this agent.^[7]

Deep desulphurization using a chlorine-free ionic liquid (anion is octylsulfate and cation *N*-octyl-*N*-methylimidazolium) is also presented^[8]. This agent is not as sensitive to water as aluminum complexes.

HEAVY OIL UPGRADING

As defined by the U. S. Geological Survey (USGS)^[9], heavy oil is a type of crude oil characterized by an asphaltic, dense, viscous nature and its asphaltene content. It contains impurities such as waxes and carbon residue that must be removed before being refined. In comparison with heavy oil, light or “conventional” oil flows naturally and can be pumped without being heated or diluted^[10]. Heavy ionic liquids are assumed to be residue from formerly light oil that has lost its low M_r components through bacterial degradation, evaporation and water leaching. Reserves are generally separated into technically recoverable or non-technically recoverable. Technically recoverable reserves are known or estimated to exist and technologies exist to recover them. Non-technically recoverable heavy ionic liquids are those that are known to exist but require more advanced technologies to remove the oil than currently exist^[11].

Heavy oil is a highly viscous liquid that is difficult to process and refine requiring a reduction in viscosity and molecular weight for conversion to products^[12]. Improving some oil properties as oil viscosity reduction and increasing API gravity are key properties to increase the wells productivity index of heavy crude oil^[13]. The thermal methods occupy an important place among enhance oil recovery techniques, especially in the production of high-viscosity oils and natural bitumen^[12]. Different versions of thermal methods are used to upgrade heavy crude oil, among the more important methods are steam drive, cycle steam injection, steam assisted gravity drainage (SAGD), conventional fire flood, toe-to-heel air injection process (THAI), aquathermolysis, and down-hole catalytic processes^[14]

Of particular interest in the current context is the potential for down-hole catalytic processes as alternatives to reduction of viscosity of the heavy crude oil improving the oil quality inside the reservoir. For example, using ionic liquids containing ions such as trivalent iron (Fe^{3+}) and hexavalent molybdenum (Mo^{6+}) a variety of interactions were observed during catalytic aquathermolysis^[15]. The results showed that reactions such as pyrolysis, depolymerization, hydrogenation, isomerization, ring opening, oxidation, and esterification were observed. It was also found that the former caused more changes in the resin, saturated hydrocarbon, and oxygen-containing groups, whereas the latter

led to more changes in the asphaltene, aromatic hydrocarbon, and sulphur-containing groups.

Moreover, in order to combine in-situ combustion process with an ionic liquid consisting only of ions of metallic salts, the ionic liquid should be distributed throughout the reservoir as a diluted salt solution. This will result in upgrading the heavy crude oil by an increase in API gravity, reduction in viscosity, and an increase in the amount of distillable fraction as well as hydrodesulphurization^[16]. Furthermore, ionic liquids could be applied into the reservoir combined with *in-situ* combustion process using unconventional wells in order to improve the recovery of heavy crude oil, producing an oil improved in-situ with lower viscosity, being easier their exploitation, increasing the productivity index in wells, and saving costs of transportation and refining at surface.

Ionic liquids have good viscosity reduction property for the heavy oil^[17]. After reaction with ionic liquids, the contents of saturates, aromatics and resins in the heavy oil increase, while the content of asphaltenes decreases. This leads to the decrease of the average molecular weight and the reduction of viscosity of the heavy oil. There are also indications that metal ion-modified ionic liquids have the catalytic effect on upgrading the heavy oil.

Furthermore, heavy oil can be upgraded by the use of ionic liquids^[18]. The experimental results show that a certain amount of sulphur in heavy oils is beneficial to the viscosity reduction. The reduction of viscosity by the ionic liquid is better when the water content of heavy oils is less than 10%. The optimum temperature to upgrade the Xinjiang heavy oil using the ionic liquid is 65 to 85°C. The combination of transition metal salts and the ionic liquid can enhance the viscosity reduction in heavy oils. The viscosity is reduced by 60% and the asphaltene content is reduced by 78%. This suggest that the ionic liquid interacts with the polar asphaltene constituents creating charged entity that is incompatible with the oil and separates out leaving an upgraded (relatively asphaltene-free) product.

One of the issues related to heavy oil processing is the belief that the asphaltene constituents are aggregated, even at the high temperatures used on the thermal processes. As a consequence, ionic liquids have been investigated as potential inhibitors in the inhibition

Review

of aggregation of petroleum asphaltenes using new ionic liquids^[19]. The ionic liquids conjugate a good solubility in nonpolar environment with strong electron donor-acceptor properties. In this study, 1-propyl boronic acid-3-alkylimidazolium bromides and 1-propenyl-3-alkylimidazolium bromides were tested. A lateral chain containing either the boronic acid or the propenyl moiety was substituted for the 1-methyl-3-alkylimidazolium bromide. The boronic acid is a weak acid but a very efficient Lewis acid. It was demonstrated that the presence of the boronic acid moiety enhances interactions between asphaltenes and ionic liquids and limits considerably asphaltene aggregation. The length of the side alkyl chain of the ionic liquid is an important parameter also. The minimum length of eight carbons was necessary to obtain steric stabilization of the ionic liquid-asphaltene complexes.

OIL SHALE PROCESSING

Oil shale is a fine-grained sedimentary rock which contains significant amounts of an organic material known as kerogen. The name *oil shale* is a misnomer as the rock does not contain oil and oil is only produced from the kerogen by pyrolysis. Pyrolysis can convert the kerogen in *oil shale* into shale oil (also known as synthetic crude oil). The process involves heating oil shale (in situ or in a surface facility) to sufficiently high temperature to yield the petroleum-like shale oil.

Kerogen is a mixture of organic material, rather than a specific chemical, and as such cannot be given a chemical formula. Its chemical composition can vary distinctly from sample to sample – labile kerogen breaks down to form heavy hydrocarbons, refractory kerogen breaks down to form light hydrocarbons and inert kerogen forms graphite^[20]. Understanding the exact chemical composition of the specific type of kerogen^[21] (Figure 1) obtained in a shale sample is key to the discovery of novel solvent systems for its dissolution. The oldest and most well known method for the processing of kerogen is pyrolysis, which is necessarily an energy intensive process^[22]. As such, alternative methods to solubilise kerogen at ambient or near-ambient temperatures are of interest. Investigations performed by *Miron et al.*,^[23] *Hues et al.*^[24] and *Nomura et al.*^[25] looked at the processing of oil shale in molten salt media. However,

most molten salts are liquid at very high temperatures and offer little advantages over traditional aqueous and

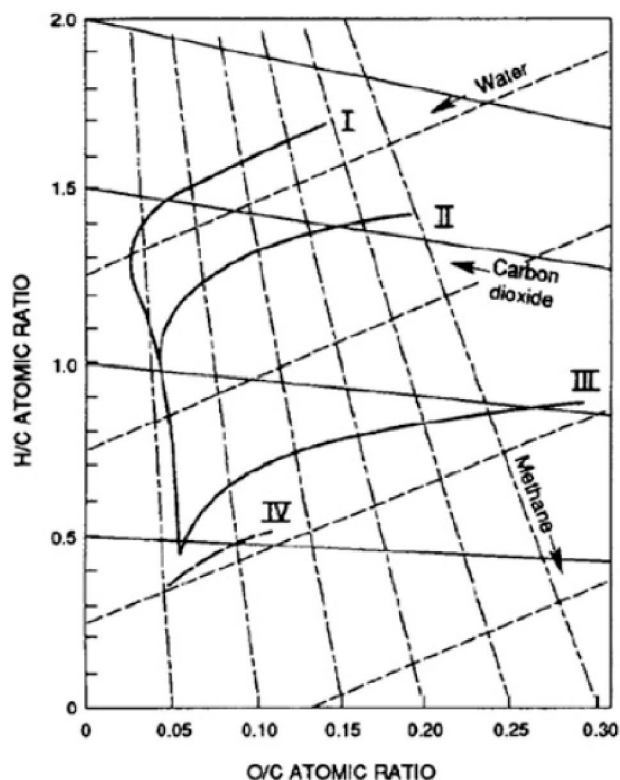


Figure 1 : Van Krevelen diagram showing types of kerogen and pathways for generation of methane and elimination of carbon dioxide and water during coalification. Liptinite corresponds to types I and II kerogen, vitrinite to type III, and inertinite to type IV. Modified from Levine (1987).

organic solvent systems.

The extraction of a particular component from a mixture consists of several steps, which includes solvation by the solvent, desorption from its tethered position and transport into the bulk liquid^[26]. Classical extraction of kerogen using organics simply solubilises and does not alter chemical properties – the latter being desirable in relation to separation of useful products. In oil shale, kerogen is tightly mixed with mineral matrix, but demineralization does not alter kerogen solubility^[27]. In the case where solvents, such as ionic liquids, are able to break bonds based on electron donor – electron acceptor interactions and hydrogen bonding, at ambient conditions with minimal noxious gas emissions, is of interest. Ionic liquids and molten salts do not only impose chemical modifications to the oil shale, but also acts as a thermal agent. The mechanism of solvation in ionic liquids has been shown to be different when compared to typical molecular

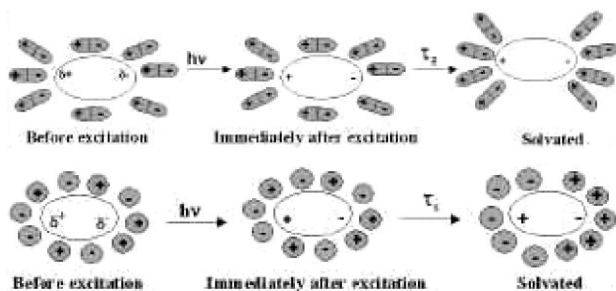


Figure 2 : Schematic representation of solvation of a dipolar solute in conventional solvents (top) and RTILs liquids (below).

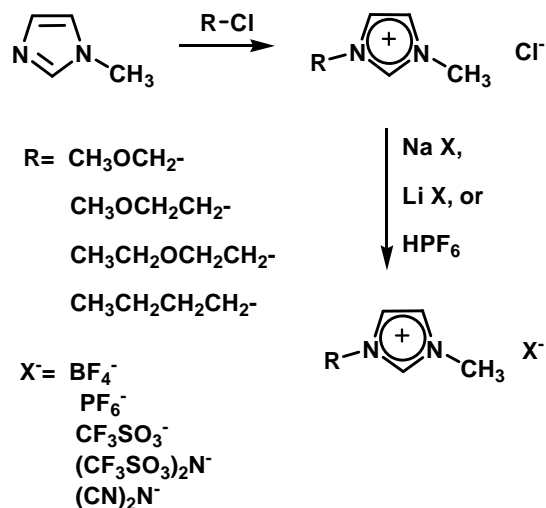


Figure 3 : Synthetic scheme showing synthesis of ionic liquids^[29]

solvents (Figure 2)^[28].

As such, the tunable properties of ionic liquids become advantages by allowing the creation of a task-specific solvent for the selective dissolution of kerogen. There are potentially over tens of thousands simple ionic liquids, but fewer than one thousand have been reported^[30]. There have been only limited studies performed involving the use of ionic liquids for oil shale treatment. In 1978, Bugle and co-workers^[31] reported on the use of a eutectic of ethyl pyridinium bromide and aluminum chloride, which has Lewis acid-base properties and acted as a base in the dissolution of Green River oil shale. A conversion of 58% of organic carbon was achieved at 320°C, and further investigations revealed the process was not driven by pyrolysis. The mechanism of degradation seemed to involve a mode of intramolecular disproportion catalyzed by the tetrachloroaluminate melt's ability to stabilize the resulting short-lived intermediates until the macromolecules involved have been sufficiently reduced in size to become

soluble in conventional solvents^[31].

The use of new solvent systems, such as ionic liquids (Ionic liquids) and supercritical fluids (SCFs) diversifies the available technology for the processing and extraction of oil shale, the reserves of which are vast, being many times greater than the proven remaining resources of crude oil and natural gas combined^[32]. In a study performed by Koel, *et al.*,^[27] the dissolution and extraction of the components of various oil shales was investigated, using supercritical fluids and ionic liquid treatment. The organic part of oil shale, kerogen, is generally of importance. The ionic liquid were able to extract organic compounds at 175°C from kerogen in amounts 10-fold greater than the usual organic solvents.

In another study performed at the University of Sussex^[33], kerogen was shown to dissolve in the acidic ionic liquid, 1-ethyl-3-methylimidazolium chloride/aluminum(III)chloride, where the mole fraction of AlCl₃ was 0.65. Dissolution of up to 95% of the kerogens occurred and treatment under microwave irradiation improved the process. Microwave heating improves the energy efficiency in the production process, because the reagents are directly heated instead of heating the reaction container, as in conventional methods. Direct heating improves energy transfer and thus reduces the amount of energy used for heating^[34].

IL's containing chloroaluminate ions are strong Lewis, Franklin and Brønsted acids. For example, protons present in 1-ethyl-2-methylimidazolium tetrachloroaluminate, [emim][AlCl₄], have been shown to be superacidic with Hammett acidities up to -18. Such highly acidic ionic liquids are, nevertheless, easily handled and offer potential as non-volatile replacements for hazardous acids such as hydrofluoric acid in several acid-catalyzed reactions^[35]. The disadvantage of such ionic liquids however, is that they are very moisture-sensitive.

Koel and co-workers^[27] looked at the solvation of oil shale using 1-butyl-3-methylimidazolium hexafluorophosphate {[bmim]PF₆}, which is relatively moisture insensitive (but subject to hydrolysis) and the 1-ethyl-3-methylimidazolium chloride-aluminum(III)chloride {[Bmim]Cl·AlCl₃} system. The hexafluorophosphate ionic liquid was a poor solvent, with better results being obtained with the chloroaluminate ionic liquids. With the latter, an increase in extraction tempera-

Review

ture increases the yield of soluble product.

Therefore, the design of an ionic liquid possessing Lewis acid properties, but which is air and water stable, has a high decomposition temperature and possess the anion/cation combination that is able to selectively dissolve kerogen will be the goal of future studies. The ability of these room-temperature ionic liquids to be easily reused and recycled will expand their portfolio in being excellent candidates for oil-shale solvents. One must take into consideration however, the toxicity of ionic liquids^[36] and the consequences of potential leaching into marine eco-systems. Mortality and perhaps more importantly, how ionic liquids alter life cycles of the biota must be fully understood, before usage becomes a reality.

CELLULOSE PROCESSING

Cellulose [$C_6H_{10}O_5$]_n is polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants and many forms of algae. Cellulose is the most naturally occurring polymer existing on earth and as such is the most abundant renewable resource in the world – approximately 33% w/wt of all plant matter is cellulose (the cellulose content of cotton is 90% w/w and that of wood is 50% w/w). For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce paper and conversion of cellulose to biofuels (such as ethanol) is under investigation as an alternative fuel source^[37].

In addition, lignocellulosic materials have been proposed as large renewable resources for chemicals and sugars to reduce society's dependence on nonrenewable petroleum-based feedstocks^[37]. Lignocellulose is a complex matrix combining cellulose, hemicellulose, and lignin, along with a variable level of extractives. Cellulose is comprised of glucose, a six-carbon sugar, while hemicellulose contains both five- and six-carbon sugars, including glucose, galactose, mannose, arabinose, and xylose. The presence of cellulose and hemicellulose therefore makes lignocellulose a potential candidate for bioconversion. The ability of the bioconversion platform to isolate these components was initially limited, as the wood matrix is naturally resistant to de-

composition.

The full potential of cellulose and its derivatives has not been realized due to the historical shift to petroleum based polymers from the 1940s and the limited number of existing solvents for dissolution^[38]. In 1934, cellulose was shown to be dissolved in molten *N*-ethylpyridinium chloride, in the presence of nitrogen containing bases^[39]. At this time, the concept of ionic liquids did not exist, so as such experiments were not revisited until decades later.

Recent research has shown that ionic liquids can be used as nonderivatizing solvents for cellulose. Ionic liquids incorporating anions which are strong hydrogen bond acceptors were most effective, especially when combined with microwave heating, whereas Ionic liquids containing 'non coordinating' anions, including $[BF_4]^-$ and $[PF_6]^-$ were not solvents. Chloride containing Ionic liquids appear to be the most effective solvents, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent^[40]. Employing a combination of NMR methods and molecular dynamic simulations on several model systems, Moyna^[41] has shown that *N,N'*-dialkylimidazolium chlorides dissolves carbohydrates through near-stoichiometric formation of hydrogen bonds between the solvent chloride ions and the solute hydroxyl groups. The presence of water in $[bmim][Cl]$ was found to greatly decrease the solubility of cellulose through competitively hydrogen-bonding its microfibrionic liquids, and as such, cellulose can be precipitated from the IL by addition of water, as well as ethanol or acetone^[42]. Ionic liquids can be recovered and reused, using various methods such as evaporation and reverse osmosis, after cellulose regeneration^[43]. This green processing of cellulose will open avenues for its derivatization and production of energy sources, such as ethanol as well as important chemicals such as ethylene.

METHANOL PRODUCTION

Methanol (methyl alcohol, CH_3OH) is a fuel typically derived from natural gas, but which can be produced from the fermentation of sugars in biomass. Methanol was originally recovered from wood as a by-product of charcoal manufacture, and was often called *wood alcohol*.

Methanol is a colorless, odorless and nearly tasteless alcohol and is also produced from crops and is also used as a fuel. Methanol, like ethanol, burns more completely but releases as much or more carbon dioxide than its gasoline counterpart. The balance is often seen as the various bi-processes that draw carbon dioxide from the atmosphere so there is no net modern release, as there is for fossil fuels.

Methanol and other chemicals were routinely extracted from wood in the 19th and early 20th centuries. However, the original route for methanol recovery from biomass was quite different to current routes. Pyrolysis (heating wood in the absence of air) to above 270°C in a retort causes thermal cracking or breakdown of the wood and allows much of the wood to be recovered as charcoal. The watery condensate leaving the retort contained methanol, amongst other compounds.

Since the 1970s, the use of homogeneous catalysis (using transition metal complexes) for the conversion of natural gas to liquid products under mild conditions has gathered much interest due to considerable scientific and industrial significance^[44]. Compounds such as PtCl₂ or PtO₂ are not often used in homogeneous catalysis as they are insoluble in organics and aqueous solvents, and even in concentrated acids, although some of them have been used as heterogeneous catalysts

In a study done at The Power, Environmental and Energy Research Center, California Institute of Technology in 2006, it was found that many of these Pt compounds could be readily dissolved in a variety of ionic liquids upon heating, and were subsequently soluble in concentrated sulphuric acid, forming a homogeneous solution.

Suitable Ionic liquids found so far include imidazolium, pyridinium, pyrazolium and triazolium-based examples, with chloride (Cl⁻) or bisulfate (HSO₄⁻) as the anion. Analyses by ¹H NMR and GC-MS on the crude reaction solutions showed that the only liquid products derived from methane, if any, were methanol and methylbisulfate (CH₃OSO₃H).

All Pt species investigated (PtCl₂, PtCl₄, PtO₂, K₂PtCl₄ and H₂PtCl₆) could exhibit significant catalytic activity depending on the nature of the IL used. In the case of PtCl₂ + [1-mim][Cl] in 96% H₂SO₄ a methanol concentration of 0.17 M was demonstrated, which was about 5 times higher than that for (bpym)PtCl₂^[45].

Using Ionic liquids in the homogeneous catalysis of methane to methanol conversion not only acted as a dissolution media for the otherwise insoluble Pt salts/oxide, but also played a key role in promoting platinum reactivity, possibly through coordination and/or intermolecular interactions. This versatile method could also be used in other chemical reactions.

In 2007, the United States Department of Energy – Energy Efficiency and Renewable Energy, embarked upon an investigation into the development of ionic liquids which seeks to replace all of the sulphuric acid reaction media with ionic liquids in the direct conversion of methane to methanol (US Department of Energy, 2007). It is predicted that by 2020, the energy savings for this technology could be as high as 30 trillion Btu per year for liquid acid alkylation alone.

REFERENCES

- [1] <http://www.planete-energies.com/content/oil-gas/refining/oil-refinery.html>; Accessed February (2010).
- [2] H.Rang, J.Kann, V.Oja; *Oil Shale*, **23(2)**, 164-176 (2006).
- [3] E.Jochen, P.Wasserscheid; *J.Green Chem.*, **6(7)**, 316-322 (2004).
- [4] W.Lo, H.Yang, G.Wei; *Green Chem.*, **5(5)**, 639-642 (2003).
- [5] Z.Shuguang, Z.C.Zhang; *Green Chem.*, **4(4)**, 376-379 (2002).
- [6] A.Bösman, L.Datsevich, A.Jess, A.Lauter, C.Schmitz, P.Wasserscheid; *Chem.Commun.*, 2494-2495 (2001).
- [7] P.Wasserscheid, A.Jess, A.Bösman, L.Datsevich, A.Lauter, C.Schmitz; *DE 101 55 281 A1*, (2003).
- [8] A.Jess, P.Wasserscheid; *Z.Umweltchem.Ökotox. Bd.*, **14(3)**, 145-154 (2002).
- [9] R.F.Meyer, E.D.Attanasi; *Heavy Oil and Natural Bitumen—Strategic Petroleum Resources*, USGS Fact Sheet PS-070-03, August (2003).
- [10] http://www.rigzone.com/news/article.asp?-a_id=35286; Tuesday, August 15, 2006, Rigzone Schlumberger Publication, Accessed January, (2010).
- [11] www.api.org; American Petroleum Institute, Accessed February, (2010).
- [12] J.G.Speight; *The Chemistry and Technology of Petroleum*, 4th Edition, CRC Press, Taylor & Francis

Review

- Group, Boca Raton, Florida, (2007).
- [13] L.Flint; Bitumen and Very Heavy Crude Upgrading Technology: A Review of Long Term R&D Opportunities. Alberta Energy Research Institute (AERI), Edmonton, Alberta, Canada. March 31, (2004).
- [14] J.G.Speight; Enhanced Recovery Methods for Heavy Oil and Tar Sands, Gulf Publishing Company, Houston, Texas, (2009).
- [15] Y.Wang, Y.Chen, J.He, P.Li, C.Yang; Energy Fuels, **24**(3), 1502-1510 (2010).
- [16] H.R.Nares, P.Schacht-Hernández, M.A.Ramírez-Garnica, M.C.Cabrera-Reyes; Proceedings International Oil Conference and Exhibition, Veracruz, Mexico, June 27-30, (2007).
- [17] H.Fan, Z.Li, T.Liang; J.Fuel Chem.and Tech., **35**(1), 32-35 (2007).
- [18] Z.Fan, T.Wang, Y.He; J.Fuel Chem.and Tech., **37**(6), 690-693 (2009).
- [19] M.Boukherissa, F.Mutelet, A.Modarressi, A.Dicko, D.Dafri, M.Rogalski; Energy Fuels, **23**(5), 2557-2564 (2009).
- [20] Article.mht; Accessed March, (2010).
- [21] V.V.Platonov, V.A.Proskuryakov, A.V.Glybina; Russian J.of Appl.Chem., **75**(3), 495-498 (2002).
- [22] J.Cummins, W.E.Robinson; Symposium on Pyrolysis Reactions of Fossil Fuels. Division of Petroleum Chemistry, Inc. Pyrolysis of Kerogen Concentrate in the Presence of Calcium Hydride. American Chemical Society Pittsburg Meeting, March 23-26 (1996).
- [23] Y.Miron; Thermochim.Acta, **65**, 213-237 (1983).
- [24] A.D.Hues, C.K.Rofer-DePoorter, R.N.Rogers; Proc.ACS Petro.Chem.Meeting, (1984).
- [25] M.Nomura, T.Muratani, Y.Tajima, S.Murata; Fuel Proc.Tech., **43**, 213-225 (1995).
- [26] Dogonadze, R.Revaz, et al. (Eds); The Chemical Physics of Solvation, Amsterdam: Elsevier. ISBN 0-444-42551-9 (Part A), ISBN 0-444-42674-4 (Part B), ISBN 0-444-42984-0 (Chemistry), **3**, (1985-88).
- [27] M.Koel, S.Ljovin, K.Hollis, J.Rubin; Pure Appl. Chem., **73**(1), 153-159 (2001).
- [28] P.K.Mandal, S.Saha, R.Karmakar, A.Samanta; Curr.Sci., **90**(3), (2006).
- [29] Q.Liu, M.H.A.Janssen, F.Rantwijk, R.A.Sheldon; Green Chem., **7**, 39-42 (2005).
- [30] <http://www.iupac.org/projects/2003/2003-020-2-100.html>; Copyright ©1997-2005 International Union of Pure and Applied Chemistry, Accessed 21st April, (2007).
- [31] R.C.Bugle, K.Wilson, G.Olsen, L.G.Wade Jr., R.A.Osteryoung; Nature, **274**, 578-580 (1978).
- [32] P.L.Russell; Oil Shales of the World, Their Origin, Occurrence and Exploitation, Pergamon Press, (1990).
- [33] (a) Y.Patell; The Dissolution of Kerogens, Thesis of M.Phil., Univ. of Sussex, (1993); (b) L.M.Dutta; The Dissolution of Liassic Kerogen and Coal, Thesis of M.Phil., Univ. of Sussex, (1994).
- [34] B.M.Khadilkar, G.L.Rebeiro; Org.Proc.Res.Dev., **6**(6), 826-828 (2002).
- [35] (a) R.Sheldon; Chem.Comm., 2399-2407 (2001); (b) M.F.Pinheiro, R.S.Mauler, R.F.de Souza; Macromol.Rapid Commun., **22**, 425-428 (2001); (c) P.Wasserscheid, C.M.Gordon, C.Hilgers, M.J.Muldoon, I.R.Dunkin; J.Chem.Soc., Chem. Commun., 1186-1187 (2001); (d) C.Gurtler, M.Jautelat; European Patent, EP 1035093 (2000); (e) P.J.Dyson, M.C.Grossel, N.Srinivasan, T.Vine, T.Welton, D.J.Williams, A.J.P.White, T.Zigras; J.Chem.Soc., Dalton Trans., 3465-3469 (1997).
- [36] D.Zhao, Y.Liao, Z.Zhang; Clean - Soil, Air, Water, **35**(1), 42-48 (2007).
- [37] J.G.Speight; Synthetic Fuels Handbook: Properties, Processes, and Performance, McGraw-Hill, New York, (2008).
- [38] S.Zhu, Y.Wu, Q.Chen, Z.Yu, C.Wang, S.Jin, Y.Ding, G.Wu; Green Chem., **8**, 325-327 (2006).
- [39] C.Graenacher; US Pat, 1943176, (1934).
- [40] R.P.Swatloski, S.K.Spear, J.D.Holbrey, R.D.Rogers; J.Am.Chem.Soc., **124**, 4974-4975 (2002).
- [41] G.Moyna; <http://tonga.usip.edu/gmoyna/research/research.html>; Department of Chemistry & Biochemistry and West Center for Computational Chemistry and Drug Discovery, University of the Sciences in Philadelphia, Accessed January, (2010).
- [42] R.P.Swatloski, R.D.Rogers, J.D.Holbrey; WO Pat., 03/029329, (2003).
- [43] K.E.Gutowski, G.A.Broker, H.D.Willauer, J.G.Huddleston, R.P.Swatloski, J.D.Holbrey, R.D.Rogers; J.Am.Chem.Soc., **125**, 6632-6633 (2003).
- [44] R.H.Crabtree; J.Organomet.Chem., **689**, 4083 (2004).
- [45] C.Jihong, L.Zaiwei, M.Haught, T.Yongchun; Chem. Commun., 4617-4619 (2006).