The Separation of Hydrocarbons from Sand Using Ionic Liquids

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ABSTRACT

The separation or extraction of hydrocarbons such as oil and bitumen from soil, sand, or other forms of mineral matter is a difficult and expensive process that also results in environmental problems associated with the disposal of waste products. For example, the separation of bitumen from tar or oil sands involves large amounts of energy and water. The process water generated in the separation is toxic to aquatic life and is a major environmental problem. Similarly, the oil and gas industry has to deal with oil contaminated sand, waste drilling muds and drill cuttings in its operations. We have developed a novel method for separating bitumen, oil or other hydrocarbons from sand or soils through the use of ionic liquids (ILs). The separation occurs at ambient temperatures and does not result in the generation of waste process water.

Keywords: oil sands, tar sands, drill cuttings, ionic liquids.

1 INTRODUCTION

The separation and recovery of hydrocarbons from "sand", a generic term often used in the oil industry to describe various types of mineral matter or silt, is a critical problem in a number of industries and crucial to the mitigation of environmental disasters, such as those associated with oil spills. For example, oil or tar sands compose a significant proportion of the world's known oil reserves. The largest deposits are found in Canada and Venezuela, which have combined oil sand reserves estimated to be equal to the world's total reserves of conventional crude oil [1]. The U.S. now imports about one million barrels a day of oil obtained from Canadian oil sands. Significant quantities (estimated to contain 32 billion barrels of oil) can also be found in the U.S., principally in Utah [1]. These deposits are complex mixtures of sand, clays, water and bitumen, a "heavy" or highly viscous oil.

Extraction and separation of bitumen from surface-mined oil sands is presently accomplished using a warm water frothing process aided by various processing additives (historically NaOH). It is much more expensive than extracting conventional oil by drilling and involves the use of significant amounts of energy and water [2-4]. Water used in the process is ultimately stored in vast tailing ponds. It is a complex mixture of water, dissolved salts, minerals, residual bitumen, surfactants released from the bitumen and other materials used in processing. It is acutely toxic to aquatic life [1-4]. Even though large quantities of tailing pond water are now recycled through the process, the recycled water can lead to scaling and corrosion problems and can adversely affect bitumen recovery. In addition, very fine mineral particles and emulsified salty water are co-extracted with the bitumen and these can also lead to problems in subsequent processing [5-7]. Furthermore, the presence of mineral fines makes the extraction of bitumen from low-grade ores difficult and uneconomic. The environmental problems associated with extracting oil from tar sands are now a source of considerable concern. Some of these problems and the need for large quantities of water have prevented the exploitation of the Utah deposits (along with the higher viscosity of the bitumen and consolidated nature of the tar sands) [8, 9].

The treatment and disposal of oil contaminated sand and soil is not only a major problem after oil spills, as in the Exxon Valdez or Deepwater Horizon incidents, but also as a result of normal drilling and refinery operations. Various methods for separating oil from contaminated sand or other mineral containing materials, such as drill cuttings or oil sludge, have been described over the years. These methods include incineration, distillation, washing with detergents or extraction using organic solvents. Some of these methods have proved to be uneconomic because of their energy requirements, others do not completely remove the oil from sand, or the chemicals used may also pose unacceptable environmental concerns. As a result, oil field or refinery wastes are often stored in pits or landfills. Removal to landfills also appears to be the fate of most of the contaminated sand removed from beaches in the Gulf of Mexico after the recent Deepwater Horizon oil spill. Long-term storage of such material is a major concern. The development of clean technology for the recovery of bitumen or oil from sand or other minerals therefore has considerable commercial potential.

2 DESCRIPTION OF TECHNOLOGY

Ionic liquids, ILs, have been widely studied in the last few years and there is now a vast literature concerning the structure and properties of these materials. The properties that directly impact the new technology are their outstanding chemical and thermal stability, very low degree of flammability and almost negligible vapor pressure [10-13]. This makes them attractive solvents for this and other chemical processes. In our work we have used a particularly versatile group of ILs is based on 1-alkyl-3-methylimidazolium cations (figure 1). The properties of these materials can be "tailored" by varying the nature of the substituents (R) on the ring and the nature of the anion.

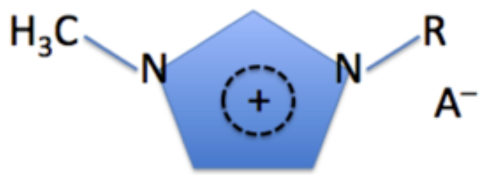

Figure 1: Schematic picture of an imidazolium ionic liquid.

We have found that bitumen can be cleanly separated from medium- and low-grade Canadian oil sands and also Utah tar sands using certain ionic liquids [20-22]. The separation of oil from drilling muds and contaminated beach sand has also been accomplished [23]. Figure 2 shows what is observed after simply stirring an oil sand sample with an IL and a hydrocarbon solvent at ambient temperatures (~22˚C) in a glass tube.

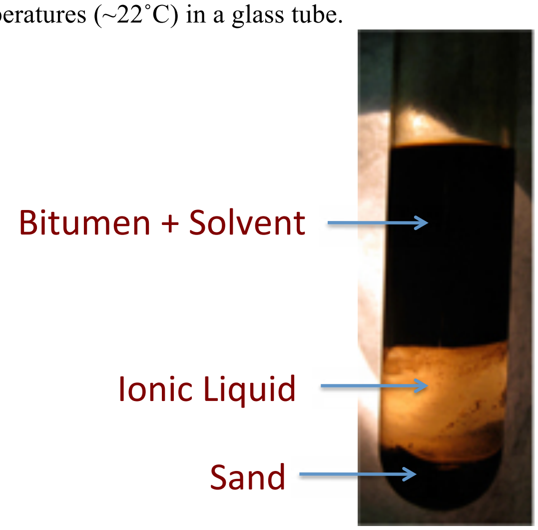

Figure 2: Phase separation of bitumen from oil sand in the presence of an ionic liquid.

Three layers are formed. The bottom layer consists of sand and clays in the form of a slurry with IL, the middle layer contains the ionic liquid with a small amount of entrained bitumen and some mineral fines, while the top layer is a solvent/bitumen mixture that contained no detectable IL. This was easily removed from the other layers using a pipette. Essentially all of the bitumen was released from the sand and fine particles could not be detected in the bitumen phase (using infrared spectroscopy). Water was not used in this stage of the separation, but relatively small amounts were used to separate residual IL from the sand and clays in the bottom layer. There was no evidence of residual bitumen or IL attached to the sand [14-18]. Because both the IL and water can be easily separated and recycled through the system (see below), this process has the potential for ameliorating many of the environmental problems associated with current extraction methods.

It was surprising to us and is no doubt surprising to others that we obtained such a remarkably clean separation under such mild conditions. The results we have obtained so far suggest that this is due to three factors: the first two involve the difference in density of the components and the solubility characteristics of the hydrophilic ILs we have used. Although small amounts of low molecular weight, largely non-polar hydrocarbons such as benzene, toluene and paraffins dissolve in some ILs, recent work has shown that the reverse is not true for hydrophilic imidazolium ILs with short side chains, which are completely immiscible with hydrocarbons [19]. This explains why we could not detect IL in the hydrocarbon phase. The final factor involves the nature of interactions in these systems, which we have recently studied using atomic forces microscopy and contact angle measurements [18]. We found that the energy of adhesion between bitumen samples obtained from both Canadian and U.S. oil sands are about an order of magnitude smaller in an ionic liquid medium than in aqueous solution. This behavior was traced to the ability of ionic liquids to form layered charge structures on mineral surfaces and is a major factor in the facile separations achieved so far. We have recently found that aqueous solutions of certain ILs work as well as more concentrated solutions (still at room temperature) and we have used IL/water mixtures in our scale-up work.

3 SCALE-UP WORK

We have built a bench-scale unit (still in the process of modification) where kilogram quantities of tar sands, drill cuttings, oil-contaminated sand or other minerals can be separated.

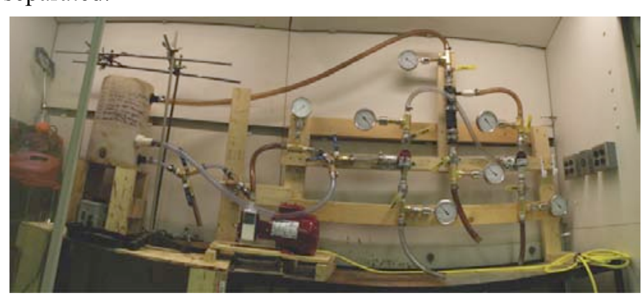

Figure 3: Picture of the initial set up for the bench scale unit

Although ILs are powerful solvents for a number of materials, non-polar polymers appear to be unaffected by the highly hydrophilic IL used in this work. We have also "soaked" various gaskets (polyethylene, fluoroelastomers, etc.) in this IL for 6 months (and counting) with no apparent dissolution. Accordingly, for our main mixing and separation vessel, we simply used a large, cheap (high density) polyethylene container, drilled some holes and installed inlet and outlet ports. We also purchased two pumps. The larger of these allows the oil sand/IL-water mixture and organic solvent (naphtha) to be pumped around a closed loop to "condition" the oil/sand mixtures and detach tar or bitumen. Some stirring and shear is necessary to mix and promote oil/sand detachment.

We have installed "Y" connections in the closed loop to allow the removal of the bitumen/solvent layer from the top and the sand from the bottom. In one experiment, an oil sand/IL/solvent mixture was pumped around the loop for 5 minutes (while the bulk of the material in the main vessel was being stirred). The contents were then allowed to settle. Upon standing, we observed a beautiful phase separation, similar to what was obtained in simple laboratory experiments, as can be seen in figure 4.

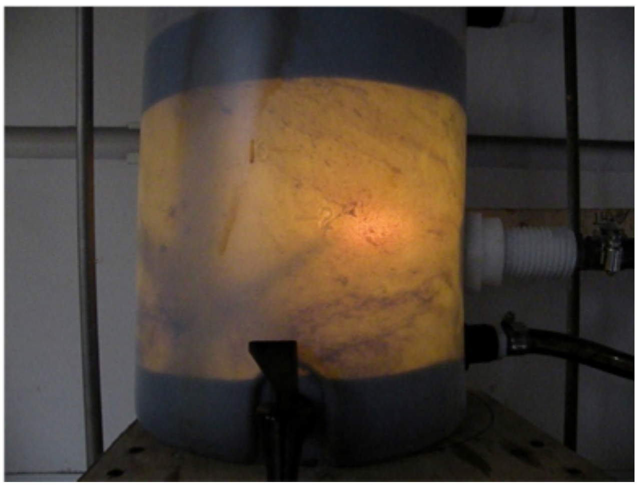

Figure 4: Phase separation of bitumen/solvent mixture from IL/water mixture and sand upon standing.

Experiments are under way to determine how much "conditioning" or shear is necessary to achieve a fast separation. Also, cyclones have been installed to separate "cleaned" sand from residual IL and oil/solvent mixtures from IL/water (see figure 2 above).

The unit we have built is simple and crude, but we suggest that this illustrates the advantages of the process. Complex procedures and pieces of equipment are not necessary in order to implement larger scale separations.

4 CURRENT STATE OF THE TECHNOLOGY AND FUTURE WORK

To summarize, in work completed so far we have shown that:

- Because of their unusual solvent properties, ILs promote the separation of oil or bitumen from sands, whether they are unconsolidated or consolidated natural deposits (Oil sands from Canada and Utah, respectively), contaminated beach sand or materials like drill cuttings.
- The separation can be accomplished at room temperature and therefore requires much less energy than current processes.
- Although water is used to wash residual sand or as part of the separation process mixed with IL, because of the extremely low vapor pressure of ILs separation and recovery of water is relatively easy and practically all of it can be recycled through a closed system, ameliorating a major environmental concern.
- Essentially complete recovery of bitumen from even low-grade tar sands, crude oil from a sand/oil mixture and oil from drill cuttings has been obtained and the hydrocarbon product is free of particle fines.
- The residual sands and clays are obtained in a very clean and uncontaminated form and can be readily used in the remediation of the environmental scars inflicted by mining.
- Other oil-contaminated minerals, such as those generated in drilling operations (e.g., drill cuttings), refinery operations or as a result of spills, can be separated cleanly into their components using the same process.
- Treatment of drill cuttings with IL also unexpectedly resulted in the generation of fine particles suitable for the manufacture of key value added products such as proppants.

Our ultimate goal is to license this technology to groups or companies that are capable of capitalizing large-scale operations. We will focus on two major initial applications, which will require similar extraction and separation methods – oil or tar sands and drill cuttings.

In order to develop the technology to the point where it can be brought to market, we need to build a demonstration unit capable of processing hundreds of pounds of material. The unit will consist of conventional mixing and separation elements (in-line mixers, holding tanks, cyclones for solids/liquid separations, continuous coalescers for oil/IL+water separations, etc.). These are all simple, relatively cheap pieces of equipment and we will operate them with two goals in mind:

- Test various configurations and operating conditions in order to specify optimum operating conditions, mass flow balances and energy needs.
- Use this information to specify the design of production facilities and hence the economics of a large-scale process. Two types of operations will be considered, processing oil sands and processing drill cuttings.
- Provide sufficient quantities of cleaned drill cuttings (a couple of tons) for processing to proppants for testing in demonstrations in well drilling operations.

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