Molten Salts as Heat Transfer Fluids

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Abstract

It has been established that increasing the operating temperature for parabolic trough electric systems or developing a heat storage option can significantly increase the efficiency of the power cycle compared to the current heat storage medium.[1] Both improvements require a new heat transfer fluid that must have a very low vapor pressure at the hot operating temperature combined with a high thermal stability, higher than 450°C. Further, the piping layout of trough plants dictates that the fluid not be allowed to freeze. Extensive insulation and heat tracing must be used unless the fluid has a freezing point near 0°C.[2] At present, it seems likely that this "ideal" fluid will have to be found among organic rather than inorganic salts. I would therefore like to investigate the chemical and thermal properties of "room temperature ionic liquids" (RTILs), which hold much promise as a new class of heat transfer or storage fluids. A large number of RTILs can be found in the class of imidazolium salts for reasons that are not completely understood, and it has been found that due to the ionic nature of these liquids, their vapor pressure is negligible, and the potential exists for a wide temperature range of the liquid state.[3] I propose a two-phase research plan. Phase 1 would be a systematic synthesis of cation/anion pairs based on various imidazolium cations and several inexpensive surfactants as anions. Phase 2 would be an investigation into the thermal properties of these fascinating fluids by thermogravimetric analysis (TGA) and molecular beam mass

spectrometry (MBMS). The successful synthesis of a viable option would necessitate a subsequent study to explore production cost, purity, and environmental safety analysis.

Background

A parabolic energy trough system consists of "trough" shaped mirrors that can focus the sun's rays onto a pipe lying within the trough, as pictured in Figure 1.

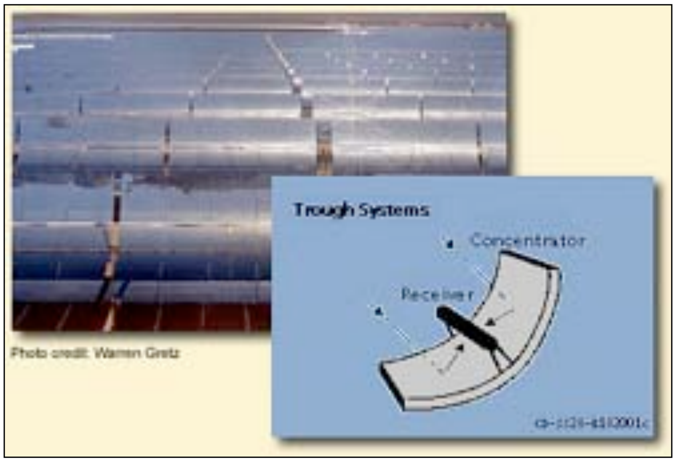

Figure 1 Trough System *from* www.eren.doe.gov/sunlab

Circulating within the pipe is a heat transfer fluid (HTF). The energy from the sun heats the HTF, which is piped through a water bath, heating the water and creating steam. The steam is then used to turn a turbine to create electricity. Energy storage is a critical factor in the advancement of parabolic trough solar technologies.[4] Storage is an important factor because during daylight hours, a parabolic trough system generates electricity solely from solar heat input. However, at night, or hours of low sunlight, an input of energy must be supplied by a natural gas heater to provide a continuous flow of energy. This heater (see

Figure 2) simply acts as a substitute or a supplement to solar heat energy. It is important to note that the heater can also be used when low temperatures threaten to freeze the HTF. Combustion of natural gas is not a “green” process, and its elimination would lower the cost of energy produced. If the solar heat energy produced during periods of high sunlight could be harnessed and distributed consistently over periods of low sunlight, the need for a natural gas heater would disappear. A possible solution is storage of a heated HTF in a large tank. This hot fluid would then be released whenever needed to produce energy. Another solution is the transfer of thermal energy from the HTF to some type of storage medium. Direct storage using the HTF as the sensible storage medium represents the simplest path forward since it eliminates a heat exchange step, and it avoids the inefficiencies of transferring heat to a storage medium. Use of the HTF as the direct

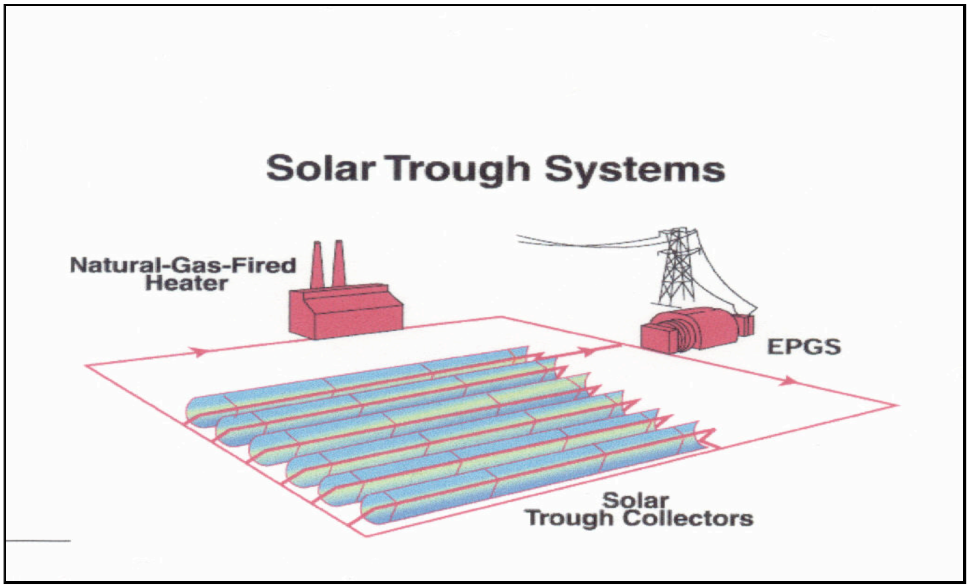

Figure 2 Trough System from www.nrel.gov/docs/legosti/fy98/22589.pdf

storage medium has been demonstrated on a large scale for power towers.[4] A power tower, as shown in Figure 3, operates in the same manner as a trough system, but with a few very important design differences. For example, the pipes containing the HTF in a power tower are vertical and located within the tower itself. This allows for easy drainage of the HTF. Another key difference between power towers and parabolic troughs lies in the specifications of the HTF/thermal storage fluid. Power towers use molten nitrate salts, while mineral oil has been used as the HTF and storage medium in parabolic trough systems. However, both types of fluid have their limitations: molten inorganic nitrate salts of the type used in power towers have freezing points above 200°C, while mineral oils have an upper temperature limit of about 300°C that significantly limits the efficiency of the power cycle.[5] Trough systems do not need to reach temperatures as high as those required by the power tower design. This relaxes requirements on the upper

Figure 3 Power Tower *from* www.nrel.gov

temperature limit of the HTF, but a low freezing point is critical. Unlike power towers, which have a compact, elevated solar receiver system that requires only simple drainage for freeze protection, parabolic trough power plants have long runs of exposed receiver tubes that cannot be easily drained. Freezing can greatly affect the efficiency of a trough system because energy input, in the form of natural gas to keep the HTF liquefied, is required.

Raising the operating temperature in a trough system to 450°C or greater would raise the efficiency of the power cycle. However, the only fluids that have been identified to date that can meet or exceed the 400°C limit are inorganic nitrate salts.[6] Due to their ionic nature, they exhibit negligible vapor pressures at elevated temperatures, but they also possess freezing points of 120°C or greater, which poses serious challenges for the design, operation, and maintenance of trough plants. The molecular composition of the current generation of organic heat transfer fluids for trough plants limits the maximum operating temperature of a storage system to about 300°C due to vapor pressures that exceed atmospheric pressure at elevated temperatures. This raised vapor pressure cannot be tolerated because it can lead to a high vapor density, which, at elevated temperatures, can lead to flash fires that are difficult to control and extinguish. Additionally, a pressure buildup will put a strain on the piping system.

Objectives

The goal of this proposed project is to identify and develop thermal storage options with improved operational characteristics for solar parabolic trough energy systems. Because of the above-mentioned limitations, I would like to investigate the thermal properties of so-called “room temperature ionic liquids” (RTILs), which hold much promise as a new class of heat transfer or storage fluids. RTILs are essentially salt-like materials that are composed of organic cations (positively charged groups) combined with organic or inorganic anions (negatively charged groups), and that are liquid at or near ambient temperature. An important component of this project is to gain a better understanding of the factors that contribute to the thermal stability of various ionic liquids, which, with their low vapor pressures and salt character, should be thermally stable above 400°C. Discovery of an RTIL with the above-mentioned thermal characteristics could revolutionize the energy-producing capacity of the parabolic trough system.

Methods

The first phase of our research work will be to synthesize a wide variety of imidazolium salts using standard methodology that can be derived from the chemical literature. The focus will be on differing substitution patterns at carbons one and three of the imidazolium cation (see Figure 4). The substituted groups (R1 and R3) to be investigated will be methyl, ethyl, butyl, hexyl, octyl, phenyl, isopropyl, silicone, and 2,4,6-trimethylphenyl in varying combinations. Simple methylation of carbons two, four, and five (R2, R4, and R5 = CH_3) will also be investigated. The commercially available cation phenyltrimethyl ammonium will be coupled to varying anions in hopes of creating an RTIL. It is known that varying the anion can have an enormous impact on the state of the molecule, i.e., whether a particular compound in its pure state will be liquid or solid at

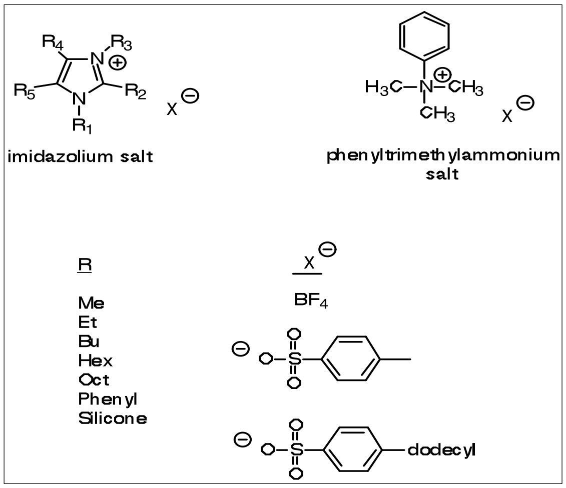

Figure 4

room temperature.[7] This cannot be determined theoretically or by research into existing literature, because many compounds I wish to study have not, to date, been synthesized. The anions to be studied (X- in Figure 3) will be chloride, tetraflouroboric acid, p-dodecylbenzene sulfonate, mesylate, and p-toluene sulfonic acid. All the synthesized ionic compounds will be characterized by standard chemical analysis techniques such as NMR-, IR-, and MS-spectroscopy to ascertain their structure and purity.

The second phase of the project will involve a study of the thermal properties of the synthesized imidazolium salts, using, e.g., thermogravimetric analysis (TGA) and molecular beam mass spectrometry (MBMS). A key issue will be the determination of the thermal stability of the salts at elevated temperatures over prolonged periods of time. While the actual onset temperature for thermal decomposition can be measured by TGA, I hope to be able to get more insight into the molecular mechanisms of the thermal breakdown by following the production of fragmentation products using MBMS techniques developed at the National Renewable Energy Laboratory (NREL).

Budget

Research:

Research technician labor for one year	$43,000	
Chemicals and specialized glassware	$7,000	
Standard NREL overhead (15%)	$7,500	
Total		$57,500

Possible Production Costs:

Glyoxal (40% aq. soln)	$ 1.00 / lb
Formaldehyde (37% aq. soln.)	$ 0.21 / lb
Ammonia	$ 0.10 / lb
Methylamine	$ 0.73 / lb
Ethyl chloride	$ 2.00 / lb
Tetrafluoroboric acid (50% aq. soln)	$ 0.65 / lb

Assuming a 1:1:1:1:1:1 molar ratio, this ionic liquid would cost $2.12/lb ($4.57/kg) for the raw materials alone.

Future Directions

Aside from the chemical parameters that might ultimately determine the choice of RTIL for use as a heat storage fluid, other key issues must be addressed following the developmental work, such as cost, purity, environmental safety, and intellectual property rights. These issues would be addressed in a subsequent study. If a viable candidate were found within the imidazolium series, synthesis routes would be scrutinized in an attempt to lower the cost of raw materials and increase purity. This might include, but would not be limited to, the study of various catalysts and variable pH control. All synthesis routes would then be evaluated using NREL's strict environmental safety guidelines to ensure that if any hazardous materials or byproducts were created, they would be disposed of properly to minimize the effect on the environment. Corrosion studies to test the feasibility of the new liquid in existing infrastructures would also be performed. The creation of a viable HTF or a novel synthesis pathway for existing compounds would be handled under the NREL "Intellectual Property Rights Handbook" guidelines. NREL's legal department would handle all patent applications.

Notes

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