Proceedings of the 11th SolarPACES International Symposium On concentrating Solar Power and Chemical Energy Technologies, September 4-6, 2002, Zurich, Switzerland

New Heat Transfer and Storage Fluids for Parabolic Trough Solar Thermal Electric Plants

Daniel M. Blake,[a]* Luc Moens[a], Mary Jane Hale[a], Henry Price[a], David Kearney[b], and Ulf Herrmann[c]
[a]National Renewable Energy Laboratory, Golden, CO 80401 USA
[b]Kearney&Associates, PO Box 2568, Vashon WA 98070 USA
[c]Flabeg Solar International GmbH, Dipl. Ing.Mühlengasse 7, D-50667 Köln
Germany

Abstract - It has been established that development of a thermal storage option and increasing the operating temperature for parabolic trough electric systems could significantly reduce the levelized electricity cost (LEC) compared to the current state of the art. Both improvements require a new heat transfer fluid if a direct storage system is to be used. The properties of a fluid that can be used for both heat collection and storage require a very low vapor pressure at the hot side operating temperature. This requirement can almost certainly only be met by an ionic fluid. Further, the piping layout of trough plants dictates that the fluid not be allowed to freeze which requires extensive insulation and heat tracing unless the fluid has a freezing point <25°C. A recent study by Kearney and Associates under subcontract to SunLab has explored the potential for use of inorganic nitrate salts that freeze at about 120°C and documented the advantages of storage and higher operating temperature. As part of that study, the LEC achievable if an "ideal" fluid having the above properties was documented. It seems likely (but not certain) at present that this ideal fluid will have to be found among organic rather than inorganic salts. This paper summarizes the results of the first year of searching for heat transfer and storage fluids in this new domain and identifies the key issues that must be addressed in the development of a new fluid.

1. Introduction

Energy storage is a critical factor in advancement of solar thermal technologies that produce electricity. Efficient use of capital requires that the hours electricity is produced be optimized. Prior work on thermal storage options was the subject of a recent review [1]. The challenge is to identify and develop new heat transfer and thermal storage fluids that will improve economics and operational characteristics for parabolic trough electric systems. This compliments near-term work that is investigating sensible heat storage in solid media or using inorganic nitrate salts. The option that would be technically the least risk for the next generation of plant is a direct storage system in which the heat transfer fluid (HTF) is also the thermal storage medium. Thermocline systems are a closely related configuration under investigation in the US Program where the thermal storage capacity of the HTF is augmented by solid thermal storage media such as quartzite particles [2]. The current generation of organic heat transfer fluid (VP-1, a mixture of biphenyl and diphenyl ether) for trough plants has a maximum operating temperature of about 400°C. The vapor pressure of current molecular heat transfer fluids exceeds atmospheric pressure at the temperatures required for use as thermal storage media. This would require impractically large pressure vessels.

Further improvements in the productivity and efficiency of trough plants could be achieved by raising the operating temperature to 450°C or greater. Inorganic nitrate salts are the only fluids that have been identified to date that can meet or exceed the 400°C limit and because they are ionic in nature they have negligible vapor pressures. However, the nitrate salts have freezing points ≥120°C which would add to the complexity of design, operation, and maintenance of a trough plant [3]. Direct thermal storage has been demonstrated for power tower systems using nitrate salts. However, power towers have a compact, elevated solar receiver system and require relatively simple measures for freeze protection [4]. Parabolic trough power plants have long runs of exposed receiver tubes that cannot be easily drained. Trough systems do not need to reach temperatures as high as those required by the power tower design which relaxes requirements on the upper temperature limit of the HTF. But a low freezing point is critical since the potential for freezing and the consequences are greater for trough plants.

There are two key challenges to meet for the next generation of heat transfer and storage fluid for trough plants. The first is raising the operating temperature above 400°C for the heat transfer fluid. The second is developing a fluid that will function as both the heat transfer fluid and thermal storage medium. If the first goal can be met, the only thing that would stand in the way of using it as the thermal storage medium would be the cost of the fluid in the quantity required for a direct storage system. A 55 MWe plant with six hours of storage would require on the order of 8 million Kg (depending on density and heat capacity). The quantity can be reduced by design options including indirect storage or a thermocline system. In these configurations the storage medium could be a lower cost inorganic salt or solid mineral media, or both.

2. Discussion

A recent study carried out by Kearney and Associates under subcontract to SunLab looked in detail at the option of using an inorganic molten salt as the heat transfer and thermal storage fluid for a trough system [3]. The commercial nitrate salt mixture Hitec XL, melting at about 120°C, was selected for use in the evaluation. Within that subcontract some effort was directed to evaluating the impact of a molten salt that had a freezing point near 0 °C. Table 1 summarizes the properties of the current working fluid in the Luz plants in California, Hitec XL, the nitrate salt with the lowest freezing point, and an organic salt of the type termed ionic liquids in the chemical community [5].

Table 1. Key Properties of VP-1™, Hitec XL™, and Octylmethylimidazolium Tetrafluoroborate [omimBF4]

Properties @ 25ºC (or other T)	**2. VP-1™**	**Hitec XL™**	**Ionic Liquid**
Freezing point (ºC)	13	120	<25
Max. applicable T (ºC)	400	>500	400[a]
Density □f (kg/m^3)	815 (300ºC)	1992 (300ºC)	1400
Specific thermal capacity C_p (J/kg K)	2319 (300ºC)	1447 (300ºC)	2500
Vapor pressure	>1 atm above 200ºC)	Nil	Nil
Storage density (MJ/m^3 K)	1.9 (300ºC)	2.9 (300ºC)	3.5
Thermal conductivity k (W/mK)	0.098479 (304ºC)	0.519 (300ºC)	Tbd
Viscosity (cp)	0.2 (300ºC)	6.27 (300ºC)	Tbd
Cost ($/kg)	3.96	1.19	4.57[b]
Heat capacity cost ($K/Mbtu) Solar field inlet T=300ºC			
□T 100	17	8.8	19.28
□T 125	-	7.4	15.42
□T 150	-	5.9	12.83

[a] Determined by thermal gravimetric analysis (tga)
[b] Sum of raw materials cost

The need for thermal storage and advantages of a HTF capable of operating at higher temperatures has been addressed in the recent subcontract work. The following is a summary of results from the Task 6 Report prepared by Kearney and Associates [6]. An ionic fluid having a freezing point <0°C and stable to 450°C. Other properties representative of imidazolium salts were used.

Taking these initial assumptions into account, some preliminary performance and LEC analyses were done to estimate the value of such fluids. Costs for all freeze protection equipment and heat tracing were set to zero and no freeze protection strategy was considered. The use of a non-oxidizing fluid will ease the requirements for specialized packing materials for valves and may also have other beneficial effects on maintenance that were not accounted for in the analysis done by Kearney and Associates.

Figure 1 shows the result of the LEC analyses. Assuming a unit cost of $4.7 /kg, which was the first estimated by NREL, the LEC is about the same as for the VP-1 reference case. When thermocline storage replaces the 2-tank storage system, the LEC is comparable to the ternary salt case even at this cost of the ionic fluid. For a 2-tank storage, the LEC becomes attractive at an ionic fluid costs under $2.7/kg.

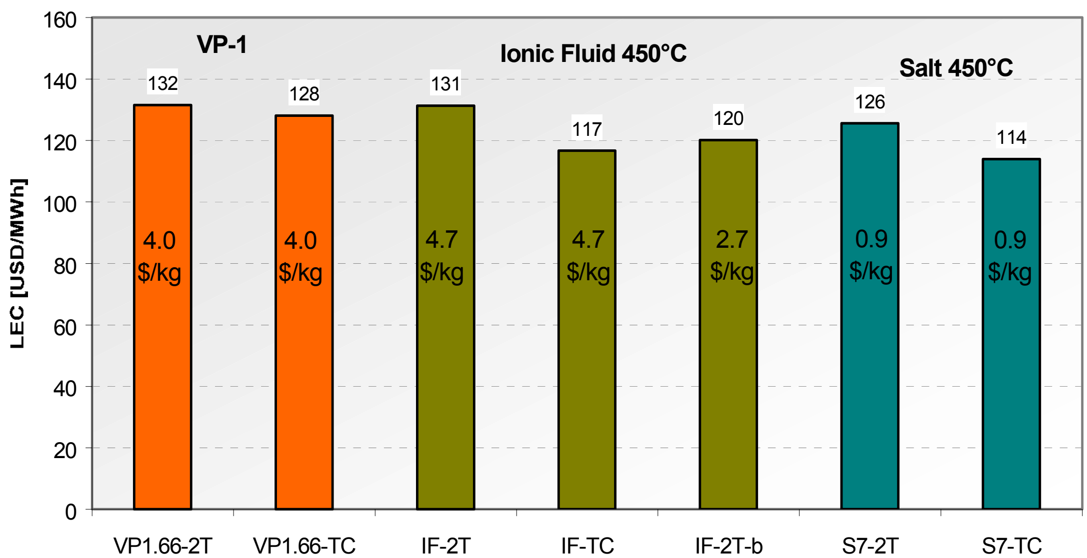

Figure 1 LEC's for Ionic Liquid compared to VP-1 and Hitec XL

(The VP1 cases assume 66 bar steam but all others assume 100 bar steam)

The above analysis concluded that, for an advanced fluid of this nature, unit costs could rise 3 to 5 times higher than the current commercial cost of inorganic salts or organic heat transfer fluids, the variation depending on the type of storage system (2-tank or thermocline). The conclusion from this evaluation is that the development of advanced fluids that may achieve the desired characteristics is justified if the projected costs fall in 2.7-4.7 $/kg range.

3. Potential Candidates For New Fluids

The search for new HTF and storage fluids was begun within the materials termed ionic liquids, (ILs) by organic chemists [7]. These are a family of salts in which the cation is an organic chemical. The anion may be organic or inorganic. Representative examples are shown in Figure 2. Within this class of salts those in which the cation was based on the imidazole ring include examples in the literature with both low freezing points and some probability of having high thermal stability [8]. Laboratory work at NREL and subcontracted work at the University of Alabama have focused on factors associated with stability, freezing point, and other properties of the imidazolium salts. NREL staff has also been looking for other kinds of organic salts or fluids that can be considered for the solar application.

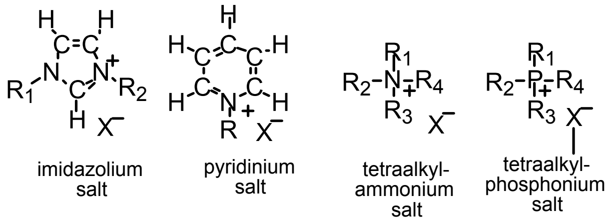

Figure 2. Quaternary ammonium and phosphonium salts (R_n = variable organic substituent and X^- = organic or inorganic negative ion)

The key issues are the usual ones that must be considered when developing any new fluid for use in a large-scale process. These include cost, availability, physical properties (such as freezing point, high temperature limit, heat capacity, and the like), materials compatibility, environmental safety and health, purity specifications, development costs, and intellectual property rights. The key issues are discussed in detail in a recent paper [5]. The limited information available to date indicates that the toxicity of imidazolium salts is comparable to that of VP-1 and nitrate salts that are currently used in solar plants. Available data from The University of Alabama, working under subcontract to NREL, indicates that with the exception of chloride salts, the imidazolium salts are compatible with the alloys currently used or contemplated for use in parabolic trough plants. Very little viscosity data is available at present and that has been measured at low temperatures. In the 20 to 80°C range representative ionic liquids have dynamic viscosities between about 20 and 80 cP [5,7]. Cost and thermal stability are likely to be the greatest challenges.

4. Conclusions

Parabolic trough solar plants impose unique constraints on heat transfer and thermal storage fluids. A low freezing point is shown to be particularly important and avoidance of freeze protection measures is demonstrated to allow a fluid cost that is significantly higher than conventional mineral oils or nitrate salts. Freezing points near 0°C seem to dictate searching for new fluids in the realm of organic salts. The imidazolium salts show promise but they are in an early stage of development. There is clearly a great deal of work that needs to be done to define the key physical and chemical parameters.

References

[1] Hermann, U. "Survey of Thermal Storage for Parabolic Trough Power Plants," September 2000, NREL, Golden, CO, NREL/SR-550-27925, 51 pp.

[2] Pacheco JE, Showalter S, Kolb W. Development of a molten salt thermocline thermal storage system for parabolic trough plants, Proceedings of the Solar Forum 2001, Washington DC, April 2001.

[3] Kearney D, et al. Evaluation of a molten salt heat transfer fluid in a parabolic trough solar field, Proceedings of the National Solar Energy Conference, Solar 2002, Reno/Sparks, Nevada, June 2002.

[4] Reilly HR, Kolb G. "An Evaluation of Molten-Salt Power Towers Including Results of the Solar Two Project", SAND2001-3674, November 2001.

[5] Moens L., Blake DM, Rudnicki DL, Hale MJ. Advanced thermal storage fluids for solar parabolic trough systems, Proceedings of the National Solar Energy Conference, Solar 2002, Reno/Sparks, Nevada, June 2002.

[6] Engineering Evaluation of a Molten Salt HTF in a Parabolic Trough Solar Field. Task 6 Report. Final System Performance and Cost Comparisons. Prepared by Kearney and Associates for NREL, August 2001, 29 pp.

[7} Wu B, Rodgers RD, Reddy RG. Novel ionic liquid thermal storage for solar thermal electric power systems, Proceedings of the Solar Forum 2001, Washington, DC, 2001.

[8] Ngo HL, LeCompte K, Hargens L, McEwen AB. Thermal properties of imidazolium ionic liquids, Thermochim. Acta 2000; 357-8: 97-102.