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Advanced Heat Transfer and Thermal Storage Fluids

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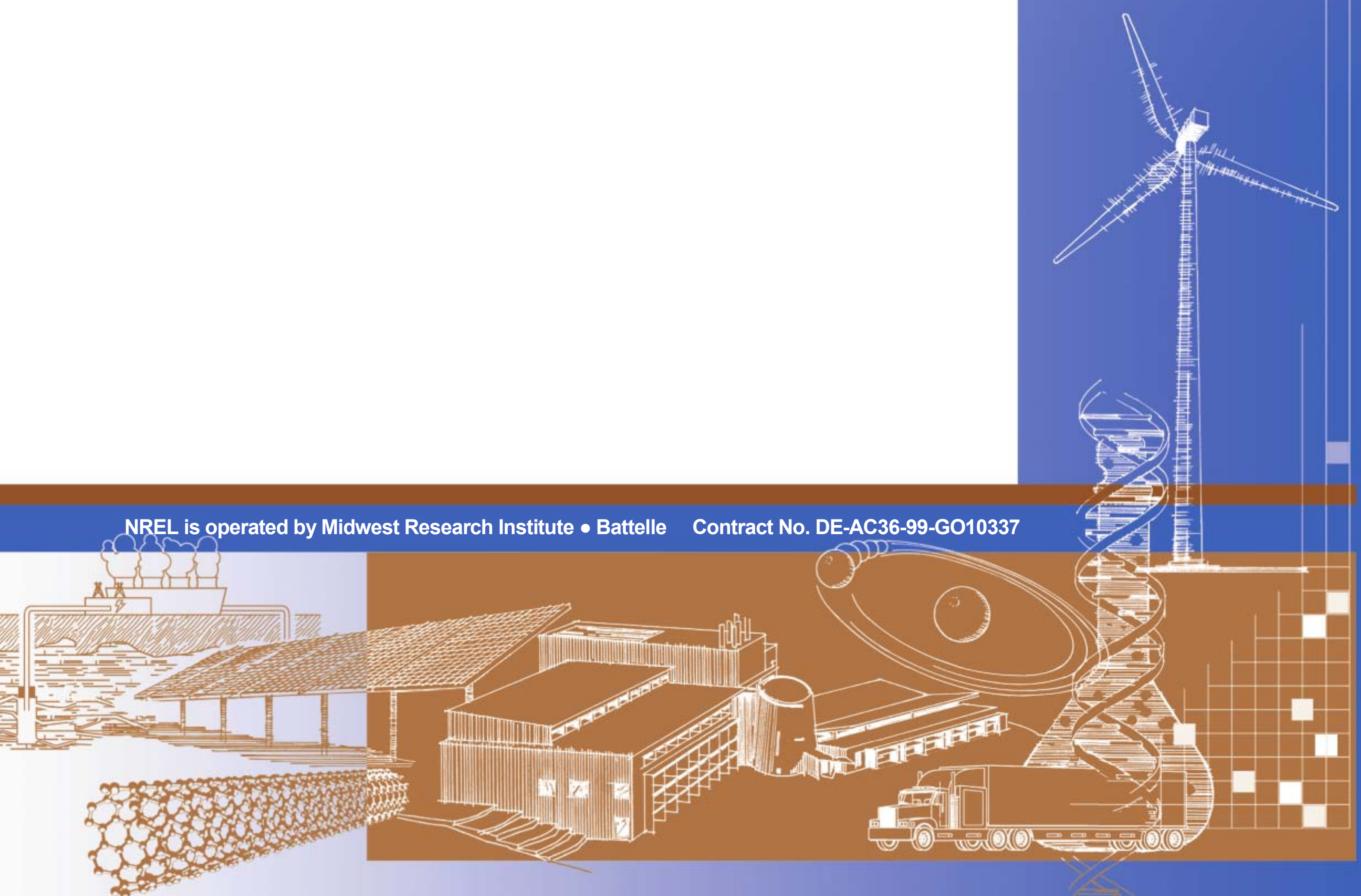

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Advanced Heat Transfer and Thermal Storage Fluids

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ABSTRACT

The design of the next generation solar parabolic trough systems for power production will require the development of new thermal energy storage options with improved economics or operational characteristics. Current heat-transfer fluids such as VP-1™, which consists of a eutectic mixture of biphenyl and diphenyl oxide, allow a maximum operating temperature of *ca.* 300°C, a limit above which the vapor pressure would become too high and would require pressure-rated tanks. The use of VP-1™ also suffers from a freezing point around 13°C that requires heating during cold periods. One of the goals for future trough systems is the use of heat-transfer fluids that can act as thermal storage media and that allow operating temperatures around 425°C combined with lower limits around 0°C. This paper presents an outline of our latest approach toward the development of such thermal storage fluids.

1. Objectives

The advanced technology development discussed in this paper is considered to be one of the most important keys to achieving reductions in the levelized energy costs (LEC) for solar parabolic trough systems. It deals with the development of new types of fluids that can operate at much higher temperatures than current systems (*i.e.*, up to 425°C) and that are suitable both as heat-transfer fluids in the solar field, as well as thermal energy storage (TES) media in the storage system [1]. The advantage of TES is that it will allow dispatching of power to meet the system peak load, and it will increase the plant capacity. The use of a fluid that can both transfer and store the thermal energy will simplify current plant designs in that no heat exchangers will be needed that add to the technical risks. A major requirement for such a new fluid beside extreme thermal stability is the need for a very low vapor pressure to avoid the need for pressure-rated tanks, as well as a freezing point at or below 0°C to avoid the risk of freezing in the collector field during cold periods.

2. Technical Approach

There are currently several classes of compounds that have been commercialized as industrial heat transfer fluids (Table 1). The organic fluids remain liquid over a wide temperature range but suffer from high vapor pressures and flammability that preclude their use above 300°–400°C. In contrast, inorganic nitrate salts have good thermal stability but high freezing points.

Table 1. Commercial heat-transfer fluids (HTF)

HTF	Application T (°C)	Properties
Synthetic oils (aromatic HC's) e.g. VP-1™	13 to 395	Flammable
Mineral oils (paraffinic HC's)	-10 to 300	Flammable
Silicone oils	-40 to 400	Expensive Flammable
Nitrate salts e.g. HITEC-XL	220 to 500	Freezing point ≥ 120°C High T stability

When we started our search for new thermal fluids, we decided to study imidazolium salts that were also known as "room-temperature ionic liquids," which are unique salts that are liquid under ambient conditions [2]. At that time, the chemical literature suggested that several ionic liquids of the imidazolium family had unusually high thermal stabilities that were believed to exceed 400°C in some cases, while many of these salts had melting points as low as –90°C. However, our study focusing on the thermal decomposition pathways of these salts revealed that their thermal stability had been greatly exaggerated and that the commercially most attractive ionic liquids quickly decompose in the 200°–250°C range. This finding caused us to abandon ionic liquids as potential thermal fluids for solar troughs. Instead, we decided to look at possible chemical modifications of the VP-1™ components, *i.e.*, biphenyl and diphenyl oxide (Fig. 1).

VP-1

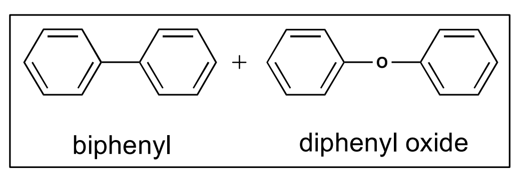

Fig. 1. Components of commercial VP-1™ fluid

As modifications, we are currently looking at salt forms of these aromatic compounds, as well as substituted analogs (Fig. 2). In addition, we also became interested in the rich literature dealing with high-performance lubricants and functional fluids for use in extreme environments (*i.e.*, jet engines and heavy engines). Because of the inherent higher thermal stabilities, we believe that the major challenges with decomposition

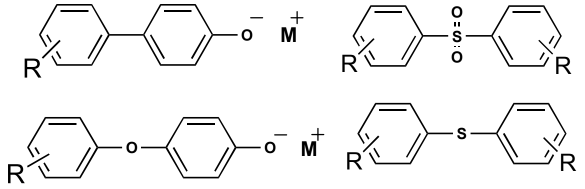

Fig. 2. Substituted biphenyl and diphenyl oxide analogs

would instead be related to oxidative and hydrolytic degradation under the extreme heat conditions due to trace contaminants such as oxygen, metal ions, or water.

The new approach requires a broad search and the synthesis of many new fluids with different molecular structures. However we also looked for high-boiling fluids with freezing points below ambient temperature that might already be known in the chemical industry. Our choice fell upon the class of commercially available phthalate esters that are commonly used as plasticizers in polymers. Phthalate esters enjoy a growing market, and have a relatively low cost (at or below $1 / lb) [3](Fig. 3).

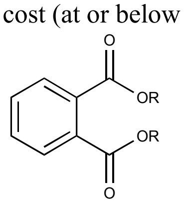
Fig. 3. Phthalate esters (R= linear or branched alkyl group)

3. Results and Accomplishments

Although the work is still in its early stages, we have already synthesized a series of compounds that are variants of the known esters that can be found in commercial lubricant formulations. Examples of esters that we are working on are derivatives of the basic building blocks shown in Figure 4, all of which have been reported in the patent literature, but we are also working on new variants that cannot be revealed at this time.

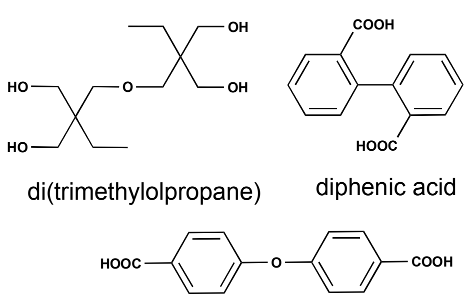

Fig. 4. Building blocks for high-performance fluids

Note that the alcohol groups (-OH) and acid groups (-COOH) allow one to synthesize a wide range of derivatives that have very high boiling points, but that also possess good fluid properties at or below room temperature. We have prepared several low-viscosity fluids with very high boiling points under high vacuum, and our plan is to study these esters in more depth using thermal analysis methods such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), with a special focus on kinetic data that can help us in evaluating their thermal behavior over extended time periods.

Among the commercially available phthalate esters, we have chosen those that are claimed to have extremely high boiling points (well beyond 450°C in some cases), and we will include these in our planned thermo-analytical studies. The material specifications needed for the solar troughs are far more extreme than any data that could be supplied by manufacturers, and even an extensive study of the chemical literature has not revealed any useful reports on this topic. In addition, the application of antioxidant packages, such as is common practice in the formulation of high-performance lubricants and fuels, requires some new thinking because the antioxidants may also undergo thermal decomposition.

4. Conclusions

We have identified and synthesized a series of compounds that may fit the specifications imposed by the next generation solar trough systems, and we have synthesized a series of fluids that are ready for extensive thermo-analytical screening. The issues of oxidative and hydrolytic stability at extreme temperatures are expected to remain a major concern for any type of organic fluid, because preventing any traces of oxygen or moisture from entering the solar trough system is a difficult technical challenge. However, although our new ester-based fluids will require long-term R&D, the phthalate esters may constitute a short-term solution because they are already commercially available as commodity chemicals with an attractive cost. The challenge will be to gain complete insight into their thermochemical behavior at extreme temperatures, and to obtain kinetic data from which we can derive their lifetime in solar thermal plants.

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