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Evaluation of Phenylnaphthalenes as Heat Transfer Fluids for High Temperature Energy Applications

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The thermodynamic properties of 1- and 2-phenyl substituted polyaromatic hydrocarbons have been measured and estimated under conditions relevant to heat transport applications almost to the critical point. Densities, vapor pressures, and heat capacity measurements were used to derive critical temperature, pressure, and density for the phenylnaphthalenes. The thermal and radiolytic stability of 1-phenylnaphthalene was examined using thermogravimetric analysis, differential scanning calorimetery, and gamma irradiation. Low melting point, low vapor pressure, high critical temperature, and resistance to thermal decomposition may make phenylnaphthalenes suitable for heat transfer applications up to 800 K, including power generation and separations processes.

Keywords concentrating solar power energy storage; high temperature heat transfer fluids; substituted naphthalenes; thermodynamic properties

INTRODUCTION

All large-scale, energy-intensive processes, including high-volume industrial separations, involve the production or absorption of energy in the form of heat. In the past the conservation of heat was not an important part of process design because energy costs were low. Now with oil prices and natural gas prices increasing, minimization of costs and discharge of waste heat through energy conservation is of renewed importance. Greater thermodynamic efficiency, new thermochemical cycles, and innovations in the generation of electricity are often dependent on equipment that can run at higher temperatures than current power plants. Both nuclear and solar power generation, extraction of hydrocarbons from complex geological matrices, and chemical cycles such as those to produce hydrogen would benefit from heat transfer fluids for cooling or energy transport that are stable to temperatures above 800 K or even higher, have good thermal characteristics, and do not react with the vessels in which they are contained. Heat transfer fluids that can be used at high temperatures have the potential of reducing both capital and operating costs of energy generation and conversion.

For example, High Temperature Heat Transfer (HTHT) fluids could be considered as candidates for parabolic troughs in solar collectors. To date, organic-based fluids used in parabolic troughs have a thermal stability limit of approximately 673 K. To trap solar energy more efficiently, a higher thermal stability limit is desirable. Recently, the potential for use of room temperature ionic liquids as engineering fluids has been reviewed by Zhao (1). He cited work where imidazolium ionic liquids demonstrated many favorable properties such as high heat capacity, low melting point, and large liquid range. However, other work has suggested that the use of ionic liquids at temperatures above 473 K would be limited by unacceptable vapor pressures and instability arising from thermal degradation (2).

New nuclear power cycles are being designed not only to provide an ample and economical source of energy but also to generate high temperatures (900–1300 K) for hydrogen production through thermochemical cycles. HTHT fluids are also being considered for secondary systems to enhance heavy oil recovery from sands and shales. Heat transfer using stable fluids could compete economically with extremely long ($\geq$1 km) electrical heating elements now being considered for oil shale extraction, the latter being subject to metal fatigue and failure. Nuclear reactor engineers use a parameter called the figure of merit to characterize possible coolants, $F = C_p^{2.8}\ \rho^2/\eta^{0.2}$, where C_p is the specific heat at constant pressure ($\mathrm{J \cdot g^{-1} \cdot K^{-1}}$), ρ is the density ($\mathrm{g \cdot cm^{-3}}$), and η is the dynamic viscosity ($\mathrm{mPa \cdot s}$). This figure of merit, one of many possible alternatives, derives empirically from the heat transfer process and the associated pumping power required. The higher the figure of merit the better the coolant performance. For example, at 573 K liquid sodium at 573 K has a value of unity; water, 60; mercury, 0.31; 5 MPa helium, 2×10^{-3}; and 5 MPa air, 4.5×10^{-5} (3). Liquid metals, though excellent coolants, present handling problems because of their chemical reactivity.

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In summary, desirable properties for a potential HTHT fluid are

- high critical temperature and thermal stability to temperatures 800–900 K
- vapor pressure, or critical pressure, of less than 20 bar above 800 K
- freezing point of less than 350 K
- specific gravity in the range 0.7 to 1.7 $g \cdot cm^{-3}$ to 800 K
- heat capacity in the range 2 to 5 $J \cdot g^{-1} \cdot K^{-1}$ to 800 K
- viscosity of about 1 $mPa \cdot s$ to 800 K
- chemical compatibility with common stainless steels
- a cost per barrel comparable to that of crude oil.

Ideally, in addition to the above properties, candidate HTHT fluids should meet environmental, safety, and health standards for toxicity or, at worse, be no more toxic than crude oil. Ideal coolants for nuclear reactors need (in addition to the earlier listed properties) low neutron absorption cross section and, for thermal reactors, a high moderating ratio, radiation stability (towards decomposition and/or polymerization), and a low induced radioactivity. Some commercially available HTHT fluids being considered for solar and nuclear power applications are given in Table 1, with properties given for a temperature at which the fluid could be used. Even though a variety of fluids are represented in the table, there are no standard commercially available high-performance heat transfer fluids that fulfill all of the above criteria.

This work focused on the thermodynamic properties of the fluid—vapor pressure, viscosity, thermal conductivity, specific heat, and density—that are important in heat transfer. Each of these is temperature dependent. Since a temperature gradient exists in a flowing stream undergoing heat transfer, a problem appears in the choice of temperature at which the properties should be evaluated. For small temperature differences between fluid and wall, and for fluids with weak dependence of viscosity on temperature, the problem is not acute. But for highly viscous fluids such as heavy petroleum oils, or where the temperature difference between the tube wall and the fluid is large, variations in fluid properties within the stream also become large, and the difficulty of calculating the heat-transfer rate increases. Therefore, the development of HTHT fluids requires a database of thermophysical properties measured over a wide temperature range and cannot rely on values obtained solely in the region of ambient temperature and pressure.

High temperature heat transfer fluids are usually required in process applications where the optimal, bulk-fluid operating temperatures necessitate safer and more efficient methods than steam, electrical, or direct flame heating methods. To date, organic types of these fluids can be categorized as either aromatics, petroleum-based paraffinic/naphthenic hydrocarbons, silicon-based, or glycol type. Of these types only the aromatics can be used above 623 K, and most of those commercially available are based on diphenyloxide $C_{12}H_{10}O$/biphenyl mixtures $C_{12}H_{10}$ (4) or the Exxon-derived terphenyl types (*o*-, *m*-, or *p*-terphenyl). Biphenyl fluids are stable to their critical temperatures, 773 ± 3 K. Some decomposition has

TABLE 1
Commercially available high temperature heat transfer fluids

Compound	T_m T_b (K)	C_p ($kJ \cdot kg^{-1}K^{-1}$)	ρ ($kg \cdot m^{-3}$)	T_c (K) p_c (bar)	p_v (bar)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	η ($mPa \cdot s$)
Dowtherm A (678 K) (4)	285.2 530.2	2.725	672.5	770 31.34	11.32	0.0771	0.12
Xceltherm 600-C_{20} paraffin oil (588.8 K) (37)	T_b range 574–741	3.001	672.36	768 10.7	0.2499	0.1122	0.252
H_2O (563 K, 7.5 MPa) (38)	273.15 373.15	5.5	732	646.95 220.64	Super-heated	0.56	0.13
Li_2BeF_4 (973 K) (39)	732 1703	2.42	1940	Not available	Not available	1.0	2.9
Na (823 K) (40)	370.95 1156	1.27	820	2503.75 256.4	~10–16	62	0.12
Helium (7.5 MPa) (41)		5.5	3.8	5 2.26	Super-heated	0.29	11.0
Biphenyl (500 K) (23,42–44)	342 559	2.03	869	773 ± 3 33.8 ± 1	0.531	0.118	0.32
p-Terphenyl (500 K) (5,23,42–44)	485 623	1.98	947	908 + 10 29.9 ± 6	0.0199	0.135	0.73

been seen with terphenyls when cycled above their critical points, 857–908 K (5). However, these stabilities are acceptable for existing reactor technology. The organics chosen for study were expected to have critical points above 800 K, with stabilities close to that region. The monosubstituted naphthalenes promise both thermal and radiation stability (6) and may become abundantly available because of pollution requirements on fuel derivatives from sources of unconventional petroleum.

Of organics, only polycyclic aromatics with small group substitutions are likely to fulfill the requirements outlined above for HTHT fluids. Unpublished work by W. V. Steele (University of Tennessee, Knoxville) supports the statement that organics with alkyl chains greater than two carbons in length will not be thermally stable above 673 K. Steele has also shown in a series of experiments using a differential scanning calorimeter (DSC) that a range of polycyclic aromatics are stable in the absence of oxygen through their critical points (7). For instance, the measured two-phase critical region for carbazole, $C_{12}H_9N$, has a recorded critical temperature of 932 K. Although carbazole itself does not fulfill the above criteria since it has a freezing temperature greater than 573 K, the same compound with a substitution of a methyl group in the 9-position is a liquid at room temperature (8) and appears stable through its critical temperature, 890 K. Phenanthrene with a substituent methyl group at the 3-position was found by Steele and colleagues (9) to have a critical temperature approaching 898 K and was thermally stable when the temperature-cycled several times to at least 873 K in the DSC.

The organics discussed here as candidate HTHT fluids are derived from petroleum (10,11) and have been shown to be present in the diesel distillate fraction. New regulations from the European Union to take effect in 2010 will ensure the removal of such polyatomic aromatics from diesel fuel because they do not burn completely in diesel engines and also tend to degrade catalytic converters. Incomplete combustion means these polyaromatic molecules can be emitted in diesel engine exhaust (12,13). Hence, separation and recovery of these heavy organics during refining for use as heat transfer fluids may have both economic and environmental drivers.

Figure 1 shows structures of the candidate HTHT fluids, 1- and 2-phenylnaphthalene, chosen for study because their normal boiling points are close to or above 598 K, higher even than those of the substituted phenanthrenes mentioned earlier. In addition, the substituted naphthalenes represent a situation where the only structural difference appears to be in the position of the phenyl group. Hence, group additivity properties would predict similar behavior, yet that appears not to be the case. 1-Phenylnaphthalene is a liquid at room temperature with a melting point at ~318 K and is easily supercooled well below that temperature. In contrast, 2-phenylnaphthalene is a solid with a melting point of 375 K and is easily crystallized. Because of their similar chemical structure, they served as a rigorous test of the thermal stability and critical point measurements in this study.

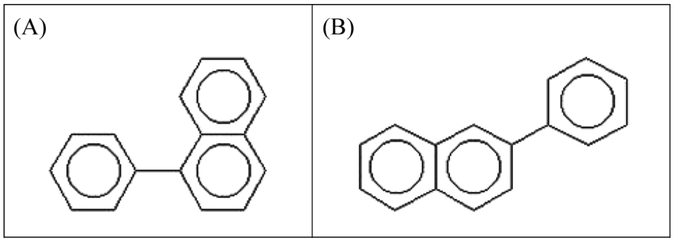

FIG. 1. Structures of 1-phenylnaphthalene (A) and 2-phenylnaphthalene (B).

EXPERIMENTAL

Thermal and radiolytic stabilities of 1- and 2-phenylnaphthalene were investigated. 1-Phenylnaphthalene (Aldrich lot #S43166-487) was irradiated in a ^{60}Co irradiator for two weeks, source strength 300 Gy · h^{-1} for a total dose of 100 kGy. The residue was analyzed using ^{1}H nuclear magnetic resonance (^{1}H-NMR) in a Bruker Avance 400. A small amount of degradation was observed, ~1.7%.

Differential scanning calorimetry and thermogravimetric analysis were used to further investigate the thermal stability of 1- and 2-phenylnaphthalene. The work done at Oak Ridge National Laboratory (ORNL) used a TA Instrument DSC Q100. Samples of weights from 4.8 to 9.3 mg were prepared and heated at 2 and 10 K · min^{-1} from 185 to 670 K. Calorimetry measurements were taken from the heat flow measurements over time, with a cover gas of nitrogen at 50 mL · min^{-1}. Both of these compounds were found to degrade at temperatures slightly below their critical points, and so heating was limited to about 800 K.

RESULTS AND DISCUSSION

Besides the experiments outlined earlier, unpublished experimental data were also used to derive physical properties to evaluate the phenylnaphthalenes as heat transfer fluids (9). Physical properties were measured on 1- and 2-phenylnaphthalene compounds that had been synthesized using a palladium-catalyzed cross-coupling reaction between a halogenated organic naphthalene precursor and phenyl boronic acid (14). The thermodynamic properties of the phenylnaphthalene compounds were measured using adiabatic calorimetry and differential scanning calorimetry for heat capacities, vapor pressures from inclined piston and ebulliometric measurements, enthalpy of combustion of 1-phenylnaphthalene by bomb calorimetry, and liquid-phase densities by vibrating tube densitometer. The experimental techniques used in these measurements are surveyed in a previous publication (7). Because of

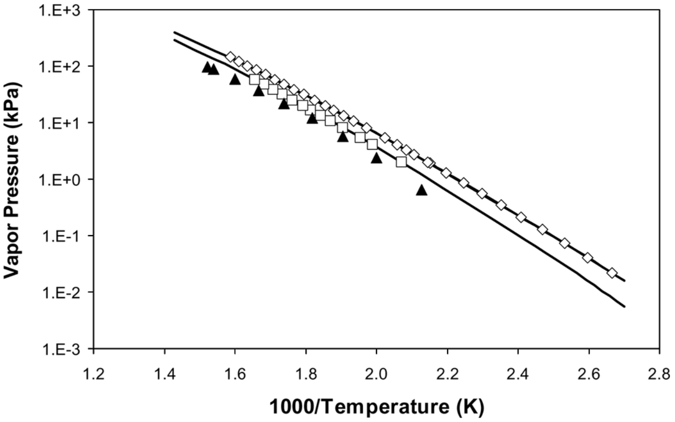

FIG. 2. Vapor pressures of 1-phenylnaphthalene (diamonds), 2-phenylnaphthalene (squares), and fluoranthene (triangles) as a function of reciprocal temperature. The solid lines are Wagner fits to the experimental pressure data (Table 2).

decomposition, measurements could not be taken at the critical point on these compounds.

Vapor pressure data is plotted on an Arrhenius plot in Fig. 2. Vapor pressure data give the normal boiling point of 2-phenylnaphthalene as 626.9 K, very close to the NIST reference value, with that of 1-phenylnaphthalene, 609.0 K, being 11 K higher than the reference. This gives an estimated uncertainty in the data of ±10%. As expected from the differing melting points, the vapor pressure of 1-phenylnaphthalene is consistently higher than that of 2-phenylnaphthalene, which in turn is higher than fluoranthene (15), a homologue also included on the plot.

As they could not be measured directly for these compounds because of decomposition, critical points were determined by simultaneously iterating functions for vapor pressure and density, as described by Steele (7). Initial guesses for critical temperature, pressure, density, and acentric factor were based on empirical relationships based on Lydersen's group contribution method as outlined by Reid et al. (16). The acentric factor is defined as $-\log[p/p_c]-1$. This estimate was used as the input for fitting the Reidel equation for density to experimental data, with the derived critical temperature and acentric factor coming from a minimization of the residuals. Using these fitted parameters, the critical density was determined by a simple ratio to minimize the deviation from experimentally measured densities. Densities were not measured for 2-phenylnaphthalene as it is solid at room temperature; hence, the intial density had to be estimated based on available data for 1-phenylnaphthalene. The latter value was measured under saturation conditions following a procedure described elsewhere by Steele and coworkers (17). The assumption of similar densities at the melting point was probably valid to within ±5%, given the difference in computed critical densities for the two isomers.

Optimization of the fit to density data was followed by a least-squares fitting of the Wagner expression for vapor pressure to determine the critical pressure, in a manner described previously (18). After iterative optimization to fit experimental data for 1- and 2-phenylnaphthalene, the Wagner expressions were characterized by both the Waring and Ambrose criteria. As density data were not available for 2-phenylnaphthalene, the final values of p_c and T_c for this compound were based on minimizations both in residuals for the vapor-pressure fit and in the Ambrose criterion. (The calculated critical point is given later in Table 4.) After finding the critical temperature, pressure, and acentric factor from optimization of the fit of vapor pressure, the critical density was calculated from the Reidel equation calibrated with a known reference density at 396 K (19). The Wagner expressions for the vapor pressures of 1- and 2-phenylnaphthalene compounds are shown in Fig. 2 and are given in Table 2.

Densities for 1- and 2-phenylnaphthalene derived from fits to the Reidel equation are given in Fig. 3 along with the experimental values for 1-phenylnaphthalene. It is obvious from the plot that the saturation densities from the vibrating-tube densitometer for 1-phenylnaphthalene only go a small fraction of the way to the critical point. Derived Reidel expressions for density are also given in Table 2. Even though the agreement between the correlation and experimental data is within $\pm 5\,\mathrm{kg}\cdot\mathrm{m}^{-3}$ at lower temperatures, because of the long extrapolation, density values have an estimated uncertainty of $\pm 20\,\mathrm{kg}\cdot\mathrm{m}^{-3}$ close to the critical point.

Thermal conductivities for the liquids were not measured directly but were estimated from critical properties using both the methods of Latini and Sato as described by Reid et al. (16). The values came from the expressions in Table 2 and are plotted in Fig. 4. In these calculations T_r is the reduced temperature and T_{br} is the reduced temperature at the boiling point.

Both correlations predicted a slightly larger thermal conductivity for 2-phenylnaphthalene than for 1-phenylnaphthalene, between 5 and 6% over the entire temperature range. The trends with temperature were very similar for all the predictions, and the correlations gave closer results at higher temperatures. The differences in the Sato and Latini expressions ranged from 2 to 4% and from 1 to 3%, respectively, for 1-phenylnaphthalene and 2-phenylnaphthalene. Although the molecular weight of the phenylnaphthalenes falls well within the range of validity of the Latini method, its accuracy is only considered to be within ±10%. Significant errors can arise with the Sato method as well, and hence the measurement of thermal conductivities would be required before using these fluids in a heat transfer application.

The thermal conductivities at 600 K, close to the boiling points of the phenylnaphthalenes, were calculated to be $0.076 \pm 0.001\,\mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}$ (for 1-phenylnaphthalene) and

TABLE 2
Correlations for thermophysical properties of liquid 1-phenylnaphthalene and 2-phenylnapthalene

Vapor Pressures – Wagner Fit (bar)

$$\ln\left(\frac{p}{p_c}\right) = \frac{T}{T_c}\left[A\left(1-\frac{T}{T_c}\right) + B\left(1-\frac{T}{T_c}\right)^{1.5} + C\left(1-\frac{T}{T_c}\right)^{2.5} + D\left(1-\frac{T}{T_c}\right)^{5}\right]$$

1-phenylnaphthalene, $p_c = 7.11$, $T_c = 818\,\mathrm{K}$
$A = 5.736$, $B = -26.89$, $C = 16.38$, $D = -14.71$
2-phenylnaphthalene, $p_c = 6.50$, $T_c = 831\,\mathrm{K}$
$A = 6.311$, $B = -29.99$, $C = 21.38$, $D = -23.28$

Liquid Density – Riedel Fit

$$\frac{\rho}{\rho_c} = 1 + 0.85\left(1-\frac{T}{T_c}\right) + (1.69 + 0.984\omega)\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}$$

1-phenylnaphthalene $\rho_c = 348\,\mathrm{kg \cdot m^{-3}}$ 2-phenylnaphthalene $\rho_c = 335\,\mathrm{kg \cdot m^{-3}}$

Thermal Conductivity ($\mathbf{W \cdot m^{-1} K^{-1}}$)

$$\lambda_L(Latini) = \frac{A(1-T_r)^{0.38}}{T_r^{1/6}}, A = \frac{A^* T_b^{\alpha}}{M^{\beta} T_c^{\gamma}}$$

$$\lambda_L(Sato) = \frac{(1.11/M^{1/2})(3 + 20(1-T_r)^{2/3})}{3 + 20(1-T_{br})^{2/3}}$$

$A^* = 0.0345$, $\alpha = 1.2$, $\beta = 1$, $\gamma = 0.167$, $M = 204\,\mathrm{g \cdot mol^{-1}}$
1-phenylnaphthalene, $T_{br} = 0.73$ 2-phenylnaphthalene, $T_{br} = 0.75$

Dynamic Liquid Viscosity (mPa · s)

$$\ln\frac{\eta_L(Orrick)}{\rho_L M} = A + \frac{B}{T}$$

$$\eta_{SL}(Letsou)\xi = 10^{-3}(2.648 - 2.725T_r + 1.309T_r^2) + 10^{-3}\,\omega(7.425 - 13.39T_r + 5.933T_r^2)$$

$$\xi = 0.176\left(\frac{T_c}{M^3 p_c^4}\right)^{\frac{1}{6}}$$

1-phenylnaphthalene, A = −10.43, B = 2019 2-phenylnaphthalene, A = −10.26, B = 1885

Heat Capacity at Constant Pressure

Condensed phase

$$\frac{C_p}{R} = -KT_r(b_0 + b_1(1-T_r) + b_2(1-Tr)^2 + b_3(1-Tr)^3)$$

1-phenylnaphthalene, $K = -98.39$, $b_o = -0.7337$, $b_1 = 0.1494$, $b_2 = -1.336$, $b_3 = 0.649$
2-phenylnaphthalene $K = -99.95$, $b_o = -0.8013$, $b_1 = 0.8634$, $b_2 = -3.808$, $b_3 = 3.160$

C_p(vapor) – C_p(liquid)(T), 1-phenylnaphthalene = $1.13 \times 10^{-3}T^2 - 0.848T$
C_p(vapor) – C_p(liquid)(T), 2-phenylnaphthalene = $8.46 \times 10^{-4}T^2 - 0.609T$

$0.082 \pm 0.001\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ (for 2-phenylnaphthalene) (shown later in Table 6). These values are similar to that of Dowtherm (Table 1) at 678 K, above its boiling point.

Liquid viscosities were estimated for liquids below $T_r = 0.75$ using the group contribution method of Orrick and Erbar (Private communication quoted by Reid et al. (16)). In this case, the reference density of liquid 1-phenylnaphthalene was taken as $1.08\,\mathrm{g \cdot cm^{-3}}$ at 318 K, while that of 2-phenylnaphthalene was taken as $1.009\,\mathrm{g \cdot cm^{-3}}$ at 396 K (19). The Letsou and Stiel correlation was used for the high temperature values for the saturated liquid. The estimates were based on the critical properties derived from vapor pressure and density measurements presented earlier. The dynamic viscosity was low for both substituted naphthalene compounds and was comparable to other fluids currently being used as heat

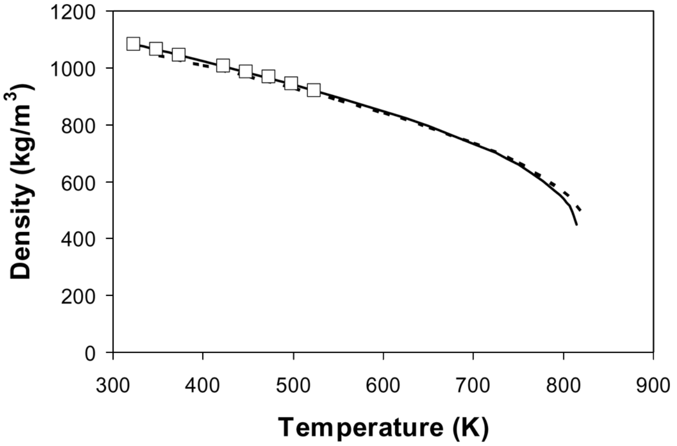

FIG. 3. Calculated liquid densities ($\mathrm{kg \cdot m^{-3}}$) for 1-phenylnaphthalene (solid) and 2-phenylnaphthalene (dashed) as a function of temperature. Densitometer data (squares) for 1-phenylnaphthalene are superimposed on the Reidel plots.

transfer fluids (Table 1). The agreement between the high and low temperature correlations was reasonable, although not perfect, for both the ortho- and meta-substituted phenylnaphthalenes (Fig. 5).

Heat capacities for liquid 1- and 2-phenylnaphthalene are presented in Fig. 6, taken from differential scanning calorimetry and adiabatic heat capacity measurements. The heat capacities for the two compounds are very similar up to 700 K and within the uncertainty of the measurement, $\Delta C_p/R = \pm 1$ as calculated from the precision of the measurements. The heat capacity curves (Table 2) were derived from a simultaneous fit to vapor pressure and the double derivative of the chemical potential.

To derive thermodynamic functions for heat capacity (gas phase), entropy, and enthalpy as a function of temperature, thermodynamic data were defined at the standard state, here taken to be 298.15 K and 1 bar (Table 3). The standard heat of formation of 1-phenylnaphthalene was derived from the heat of combustion measured in a rotating bomb calorimeter, using expression (1). The heat of combustion of 2-phenylnaphthalene was not measured in the same way, and so was derived from that of its ortho isomer as the stoichiometry of the combustion reaction is the same (1).

$$C_{16}H_{12} + 19O_2 \rightarrow 6H_2O + 16CO_2$$
$$\Delta_f H_m^0(C_{16}H_{12}) = -\Delta_c H_m^0 + 6\Delta_f H_m^0(H_2O) + 16\Delta_f H_m^0(CO_2) \tag{1}$$

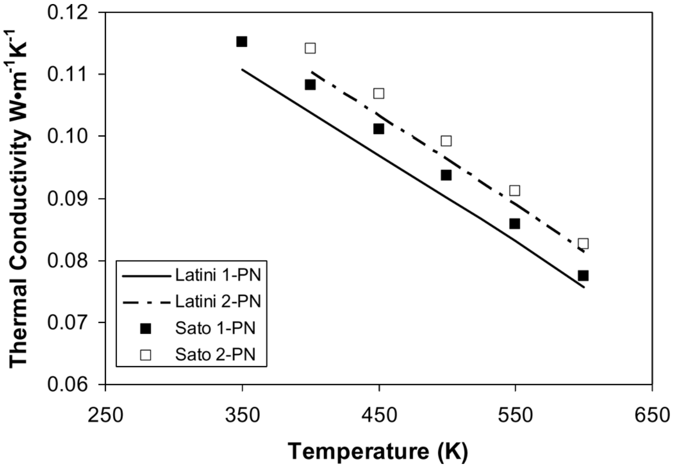

FIG. 4. Calculated thermal conductivity ($\mathrm{W \cdot m^{-1} K^{-1}}$) as a function of temperature (K), for 1-phenylnaphthalene (1-PN) and 2-phenylnaphthalene (2-PN).

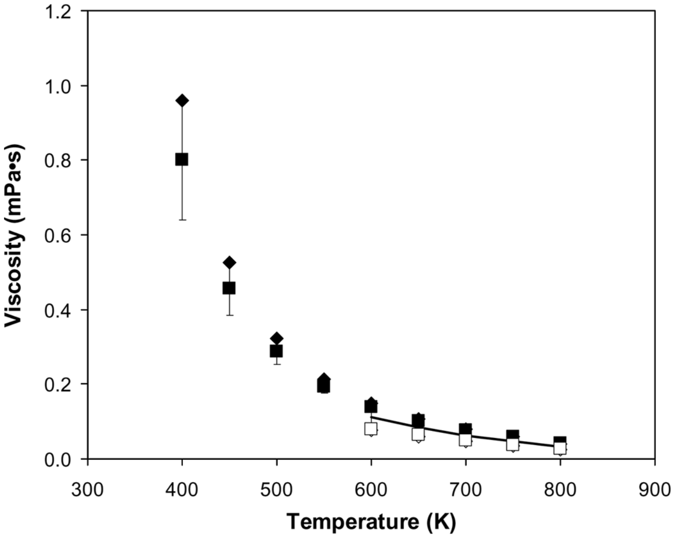

FIG. 5. Estimated dynamic liquid viscosities for 1-phenyl (diamonds) and 2-phenyl (squares) substituted naphthalenes as a function of temperature. The low temperature estimates are the filled symbols, and the high temperature estimates for the saturated liquid are the unfilled symbols. The solid line at higher temperatures is the average of the two simulations to show convergence of the values.

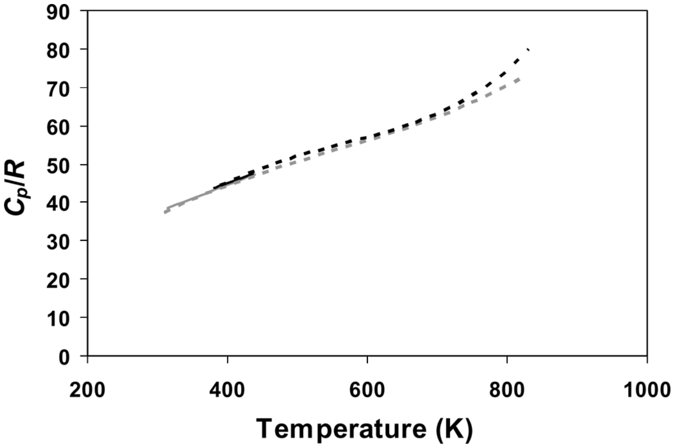

FIG. 6. Heat capacities C_p/R for saturated liquid 1-phenylnaphthalene (grey) and 2-phenylnapthalene (black) by adiabatic calorimetry (solid) and differential scanning calorimetry (dashed) as a function of temperature.

TABLE 3
Computed thermodynamic functions for saturated liquids

Molar properties at standard state: 298.15 K, 1 bar (unless noted otherwise)	Notes
1-phenylnaphthalene	
$\Delta_f H_m^\circ = 161.8 \pm 3\,\mathrm{kJ \cdot mol^{-1}}$	Based on energy of combustion from rotating bomb calorimeter (45)
$S_m^\circ = 31 \pm 4\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	(W.V. Steele 2009, private communication)
$\Delta_c^g S_m^\circ = 218\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	From ΔC_p data from vapor pressures
$\Delta_l^g H_m^\circ = 78.0\,\mathrm{kJ \cdot mol^{-1}}$	(23)
$\Delta_g^l H_m^\circ = 81.0 \pm 1.8\,\mathrm{kJ \cdot mol^{-1}}$	(46)
$\Delta_{fus} H_m^\circ\ (318\,\mathrm{K}) = 18.7 \pm \mathrm{kJ \cdot mol^{-1}}$	(23,47)
$\Delta_{fus} S_m^\circ\ (318\,\mathrm{K}) = 58.8 \pm 1.8\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	(23)
2-phenylnaphthalene	
$\Delta_f H_m^\circ = 146 \pm 15\,\mathrm{kJ \cdot mol^{-1}}$	Based on $\Delta_f H_m^\circ$ of 1-phenylnaphthalene, C–C bond rotational energy (20,21)
$S_m^\circ = 30 \pm 2\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	(W.V. Steele 2009, private communication)
$\Delta_c^g S_m^\circ = 211.5 \pm 1.8\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	(46)
$\Delta_c^g S_m^\circ = 206\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	From ΔC_p data from vapor pressures
$\Delta_l^g H_m^\circ = 95.5 \pm 0.6\,\mathrm{kJ \cdot mol^{-1}}$	(46)
$\Delta_c^g H_m^\circ = 107.8 \pm 0.6\,\mathrm{kJ \cdot mol^{-1}}$	(46)
$\Delta_{fus} H_m^\circ\ (373.5\,\mathrm{K}) = 17.90 \pm 0.12\,\mathrm{kJ \cdot mol^{-1}}$	(46)
$\Delta_{fus} S_m^\circ\ (373.5\,\mathrm{K}) = 47.9 \pm 0.3\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	(46)

The heats of formation were thus calculated as being $161.8 \pm 3\,\mathrm{kJ \cdot mol^{-1}}$ for 1-phenylnaphthalene and $146 \pm 15\,\mathrm{kJ \cdot mol^{-1}}$ for 2-phenylnaphthalene. The difference in ground state stability between the two isomers arises from the orientation of the phenyl group substituent on the naphthalene moiety, and the C–C bond linking the

TABLE 4
Thermodynamic properties of 1-phenylnaphthalene

T/K	C_{sat}/R	H(T) – H(298.15 K) (kJ/mol)	S/R	C_p/R	H(T) – H(298.15 K) (kJ/mol)	S/R
		Solid			*vapor*	
298.15	36.31	0	30.81	17.98	0.00	57.03
		Saturated liquid				
320	38.19	25.47	40.51	19.47	12.15	65.95
340	39.82	31.95	42.88	20.85	18.63	66.82
360	41.37	38.71	45.20	22.27	25.39	67.82
380	42.85	45.71	47.48	23.72	32.39	68.90
400	44.26	52.95	49.71	25.21	39.63	70.07
420	45.61	60.43	51.90	26.75	47.11	71.29
440	46.90	68.12	54.05	28.33	54.80	72.56
460	48.14	76.02	56.17	29.98	62.70	73.87
480	49.33	84.12	58.24	31.69	70.80	75.20
500	50.49	92.42	60.28	33.47	79.10	76.56
520	51.62	100.91	62.28	35.33	87.59	77.94
540	52.73	109.59	64.25	37.28	96.27	79.33
560	53.83	118.45	66.19	39.33	105.13	80.73
580	54.93	127.49	68.09	41.49	114.17	82.13
600	56.04	136.71	69.98	43.77	123.39	83.55

TABLE 5
Thermodynamic properties of 2-phenylnaphthalene

T/K	C_{sat}/R	H(T) – H(298.15 K) (kJ/mol)	S/R	C_p/R	H(T) – H(298.15 K) (kJ/mol)	S/R
		solid			*vapor*	
298.15	35.17	0	30.12	19.48	0.00	54.90
300	35.38	0.5372	30.34	19.64	0.54	57.32
320	37.57	6.543	32.67	21.43	6.54	57.96
340	39.64	12.9	34.98	23.19	12.90	58.79
		saturated liquid				
380	43.41	44.49	45.32	26.57	16.74	66.62
400	45.10	51.77	47.52	28.19	24.02	67.76
420	46.68	59.33	49.78	29.77	31.58	69.06
440	48.13	67.13	51.96	31.31	39.38	70.36
460	49.47	75.17	54.11	32.82	47.42	71.71
480	50.71	83.21	56.22	34.32	55.46	73.09
500	51.86	91.86	58.30	35.80	64.11	74.49
520	52.93	100.48	60.33	37.29	72.73	75.90
540	53.95	109.28	62.32	38.80	81.53	77.31
540	54.93	118.24	64.29	39.78	90.49	79.28
580	55.89	127.36	66.21	41.99	99.61	80.17
600	56.87	136.64	68.10	43.70	108.89	81.59

two. Holloway and co-workers (20,21) determined that 2-phenylnaphthalene has a conformation very close to planar at 300 K with a very small barrier to rotation, $21.0\,\mathrm{kJ\cdot mol^{-1}}$ and a bond length of 1.5 Å. At the same bond length, 1-phenylnaphthalene was predicted by Tinland (22) to have a much greater barrier to rotation, $527\,\mathrm{kJ\cdot mol^{-1}}$. Holloway and colleagues surmised that when energy is absorbed by 2-phenylnaphthalene, it excites rotation about the C–C bond. This energy is not recovered during fluorescence, which is red-shifted from the absorption spectrum. From spectral analysis, Holloway estimated the rotational energy going into the bond as $\sim 1290\,\mathrm{cm^{-1}}$, or $15.4\,\mathrm{kJ\cdot mol^{-1}}$. Following through with the same analysis would suggest that the heat of formation of 2-phenylnaphthalene will be lower than that of 1-phenylnaphthalene as there is less steric hindrance, by an amount similar to the rotational energy of the C–C bond linking the naphthalene and phenyl moieties. A similar analysis applies to the ortho-, meta-, and para-terphenyl compounds, which have standard heats of formation in the condensed phase: 180, 162, and $158\,\mathrm{kJ\cdot mol^{-1}}$ respectively (23).

Further analyses to derive thermodynamic functions from heat capacity data were carried out as outlined by Steele and colleagues (17) (Tables 4 and 5). Enthalpy increments relative to 298.15 K for 1- and 2-phenylnaphthalene were very similar except for the phase transitions, corroborating the very similar Clausius-Clapeyron slopes observed in the Arrhenius plot (Fig. 2).

A summary of physical properties of 1- and 2-phenylnaphthalene at 600 K that are important for their evaluation as heat transfer fluids is given in Table 6. Although

TABLE 6
Overview of physical properties of 1- and 2-phenylnaphthalenes at 600 K

Compound	T_m T_b (K)	C_p/R (±1)	ρ_c ($\pm 20\,\mathrm{kg\cdot m^{-3}}$)	T_c (±20 K) P_c (±1 bar)	p_v (±0.08 bar)	λ ($\pm 0.002\,\mathrm{W\cdot m^{-1}K^{-1}}$)	η ($\pm 0.04\,\mathrm{mPa\cdot s}$)
$C_{16}H_{12}$	297–318	57	348[a]	818	0.820	0.077	0.11
1-Phenylnaphthalene	598			7.1			
$C_{16}H_{12}$	375	58	335[b]	831	0.563	0.083	0.11
2-Phenylnaphthalene	627			6.5			

[a] From fit of experimental density data to get critical point.

[b] From Riedel equation calculation using calculated critical temperature and acentric factor, and reference density at 396 K.

their structures are similar, the melting and boiling points for 1-phenylnaphthalene are significantly lower than those of 2-phenylnaphthalene. The reason for this may be the distortion of the 1-phenylnaphthalene molecular structure from planar because of the steric hindrance between the protons on the C8 and C12 positions. Nori-shargh and coworkers (24) modeled the structure of 1-phenylnaphthalene as well as other biaryl compounds to explain the apparent twist angle of at least 50°. Although the modeling was not done for the 2-phenylnaphthalene, it is expected that steric hindrance would be much lower, leading to a more uniformly planar crystalline solid with a higher melting point than that of 1-phenylnaphthalene. For instance, other planar aryl compounds, such as anthracene and phenanthrene, have melting points of 490 and 372 K respectively. It was also found, both experimentally and through correlations, that at higher temperatures approaching the critical points, the properties of the two compounds become increasingly similar.

The figures of merit for use as a heat transfer fluid were calculated for the 1-phenylnaphthalene and 2-phenylnaphthalene as both being close to 9.1 at 600 K, and 7.8 and 7.9 at 500 K, respectively. These values are lower than that of pressurized water, calculated as 95 (563 K and 7.5 MPa), but are better than values of 6.9 and 6.5 for comparable organic fluids biphenyl and terphenyl at 500 K. The figure-of-merit for Dowtherm, a commercial heat transfer fluid, was calculated as 8.0 at its peak temperature of 678 K. Because the phenylnaphthalenes are in the gas phase at this point, the heat capacities are lower, and so the figures-of-merit values drop to 3.7 and 3.6 respectively at 700 K. These calculations suggest that the substituted naphthalenes have potential as candidates for heat transfer fluids in the temperature range of 500 to 700 K.

CALCULATION OF RANKINE CYCLE EFFICIENCY

Figure 7 shows the temperature versus entropy plots of the type used in calculating the ideal thermodynamic efficiency of a heat pump cycle. In this case, entropy data is only available up to the boiling point. However, the saturated vapor line of both phenylnaphthalene compounds appears to have a positive slope, ensuring that there will be no condensation at the turbine outlet.

The nonoptimized efficiency of a Rankine cycle operating with 1-phenylnaphthalene was calculated to be 33% based on the following stages: isentropic compression of the saturated liquid at 323 K to 0.742 MPa; isobaric evaporation 800 K; isentropic compression to 3.6×10^{-7} MPa, 500 K; and isobaric condensation to 323 K. A Peng-Robinson equation of state based on the critical data derived in this work was used to model the 1-phenylnaphthalene vapor phase. A lower Rankine cycle efficiency was calculated for 2-phenylnaphthalene, 22%, because the lowest attainable temperature above the melting point would be approximately 380 K. These values are lower than the calculated thermal efficiency of 44% for a pressurized steam cycle operating up to 811 K and 24 MPa. However, optimized cycles for the organic fluids should be able to achieve higher efficiencies, as long as the fluid does not degrade over time (25).

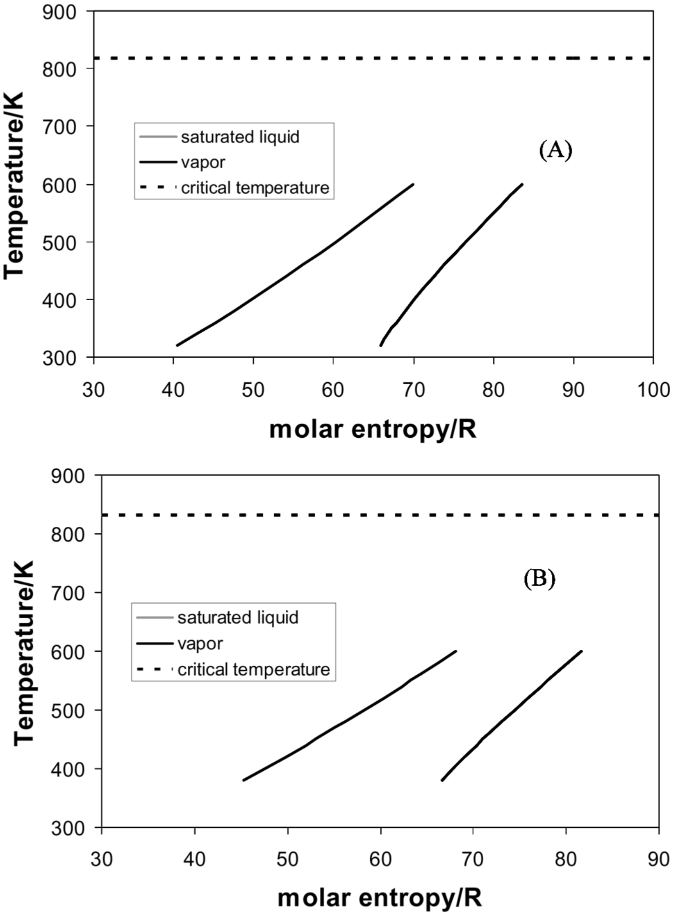

FIG. 7. Temperature-entropy plots for 1-phenylnaphthalene (A) and 2-phenylnaphthalene (B).

THERMAL AND RADIOLYTIC STABILITY

At high enough temperatures, C–H bond breakage will occur and aromatic hydrocarbons will undergo polymerization to form complex mixtures (26). Rearrangements and decomposition of arylnaphthalene and similar compounds have been investigated by Senthilnathan and Stein (27). The kinetics of 1-phenylnaphthalene condensation to fluoranthene, decomposition to naphthalene, and isomerization to 2-phenylnaphthalene have been compared, in the presence of single-hydrogen donors xanthene or fluorene at 713 K, the structures of which contain one aliphatic carbon or $-CH_2-$. In purely aromatic systems, without hydrogen donor molecules, the rates for degradation through isomerization and rearrangement will be much lower. Dissociation to naphthalene would likely predominate in a reaction

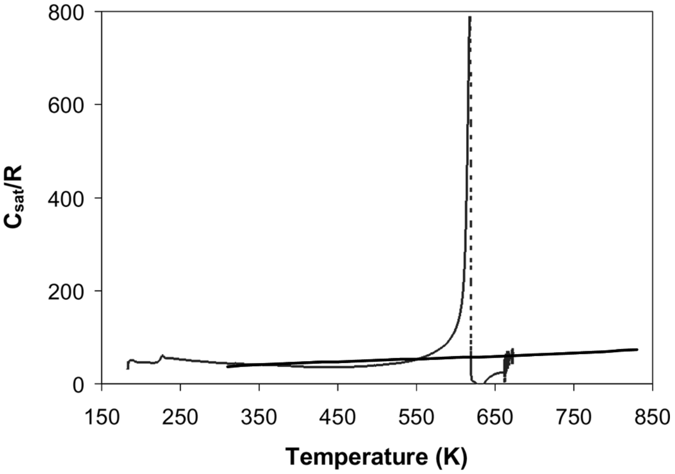

FIG. 8. Differential scanning calorimetry endotherm for 1-phenylnaphthalene showing phase transition at normal boiling point, dashed grey line. The solid black line is a scan with phase transition data removed to illustrate the saturated two-phase heat capacity up to 800 K.

mechanism based on free hydrogen atoms that could be generated at high temperatures >700 K.

The raw endotherm from differential scanning calorimetry measurements is given in Fig. 8, showing little degradation up to the normal boiling point, the grey dashed line. The solid line shows the heat capacity curve after subtracting phase transition enthalpies. The temperature range is different because the data were collected on two separate calorimetric systems, one only operating to 673 K.

1-Phenylnaphthalene was irradiated in a 300 Gy · h^{-1} ^{60}Co irradiator for two weeks, subjected to a total dose of 100 kGy. This corresponds to about a quarter of the benchmark dose used to test the stability of tributylphosphate and kerosene mixtures used in the reprocessing of nuclear fuel (28). The organic was analyzed by ^{1}H-NMR spectroscopy before and after irradiation, with signal from the 14 aromatic protons appearing bunched at a shift between 7.5 and 8.2 relative to tetramethylsilane (TMS). The irradiated sample also showed a small peak appearing at $\delta = 1.4$, corresponding to an aliphatic $-CH_2-$ group (Fig. 9). The degradation of 1-phenylnaphthalene was determined to be 1.7%, by comparison of the integrated peak areas and correction for the number of protons represented by each peak. Assuming a linear response to dose, about 7% of the 1-phenylnaphthalene would be expected to degrade after 400 kGy, which is less than the 15% observed for tributylphosphate/kerosene but more than that observed by Allen and co-workers for imidazolium ionic liquids (28). The mechanism by which the arylnaphthalene decomposed is probably similar to high temperature phenyl migrations as reported by Preda and Scott (29), with the eventual formation of fluoranthene and liberation of hydrogen (30). Although fluoranthene appears to be more stable than the phenylnaphthalenes and has a lower vapor pressure, it would not be a good candidate as a heat transfer fluid because it has a melting point, 383 K, that is well above ambient condition (23).

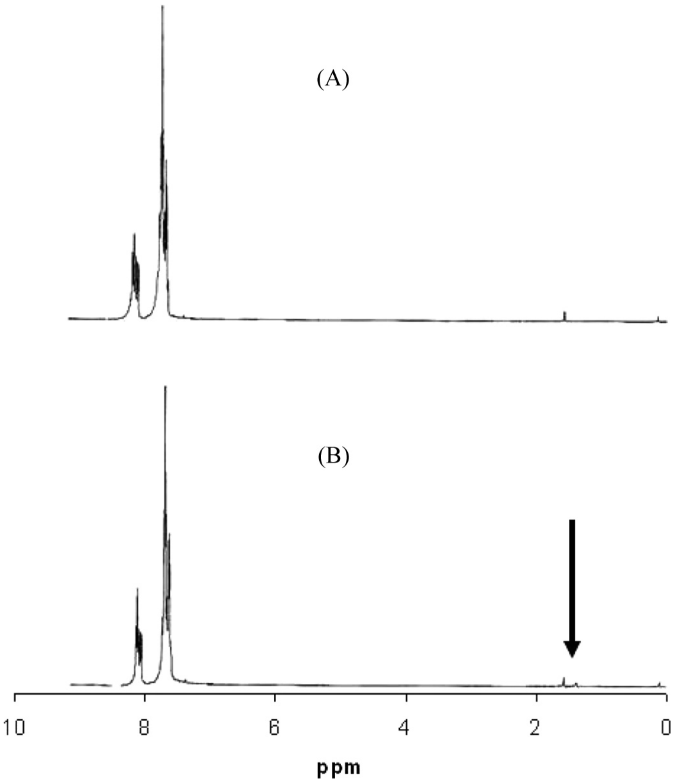

FIG. 9. NMR of 1-phenylnaphthalene: (A) unirradiated and (B) irradiated. The arrow points to the decomposition product. The small peak to the left is from H_2O impurity in the solvent $CDCl_3$, present in both samples.

SEPARATION AND PURITY OF POLYAROMATIC HYDROCARBONS

The efficient separation of phenylnaphthalenes from other diesel components will be an important factor in their being used as heat transfer fluids. As mentioned earlier, because of poor combustion characteristics, removal of these compounds from diesel fuel has been mandated because of potential environmental impacts of vehicle exhaust. Rather than synthesizing compounds, as done to produce chemicals for thermodynamic measurements, phenylnaphthalenes will most likely be produced during refining of petroleum. Phenylnaphthalene, along with similar polyaromatic hydrocarbons, are present in the atmospheric gas oil fraction, or the heaviest components of crude oil removed before vacuum refining (31). Hence, distillation by removal at the refinery will be the method of choice for the first stage of separation, with the boiling point cut between 594 and 606 K capturing about 2% of the total volume of crude oil. Secondary processing could be done with further distillation, but other methods such as using pressurized hot water (32–34) or supercritical CO_2 extraction (35) have been tested for the separation of polyaromatic hydrocarbons. Alternatively, catalytic upgrading of the unprocessed diesel may lead to building block chemicals for phenylnaphthalene synthesis (36). These novel methods may be less energy intensive and may be more selective for classes of compounds with similar physical properties. Along with testing of 1-phenylnaphthalene in a heat transfer loop, methods of producing pure material from oil are needed before consideration of these materials in a commercial heat transfer operation. Finally, properties of a mixture of substituted naphthalene compounds should be considered as high temperature heat transfer fluids, as isomers that may be difficult to separate may perform well as composite fluids.

CONCLUSIONS

The polyaromatic compounds 1- and 2-phenylnaphthalene have been evaluated as high temperature heat transfer fluids based on measured and calculated thermophysical property data. These have been compared to the list of performance indicators listed in the introduction. Based on this analysis, these compounds could be useful candidates for solar power applications, and engineering testing is planned in the future. This study has found gaps in the available literature on experimental thermodynamic data on the phenylnaphthalene compounds; for example, properties such as the density of 2-phenylnaphthalene and thermal conductivity. Although these thermophysical properties can be estimated using empirical correlations, the uncertainty in such correlations means that the data will need to be measured before these fluids can be used in heat transfer applications.

Thermal and radiolytic stabilities were also investigated. The apparent degradation of 1-phenylnaphthalene after 100 kGy irradiation, although slight, suggests that this material would not be appropriate for long-exposure or high-field nuclear applications. In addition, the maximum operating temperature of these fluids would preclude them from being used in the manufacture of hydrogen in chemical cycles that require temperatures above 1100 K (48). However, these fluids may show promise for use as solvents in separations of hydrocarbons from oil shale or sands, as they are stable at the temperatures of 500 to 800 K needed for these processes (49).

In summary, 1-phenylnaphthalene has an advantage over high temperature inorganic salts for heat transfer applications up to 800 K because it is a liquid at temperatures at or close to ambient. However, thermal cycling would have to be restricted to temperatures below the critical point, 813 K, to avoid degradation of the fluid. Thermal stability can be tested in lab-scale and pilot-scale instrumented loops, planned in future experiments. In addition, properties of mixed polyaromatic hydrocarbons will be investigated for optimization of thermophysical properties for heat transfer.

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NOMENCLATURE

C_p	heat capacity
F	figure of merit
H	enthalpy
S	entropy
P	pressure
p_v	vapor pressure
p_c	critical pressure
R	Gas constant
T_b	normal boiling point
T_{br}	reduced temperature at the boiling point
T_m	melting point
T_r	reduced temperature
λ	thermal conductivity
η	dynamic viscosity
ρ	density
ω	acentric factor

Superscripts and Subscripts

$^\circ$	standard state
c	condensed
fus	fusion
f	formation
g	gas
l	liquid
m	molar
sat	saturated liquid

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