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Performance evaluation of organic and titanium based working fluids for high-temperature heat pumps

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ABSTRACT

In this paper, selected organic and titanium based fluids (biphenyl, biphenylmethane, naphthalene, isoquinoline, titanium tetrabromide and titanium tetraiodide) are assessed thermodynamically as potential working fluids for high temperature mechanical heat pumps. Various applications, such as thermochemical cycles for hydrogen production, chemical processes comprising endothermic reactions, steam generators and metallurgical processes, can benefit from such heat pumps as "green" sources of high temperature heat. The environmental benefit occurs from avoiding fossil fuel heating and therefore reducing carbon dioxide and other pollutant emissions. Through heat pumps, a low-grade heat source from nuclear reactors, industrial waste, geothermal, etc. can be upgraded to high temperatures through a work-to-heat conversion. The work itself can originate from any source of renewable energy (wind, hydro, biomass, solar, etc.). In this paper, available thermo-physical parameters of the selected fluids are presented and appropriate equations of state are constructed to allow a heat pump thermodynamic analysis. Among these working fluids, only biphenyl, naphthalene, titanium tetrabromide and titanium tetraiodide have promising potential. For these fluids, a further parametric study is conducted to investigate the COP for a range of relevant operating conditions, in terms of temperature and pressure. The range of COP values is large, ranging from 1.9 to 7.3, depending on the fluid and temperature levels; the highest COP is obtained with TiI_4.

1. Introduction

High-temperature heat supply is a major necessity in many industrial and power generation processes and it is predominantly derived from combustion of fossil fuels. A promising "green" alternative to combustion for this heat supply is the use of high-temperature heat pumps that have the ability to recover low-grade heat and upgrade its temperature level through mechanical work, which can be derived from any type of cleaner energy source (i.e., nuclear power, geothermal, solar, wind, hydro, biomass). The capacity to upgrade heat can make heat pumps a better alternative than high-temperature electrical heating, since they require less electrical energy consumption for the same useful heat output. A parameter that directly compares electrical heaters with heat pumps is the coefficient of performance (COP), defined as the useful heat output vs. the consumed (shaft or electrical) power input: $\mathrm{COP} = \dot{Q}/\dot{W}$. For mechanical heat pumps in a conventional vapor compression cycle, a typical COP is over 2, meaning that more than 50% electrical savings can be achieved when using heat pumps. Savings in electrical energy correspond to a fossil fuel savings in power plants, and thus emission reductions of combustion pollutants.

Luickx et al. [1] outlined the benefits of heat pumps over fossil fuel and electrical heating, in terms of exergy efficiency. Many types of mechanical heat pumps have been reported for various high-temperature applications, such as pasteurization [2], distillation [3,4], steam generation [5,6] and paper drying [7]. In the layout of a thermodynamic cycle, mechanical heat pumps include a compression process, during which the temperature of the working fluid is augmented through mechanical work input. Several kinds of cycles have been considered in past studies, including the vapor compression cycle, Lorentz cycle [5,6], reversed Brayton [8] and Stirling cycles [9,10]. Another category of heat pumps for high-temperature applications is called "chemical heat pumps". In these devices, by adjusting the pressure at which certain reversible endothermic/exothermic reactions are conducted, the chemical equilibrium is shifted in a desired direction. Using this method, the system upgrades heat from low to high temperatures [11–16].

A promising application of high-temperature heat pumps is hydrogen production via thermo-chemical water splitting [17]. The copper–chlorine (Cu–Cl) cycle requires heat input at about 500 °C [18]. Other thermo-chemical cycles generally have much higher operating temperatures, such as the sulfur–iodine (S–I) cycle (involving hydrogen sulfide, iodine–sulfur, sulfuric acid–methanol)

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and Br–Ca–Fe cycle [19,20]. Kasahara et al. [21] reported a maximum thermal efficiency of 56.8% for the S–I cycle. A continuous stable operation of a bench-scale S–I cycle was demonstrated [22]. Future supercritical water-cooled reactors (SWCR; Canada's Generation IV nuclear reactor) can provide the required source of high-temperature heat for the Cu–Cl cycle, or else heat pumps could be used to upgrade heat from existing nuclear reactors. Granowskii et al. [23,24] presented a chemical heat pump that was integrated with the secondary Rankine cycle loop of an SWCR. A reverse exothermic methane-synthesis reaction was carried out at a high temperature in the process. Water splitting in the Cu–Cl cycle was driven by the high-temperature heat of methane synthesis. Some work was consumed from the Rankine turbine shaft to drive a compressor, which pressurizes the fluid and shifts the chemical equilibrium in the desired direction, by adjusting the reaction pressure. Additional studies on integrated heat pumps have been conducted by Tahat et al. [25] and de Boer et al. [26].

In this paper, six organic and titanium based fluids are proposed as potential working fluids for mechanical heat pumps, and studied thermodynamically for their performance assessment up to or over 400 °C. The fluids are examined with respect to their thermophysical properties and other issues like safety, availability, etc. Then a suitable equation of state is selected and used to assess the fluid's potential as a possible working fluid for the high-temperature heat pumps. It is shown four of the six selected fluids were found to be suitable. The paper examines the heat pump performance under a range of operating conditions and investigates the linkage between mechanical heat pumps and CANDU nuclear reactors for electricity and hydrogen cogeneration. Other high-temperature applications of the high pumps are also considered.

2. Potential working fluids of high-temperature heat pumps

The selection of working fluids for high-temperature heat pumps requires an analysis of a number of parameters related to thermodynamic properties, as well as aspects regarding safety issues (toxicity, flammability, thermo-chemical stability, etc). In this section, properties relevant to fluid choice will be examined.

2.1. Thermophysical properties of working fluids

Molecular mass provides a measure of the fluid's molecular complexity and it is important when analyzing thermo-chemical stability. Complex fluids are formed from many atoms. As a consequence, chemical instability may occur at high temperatures, i.e., atoms may recombine and form a derivative product. Based on observations from past studies [10,27], one may conclude that molecularly complex organic fluids can be used safely up to temperatures about 50–100 °C higher than the critical point. Over this threshold, the risk of decomposition may appear, depending on the case. Due to their capacity to store large amounts of energy, the gas dynamic behavior of complex molecular fluids is quite different than that of simple fluids [28]. This must be considered or exploited (if possible) when designing energy conversion systems such as heat pumps and other turbomachinery.

A second major parameter when analyzing the working fluids for high-temperature applications is the melting point. Many heat transfer fluids are either very viscous at ambient temperature (i.e., heavy hydrocarbons) or exist in solid form (i.e., all fluids analyzed herein). Special design precautions have to be taken if a heat pump is off-operation and the temperature drops below the melting/solidification point of the working fluid. Prior to start-up, the working medium in the solid form must be preheated up above its melting temperature.

Another important parameter is the normal boiling point of the working fluid, defined as the temperature at which the fluid boils under an absolute pressure of 1 atm. This parameter impacts the temperature at the source because heat pump operation under a vacuum condition can lead to fluid contamination, malfunctions and reduced lifetime. Ideally, the lower pressure in the system should be slightly above 1 atm. The normal boiling point is a valuable data point when fitting parameters of the adopted equation of state (EoS) for fluid modeling.

The magnitude of the critical temperature is also essential for heat pumps that include phase change processes (i.e., vapor compression or Lorentz cycles). When a high temperature is required at the heat sink, the critical temperature must be sufficiently high. In general, perfluorocarbons, heavy hydrocarbons and siloxanes are known to have a high critical temperature. Most of these chemical compounds have cyclic molecules, which leads to better stability at a high temperature.

Critical pressure is another issue that affects the performance and design of a heat pump. Heavy molecular fluids and metallic compounds are characterized by a low critical pressure, which favors a cheaper construction and better safety. However, low critical pressure implies low pressure at the source, so either the heat pump operates under a reduced temperature differential, or in a vacuum at the source heat exchanger. Thus, there is a tradeoff in choosing the working fluid according to the desired temperatures.

Other significant parameters for fluid modeling and fitting the parameters to an equation of state are the critical specific volume, critical compressibility and accentric factors. The accentric factor accounts for the molecular structure of the fluid [29],

$$\omega = -\log_{10}(P''_{\mathrm{r}}(T_{\mathrm{r}})) - 1 \tag{1}$$

$$T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}} = 0.7 \tag{2}$$

$$P''_{\mathrm{r}} = \frac{P''}{P_{\mathrm{c}}} \tag{3}$$

where the double prime stands for vapor pressure at the specified temperature and the index r stands for the reduced temperature or pressure.

With respect to safety issues, two parameters are most relevant: (1) flash point – representing the lowest temperature at which the liquid can ignite in atmospheric air under the presence of a spark and (2) autoignition temperature – at which the material autoignition occurs in the open atmosphere, without the presence of any spark.

Since vapor compression heat pumps involve vapor–liquid phase change processes, the primary factor for choosing the fluids is based on the critical temperature. Six fluids with critical temperatures over 400 °C were selected: biphenyl ($C_{12}H_{10}$), biphenylmethane ($C_{13}H_{12}$), naphthalene ($C_{10}H_8$), isoquinoline (C_9H_7N), titanium tetrabromide ($TiBr_4$) and titanium tetraiodide (TiI_4). The relevant properties of the working fluids are summarized in Table 1, including the chemical formula, molecular mass, melting point, normal boiling point, critical properties, accentric factor, flash point and the autoignition temperature.

2.2. Sample organic working fluids

Biphenyl is an aromatic hydrocarbon that naturally occurs in coal, crude oil and natural gas. It can be produced via biological methods or by distillation of fossil fuels. Biphenyl is insoluble in water but soluble in organic solvents. It is mildly toxic (but can be degraded biologically by conversion into nontoxic compounds) and less reactive. The industrial uses include production of a host of emulsifiers, plastics and food preservatives. From Table 1, it is observed that biphenyl appears more suitable in heat

Table 1
Thermophysical properties of selected working fluids.

Properties	Biphenyl	Biphenyl methane	Naphthalene	Isoquinoline	Titanium tetrabromide	Titanium tetraiodide
Chemical formula	$(C_6H_5)_2$	$(C_6H_5)_2CH_2$	$C_{10}H_8$	C_9H_7N	$TiBr_4$	TiI_4
Molecular mass (kg/kmol)	154.2	168.2344	128.1705	129.16	367.483	555.485
Melting point (°C)	69.05	25.24	80.26	27	38.3	155
Normal boiling point (°C)	256	264.272	217.51	243.22	233.55	376.85
Autoignition temperature (°C)	540	485	525	476.85	Non-flammable	Non-flammable
Flash point (°C)	113	130	79	107	Non-flammable	Non-flammable
Critical temperature (°C)	499.85	486.85	475.20	530.00	522.55	766.85
Critical pressure (bar)	33.8	27.1	40.5093	51.0	62.72$^{(*)}$	55.03$^{(*)}$
Critical volume (m^3/kmol)	0.497	0.563	0.477887	0.374	0.391	0.505
Critical compressibility	0.261	0.241	0.311129	0.286	0.3214$^{(*)}$	0.3214$^{(*)}$
Accentric factor	0.402873	0.481608	0.30295	0.303484	0.295$^{(*)}$	0.109$^{(*)}$
Reference	[30]	[30]	[30]	[30]	[31]	[31]

Asterisk indicates values that were not found in the literature and therefore are estimated in the present paper; the other values where taken from literature reference indicated in the same table.

pumps if the heat at the source is available at over 260 °C. This is the level of steam temperature available in secondary circuits of CANDU nuclear reactors. Its critical temperature is about 500 °C. Its molecule is cyclical, so one may expect that biphenyl is thermally stable up to at least ~600 °C. Hence, it can be used as a working fluid in supercritical heat pumps. It has a moderate level of critical pressure.

Biphenylmethane has a cyclic molecule consisting of two phenyl groups, thus similar features as biphenyl regarding safety aspects. However, it will be shown afterwards that from a thermodynamic point of view, biphenylmethane is not a good choice for mechanical heat pumps because of its relatively low heat of vaporization at vapor–liquid phase change.

Naphtalene's molecule is formed from two attached benzene rings and it has a known property to sublimate in atmospheric conditions. Its vapors are detectable by smell, even in low concentrations of 0.08 ppm, which is a self-alarming feature that is good for detecting leakages of working fluid. There are some safety issues related to the use of naphthalene, because this substance is considered a carcinogen and in some concentrations in air may create explosion danger. Naphthalene is produced from coal tar or heavy petroleum fractions obtained during oil refining. In general, this substance has multiple uses in industry, agriculture and medicine, but to date there has not been any documented evidence of applications to heat pumps. Since its normal boiling point is 218 °C, it appears feasible to use naphthalene for heat pump applications, whenever the heat source is available at above 200–230 °C.

Isoquinoline is an isomer of quinoline, an aromatic organic compound with a cyclic molecule formed from a benzene ring attached to a pyridine ring. The compound is hygroscopic, with low solubility in water, and it has a specific unpleasant odor. It is produced by chemical synthesis from various organic substances with cyclic molecules, among which benzaldehyde is the most used. Isoquinoline has been used predominantly in medicine, pharmacy, manufacturing of dyes and it is a corrosion inhibitor.

Titanium tetrabromide is relatively simple (five atoms) but a heavy molecule containing one transition metal (titanium) and five heavy halogen atoms (bromine). It is diamagnetic and highly soluble in non-polar organic solvents. This component has been proposed as a high-temperature heat transfer fluid for special applications such as aerospace, because it has a high critical point (522 °C) and good thermo-chemical stability [32].

Titanium tetraiodide shows stronger molecular bonds than titanium tetrabromide because of iodide's characteristic of higher Van der Waals intermolecular forces. Hence, the melting, boiling and critical points have a higher temperature. Among the fluids analyzed in this paper, TiI_4 has the highest molecular weight. The main hazard of using this substance as a working fluid in heat pumps comes from its violent hydrolysis (hence contact with water must be avoided). Moreover, TiI_4 is corrosive.

2.3. Equations of state

The critical pressure data and the accentric factors of $TiBr_4$ and TiI_4 were not found in the literature (having this data from experimental sources is important with respect to having a suitable equation of state for fluid modeling). Hence, Peng–Robinson the EoS [29] is used to evaluate the critical pressure based on the critical temperature and critical specific volume reported in Ref. [31]. This EoS gives reasonable accuracy in the vicinity of the critical point. The following non-linear system of equations, which relates the Peng–Robinson EoS, pressure, specific volume and temperature at the critical point, have been solved iteratively for P_c, a and b,

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2 - 2bv_c - b^2} \tag{4}$$

$$a = 0.45724\frac{R^2T_c^2}{P_c} \tag{5}$$

$$b = 0.0778\frac{RT_c}{P_c} \tag{6}$$

where $R = 8314.472$ kJ/mol K is the ideal gas constant and the subscript c stands for critical property. The specific volume is expressed in m^3/kmol, temperature in K and pressure in Pa. In Table 1, the critical compressibility for $TiBr_4$ and TiI_4 has been further computed by the calculated P_c and the known formula $Z_c = P_c v_c / RT_c$. For the accentric factor evaluation, a trial and error procedure has been applied (to be described afterwards).

In order to completely fix the thermodynamic state, at least two equations are needed: thermal (relating P, v and T) and calorimetric (involving internal energy, entropy, enthalpy, or specific heat) equations of state. This paper uses StanMix subroutines included in FluidProp software [33] to include both caloric and thermal EoS. The subroutines implement the Peng–Robinson EoS, improved by Strjek and Vera [34]. The input data files for each fluid comprise the molecular mass, critical pressure, temperature, accentric factor and a fluid dependent empirical parameter (k_1) introduced by the Peng–Robinson–Strjek–Vera (PRSV) EoS. The parameter k_1 must be determined by trial and error such that the PRSV equation predicts, as accurately as possible, the vapor–liquid equilibrium data. The parameter is defined by the following set of equations [34]

$$P = \frac{RT}{v - b} - \frac{(0.457335R^2T_c^2/P_c)[1 + k(1 - \sqrt{T/T_c})]^2}{v^2 + 2bv - b^2} \tag{7}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{8}$$

Table 2
Coefficients for Eq. (5) and the fluid parameter k_1 of PRSV EoS.

Fluid	$(C_6H_5)_2$	$(C_6H_5)_2CH_2$	$C_{10}H_8$	C_9H_7N	$TiBr_4$	TiI_4
A	−97.07	−381.957	−68.8	−192.73	0.1794	0.294
$B \times 10^{-3}$	1106	5990.5	849.9	4300.5	0.3	0
$C \times 10^{-6}$	−885.5	−3818.8	650.6	−2700	−0.3	0
$D \times 10^{-9}$	279	900	198.1	600	0.1	0
Source	[30]	[30]	[30]	[30]	[35]	[35]
k_1	0.288736	−0.31	0.03297	0.061537	0.46	0.02

$$k = k_0 + k_1(1 + \sqrt{T/T_c})(0.7T/T_c) \tag{9}$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{10}$$

Additionally, the ideal specific heat, C_{p0} (specific heat at constant pressure for low pressure and high-temperature conditions) must be given as an input to the StanMix subroutines [33] in the form of coefficients of a third degree interpolation polynomial,

$$C_{p0} = A + BT + CT^2 + DT^3 \tag{11}$$

where the temperature T is given in Kelvin and the specific heat units are kJ/kg K. For the subroutines [33], the $C_{p0}(T)$ function is essential for deriving the caloric equation of state in the form of the free energy. Table 2 gives the interpolation coefficients obtained within this paper for the ideal gas specific heat of working fluid. The table also indicates the bibliographic sources containing the tabulated C_{p0} data.

Table 2 also indicates the optimized value of the fluid specific parameter k_1, which is used in PRSV EoS. A standard method to determine the best value of k_1 proceeds by trial and error (Strjek and Vera [34]). Using experimental data for the vapor pressure, one iterates the value of k_1 such that the equation predicts the data as closely as possible. In general, the range of k_1 lies from −1 to 1. Due to a lack of data, in this paper only the normal boiling point (NBP) to fit the parameter k_1 is used for the working fluids. According to Ref. [34], fitting with respect to NBP provides sufficient accuracy for PRSV EoS.

For $TiBr_4$ and TiI_4, no past documented information was available for the accentric factor. Therefore, a trial-and-error fitting procedure was used for both the accentric factor and k_1, simultaneously. The range of accentric factor has been restrained with the help of Eq. (2) and the inequality $T_{r,NBP} < 0.7$ for all fluids (following from Table 1). With $T_{r,NBP} = T_{NBP}/T_c$, the reduced temperature at the normal boiling point leads to

$$-1 \leq \omega \leq -\log_{10}(P_{r,NBP}) - 1. \tag{12}$$

Using the optimized k_1 values reported in Table 1, the NBP predictions were accurately predicted (with an error smaller than ±0.1%) for all fluids except TiI_4. In the TiI_4 case, there was a lack of C_{p0} data and therefore a constant value available from Ref. [35] was used (see also Table 2). For titanium tetraiodide, the NBP prediction was acceptable (error <±4%), so the constructed PRSV equation is believed to be accurate enough for thermodynamic modeling of the heat pump cycle.

The PRSV equations were first used to develop T–s diagrams for all fluids. These diagrams are presented in Fig. 1. Two isobars, namely P = 1 bar and $P = 2P_c$ (or $P = P_c$ for $TiBr_4$ and TiI_4) are indicated on the diagram for the purpose of analyzing how a thermodynamic cycle can be constructed. The following observations result from Fig. 1. All of the illustrated organic fluids are retrograde (compression of their saturated vapor occurs with condensation). This feature opposes the trend of regular fluids, for which compression superheats the saturated vapor (see diagrams of $TiBr_4$ and TiI_4, which are regular fluids). The two-phase region of biphenyl methane and isoquinoline is relatively small. This suggests that these fluids are not suitable to be used in usual mechanical heat pumps that exploit the existence of vapor–liquid phase transition. If internal heat recovery is used (i.e., liquid exiting the condenser preheats the vapor prior to compressor suction), biphenyl and naphthalene may be feasible as working fluids. Two-phase compression may be also considered as an option for biphenyl or naphthalene.

In Fig. 1, both titanium based fluids show an interesting feature: the isobars in the vapor phase are almost coincident with the isentropes. Hence, compression of the saturated vapor produces extremely high superheating for small pressure differentials. This feature has a drawback: it does not allow a large enough pressure differential so that the saturation temperature of the heat sink is essentially higher than the saturation temperature at the source. Also, it appears that compression in the two-phase region leads to feasible heat pump cycles with both titanium tetrabromide and titanium tetraiodide.

In the following section, two thermodynamic cycles will be analyzed: (1) heat pump with internal heat recovery for biphenyl and naphthalene, and (2) heat pump with two-phase compression for titanium based working fluids. Due to their reduced phase change region, isoquinoline and biphenyl methane will no longer be considered in the analysis.

3. Performance of vapor compression cycles

In this section, two thermodynamic cycles of high-temperature heat pumps and their modeling will be presented. The first cycle (denoted with HP_1) involves biphenyl or naphthalene. It includes an internal heat recovery heat exchanger to preheat the working fluid prior to compression. The second cycle (denoted with HP_2) is designed for titanium based working fluids ($TiBr_4$ and TiI_4). It includes a positive displacement compressor, operating completely within the two-phase region.

Fig. 2 illustrates the phase diagram for the thermodynamic cycle HP_1 comprising an internal heat recovery heat exchanger to preheat the working fluid (processes 1–2 and 4–5), a turbo-compressor (processes 2–3), sink side heat exchanger (condensation 3″–3′ and sub-cooling 3′–4), throttling valve (5–6) and the source side heat exchanger (evaporator 6–1). A unique feature of the proposed cycle consists of preheating the working fluid prior to compression. This approach is technically feasible, as such current technology is available for turbomachinery and high-temperature compressors.

The process 3″–3′–4 can be performed either by a sole heat exchanger, or two separate units. It would reject heat to a separate stream (such as chemical reactants) that is heated (process 1_{si}–2_{si}). Define the coefficient of performance (COP) of the heat pump HP_1 in the following way,

$$\mathrm{COP} = \frac{h_3 - h_4}{w_c} \tag{13}$$

$$w_c = h_{3''} - h_2 \tag{14}$$

where h represents the specific enthalpy in the respective state. The exergetic coefficient of performance (COP_{ex}), based on the second-law of thermodynamics, is defined as

$$\mathrm{COP}_{ex} = \frac{(h_3 - h_4)(1 - T_0/\bar{T}_{3-4})}{w_c} = \mathrm{COP}(1 - T_0/\bar{T}_{3-4}) \tag{15}$$

where $\bar{T}_{3-4}$ is the average temperature of the sink (3–4).

The energy balance equations are written together with other auxiliary equations expressing the isentropic efficiency of the compressor, isenthalpic expansion 5–6, and the saturation pressure and enthalpy as functions of temperature.

$$h_2 - h_1 = h_4 - h_5 \tag{16}$$

$$h_5 = h_6 \tag{17}$$

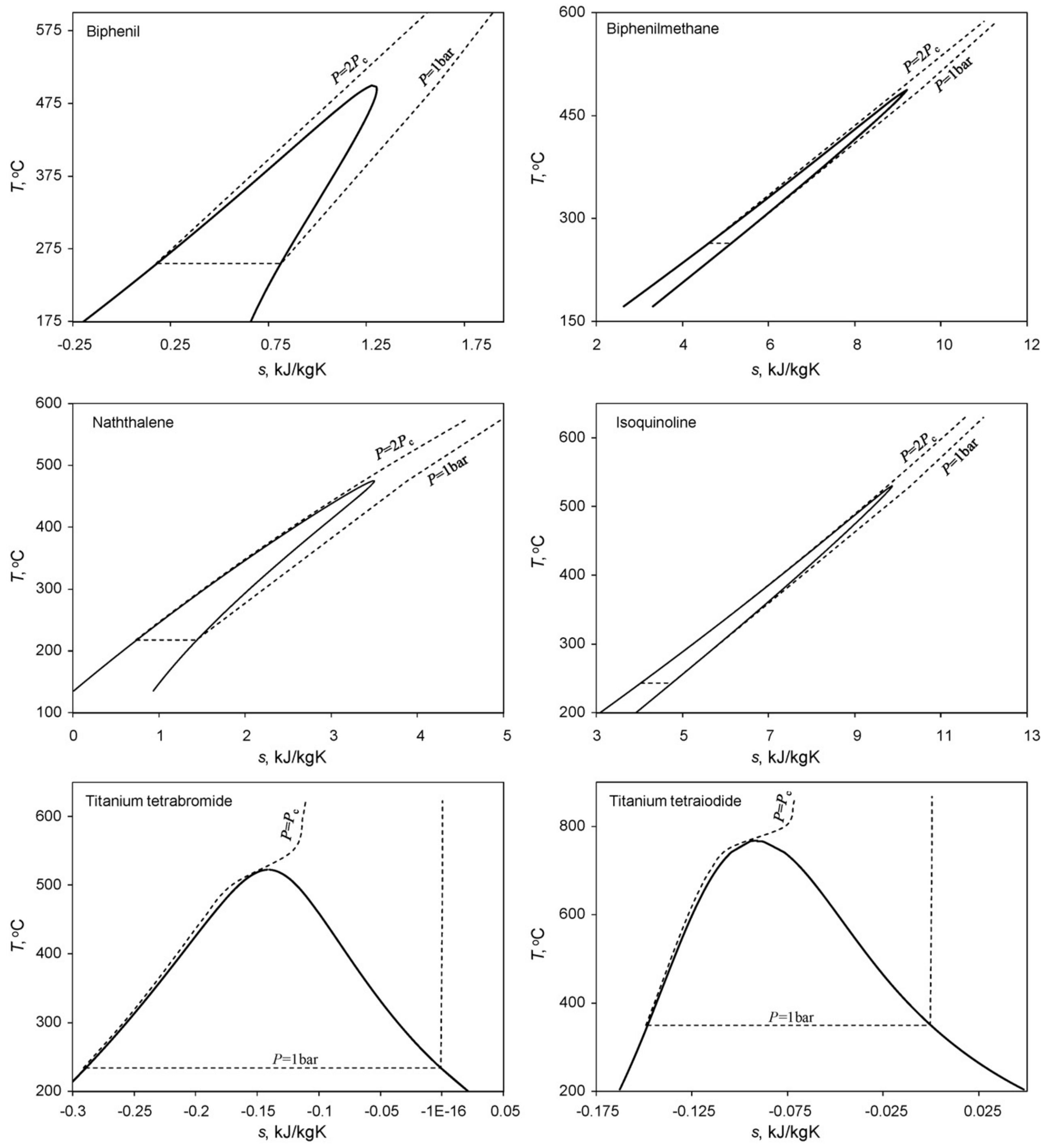

Fig. 1. *T–s* diagrams of selected working fluids for high-temperature heat pumps.

$$\eta_{\mathrm{is}} = \frac{h_{3s} - h_2}{h_3'' - h_2} \tag{18}$$

$$h_{3\mathrm{s}} = h(s_2, P_{\mathrm{H}}) \tag{19}$$

$$P_{\mathrm{H}} = P''(T_{\mathrm{si}}) \tag{20}$$

Also, the temperature at state 4 is higher than temperature 2, since stream 4–5 heats the fluid stream 1–2. Hence,

$$T_4 = T_2 + \Delta T; h_4 = h(P_H, T_4) \tag{21}$$

The equations are solved simultaneously for the pressure and temperature at all states, starting from a set of input values including the temperature level of the heat sink and source (T_{si} and T_{so}), isentropic efficiency of the compressor η_{is} and the temperature difference $\Delta T = T_4 – T_2$. A sample result is presented in Fig. 2 for $T_{\mathrm{si}} = 450\,^\circ\mathrm{C}$, $T_{\mathrm{so}} = 255\,^\circ\mathrm{C}$, $\Delta T = 10\,^\circ\mathrm{C}$ and $\eta_{\mathrm{is}} = 0.8$. The calculated coefficients of performance are 3.0 (energetic) and 1.7 (exergetic). For an energy based COP higher than 2.5–3, the heat pumps become an attractive option with respect to overall energy utilization. The efficiency of thermal power plants is typically between 30 and 40%, so lower values of COP would suggest heat used directly from the primary energy source rather than conversion to electricity for a subsequent heat pump.

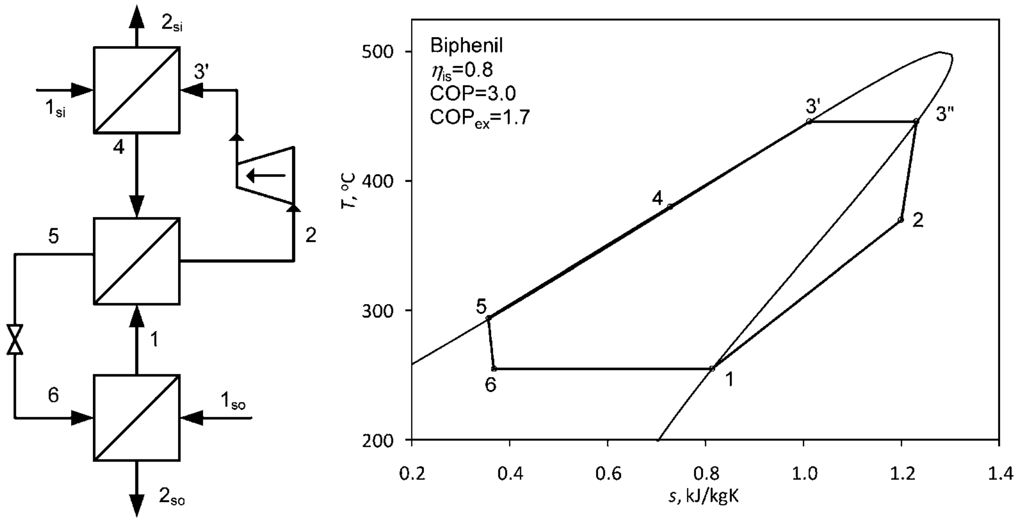

Fig. 2. Schematic of heat pump HP_1 and its thermodynamic cycle.

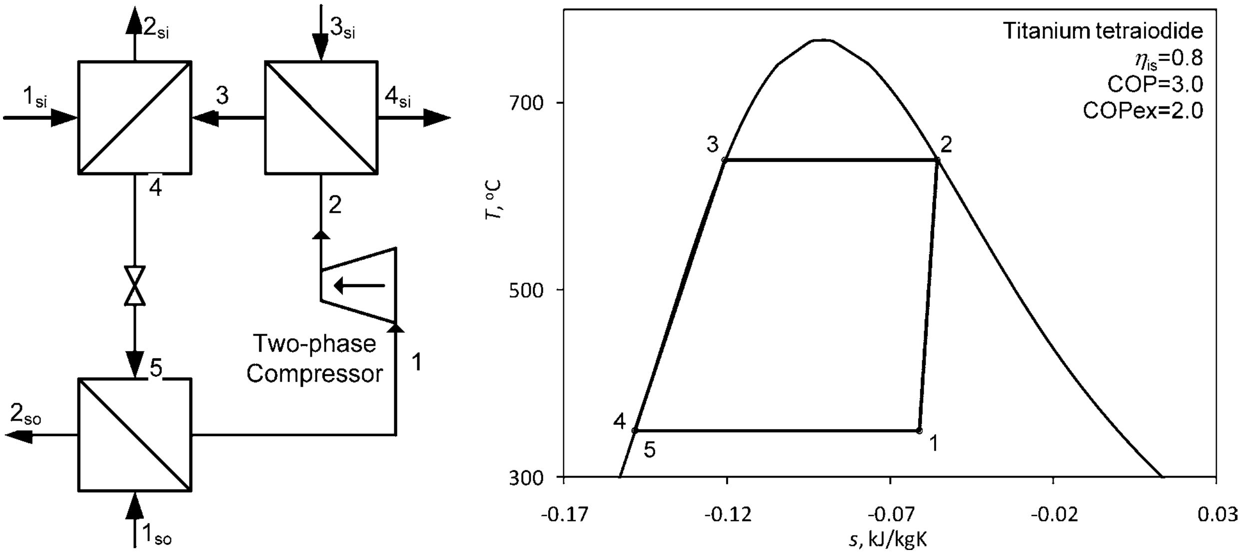

Fig. 3. Diagram of heat pump HP_2 and its thermodynamic cycle.

The heat pump cycle operating with $TiBr_4$ or TiI_4 is shown in Fig. 3. This cycle comprises four elements, namely: two-phase compressor (process 1–2), condenser (process 2–3), sub-cooler (3–4), throttling valve (4–5) and the evaporator (5–1). Positive displacement compressors for processes that evolve completely in two-phase flow have been used previously for ammonia–water mixtures [6]. A screw machine was used as the compressor. The liquid phase was supplied in excess so that the need of lubrication oil

Table 3
Equations for HP_2 modeling.

Index	Equation	Comments
1	$h_4 = h_5$	Isenthalpic expansion
2	$\eta_{is} = \frac{h_{2s}-h_1}{h_2-h_1}$	Isentropic efficiency of the compressor
3	$h_3 = h''(T_{si})$	Enthalpy at state 2 is a saturated vapor
4	$h_3 = h'(T_{si})$	At state 3, there is saturated liquid at the sink temperature
5	$h_3 = h'(T_{so})$	At state 5, there is saturated liquid at the source temperature
6	$h_{2s} = (1 - x_{2s})h_3 + x_{2s}h_2$	Enthalpy for isentropic discharge obeys the mixing rule
7	$(1 - x_{2s})s_3 + x_{2s}s_2 = s_1$	Entropy at 2s is the same as 1 and obeys the mixing rule
8	$h_1 = (1 - x_1)h_5 + x_1 h''(T_{so})$	Enthalpy at state 1 obeys to mixing rule
9	$s_1 = (1 - x_1)s_5 + x_1 s''(T_{so})$	Entropy at state 1 obeys to mixing rule
10	$s_2 = s''(T_{si})$	Enthalpy at state 2 is a saturated vapor
11	$s_3 = s'(T_{si})$	At state 3, there is a saturated liquid at the sink temperature
12	$s_5 = s'(T_{so})$	At state 5, there is a saturated liquid at the source temperature

Table 4
Range of operating condition for the high-temperature heat pumps.

Parameter	Biphenyl	Naphthalene	$TiBr_4$	TiI_4
T_{so} (°C)	250–260	210–220	230–240	345–355
T_{si} (°C)	380–480	300–450	300–500	450–650
COP	2.5–4.8	1.9–4.6	2.7–6.5	2.8–7.3
COP_{ex}	1.3–2.6	1.1–2.2	1.5–3.5	1.6–4.3
P (bar)	8–30	5–30	4–26	5–52

was eliminated. The screw machines can operate in either compression or expansion modes. Compression in two-phase conditions with titanium tetrabromine or tetraiodide represents a challenge. It requires a special construction because the density of the fluid in two-phase flow is above the density of liquid water. Hence, reciprocating compressors might be suitable. The structural integrity of the compressor must be sufficient to handle large inertial forces.

For the heat pump cycle HP_2, assume that heat is rejected during processes 2–3 and 3–4. The exergetic COP calculation for sub-cooling in process 3–4 has been considered at the average temperature $\bar{T} = (T_{si} + T_{so}/2)$. Hence, the COPs are defined by

$$\mathrm{COP} = \frac{h_2 - h_4}{w_c} \tag{22}$$

$$w_c = h_2 - h_1 \tag{23}$$

$$\mathrm{COP_{ex}} = \frac{(h_2 - h_3)(1 - T_0/T_{si}) + (h_3 - h_4)(1 - T_0/\bar{T})}{w_c} \tag{24}$$

In Table 3, the equations expressing the energy balances, isentropic efficiency, vapor quality and saturation conditions are shown. The 12 equations can be solved simultaneously for 12 unknowns, namely h_1–h_5, s_1–s_5, x_{2s} (vapor quality at compressor discharge for isentropic process) and x_1 (vapor quality at compressor's suction). The following parameters are input parameters: temperatures at source T_{so} and sink T_{si} and the compressor's isentropic efficiency. Additional results are the pressures at the sink and source, as well as the energetic and exergetic coefficients of performance.

Fig. 3 represents a case of a high-temperature heat pump working with titanium tetraiodide for which the source and sink temperatures are 350 and 650 °C, respectively, and the isentropic efficiency of the compressor is 0.8. The calculated results are given as follows: low pressure – 1 bar, high pressure – 25.6 bar, and coefficients of performance are 3.0 (energetic) and 2.0 (exergetic).

The calculation of COP for HP_1 operating with biphenyl and naphthalene, and HP_2 operating with titanium tetrabromide and tetraiodide, are reported in Table 4. The compressor isentropic efficiency lies in the range of 0.6–1.0. Hence, the highest values reported for the coefficient of performance correspond to the ideal maximum.

The range of source temperature has been chosen so that the heat pump operates at around 1 bar vapor pressure at the compressor suction. The temperature of the heat source has been increased until it reaches the critical point with a difference of 10 °C. The higher pressure in the plant is reported also in Table 4. The highest values of COP were obtained with titanium tetraiodide, which shows also the highest temperature at the sink among all fluids considered in this study.

Figs. 4 and 5 show the variation of COP and COP_{ex} over a range of temperatures at the sink. Fig. 4 refers to biphenyl, while Fig. 5 refers to titanium tetraiodide. For both graphs, the pressure at the suction has been assumed as 1 bar. Three values of the isentropic efficiency of the compressor have been assumed, namely 0.6, 0.8 and 1.0. The continuous lines in Figs. 4 and 5 represent ideal maxima that would not be reached in practice.

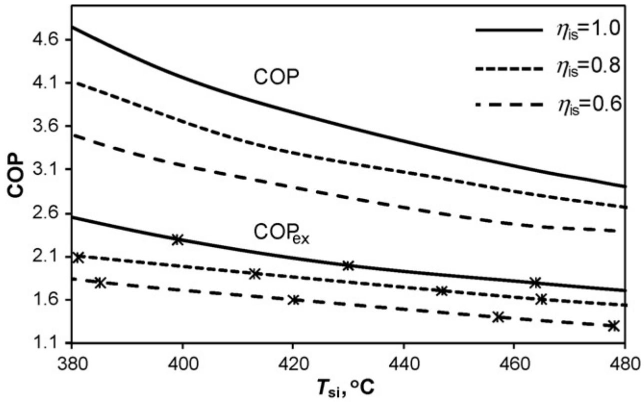

Fig. 4. Energetic and exergetic COP for biphenyl over a range of sink temperatures, for three values of isentropic efficiency and a fixed source temperature of 255 °C.

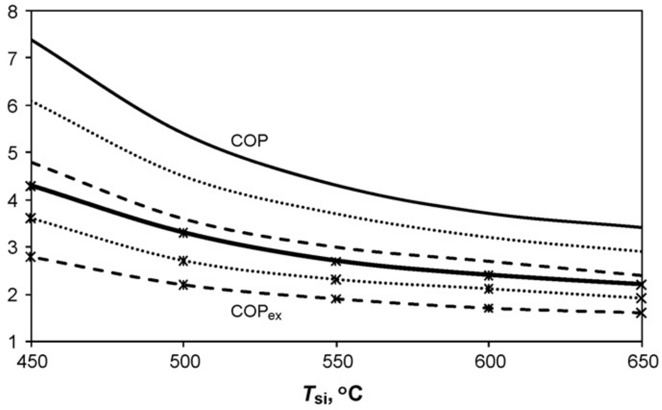

Fig. 5. Energetic and exergetic COP for TiI_4 over a range of sink temperatures, three values of isentropic efficiency and a fixed source temperature of 255 °C.

4. Conclusions

This paper identified and analyzed six potential working fluids for high-temperature heat pumps, which represent a promising cleaner alternative to fossil fuel heating. It was found that biphenyl methane and isoquinoline were not suitable as working fluids in vapor compression heat pumps. Naphthalene and biphenyl are retrograde fluids, as saturated vapor condensate forms during compression. Naphthalene and biphenyl may be used as working fluids in heat pumps with internal heat recovery, where the saturated vapor is superheated prior to suction, with heat recovered from the high-temperature liquid that leaves the heat exchanger at the heat sink. Titanium tetrabromide and tetraiodide have a unique feature in the vapor phase, whereby along the isentropes the pressure remains quasi-constant. Due to this reason, heat pumps that compress saturated vapor of these substances are not feasible. Two-phase compression has been suggested as a process to compress the fluid and raise its temperature. Both titanium based fluids have high energetic and exergetic COPs. With titanium tetraiodide, one can obtain the maximum temperature among the fluids studied, namely 650 °C with a COP over 3 (see Fig. 4). This suggests that TiI_4 is a promising working fluid for a heat pump that upgrades low-temperature heat for later use in the thermo-chemical Cu–Cl cycle of hydrogen production. Future research with experimental studies like Refs. [36,37] can provide further validation of the findings in this paper.

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