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SCIENTIFIC PAPER

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THERMAL PERFORMANCE EVALUATION OF HOT OILS AND NANOFLUIDS BY SIMULATION OF AN INDIRECT HEATING PLANT

Article Highlights

- Performance evaluation of heat transfer fluids by steady-state simulation of a hot oil system
- Thermal performance comparison between two nanofluids and a paraffinic oil
- A hot oil system in a real industrial plant was considered in the study performed
- Paraffinic oil showed better adjustment to heat duty required by the system
- Paraffinic oil presented operational clearance when compared with the current heat transfer fluid

Abstract

This paper aims to analyze the thermal performance of four different heat transfer fluids in a hot oil system located in a paraffin hydrotreatment and fractionation plant of a petroleum refinery. The software Petro-SIM® (KBC--Yokogawa) was employed to elaborate steady-state simulations intended to compare the heat transfer fluid currently used (eutectic of biphenyl and diphenyl oxide) and three fluids proposed as substitutes: paraffin oil (namely n-C_{13}^{+}) produced in the same industrial unit, a nanofluid of eutectic of biphenyl and diphenyl oxide and copper at a 6% volume fraction, and a CuO/polydimethylsiloxane nanofluid at a 6% volume fraction. The results showed that n-C_{13}^{+} was the only heat transfer fluid that could replace the eutectic diphenyl oxide/biphenyl in the system under analysis since it absorbed the heat duty of 13.79 Gcal/h, which exceeded the thermal energy of 10.57 Gcal/h absorbed by the heat transfer fluid currently used at the same operating parameters. The Cu/eutectic of biphenyl and diphenyl oxide and CuO/polydimethylsiloxane nanofluids presented lower heat duty than the energy needed for the operation of the hot oil system, which was 8.31 and 8.51 Gcal/h, respectively.

Keywords: heat transfer, heat transfer fluid, hot oil, nanofluids, simulation.

Heat transfer fluids, also known as hot oils, are used for heating or cooling in industrial and household applications. They are of great importance to the world's energy demand as more than 70% of all energy consumed is *produced* by heat transfer [1].

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In industrial processes, heat transfer fluids are employed as either vapor or liquid or phase equilibrium of both. Besides water and steam, other substances such as mercury, sodium, potassium, molten salts, and synthetic oils are used for both heating and cooling, each one possessing suitable characteristics for the different application fields according to the desired temperature range [2]. Figure 1 presents the categories discussed by Álvarez [1] as the most commonly used heat transfer fluids in industrial processes.

The oils mentioned in this work belong to the categories of thermal oils and nanofluids. These heat transfer fluids are represented in the figure below as

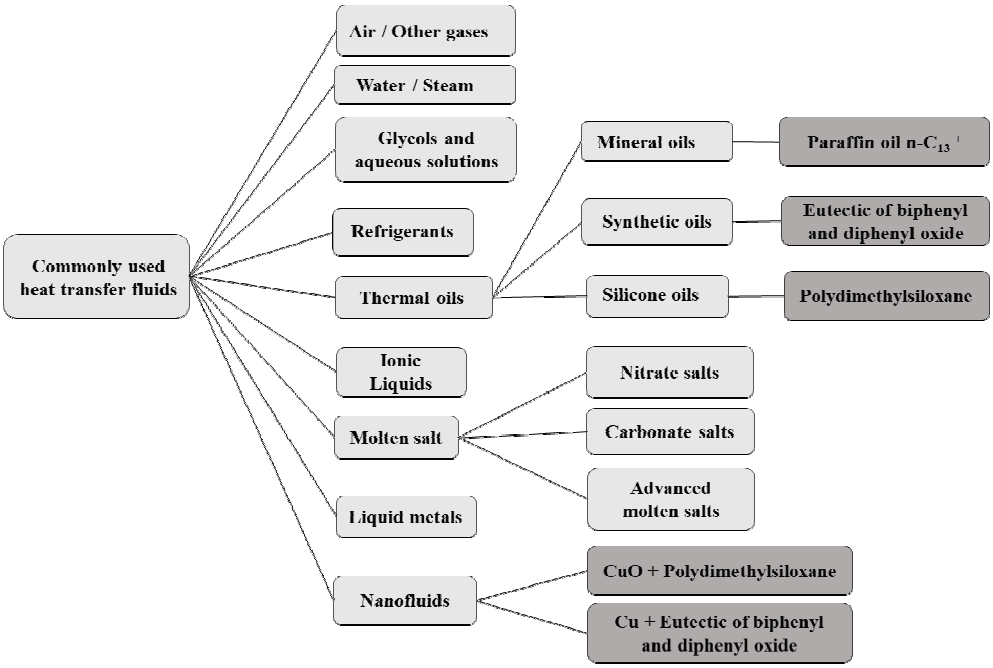

Figure 1. Most commonly used heat transfer fluids. Adapted from Alvarez [1].

the mineral paraffin oil *n*-C_{13}^{+}, the synthetic oil eutectic of biphenyl and diphenyl oxide, the silicon oil polydimethylsiloxane, the nanofluid of copper/eutectic of biphenyl and diphenyl oxide, and the nanofluid of polydimethylsiloxane with copper oxide particles.

Synthetic oils such as Malotherm® TH, Syltherm® 800, Therminol® VP-1, Dowtherm® A and Sandotherm® 59 are commonly used in closed indirect heating systems of industrial processes in general [3]. Besides their application in petroleum plants, petrochemical plants, and refineries, these thermal oils are currently employed in solar power plants, which are considered promising sources of alternative and renewable energy. The fluid acts as a medium for transferring and storing the heat captured by the solar parabolic trough collectors for later conversion into electrical energy [4].

The selection of the most suitable type of hot oil is of great importance to minimize costs and obtain the maximum performance from industrial facilities [1]. Requirements include low reactivity, long-term stability, and low freezing point. Proper characterization of the physical-chemical properties of the fluid is paramount for the design and monitoring of the operation of the industrial unit. The most significant parameters in the evaluation of heat transfer are density, heat capacity, viscosity, and thermal conductivity [5].

The heat transfer fluids currently used have maximum working temperatures of about 400 °C [3]. Molten salts can be used in applications where the temperature can reach 500 °C. However, corrosion and erosion of piping and equipment should be previously evaluated [6]. Liquid metals, such as pure, binary, and eutectic mixtures are suitable for high-temperature operation, above 1000 °C, because their boiling temperature can reach 1300 °C, approximately [6].

An alternative way to increase the allowable operating range for these heat transfer fluids is the addition of nanoparticles of up to 100 nm, which turns them into nanofluids [7].

Research related to nanofluids began in the 1990s, when this nomenclature was used by Choi and Eastman [8] to categorize heat transfer fluids containing nanoparticles in suspension in order to increase their thermal conductivity.

Solid nanoparticles incorporated at low concentrations into conventional heat transfer fluids are generally metals, metal oxides, and carbon-based structures (including nanotubes). This modification of the base substance results in better heat and mass transfer performance by changing the physical-chemical properties of the fluid [9].

Studies in this field of application have been developed looking for novel heat transfer fluids that could provide higher thermal conductivity and thermal stability, which could result in a better thermal performance of the nanofluids. Some of these studies are discussed below.

Kumar *et al.* [7] performed an experimental study with aluminum oxide nanofluids at 0.02, 0.04, 0.06 and 0.08% volume fractions using water, ethylene-glycol and paraffin oil as base fluids. Improve-

ment in the convection heat transfer coefficient was observed in all nanofluids evaluated, influenced by the nanoparticle concentration and higher turbulence.

Using the eutectic mixture of biphenyl and diphenyl oxide as base fluid, Navas *et al.* [10] obtained an 11% increase in the convection heat transfer coefficient by adding copper nanoparticles at a concentration of 5 ppm. Yasinskiy *et al.* [4] documented a 35.4% improvement for the same coefficient in a nanofluid containing 2.44 vol.% of titanium oxide.

Mwesigye *et al.* [11] evaluated the thermal and thermodynamic performance of Cu-Therminol® VP-1 at a high concentration ratio parabolic solar trough collector by means of a numerical study. The authors were able to enhance the heat transfer by 32% with the nanoparticle volume fraction of 6% in the nanofluid.

Bellos and Tzivanidis [12] analyzed different fluids aiming to optimize a solar-driven trigeneration system that featured the organic Rankine cycle (ORC), an absorption heat pump and parabolic trough solar collectors operating with nanofluids. The study investigated nanofluids of polydimethylsiloxane added with CuO and Al_2O_3 in the solar field loop of the trigeneration system. The optimum combination found was with the use of toluene in the ORC and CuO nanofluid at 4.35% in the parabolic trough collectors, which led to the maximum energy efficiency of 24.66%.

Sarafraz *et al.* [13] experimentally evaluated the flow boiling heat transfer coefficient, pressure drop, and fouling resistance of an MgO/Therminol® 66 nanofluid. The authors observed that the nanofluid, at 0.1, 0.2 and 0.3% mass fractions, caused an improvement of the characteristics under evaluation compared to pure Therminol® 66. The lowest concentration nanofluid led to the highest enhancement (about 23.7%) of the heat transfer coefficient.

Sarafraz and Arjomandi [14] experimentally examined the use of gallium and aluminum oxide nano-suspensions to replace water as the heat transfer fluid of a microchannel solar thermal receiver. The nanofluids were prepared at 5, 10 and 15% mass fractions and the authors observed that the nanosuspension at 10% mass fraction presented the best thermal performance to that application. Sarafraz *et al.* [15] experimentally studied gallium and copper oxide nano-suspensions using the same methodology as Sarafraz and Arjomandi [14] and found that the CuO nanofluid at 10% mass fraction had the best performance in heat transfer. Sarafraz and Arjomandi [16] experimentally assessed the thermal performance, pressure drop, and friction factor of a CuO/In nanofluid in microchannel heat exchanging systems as a plausible coolant to be used in solar thermal receivers. The authors' investigation showed that the studied nanofluid had great potential for applications in the temperature range from 170 to 300 °C.

Jalali *et al.* [17] numerically examined the laminar heat transfer of oil and multi-wall carbon nanotubes (MWCNT) nanofluids varying from 0 to 4% volume fractions to be used as cooling fluid jet. The authors observed that the enhancement in the conductivity provided by the increase in the nanoparticle concentration had positive effects in the heat transfer and promoted a better performance of the cooling fluid jet.

In this paper, a closed indirect heating system is analyzed, similar to that shown in Figure 2, concerning the thermal performance of hot oils and nanofluids. The objective is to verify if the oils under investigation can replace Dowtherm® A (fluid currently used), considering the operating conditions of the industrial unit, ensuring that the temperatures required by the four heat exchangers of the system are met.

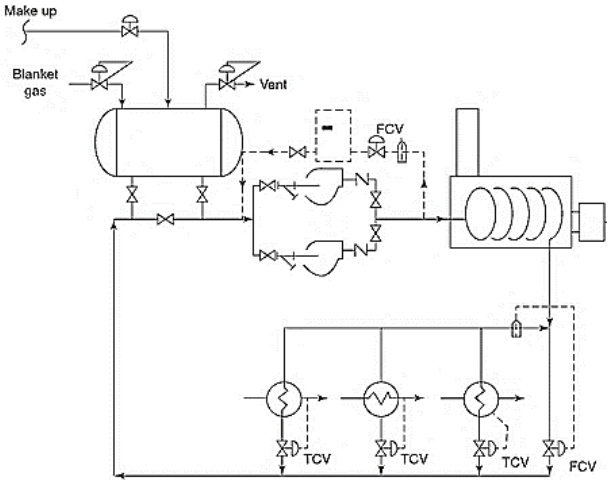

Figure 2. Typical hot oil system. Adapted from Bahadori [2].

In order to check how well the hot oils and nanofluids studied in this work suit the application of interest concerning heat transfer performance, the Petro-SIM® process simulator version 6.2 (KBC-Yokogawa) was employed. This tool has the key feature of providing thermodynamic packages to characterize hydrocarbons and substances present in petroleum refining processes in general. This allows the prediction of the properties of these compounds under different pressure, temperature, and concentration conditions through robust and reliable calculations [18].

Petro-SIM® provides information to determine whether the proposed heat transfer fluid suits the process by using operating and design data of the industrial plant analyzed in this study.

The fluids evaluated in this work are the eutectic mixture of biphenyl and diphenyl oxide (commercially known as Dowtherm® A or Therminol VP-1) [19,20], the paraffin fluid *n*-C_{13}^{+}, the nanofluids made of Dowtherm® A and copper particles, and Syltherm® 800 (polydimethylsiloxane) [21] containing copper oxide particles.

METHODOLOGY

Designing the simulations

The hot oil system studied in this paper was designed to use a eutectic mixture of diphenyl and biphenyl oxide as an indirect heat transfer medium into four heat exchangers, namely HT-01, HT-02, HT-03 and HT-04. The system provides thermal energy to a paraffin hydrotreatment and fractionation plant in a range from C_8 to C_{18}. Exchangers HT-01 and HT-02 preheat the process streams that feed a reactor, whereas HT-03, HT-04 are distillation column reboilers.

The heating process occurs as discussed by Bahadori [2] and Couto [22]. The oil is pumped and heated in a furnace (or some other heat source that forms the very process, such as steam exhausted from a turbine, for instance). The temperature of the heat transfer fluid typically rises from 11 to 55 °C at the furnace outlet and is distributed to the heat exchangers to meet the heat transfer requirements of the process. After that, the oil returns to an expansion vessel from where it is pumped again, restarting the cycle.

The first piece of information to be provided to Petro-SIM® in assembling simulation is the thermodynamic model that will represent the substances involved. The method for calculating the density of liquid substances should also be chosen in this step of the simulation setting.

The Peng-Robinson equation of state (1976), presented in Eq. (1), was chosen because it is a system primarily composed of nonpolar organic molecules, especially hydrocarbons in the liquid and gas phase at low-pressure conditions:

$$P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

The density of the liquid substances was calculated by the software according to Eqs. (2)–(5), which represent the correspondent state correlation (COSTALD), published in 1979 by Hankinson and Thompson, and which exhibits good reliability for gases in general as well as saturated and subcooled liquids [23]:

$$\frac{1}{\rho_s} = \frac{V_{sm}V_{rm}\left[1-\omega f\left(T_{rm}\right)\right]}{M_m} \tag{2}$$

$$V_{rm} = 1+\sum_{k=1}^{4}\left(\alpha_k \theta^k\right) \tag{3}$$

$$\theta = \left(1-T_{rm}\right)^{1/3} \tag{4}$$

$$f\left(T_{rm}\right) = \sum_{k=1}^{4}\left(\frac{b_k T_{rm}^{(k-1)}}{T_{rm}-1}\right) \tag{5}$$

In the hydrotreatment and fractionation process, the paraffin heated by the hot oil consist of mixtures whose compositions are complex and variable within ranges considered suitable as specifications. Therefore, some simplifications were made to design the simulations. Table 1 shows which compounds and substances were considered cold fluids in each of the heat exchangers of the hot oil system.

Table 1. Cold fluid of each heat exchanger in the hot oil system

Heat exchanger	Cold fluid
HT-01	*n*-C_8 to *n*-C_{18}
HT-02	Hydrogen
HT-03	*n*-C_9 to *n*-C_{18}
HT-04	*n*-C_{13} to *n*-C_{18}

For an easier characterization of the composition of each of the hydrocarbon streams present in the exchangers HT-01, HT-03 and HT-04, only linear paraffins were assumed to be part of their compositions, as these alkanes represent more than 90% in mass of the streams mentioned.

The present work employed a simulation of the paraffin fractionation distillation columns T-01 and T-02, whose reboilers are HT-03 and HT-04, respectively. For this step, shown in Figure 3, it was needed to obtain the composition of these exchangers' paraffin streams as only the linear paraffin feed stream for T-01 is characterized by routine laboratory analyses. Table 2 contains the standardized feed stream composition of T-01 considered in this study.

Figure 3 contains the distillation columns T-01 and T-02 and the process streams, which are called FEED (n-paraffins C_8 to C_{18}), N-C10-, GAS-C10-, N-C10C13, N-C13+. The energy streams to reboiler were labeled E-HT-03 and E-HT-04. The other streams of this kind were represented E-*n*, (where *n* is a two-digit number from 05 to 08).

By analyzing the datasheets and technical documentation of the equipment that makes up this section of the industrial plant, it was possible to obtain

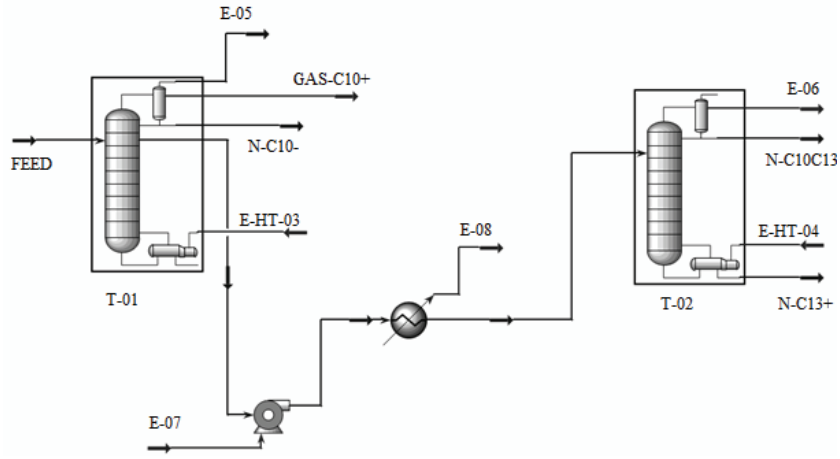

Figure 3. Simulation on Petro-SIM® for fractionation system which contains the reboilers HT-03 and HT-04.

the flow rate, pressure, temperature, pressure drop, and heat transfer area that constitute the design basis of each piece of equipment. Tables 3 and 4 show the data used as inputs to represent these operating conditions in Petro-SIM®.

Table 2. Composition of feed stream to T-01

Component	Feed stream to T-01, mass%
C_8H_{18}	1.65
C_9H_{20}	3.86
$C_{10}H_{22}$	10.98
$C_{11}H_{24}$	21.20
$C_{12}H_{26}$	21.71
$C_{13}H_{28}$	20.54
$C_{14}H_{30}$	14.09
$C_{15}H_{32}$	5.08
$C_{16}H_{34}$	0.79
$C_{17}H_{36}$	0.09
$C_{18}H_{38}$	0.01

Table 3. Input data for pump, furnace, expansion vessel and control valve of the hot oil system

Parameter	P-01	F-01	V-01	PV-01
Flow rate, m³/h	533.0	-	-	-
Inlet pressure, MPa g	1.11	2.30	-	1.52
Outlet pressure, MPa g	2.82	1.57	1.11	1.12
Inlet temperature, °C	350.0	350.0	-	350.0
Outlet temperature, °C	-	385.0	-	-

The simulator calculated the heat exchangers by the steady state rating, which assesses steady-state heat transfer for shell-and-tube-type heat exchangers, considering the stream arrangement, the heat transfer resistance by deposits, and its construction model [24].

The convergence criterion in the exchanger's heat transfer calculation is informed to satisfy the degrees of freedom to the system of equations. The standard configuration of the equipment block in the simulator recommends using the energy balance for hot and cold fluid (Eq. (6)) and the heat transfer equation (Eq. (7)) [24]:

$$\dot{m}_{hot} C_{phot} \Delta T_{hot} - \dot{m}_{cold} C_{pcold} \Delta T_{cold} = 0 \tag{6}$$

$$\dot{Q} = U A f_t \Delta T_{ml} \tag{7}$$

Based on all the information obtained and assumptions made, the hot oil system was represented in the simulations as shown in Figure 4. Considering the substitute heat transfer fluids proposed in this work, the system was represented in four different operating conditions, where the first one was exactly as foreseen in the design and the others modifying only the heat transfer fluid that circulates through the system.

The devices P-01, F-01, V-01, and the control valve PV-01, were tagged in Figure 4. Heat losses and pressure drops were represented using the terms HLOSS and PDROP, respectively. All the energy

Table 4. Input data for heat exchangers of the hot oil system

Parameter	HT-01		HT-02		HT-03		HT-04	
	Shell	Tubes	Shell	Tubes	Shell	Tubes	Shell	Tubes
Flow rate, m³/h	22.01	46.08	6.66	6.08	77.67	23.78	562.60	237.80
Inlet pressure, MPa g	10.79	1.57	10.79	1.51	0.14	1.52	0.14	1.51
Pressure drop, MPa	0.05	0.02	0.01	0.01	0.00	0.16	0.00	0.18
Inlet temperature, °C	203.0	370.0	38.0	370.0	385.0	255.0	385.0	302.1

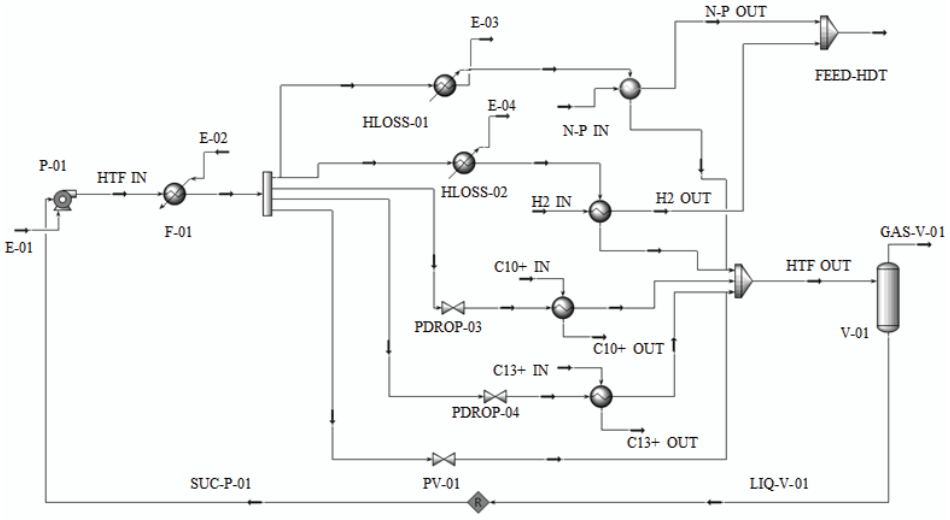

Figure 4. Petro-SIM® simulation for the hot oil system.

streams were labeled E-*n*, (where *n* is a two-digit number from 01 to 04), and the process streams as N-P (for *n*-paraffins), H_2, C10+ and C13+.

The validation of the first simulation was necessary to guarantee that Petro-SIM® reliably represented the cases where the thermal oil is not the eutectic mixture of biphenyl and diphenyl oxide.

The first option was the paraffin oil obtained at the bottom stream of tower T-02. As it is a by-product of the industrial unit where the hot oil system is located, there would be no additional costs for the production of the replacement fluid. In fact, the costs would be reduced since an inventory of synthetic oil from the current heat transfer fluid manufacturer would become unnecessary.

Nanofluid 1 (Cu + eutectic of diphenyl oxide and biphenyl) was selected as a possible substitute as it showed a 12.5% increase in heat transfer efficiency in parabolic solar collectors compared to the base thermal oil reported by Mwesigye *et al.* [11]. This case was simulated to evaluate if the modification of the thermophysical properties of the current working fluid with the addition of copper particles (6 vol.%) could represent a possible increase in productivity gains for the industrial unit due to the more efficient heat transfer.

Nanofluid 2 (composed of CuO + polydimethylsiloxane) was chosen because it achieved a maximum efficiency increase of 24.66% when applied to a trigeneration system as discussed by Bellos and Tzivanidis [12]. Thus, a simulation of the hot oil system was elaborated for this case, aiming to check the performance of this nanofluid at a concentration of 6.0% so as to find positive results, similar to those reported by those authors.

Inclusion of hypothetical components for the evaluation of nanofluids

The addition of nanometer-sized particles in conventional heat transfer fluids causes the enhancement of thermophysical properties, which in turn leads to greater efficiency in heat transfer processes [11].

The nanofluids selected for performance simulations in the studied system were polydimethylsiloxane with CuO (6 vol.%) and a eutectic mixture of biphenyl and diphenyl oxide containing Cu (6 vol.%) developed by Bellos and Tzivanidis [12] and Mwesigye *et al.* [11], respectively.

Since nanofluids are not present in the simulator database, it was necessary to characterize each studied nanofluid as a pure hypothetical component whose density, viscosity, thermal conductivity, and heat capacity properties could be adjusted by data regression so that there was an agreement with the data presented in above cited studies.

Petro-SIM® uses the UNIFAC method to construct the hypothetical component molecule and, based on the contributions of the subgroups added to the structure, calculates the thermodynamic parameters to the new substance [24].

Considering that the base fluids are, respectively, a siloxane-type polymer and a eutectic mixture of aromatic compounds, specific strategies to configure each of them as hypothetical components were needed.

The eutectic mixture of biphenyl and diphenyl oxide was represented by counting the subgroups that constitute both molecules. After this procedure, the proportionality of the mixture was applied according to Table 5 [5], where the sum of the results represents the number of subgroups that were supplied to

the simulator for the hypothetical molecule, according to Table 6.

Table 5. Eutectic mixture of biphenyl and diphenyl oxide

Component	Content, mol%
Biphenyl	26.5
Diphenyl oxide	73.5

Table 6. Composition and subgroups for eutectic of biphenyl and diphenyl oxide and hypothetical compound configured on Petro-SIM®

Subgroup	Eutectic mixture		Hypothetical compound
	Biphenyl	Diphenyl oxide	Hypothetical molecule
	Content, mol%		
	26.50	73.50	100.00
ACH	5.00	10.00	10.00
AC	1.00	1.00	1.26
CHO	-	1.00	0.74

The adherence of the proposed component to the characteristics of the actual eutectic mixture was verified by comparing the critical properties and molecular mass calculated by the simulator with the values reported by the manufacturer according to Table 7.

Table 7. Comparison of critical properties and molecular weight for eutectic of biphenyl and diphenyl oxide and hypothetical compound

Property	Eutectic of biphenyl and diphenyl oxide	Hypothetical compound	Error %
Molecular weight, g/mol	166.0	162.0	2.41
Critical temperature, °C	497.0	497.1	0.02
Critical pressure, MPa g	3.13	3.50	11.64
Critical volume, L/mol	0.526	0.449	14.65

In order to construct a representative structure of polydimethylsiloxane (commercially known as Syltherm® 800), the subgroups present in Figure 5 [21] were identified, and their quantity estimated according to Table 8 so that the critical properties were as close as possible to the information in the manufacturer's catalog. Table 9 contains the results obtained with the percentage error associated with each parameter.

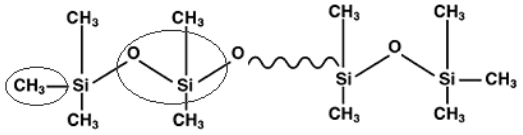

Figure 5. Polydimethylsiloxane polymeric structure. Adapted from Syltherm® 800 Heat Transfer Fluid [21].

Table 8. Representative (hypothetical) structure for polydimethylsiloxane

Subgroup	Structure
SiO	9
CH_3	33

Table 9. Comparison of critical properties and molecular weight for polydimethylsiloxane and hypothetical compound

Property	Polydimethyl-siloxane	Hypothetical compound	Error %
Molecular weight, g/mol	-	980.2	-
Critical temperature, °C	367.0	367.9	0.25
Critical pressure, MPa g	1.09	1.06	3.21
Critical volume, L/mol	3.22	2.93	9.00

Adjustment of the thermophysical properties of the nanofluids

The characterization of the density, viscosity, thermal conductivity, and specific heat of nanofluids is crucial to evaluate their efficiency in the heat transfer phenomena involved in industrial applications [10].

Mwesigye *et al.* [11] calculated the thermophysical properties for the suspension of copper nanoparticles in the eutectic mixture of biphenyl and diphenyl oxide by means of three sets of equations: one for the base fluid, one for the nanoparticles, and another one for the nanofluid.

The polynomials obtained for the base fluid as a function of the temperature (Eqs. (8)-(12)) were derived considering values between 285.15 to 698.15 K based on the data provided by the manufacturer in the product catalog. Eqs. (13)-(15), for copper particles, can be found in the property tables of Incropera *et al.* (2006) [11,25]:

$$\rho = 1.4386\times10^{3} - 1.8711T + 2.737\times10^{-3}T^{2} - \\ -2.3793\times10^{-6}T^{3}\,(\mathrm{kg/m^3}) \tag{8}$$

$$k = 0.14644 + 2.0353\times10^{-5}T - 1.9367\times10^{-7}T^{2} + \\ +1.0614\times10^{-11}T^{3}\,(\mathrm{W/m\,K}) \tag{9}$$

$$C_p = 2.125\times10^{3} - 11.017T + 0.0499T^{2} - \\ -7.766\times10^{-5}T^{3} + 4.394\times10^{-8}T^{4}\,(\mathrm{J/kg\,K}) \tag{10}$$

$$\mu = 366.1 - 3.0154T + 8.3409\times10^{-3}T^{2} - \\ -7.723\times10^{-6}T^{3}\,(\mathrm{mPa\,s}) \\ (285.15\ \mathrm{K} \le T \le 373.15\ \mathrm{K}) \tag{11}$$

$$\mu = 23.165 - 0.1476T + 3.617\times10^{-4}T^{2} - \\ -3.984\times10^{-7}T^{3} + 1.654\times10^{-10}T^{4}\,(\mathrm{mPa.\,s}) \\ (373.15\ \mathrm{K} \le T \le 698.15\ \mathrm{K}) \tag{12}$$

$$\rho_{Cu} = 8993.0 \text{ kg/m}^3$$

$$k_{Cu} = 441.6 - 0.17119T + 1.5446\times10^{-4}T^2 - \\ -7.2917\times10^{-8}T^3 \left(\text{W/m K}\right) \quad (14)$$

$$C_{pCu} = 258.8 + 0.44631T - 5.2054\times10^{-4}T^2 - \\ -2.3958\times10^{-7}T^3 \left(\text{J/kg K}\right) \quad (15)$$

The calculation of nanofluid properties (nf index) considers the base fluid (bf index), nanoparticles (np index), and volume concentration of particles (φ) in Eqs. (16)-(20) [11]:

$$\rho_{nf} = \left(1-\varphi\right)\rho_{bf} + \varphi\rho_{np} \quad (16)$$

$$k_{bf} = 0.25\left[\left(3\varphi-1\right)k_{np} + \left(2-3\varphi\right)k_{bf} + \sqrt{\Delta}\right] \quad (17)$$

$$\Delta = \left[\left(3\varphi-1\right)k_{np} + \left(2-3\varphi\right)k_{bf}\right]^2 + 8k_{bf}k_{np} \quad (18)$$

$$C_{pnf} = \frac{\left(1-\varphi\right)C_{pbf}\rho_{bf} + \varphi C_{pnp}\rho_{np}}{\left(1-\varphi\right)\rho_{bf} + \varphi\rho_{np}} \quad (19)$$

$$\mu_{nf} = \mu_{bf}\left(123\varphi^2 + 7.3\varphi + 1\right) \quad (20)$$

Bellos and Tzivanidis [12] characterized the thermophysical properties of a polydimethylsiloxane nanofluid containing copper oxide particles. Base fluid parameters are temperature dependent and were obtained from data provided by the manufacturer's catalog. The properties of the nanofluids are calculated through Eqs. (16) and (21)-(23) [12]:

$$k_{nf} = k_{bf}\frac{k_{np} + 2k_{bf} + 2\left(k_{np} - k_{bf}\right)\left(1-\beta\right)^3\varphi}{k_{np} + 2k_{bf} - \left(k_{np} - k_{bf}\right)\left(1-\beta\right)^3\varphi}$$

$$\left(\beta = 0.1\right) \quad (21)$$

$$C_{pnf} = \frac{\rho_{bf}\left(1-\varphi\right)}{\rho_{nf}}C_{pbf} + \frac{\rho_{np}\varphi}{\rho_{nf}}C_{pnp} \quad (22)$$

$$\mu_{nf} = \mu_{bf}\left(1 + 2.5\varphi + 6.5\varphi^2\right) \quad (23)$$

Copper oxide nanoparticles are present in the nanofluid at a concentration (φ) of 6.0% by volume and were characterized with a density (ρ_{np}) of 6320.0 kg/m³, thermal conductivity (k_{np}) of 77.0 W/(m K) and specific heat ($C_{p\,np}$) of 532.0 J/(kg K) [12].

With all the mathematical framework presented, data was regressed in Petro-SIM® in the temperature range from 303.15 to 653.15 K. Thus, each of the configured hypothetical compounds well represented the thermophysical properties of the respective nanofluids in the elaborated steady-state simulations.

RESULTS AND DISCUSSION

Representation of design conditions

The representation of the design parameters in the simulation was validated based on two main criteria: the heat duty associated with each heat exchanger and the comparison between the temperature at the beginning of the cycle (suction of pump P-01) and at the end of the cycle (liquid stream from the expansion vessel V-01).

Table 10 presents the percentage difference between the simulated heat duty values and those reported in the datasheets of each one of the exchangers that make up the hot oil system.

Table 10. Percentage Error, comparing heat exchanger duty simulated and from the equipment datasheet

Heat exchanger	Error, %
HT-01	0.00
HT-02	+3.58
HT-03	+8.00
HT-04	-1.48

All the heat exchangers showed satisfactory adherence, with the largest deviation being 8.0% for reboiler HT-03. This result can be justified by the lack of data on the composition of the *n*-paraffin streams used as a cold fluid for HT-03 and HT-04, and therefore it was necessary to obtain them from previous simulations of the fractionation towers T-01 and T-02, illustrated in Figure 3.

The T-01 feed stream was considered to be an average mass composition based on various results of routine laboratory analysis. The greater number of uncertainties associated with these exchangers may have caused a higher percentage error for HT-03, although it was still possible to obtain good adjustment for HT-04.

The temperature found for the liquid stream of the expansion vessel was exactly 2.0% higher than the suction temperature of pump P-01. Since these streams are actually only one and as the present study deals with a closed-loop system, this result indicates a good representation of the cycle, and the deviation can be explained by heat losses to the environment that were not represented in the simulation.

The heat duty supplied by furnace F-01 to the hot oil was 10.57 Gcal/h and served as a parameter for comparison with the other fluids evaluated in this paper because this energy demand is directly linked to the heat that is transferred from the heat exchangers to the process streams, considering Eq. (24) when losses to the environment are negligible:

$$Q_{F-01} = Q_{HT-01} + Q_{HT-02} + Q_{HT-03} + Q_{HT-04} \quad (24)$$

Since the simulation of design basis in Petro-SIM® presented satisfactory representativeness, it was possible to develop, with good reliability, the following topic in which possible substitutes for the eutectic mixture of biphenyl and diphenyl oxide are analyzed.

Performance evaluation of proposed heat transfer fluids

In this section, the term "paraffin fluid" refers to the *n*-C_{13}^{+} stream. The eutectic mixture of biphenyl and diphenyl oxide with 6 vol.% copper nanoparticles was labeled "Nanofluid 1", and the mixture composed of polydimethylsiloxane and 6 vol.% copper oxide nanoparticles was labeled "Nanofluid 2" in the tables presented.

According to the methodology used for the elaboration of the simulations of this study, the initial and final temperatures of the cycle for each of the proposed fluids were analyzed first.

It was observed that all substances had a lower end-cycle temperature compared to the eutectic mixture of biphenyl and diphenyl oxide. To adjust the simulation, the beginning of the cycle was equalized with the lowest temperature conditions so that there was a new convergence of the equipment blocks.

This change in temperature represents an increase in heat duty transferred to the hot oil in furnace F-01; however, as they are substances with different thermophysical properties, it does not necessarily mean that the absorbed heat will be greater than it would be with the eutectic mixture of biphenyl and diphenyl oxide.

The percentage difference between the pump P-01's suction temperature of each simulated heat transfer fluid and the design condition with the eutectic mixture of biphenyl and diphenyl oxide was calculated through Eq. (25):

$$\Delta T_{suctionP-01} = 100\frac{T_{V-01simulated} - T_{P-01design}}{T_{P-01design}} \quad (25)$$

To be a suitable replacement, the fluid under evaluation must be able to meet or exceed the design's heat duty value for each of the system's heat exchangers. Based on this criterion, the percentage gain in heat duty was defined by Eq. (26):

$$GainQ\% = 100\frac{Q_{FTsubstitute} - Q_{design}}{Q_{design}} \quad (26)$$

It was considered that the heat duty of the exchanger was met without operating clearance for percentage gains between -5 and +5%, attributing this margin of error to the approximations and assumptions made during the whole process of elaboration and convergence of the simulation calculations.

The summary of the compared criteria for the *n*-C_{13}^{+}, the proposed nanofluids, and the simulation of design conditions are represented in Table 11.

As previously shown, paraffin oil has demonstrated to be a promising substitute candidate for the eutectic mixture of biphenyl and diphenyl oxide, even providing a higher heat duty than that of the design for reboilers HT-03 and HT-04.

In this case, the heat duty transferred to the fluid by the furnace, in order to reach the same outlet temperature, was higher than for the thermal oil currently used, which justifies the higher heat availability for the heat exchangers and operating clearance.

Nanofluid 1 presented 1.37% lower temperature at the beginning of the cycle, and the heat duty supplied by F-01 is 21.4% lower than in the design condition.

The results presented showed that the same behavior observed by the Cu nanofluid + the eutectic mixture of biphenyl and diphenyl oxide occurred for Nanofluid 2; the suction temperature of the pump P-01 is 8.14% lower, and the heat duty provided by the furnace is 20.88% below expected.

The simulations have demonstrated that the nanofluids under study are not suitable for use under the design conditions as they could not provide the proper heat duty for three of the four exchangers that make up the hot oil system. More severe conditions would be required to obtain satisfactory performance,

Table 11. Performance evaluation for the proposed heat transfer fluids

Parameter	Equipment	Current fluid	Paraffinic fluid	Nanofluid 1	Nanofluid 2
$\Delta T_{\text{suction P-01}}$, %	P-01	-	-1.71	-1.37	-8.14
Heat duty, Gcal/h	F-01	10.57	13.79	8.31	8.51
Gain $Q_{\%}$, %	HT-01	0.00	-3.13	+1.84	-3.74
	HT-02	+3.58	0.00	-35.81	-43.65
	HT-03	+8.00	+9.33	-23.10	-26.64
	HT-04	-1.48	+40.05	-25.83	-20.79

but this, in turn, would require an assessment of system equipment and components to determine whether it would be possible to operate under more severe operating conditions without damage.

CONCLUSION

Thermal performance evaluation by static simulation of the studied hot oil system demonstrated that paraffin oil stood out when compared to the nanofluids evaluated and the eutectic mixture of biphenyl and diphenyl oxide, because the oil reached a heat duty of 13.79 Gcal/h, surpassing by 30.46% the thermal energy absorbed by the synthetic oil currently used (10.57 Gcal/h). The *n*-C13+ presented a satisfactory performance for all heat exchangers, providing higher heat duty than expected for HT-03 and HT-04.

Both nanofluids did not perform satisfactorily at the same operating conditions as the system. The Cu/eutectic of biphenyl and diphenyl oxide nanofluid only enhanced thermal energy in 8.31 Gcal/h and the CuO/polydimethylsiloxane nanofluid in 8.51 Gcal/h. The operating conditions might have to be modified to reach a higher temperature at the furnace outlet so that satisfactory thermal performance of these fluids could be obtained, but it should be preceded by a study on whether the devices and components of the system could endure such conditions.

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NAUČNI RAD

EVALUACIJA TERMIČKIH PERFORMANSI TOPLIH ULJA I NANOFLUIDA SIMULIRANJEM INDIREKTNOG TOPLOTNOG POSTROJENJA

Ovaj rad analizira termičke performanse četiri različite tečnosti za prenos toplote u sistemu sa vrelim uljem postrojenju za hidrotretman i frakcionisanje u rafineriji nafte. Softver Petro-SIM® (KBC-lokogava) je korišćen za izradu simulacija stacionarnih stanja namenjenih poređenju tečnosti za prenos toplote koje se trenutno koriste (eutektik bifenil- i difenil-oksida) i tri tečnosti predložene kao zamene: parafinsko ulje (n-C_{13+}) proizvedeno industrijski, nanotečnost eutektik bifenil i difenil oksida/bakar (zapreminski udeo 6%) i nanotečnost CuO/polidimetilsiloksan (zapreminski udeo 6%). Rezultati su pokazali da je n-C_{13+} jedina tečnost za prenos toplote koja može da zameni eutektik difenil oksid/ /bifenil u analiziranom sistemu, jer je apsorbovala toplotu od 13,79 Gcal/h, što je premašilo toplotnu energiju od 10,57 Gcal/h koju je apsorbovala tečnost koja se trenutno koristi pri istim radnim uslovima. Nanotečnosti Cu/eutektika bifenil- i difenil-oksida i CuO/polidimetilsiloksan pokazale su slabije performance u odnosu na vrelo ulje (8,31 i 8,51 Gcal/h, redom).

Ključne reči: prenos toplote, tečnost za prenos toplote, vrelo ulje, nanotečnosti, simulacija.