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Comparing the Thermal Stability and Oxidative State of Mineral and Biphenyl Diphenyl Oxide Based Heat Transfer Fluids

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Abstract

Many industrial processes (i.e., concentrated solar power [CSP] plants) require indirect heating of the product to temperature above ambient temperature. A heat transfer fluid (HTF), such as a Globaltherm™ Omnitech (Global Heat Transfer; Staffordshire, UK), is used in such plants and flows from the heater to source requiring the heat. Not all HTFs are the same, however, and so understanding the difference between fluids is important to ensure that end-users use the correct fluid for the correct operation. This is especially true in CSP plants where HTFs operate at high temperatures for long periods of time and therefore need to be stable under such conditions. Indeed, biphenyl diphenyl oxide (BDO) mixtures are commonly used in CSP plants as they can be heated to 400 degrees Celsius, which is higher than the upper operating temperature for a mineral-based HTF (i.e., ~400 degrees Celsius). It is a fact that all HTFs will thermally degrade over time and so it is important to monitor this to ensure that an early intervention can be taken if a problem starts to appear. The objective of HTF monitoring being to keep the HTF and plant operational for as long as is possible. Routine sampling and chemical analysis is used to assess the physiochemical properties of a HTF. For this to be done effectively, it is important to understand the properties of a virgin HTF and then to assess the rate of thermal degradation over time. Carbon residue, total acid number and closed flash point temperature are routinely measured in the laboratory and the current study proposes their use to assess the extent of thermal cracking and oxidation, two common pathways through which a HTF thermally degrades. The findings of this assessment are presented herein. Future work should consider using a similar approach to assess the condition of other HTFs commonly used in industrial applications.

Keywords: Heat transfer fluid; Thermal heat transfer fluid; Thermal degradation; Oxidation; Sampling and chemical analysis

Introduction

The electricity produced by concentrated solar power (CSP) plants is growing with ~430 MW produced in 2008 [1] and an estimated 20 to 630 GW to be produced by 2020 [2] and 2050 [3,4] respectively. CSP plants use a heat transfer fluid (HTF) to collect heat from the sun. The main types of HTF being: 1) air/other gases; 2) water/steam; 3) mineral based HTFs (e.g., Globaltherm M); 4) synthetic based HTFs; 5) molten salts (e.g., Globaltherm Omnistore); and, 6) liquid metals [3]. Synthetic HTFs that contain a eutectic mixture of biphenyl and diphenyl oxide (BDO), such as Dowtherm A, Therminol VP-1 and Globaltherm Omnitech [4], are commonly used as a heat carrier in CSP plants [5].

The sheer size of CSP plants, for example the first CSP plant built in India used a solar field consisting of three loops with parabolic troughs and measured 1,500 meters in length and covered 8,000 m^2 [6] means that the HTF is an expensive asset [3]. Commercial operations therefore need to work to minimize the cost of the HTF as well as maximize the performance of the CSP plant [3].

It is a fact that HTFs will age with usage and is influenced by a number of factors including elevations in temperature above the HTFs bulk operating temperature, oxidative stress and HTF contamination [7]. Being able to slow the process of degradation is critical to maintaining an effective and efficient operation. Laboratory chemical analysis is routinely used in the condition monitoring of HTFs. Indeed, a HTF that undergoes thermal degradation will form heavy (i.e., carbon formations) and light-chain (flash point components that can be assessed from open and closed flash point temperatures). Organic HTFs operating at high temperatures are susceptible to air oxidation and it is possible to assess the extent of HTF oxidation by looking at its neutralization number (i.e., total acid number [TAN]) (Table 1). Other tests can also be used to assess foreign contaminants and kinematic viscosity [5].

Aluyor and Ori-jesu [8] describes "thermal stability" as the resistance posed by a fluid to either molecular breakdown or the rearrangement of molecules at elevated temperatures in the absence of oxygen (i.e., thermal degradation). Synthetic HTFs, such as eutectic mixtures of BDO, are generally considered to exhibit better thermal stability than mineral-based HTFs [9]. They are also considered to be more resistant to fouling (for example, please see reference [10].

Objectives for This Article

This article aims to compare mineral-based and synthetic (i.e.,

Chemical test	What is assessed?
Carbon residue	Heavy-chain hydrocarbons
Closed flash point temperature	Light-chain hydrocarbons
Open flash point temperature	Light-chain hydrocarbons
TAN	The extent of HTF oxidation

Table 1: What the chemical testing says about the condition of a HTF.

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BDO-based) HTFs to ascertain the following:

a) Their physicochemical properties.

b) To understand how these HTFs should be maintained and if there are any differences.

c) To compare the thermal stability (from plots of carbon residue versus open and closed flash point temperatures) and anti-oxidative capacity (from plots of carbon residue versus TAN) of these HTFs.

Materials and Experiments

Materials and methods

The sampling of HTFs: A 500 ml of the HTF was sampled from the plant whilst the HTF was in circulation. These samples were then taken to the laboratory for subsequent chemical analysis [7]. This was performed using a closed sampling device to prevent the HTF coming into contact with air and thus ensuring a representative sample of the HTF was collected. This technique has been presented previously [11]. All laboratory analysis was conducted according to ISO14001 [12] and ISO17025 [13].

HTFs sampled and chemically analyzed: Mineral-based (i.e., Globaltherm M) and BDO-based HTFs (i.e., Dowtherm A) were included in this analysis.

Contrast and comparison

Physicochemical properties: The physicochemical properties of virgin mineral and BDO-based HTFs were compared by extracting key data from safety data sheets for Globaltherm M (mineral-based) and Globaltherm Omnitech HTFs (BDO-based) [14].

Comparing the maintenance and management programs required for mineral and BDO-based HTFs: The maintenance guidelines for mineral and BDO-based HTFs were compared based on guidance for usage, routine sampling, chemical analysis and handling. The objective was to determine if these HTFs should be treated any differently in the real-world setting.

Assessments of thermal stability and anti-oxidative capacity: Retrospective test reports were analyzed to assess the thermal stability and anti-oxidative capacity of mineral and BDO-based HTFs. Thermal stability was determined from x-y plots of carbon residue against closed flash point temperature. Likewise, anti-oxidative capacity was determined from x-y plots of carbon residue against TAN.

Comparisons were made by constructing x-y plots and grouped according to carbon residue values: Closed flash point temperatures and TAN were grouped according to carbon residue, which was organized based on 5 groups:

a) Group 1, <0.05% carbon residue and typical of a virgin HTF.

b) Group 2, ≥0.05 and <0.5% and considered a satisfactory rating.

c) Group 3, ≥0.5 and <0.75% and considered a cautionary rating.

d) Group 4, ≥0.75 and <1.0% and action to correct the issue should be considered.

e) Group 5, ≥1.0% and this is considered to be severe and an immediate intervention is required [11].

Results and Discussion

Physicochemical properties

Some typical physicochemical properties for mineral and BDO-based HTFs are compared in Table 2.

It is claimed that eutectic mixtures of BDO have been used in industrial HTF systems for over 60 years [15]. Eutectic mixtures of BDO are commercially available [16,17] and traded under many different brand names. One example is Globaltherm Omnitech [14] which contains a uniform eutectic mixture of biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$) [5,16] with a melting point of roughly 12 degrees Celsius and an upper operating temperature around 400 degrees Celsius [5,18]. This means the operating range is above 12 degrees Celsius as below this temperature the HTF solidifies. This is in contrast to a mineral-based HTF which has a lower operating temperature of -10°C, which means it has the advantage of being able to be used without steam tracing in most cases and less prone to solidifying during storage or cold operating climates. Although, solidification will not present an issue in plants are protected from the weather.

The upper operating temperature of the BDO-based HTF is 400°C and is a reflection of the fluid's superior thermal stability as compared with a mineral-based HTF (i.e., +120°C higher than a mineral-based HTF (Figure 1 and Table 2).

BDO-based HTFs can also be used effectively as a liquid HTF (below boiling point), a vapor phase (above its boiling point) or as a mixture of liquid plus vapor, which is defined by the overall design of the plant [14]. This is compared with a mineral-based HTF which operates in the liquid phased.

BDO-based HTFs also have lower flash point temperatures and higher bulk and auto-ignition temperatures (Figure 1 and Table 2). Indeed, the BDO-based HTF provides a safety margin of 221°C above its upper operating temperature [19] as compared with the 40°C normally provided by a mineral-based HTF [20].

Parameter	Unit	Mineral-based HTF	BDO-based HTF
Other HTF examples	Descriptive	BP Transcal N, Globaltherm M, Shell Thermia B	Dowtherm A, Globaltherm Omnitech, Therminol VP-1
Operating range	^{0}C	-10 to 320	15 to 400
Appearance	Descriptive	Viscous clear-yellow liquid with a mild odor	Clear-to-light yellow liquid with a geranium-like odor
Density at 25^{0}C	kg/m^3	873	1056
Kinematic viscosity (at 40, 100^{0}C)	mm^2/s	29.8, 4.5	2.5, 0.97
Auto-ignition	^{0}C	>320	621
Maximum film	^{0}C	330	425
Boiling point at 1013 mbar	^{0}C	365	257
Open flash point	^{0}C	230	123
Closed flash point	^{0}C	210	113

Table 2: A comparison of the typical physicochemical properties of a mineral and BDO-based HTF.

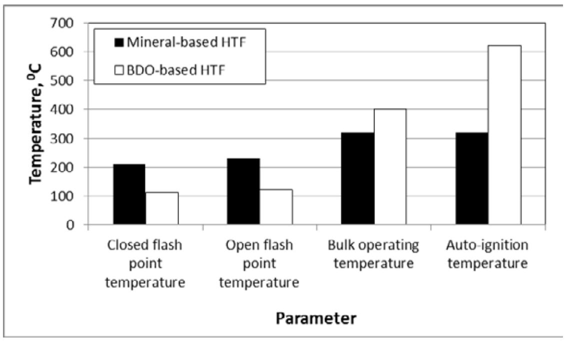

Figure 1: Comparison of flash point, bulk operating and auto-ignition temperatures for mineral and biphenyl and diphenyl oxide (BDO)-based heat transfer fluids (HTFs).

Both mineral and BDO-based HTFs are combustible materials, but the both have relatively high open flash points 230 and 123°C (mineral and BDO-based HTF, respectively) [19]. The flash points for BDO-based HTFs are lower compared with mineral based HTFs, but it is also important to factor the greater thermal stability of BDO-based HTFs.

Table 2 compares the kinematic viscosity for mineral and BDO-based HTFs. For BDO-based HTFs, the kinematic viscosity is lower than mineral-based HTFs and only changes slightly between the lower and upper operating temperatures. For comparative purposes this is seen in Table 2 where the factor of change in kinematic viscosity between 40 and 100°C is 2.6 (0.97 divided by 2.5 mm^2/s) and 6.6 (4.5 divided by 29.8 mm^2/s) for BDO and mineral-based HTFs, respectively. A benefit of the lower viscosity for BDO-based HTFs is that problems on start-up are minimized as the fluid has a lower viscosity than a mineral-based HTF [19].

The carbon residue, water and neutralization number (indicating the TAN for a HTF) are ideally as close to zero as possible. Contamination of a HTF, and potentially subsequent HTF system corrosion and HTF degradation, can be caused by the introduction of foreign particles (e.g., water) or chemicals during system flushing and cleaning [19] as a result of process leaks [19] or during the building of new HTF plants (e.g., welding slag and environmental contaminations) [21,22]. Hence, even at the early stages in the construction of a plant it is important to sample and chemically analyze the HTF to mitigate the exposure to and manage the removal of any identified contaminants [21,22].

Maintenance and management programs for mineral and BDO-based HTFs

The thermal stability of a HTF depends not just on the chemical structure, but also on sound engineering practices [19] and sound maintenance programs to monitor and manage the rate of thermal degradation and degree of oxidation [11].

The advice from manufacturers (from example see [19] when sampling and analyzing HTFs is summarized below:

a) A 500 ml is required to chemically analyze the condition of the HTF.

b) Closed sampling devices should be used to get a representative sample of the HTF.

c) Before sampling, the sampling device should be thoroughly washed.

d) A HTF should be taken from the main circulating line of the HTF system, but samples may be required from other parts of the system if a specific issue is being investigated.

e) Analysis of a HTF provides insights, as discussed above, into the condition of the fluid and is used to identify problems (e.g., contamination) as well as to monitor the state of the HTF and to help define suitable interventions if a correct to the HTF condition is required.

f) Following sampling of a HTF, is should be allowed to cool (to below 40 degrees Celsius) before handling and chemical analysis. This will also work to keep light-ends in solution and stop them escaping from the sample.

g) HTFs should be sampled routinely and research has shown that the condition of mineral-based HTFs improves if sampled every 3 months [7].

h) The chemical analysis conducted on the HTF sample should be defined in consultation with the manufacturer of the fluid.

Assessments of thermal stability and anti-oxidative capacity

Figure 2 plots carbon residue against TAN and closed flash point temperature to provide visual assessments of the thermal stability (bottom panel) and anti-oxidative capacity (top panel) for a mineral and BDO-based HTF. From Figure 2 it is clear that for a mineral-based HTF, carbon residue increases at twice the rate of TAN. Thus demonstrating the need to assess carbon residue closely for mineral-based HTFs as this appears to be an early and sensitive marker for assessing the condition of the HTF. Moreover, once a mineral-based HTF gets to a carbon residue value of ≥1% weight, the HTF will need to be replaced. This can be achieved by monitoring the fluid and this

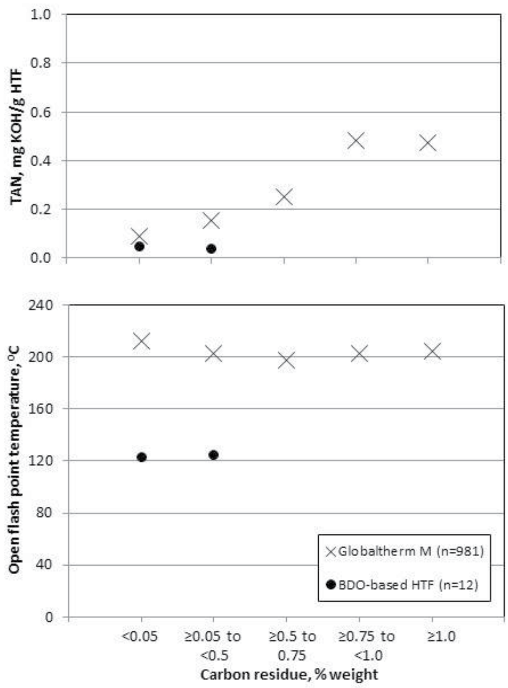

Figure 2: Plots of carbon residue against total acid number (TAN; top panel) and closed flash point temperature (bottom panel) for Globaltherm M and a biphenyl diphenyl oxide (BDO) based HTF.

	Carbon residue, % weight				
Parameter	<0.05	≥0.05 to <0.5	≥0.5 to <0.75	≥0.75 to <1.0	≥1.0
Number of samples chemically analyzed	82	793	46	30	30
Water content, ppm	90.43	84.49	83.60	63.00	182.89
Kinematic viscosity, mm^2/s	30.3	30.2	30.9	33.8	36.2
Elements, e.g., silicon (ppm less than 5 μm)	11.8	14.3	18.3	11.5	16.0
TAN	0.1	0.2	0.3	0.5	0.5
Ferrous debris, insolubles	7.0	15.6	20.9	17.8	29.1
Open flash point temperature, ^0C	212.0	203.1	197.3	202.8	204.2
Closed flash point temperature, ^0C	165.5	155.6	150.4	164.6	160.5
Fire point temperature, ^0C	244.1	243.9	236.6	240.0	240.2

Table 3: The physicochemical properties of the mineral-based HTF for each carbon level.

is an important part of HTF system planned preventative maintenance [23] and offers the opportunity to be able to detect problems and take appropriate action when needed. In the current case this would be maintaining carbon residue as close to the values for a virgin HTF (see typical values presented in Table 1) as possible.

Although, the current data shows that both carbon and TAN were increasing and this raises the question as to whether these changes were primarily driven by oxidation or by thermal cracking. This can be assessed by looking at plots of carbon against closed flash point temperature. Indeed, the bottom panel of Figure 2 shows the thermal stability of the HTF was relatively constant with closed flash point temperature constant at each level of carbon. This data suggests that the degradation of HTF was driven largely by oxidation rather than cracking of the HTF [24]. This is supported by the fact that carbon increases linearly with TAN (i.e., oxidative state) but is stable against closed flash point temperature. This is further supported by Table 3 where kinematic viscosity increases as opposed to decreases. The increase denoting the formation of carbon in solution, as would be occurring through oxidation of the HTF [24].

The comparison of mineral and BDO-based HTFs over the full range of carbon residue values was not possible because of the limited number of samples for the BDO-based HTF. From Figure 2, however, thermal stability and oxidative state are relatively stable over the range of carbon values investigated. The data for BDO-based HTFs highlights the need for further work to allow the comparison of different HTFs Table 3.

Conclusions

The current study highlights three important aspects for every HTF:

i. The importance of referring to the safety datasheet to understand the thermochemical physicochemical properties and performance of a virgin HTF. This is an important reference source to understand a fluid or to compare fluids, such as was done herein to understand the differences between mineral and BDO-based HTFs.

ii. All HTFs need to be maintained as part of the overall maintenance of a plant. All HTFs need to be managed as their condition is directly related to the condition of the overall plant. Indeed, Wagner [5] states that “Relevant regular maintenance services of the system components are necessary and to be carried out by experienced personnel to ensure trouble-free operation of the plant over a longer period.” This needs to be done by experienced engineers, such as Global Heat Transfer (www.globalheattransfer.co.uk) using suitable equipment so that a representative sample can be obtained safely whilst the plant is still in operation [22].

iii. Chemical analysis can be used to assess the condition of the HTF and to make early decisions regarding the maintenance of the HTF and the plant. The results of tests for carbon residue, TAN and closed flash point temperature can be used to assess both the extent of thermal cracking (x-y plots of carbon residue versus closed flash temperature) and oxidation (plots of carbon residue versus TAN). The data presented in this paper suggested that the degradation of HTF was driven largely by oxidation as opposed to thermal cracking [24] and these insights were achieved the 11-point test offered by Global Heat Transfer.

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