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Safe Sampling, Handling and Storage of Biphenyl Diphenyl Oxide Heat Transfer Fluids

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Abstract

Background: The heat transfer fluid (HTF) most commonly used in concentrated solar power (CSP) plants is eutectic mixtures of biphenyl and diphenyl oxide (BDO) such as Globaltherm® Omnitech, which can be used up to 400 degrees Celsius. Routine sampling and chemical analysis of solar HTFs plays a critical role in maximizing the profitability of CSP plants. *Objectives*: The current article outlines the sampling and chemical analysis of solar HTFs containing a eutectic BDO mixture and how to safety handle and store BDO HTFs. *Methods*: The Company's database was searched to identify risk and method statements detailing the safe sampling of BDO HTFs and to identify the parameters to measure. Likewise, the safety datasheets for the company's BDO HTFs were searched and used to outline how this type of HTF should be handled and stored. *Results*: Like any HTF, the sampling of a BDO HTF needs to be conducted in a standardised manner to ensure it is done safely. The chemical testing of a HTF should include assessments of both 'light' and 'heavy-ends' (i.e., short and long-chain hydrocarbons); oxidative state; and, the potential flammability risk posed by light-ends. Other assessments include kinematic viscosity, contamination and component wear particles. In terms of safety, it is recommended that engineers are proficient with the safety data sheet for a BDO HTF to ensure they are sampled, handled and stored safely. General safety advice included: not allowing clothing soaked with a HTF to come into contact with or remain in contact with the skin; avoiding all personal contact with the HTF, including inhalation; wearing protective clothing; being vigilant that the decomposition of BDO HTFs may be flammable and hazardous to human health; and, knowing that personal protective equipment should be worn when sampling and handling a BDO HTF. *Conclusions*: Routine sampling of HTFs should be done whilst the HTF is live and conducted by a trained engineer that knows how to safely take a live sample as well as how to safely manage a BDO HTF. This includes being proficient in first aid should the BDO HTF come into contact with the skin, be ingested or inhaled. Lastly, BDO HTF condition should be tested on a regular basis and it is also advised to have this done by a company that specialises in this sector such as Global Heat Transfer, which has over 25 years of experience in this area of thermodynamics.

Keywords

Heat Transfer Fluid, Heat Transfer Fluid System, Sampling and Chemical Analysis, Concentrated Solar Power, Eutectic Mixtures of Biphenyl and Diphenyl Oxide

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1. Introduction

1.1. Background

A heat transfer fluid (HTF) is liquid substance used to carry heat away from its source to be cooled, usually by another fluid, as in a heat exchanger [1]. The transfer of heat energy between a HTF and process equipment is a basic requirement. Traditionally, steam was used as a HTF; HTFs based on mineral oil, silicone, aromatics, polyalkylene glycols and glycol fluids are often preferred because they can be used at relatively low pressures [2]. They are used for

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purposes as diverse as pharmaceutical production, the manufacture of fine chemicals and polymers, biodiesel production and the generation of electricity from concentrated solar power (CSP) plants [2]. The HTFs most likely to be used in such operations are eutectic mixtures of biphenyl and diphenyl dioxide (BDO) [3]. For instance, The Jawaharlal Nehru National Solar Mission used a BDO mixture in a parabolic trough power plant [4]. This particular HTF provides has an operational range between 12 and 400 degrees Celsius [5]. This is one of a wide array of HTFs, which includes gases (air or other gases), water or steam, mineral and synthetic based HTFs (e.g., BDO mixture), molten salts and liquid metals [6]. The building of a CSP plant is a major undertaking and technical and cost effective criteria for HTFs need to be considered [7] (please see Tab. 1). However, the profitability of a plant also needs to be considered. This includes the maintenance costs associated with CSP plant operation and maintenance [8], which includes the HTF as well. The objective being to maximise profitability and this is achieved by reducing the cost of maintenance and extending operational times so more energy can be provided for longer periods of time.

Tab. 1. Technical and cost effectiveness criteria for CSP plants.

Criteria	Influencing factors
Technical aspect	1. High thermal energy storage capacity (the most important). 2. Efficient heat transfer rate between HTF and storage material. 3. Good mechanical and chemical stability of storage material. 4. Compatibility between HTF, heat exchanger and/ or storage material. 5. Complete reversibility of a large number of charging and discharging cycles. 6. Low thermal losses and ease of control.
Cost-effectiveness aspects	1. The cost of thermal energy storage materials. 2. The cost of the heat exchanger. 3. The cost of the space and/or enclosure for the thermal energy storage.

The routine sampling and chemical analysis of HTFs is critical to maximizing the profitability of such plants as it can be used to monitor the condition of a HTF and to drive interventions to mitigate adverse changes in the condition of a HTF [9].

1.2. Objectives

Engineers work in close proximity to BDO mixtures and they need to understand how to safely sample, handle and store BDO HTFs. The two broad objectives were to i) identify how to safely sample and chemically analyse BDO HTFs; and, ii) how to safely manage, including both handling and storage, of BDO HTFs.

2. Materials and Methods

2.1. How to Sample and Chemically Analyse BDO HTFs

Global Heat Transfer [10] is a thermal fluid specialist, providing heat transfer engineering assistance and thermal fluid supplies. Services offered include sampling and chemical analysis of HTFs to monitor the condition of a HTF. The Global Heat Transfer database was searched to identify risk and method statements for the safe sampling of BDO HTFs and to identify the parameters to measure.

2.2. How to Safely Handle and Store BDO HTFs

Global Heat Transfer is a supplier of HTFs. The safety datasheets for BDO HTFs were searched and used to outline how this type of HTF should be handled and stored.

3. Results

3.1. Sampling and Chemical Analysis of BDO HTFs

At high temperatures, HTFs may degrade to produce corrosive oxidation products and a mixture of heavier and lighter fractions as a result of thermal cracking. The formation of heavier hydrocarbon chains may result in sludge deposits, and the build-up of lighter hydrocarbon chains (commonly referred to as “light-ends”) increase the potential flammability of the HTF [11] as they lead to a reduction in the flash point of a HTF [12]. Regular sampling and chemical analysis of a HTF is used to monitor and manage these decomposition products and can help to maximise the life of the HTF. It is important that the sampling technique can be used to obtain a representative sample. This means that the HTF sample reflects what is circulating in the HTF system and so this needs to be taken whilst the HTF is in operation (i.e., circulating in the system and hot) so that the operation is not interrupted. Fig. 1 shows a sampling device designed to take approximately 500 ml of HTF. Sampling is performed in a closed system to prevent the loss of volatile components that may be present in the HTF [13] and build-up as a fluid thermally degrades over time.

The proportion of light-ends in the HTF can be evaluated by measuring flash point temperatures. The lower the flash point temperature, the higher the proportion of light-ends in the HTF and the higher the flammability risk posed to the HTF system and plant as a whole. Heavy-ends can be quantified by measuring the mass of solids in a sample and the extent of a fluids oxidation can be qualified using acid-base titration to measure total acid number (TAN). Organic

acids commonly cause corrosion in metal components of the heat transfer system.

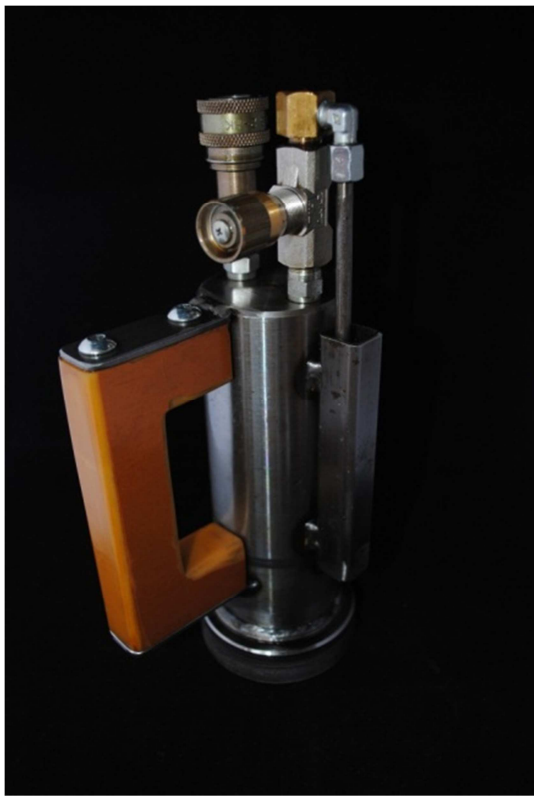

Fig. 1. The sampling device used by Global Heat Transfer to take live HTF samples.

Regular sampling and chemical analysis of hot HTFs is used to gauge the condition of a HTF. Chemical analysis is routinely used to monitor changes in:

a. Both light and heavy-ends in a HTF.

b. Oxidative state of the HTF.

c. The potential flammability hazard posed by a HTF.

Chemical analysis is used to assess the current condition of a HTF and with repeat testing it is possible to assess the changes in condition over time. This can then be used as a predictive tool and enables a plant operator to plan interventions to correct adverse changes in, for example, carbon residue (heavy-ends). The advantage to the customer is that this approach can be used to sustain the life of a HTF and to prevent unnecessary damage to expensive equipment. For example, when a HTF starts to thermally degrade it will form heavy and light-ends-ends. These heavy-ends have a number of potentially detrimental effects including:

a. Increased kinematic viscosity of the HFT – this leads to a reduction in heat transfer and efficiency, which then requires more energy to reach previous performance and further HTF degradation. Increased viscosity also increases the resistance to flow.

b. Carbonization of the internal surfaces of the HTF system – this adds to the resistance to flow. The internal coating also results in poor heat transfer rates and possibly higher film temperatures and further thermal degradation of the HTF [11].

3.2. Safe Sampling of Hot BDO HTFs

It is critical that personal protective equipment (PPE) is worn when sampling live HTFs. PPE is defined as any equipment that offers protection against hazards and are there to protect employee health and safety at work according to the Work Regulations Act 1992.

Global Heat Transfer (www.globalheattransfer.co.uk) provides HTFs and engineering services to the heat transfer sector. This means that engineers sampling HTFs may need to manage fluids that operate to 400 degrees Celsius [10]. Engineers also come into chemicals on a regular basis and must take the appropriate protection when entering potentially hazardous environments.

Potential eye hazards are the first thing that must be taken into consideration. Risks can include the splashing of hot fluids and chemicals, as well as exposure to dust and gas. Best practice dictates that prior to entering a hazardous environment an engineer should put on safety spectacles. These spectacles are covered by a facemask to protect the eyes against any adverse vapours or splashes. The mask also protects the wearer's skin and offers further protection when sampling a HTF. On entering any facility, it is compulsory that all relevant staff wear a hard hat to prevent any form of head injury. This includes bumping the head on stationary objects, hair entanglement or impact from falling / flying objects. An engineer's uniform should include a disposable filtering face piece or respirator (half or full-face), an air-fed helmet and breathing apparatus. Global Heat Transfer's engineers wear 3M respirators, which work to filter fumes from the HTF that is being sampled (please see Fig. 2).

Fig. 2. The personal protective equipment worn whilst sampling a HTF.

Other protective equipment should include disposable Supertex coveralls and high-visibility clothing. Hazards to

hands and arms include abrasion, temperature extremes, cuts, contact / contamination with chemicals. Hence, when taking a live sample of a HTF it is recommended that heat-rated gauntlets are worn. These need to be non-porous and to resistant the fluid penetrating the gauntlet. A cotton inner glove is also recommended as this serves as an additional layer against the gauntlet should it come into contact with a live HTF. Furthermore, the cotton glove helps to stop moisture from pooling in the gauntlet.

Much like hands and arms, the feet and legs also need protection from safety risks such as chemical splashes and falling objects. Hence, wearing tight fitting boots is recommended. These need to provide some heat resistance and must have a non-slip sole. Boots should also have a steel toecap to protect the toes and penetration-resistant mid-soles. Open-topped footwear, such as rigger boots, must not be worn when sampling HTFs as a sampled fluid can potentially penetrate this type of boot.

In addition to the above items, ear defenders should be worn to protect hearing. Indeed, factories can be very noisy places.

Safe hot fluid sampling is critical to the safety of engineers and compulsory training should be run to ensure that best practices are being followed. It is also important that refresher training is run to emphasise its importance and to ensure that practices are being followed in the field. The anonymous reporting of unsafe practices to senior management should be encouraged and the reporting procedure should form part of all refresher training.

3.3. Safe Handling of BDO HTFs

Eutectic BDO mixtures can be used in both vapour and liquid phases. It is miscible and interchangeable (i.e., in the case of top-ups or HTF system design extensions or additions) with other BDO HTFs with the same chemical structure and composition. Safety considerations specific to BDO HTFs are detailed below:

3.3.1. If the BDO HTF Is Accidentally Ingested

Accidental ingestion of the material may be damaging to the health of the individual. Biphenyl is absorbed by the gastro-intestinal tract and is rapidly metabolised to 4-hydroxybiphenyl, 4-phenylcatechol and 4.4'-dihydroxyphenyl which are excreted in the bile as the glucuronide and mercapturic conjugates. After single large oral doses experimental animals showed increased rate of respiration, lachrymation, and anorexia and weight loss, muscular weakness and ataxia, with death in coma occurring between 2 hours and 18 days.

If swallowed, first aid should not be used to induce vomiting. If vomiting occurs, lean patient forward or place on left side (head-down position, if possible) to maintain open air way and prevent aspiration.

3.3.2. If the BDO HTF Gets into the Eye

Evidence exists, or practical experience predicts, that the material may cause eye irritation in a substantial number of individuals. Prolonged eye contact may cause inflammation characterized by a temporary redness of the conjunctiva (similar to windburn). The liquid produces a high level of eye discomfort and is capable of causing pain and severe conjunctivitis. Corneal injury may develop, with possible permanent impairment of vision, if not promptly and adequately treated.

If this product comes in contact with the eye, first aid measures include washing-out the eye immediately with fresh running water. Also ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids.

3.3.3. If the BDO HTF Comes into Direct Contact with the Skin

The material may cause mild but significant inflammation of the skin either following direct contact or after a delay of some time. Repeated exposure can cause contact dermatitis which is characterized by redness, swelling and blistering. Skin contact with the material may damage the health of the individual; systemic effects may result following absorption. Entry into the blood-stream via cuts, abrasions or lesions, for example, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

If skin contact occurs, first aid measures include the immediate removal of all contaminated clothing, including footwear, flush skin and hair with running water (and soap if available).

3.3.4. If the BDO HTF Is Inhaled

BDO can cause respiratory irritation in some persons. The body's response to such irritation can cause further lung damage. Inhalation of aerosols (mists, fumes), generated by the material during the course of normal handling, may be damaging to the health of the individual. Inhalation hazard is increased at higher temperatures (i.e., from liquid to vapour phase). Workers exposed to BDO vapour during paper impregnation, for example, complained of transient nausea, vomiting and bronchitis. When air concentrations of biphenyls were below 1 mg/m3 there was no detectable difference between exposed and unexposed workers in blood pressure, pulmonary function tests, serum creatinine values, urinary protein levels and standard blood cell counts.

If fumes or combustion products are inhaled first aid measures should focus on removing the engineer from the

contaminated area, lay engineer down and keeping them warm while they rest.

3.4. Storage of HTFs

The advice offered in the safety data sheet on how to safely store Globaltherm® Omnitech [5] is as follows:

a. Metal drum or its original container.

b. The advice of the manufacturer should be followed.

4. Discussion

CSP plants need to be operational for long periods of time to generate electricity and remain profitable.

Maintenance includes the management of HTF condition and past research has shown that condition is improved when sampled more frequently. Therefore, routine sampling of HTFs needs to be part of the maintenance of CSP plants so that plants remain in operation for extended periods of time.

HTFs need to be sampled using a closed sampling device to gain a representative sample of the fluid.

Engineers need to be trained on how to safely sample a HTF and they require regular top-ups in training to ensure safe practices are being followed.

Eutectic mixtures of BDO are commonly used in CSP plants and need to be handled and stored safely. The safety data sheet is the "bible" when determining how a fluid should be managed. Again, this needs to be considered as part of the regular training of engineers coming into contact with HTFs.

5. Conclusions

It is generally good advice to avoid the detrimental effects of thermal degradation and this can be done by routine monitoring of HTF condition. Maintenance plan needs to be conducted on a regular basis and need to assess both the condition and contamination of a HTF. Sample reports can then be used to build a picture of the HTF's condition over time and used to plan interventions to help sustain the working life of the HTF. This will help to avoid unnecessary and costly system shut-downs.

It is also advisable to have your HTF sampled and chemically analysed by a company that specialises in this sector such as Global Heat Transfer. This will allow a live sample to be taken and this allows a representative sample to be gained whilst the HTF is in operation.

Engineers should consult the safety data sheet for a BDO HTF to ensure they know how to safely handle and store the fluid. General advice offered in the safety data sheet for Globaltherm® Omnitech [5] is as follows:

a. Do not allow clothing soaked with a BDO HTF to come into contact or stay in contact with skin.

b. Avoid all personal contact with a BDO HTF, including inhalation and ingestion.

c. To wear protective clothing as there is a risk of exposure to the BDO HTF when sampling and when handling this fluid.

d. The decomposition products of BDO HTF are potentially flammable and hazardous to humans.

e. To ensure that PPE is worn when sampling, handling and storing a BDO HTF.

Abbreviations

BDO, biphenyl and diphenyl oxide; CSP, concentrated solar power; HTF, heat transfer fluid; HTF system, heat transfer fluid system; PPE, personal protective equipment.

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