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Heat transfer fluid life time analysis of diphenyl oxide/biphenyl grades for concentrated solar power plants

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Abstract

To gain a better understanding of how purity affects fluid degradation in concentrated solar power (CSP) plants, commercially available eutectic diphenyl oxide/ biphenyl heat transfer fluids were tested for their thermal stability at different temperatures and for their chlorine content. A model for thermal degradation of the eutectic diphenyl oxide/ biphenyl fluids in a parabolic trough CSP plant was built based on laboratory testing results and average fluid analysis results from operating CSP plants. Fluid degradation was compared between high quality product at 99.9% purity such as DOWTHERM™ A Heat Transfer Fluid and commercially available products with purities around 99.5%. A range of 1.7-2.4 times more degradation was determined for 99.5% purity fluids compared to the 99.9% quality for the operating conditions in a CSP plant. More frequent degradation separation operations are needed for lower 99.5% purity fluids, which ultimately means extra operating cost. In addition to that, the additional new fluid refills needed over a 25 years of operation is $2/kg.

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Keywords: Heat transfer fluids; diphenyl oxide; biphenyl; degradation; purity; chlorine

1. Introduction

A synthetic organic heat transfer fluid (HTF) consisting of 73.5% diphenyl oxide (DPO) and 26.5% Biphenyl is used by today's parabolic trough concentrated solar power (CSP) technology to transfer the heat from the solar collectors to the power cycle. The most commonly used grades of HTF in CSP plants have a purity as high as 99.9% and chlorine levels below the detection limit of 0.2 parts per million (ppm) and have been successfully used for over

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20 years. This grade contains high purity DPO with the lowest impurity level which is usually produced by the reaction of phenol over a catalyst. This process does not involve any chlorinated organic compounds. High quality material produced by this process will typically have non-detectable levels of chlorine since none is used in this production process.

A second method to produce DPO involves the reaction of monochlorobenzene with phenol. In this process, it is common to have some residual chlorine containing compounds left in the finished product. In reviewing producer specifications, chlorine levels of 40 ppm or even higher have been allowed in some DPO grades. These residual chlorine containing compounds can break down at elevated temperatures and result in chloride being present in the system. The reaction of the second method is also less selective, which requires a more complex separation process and leads to higher impurity concentrations such as 0.5%.

As grades with lower purity may bring advantages in regards of lower HTF cost, the effects of these alternative grades have been investigated and are discussed in this report. The most relevant HTF property is the degradation of the HTF which causes a change in the fluid properties that mostly have a negative impact to the system resulting in higher operating costs. Degradation is a chemical change of the HTF's molecules caused by many factors such as heat, oxygen, impurities and many more.

This report discusses the impact of the purity of different DPO/biphenyl grades on parabolic trough based CSP plants. The degradation behavior of other purity grades was tested [1, 2] in the past, but the meaning for the complex operation of a parabolic trough solar CSP plant has not been studied.

Laboratory test data for different DPO/biphenyl grades and sample analysis data from CSP plants were used to build a fluid life time model.

Additionally, the effects of chloride contaminants in DPO/biphenyl blends on carbon steel and stainless steel is discussed in relation to pitting corrosion and chloride stress corrosion cracking at high temperature.

2. Assumptions and analysis

2.1. Degradation testing

Thermal degradation is impacted by many factors that have been studied in diverse DOW internal reports and DOW customer feedback:

- Fluid temperature
- Initial impurity concentration (organic and inorganic)
- Concentration of degradation products in HTF
- Low boiler / high boiler ratio in the HTF
- Degradation product composition
- Oxygen accessed to the fluid (e.g. lack of Nitrogen quality)
- Metal surface to HTF mass ratio due to catalytic effects from construction materials
- Contamination of HTF (e.g. pipe conservation oil, residues from construction, oil from pump seal system, etc.)

The first three points from the above list have been covered in this study. Unused DOWTHERM™ A HTF (99.9% purity) and 5 commercially available samples of DPO/biphenyl fluids at 99.5% purity were degraded at 400°C. The degradation concentration of the samples was determined after 6 weeks. Then further degradation testing at different time periods of heat exposure at 371°C, 399°C and 427°C were performed for unused DOWTHERM™ A HTF and one representative grade with 99.5% purity. The tests were performed according to DIN 51528 and ASTM D-6743. Cleaned stainless steel pins of 1" diameter were filled with the HTF samples. Before the pins were closed the vapor spaces were filled with nitrogen at 99.9% purity. By these actions the oxygen level, the metal surface to HTF mass ratio and the contamination level were put constant in the laboratory test.