DECISIONS, DECISIONS

Edward Cass, Paratherm, USA, looks at the chemistry of heat transfer fluids and what must be considered when selecting them.

In the oil and gas sector, the term 'downstream' generally refers to the facilities responsible for removing impurities and converting oil and gas raw materials into useful products for other industries and the general public. Critical outputs of the downstream sector include gasoline, jet fuel, heating oil, asphalt products, lubricants, and myriad others. While they account for only a very small portion of hydrocarbon end-uses, heat transfer fluids (HTFs) are a niche but important output of downstream production.[1] Hydrocarbon-based HTFs have well-established advantages over steam, glycol or direct heating process operations. These fluids are specifically engineered for heat transfer service, with an ideal combination of purity, stability and efficiency to meet the demands of various industrial heating processes. There are many suppliers and product options available to the end-user when it comes to choosing an HTF, but there are several criteria the specifier should be aware of before making a final decision. Herein is a look at the various types of hydrocarbon fluids available on the market, key performance differences, and recommendations for matching a fluid to an application.

Hydrocarbon HTFs

The chemistry of a given HTF dictates its specific physiochemical properties and operating range. HTFs have historically been divided into two categories – mineral oil and synthetic. Most of the time, the minimum and maximum operating temperatures are enough to help narrow whether a synthetic or a mineral oil will be most suitable for a given application. However, there are subcategories of both fluid types worthy of further examination. Mineral oil is a catch-all term, which includes different grades and purities of paraffinic oils, naphthenic oils, and blends thereof. Synthetic is also a catch-all term, collectively accounting for benzene derived fluids with favourable heat transfer characteristics. Mineral oil fluids are generally considered cost-effective robust choices for applications operating to a maximum 550 – 600˚F. Synthetic fluids are generally more expensive but can provide fill-for-life performance in the mineral oil operating range in a well-designed and maintained system. Synthetic fluids are also the obvious choice when operating above 600˚F.

Mineral oil HTFs

Mineral oil HTFs (also known as hot oils) are those formulated from the base oils produced in the downstream refining processes. The American Petroleum Institute (API) classifies petroleum base oils into three groups:

- Group I – base oils with a viscosity index of 80 – 120, and containing less than 90% saturated hydrocarbons and/or more than 0.03% sulfur.[2]
- Group II – base oils with a viscosity index of 80 – 120, and containing at least 90% saturated hydrocarbons and no more than 0.03% sulfur.
- Group III – base oils with a viscosity index of 120 minimum, a minimum 90% saturated hydrocarbons and maximum 0.03% sulfur.

Mineral oil HTFs derived from all three groups are available from various suppliers. The least expensive fluids on the market are Group I based, but these are generally considered inferior to Group II and III type fluids due to lower thermal stability and higher fouling potential. Most global base oil production has shifted to Group II or better base oils, largely driven by modern engineering and regulatory requirements. This shift is advantageous since higher saturates content and reduced heteroatoms (sulfur/nitrogen-containing species) means improved purity and stability.

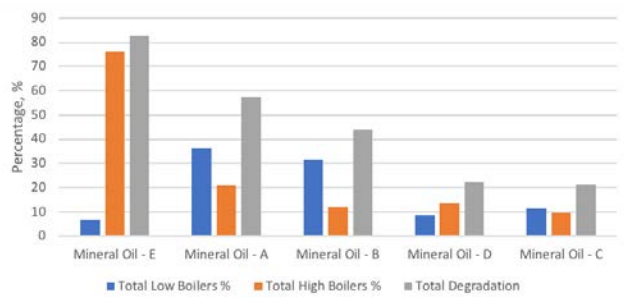

Figure 1. Thermal stability results of five commercially available mineral oils. Samples were held at 343˚C for 500 hours.

It is important to note that mineral oil HTFs are distinctly different formulations than lubricant oils. Base oil chemistry may be similar, but many commonly used lubricant additives such as extreme pressure and anti-wear agents (EP/AW), defoamers, demulsifiers, viscosity index improvers, corrosion inhibitors, etc. are not rated for the high temperatures experienced in heat transfer systems. Many additive chemistries tend to foul heat exchange surfaces or may decompose into reactive species that can catalyse fluid degradation. For this reason, it is important to specify an HTF from a reputable supplier offering fluids that have been specifically formulated for heat transfer service. If the supplier cannot provide thermal property data over the operating range of the fluid, it is likely that the fluid is not ideally suited for heat transfer service.[3]

Narrowing the field comes down to considerations such as cost, operating range, and thermal stability. The cost of a mineral oil fluid is generally tied to its expected performance, with the top tier being highly refined white oils and specialty naphthenic blends. These fluids have proven stability advantages, and many achieve food grade status.

Thermal stability is often determined using laboratory ampoule tests. A candidate fluid is sealed in a test cell and continuously held at high temperatures. Degradation is measured using gas chromatography to quantify low and high boiling species formed as a result of the thermal stress. The lower the 'total degradation', the better the stability. Figure 1 illustrates the results of such testing, comparing several commercially available mineral oils. The samples were held continuously at 343˚C for 500 hours. All fluids tested are considered mineral oils, however their results vary greatly as a result of the differences in their molecular structure. Mineral oil E is a paraffinic mineral oil that experienced nearly 83% degradation. Under identical conditions, mineral oil C experienced only 21% degradation. There is no proven correlation between ampoule tests and fluid lifetime in practice, however an extrapolation of laboratory results to real-life would indicate that mineral oil C is likely to last three to four times longer in a well-designed and maintained system.[4] The highest performing mineral oils will generally have a wider operating range and will exhibit minimal degradation at the recommended operating temperature.

Table 1. Typical properties of the most commonly used synthetic HTFs

Synthetic fluids in heat transfer	Temperature range (˚F)	Vapour pressure at maximum temperature (psia)	Boiling range (˚F)
Hydrogenated terephenyl blends	25 – 650	Below atmospheric	> 700
Diphenylethane blends	-40 – 650	> 50	< 525
Diphenyl oxide / biphenyl blends	60 – 750	> 100	< 500
Dibenzyl toluene blends	25 – 660	Below atmospheric	> 700
Alkylated biphenyls	-25 – 660	Below atmospheric	600 – 700
Diaryl / triaryl ether blends	10 – 715	> 20	< 600
Alkylated benzene blends	-15 – 575	Below atmospheric	> 600

Synthetic HTFs

Table 2. Summary comparison of mineral oil and synthetic HTFs		
Fluid type	**Mineral oils**	**Synthetics**
Pros	n Cost-effective n Capable to 550 – 600˚F n Low vapour pressures n High boiling points n High flash points n User friendly/low toxicity n Little to no regulatory restrictions n Broad material compatibility n Food grade available	n High thermal stability n Capable to 750˚F n Good low temperature performance n High solvency n Vapour phase operation n Soluble degradation by-products n High flash and autoignition temperatures n More efficient vs mineral-based
Cons	n Limited low temperature performance n Low to moderate solvency n Insoluble degradation by-products n Low boiler accumulation n Often relabelled/improperly formulated n Higher fouling tendency n Less efficient vs aromatics	n Handling and disposal n Regional regulatory restrictions n Can have high vapour pressure n Higher cost vs mineral-based n System engineering complexity n Narrowed material compatibility n Narrowed supplier options

The downstream segment produces another class of hydrocarbons known as aromatics. In heat transfer, synthetic fluids are also known as 'aromatics' since they are benzene-based chemistries. These fluids tend to have narrow boiling ranges vs their mineral oil cousins, so operation in both the liquid and vapour phase is possible. Synthetic aromatic fluids can offer many benefits over conventional mineral oil-based fluids, such as enhanced thermal stability, better low temperature performance, wider operating ranges and extended fluid lifetimes. These fluids tend to be more hazardous in terms of handling, disposal and environmental impact.

There are a wide range of synthetic HTFs available on the market, but there are less suppliers of these specialty fluids. Table 1 highlights the most popular synthetic varieties in use globally. For these fluids, maximum temperature, boiling point and vapour pressure vary widely, and many of these fluids are suitable for operation in both liquid and vapour phase. Cost generally increases with performance, so fluids that can operate at temperature extremes or over a wide operating range tend to be more expensive. Temperature ratings for synthetics are set based on laboratory tests and established field performance.

There are a handful of other synthetic chemistries used for more niche applications such as silicones, cycloalkane blends, polyalkylene glycols, isomerised alkanes, fluorocarbons, esters, and polyalphaolefins to name a few. Since their use is limited to special applications, they will not be discussed here. Table 2 summarises the pros and cons of mineral oil and synthetic fluids.

Considerations for HTF selection

There are several considerations for proper HTF selection, however, the following provide a good starting point when reviewing candidate fluids:

Maximum bulk temperature

A critical fluid property directly related to thermal stability. Operating at or above the bulk temperature will ensure rapid degradation of the fluid. The wider the gap between the operating temperature and maximum bulk temperature, the longer the fluid will last in a well-designed and maintained system.

Low temperature properties

These are typically reported as minimum operating temperature, minimum start-up temperature, pumpability and/or pour point depending on the manufacturer. The key thing to consider is the lowest temperature that any part of the process will experience. The circulation pump needs to be capable of moving fluid at its highest possible viscosity depending on the environment. Heat tracing can help overcome low temperature limitations of a fluid but can be expensive to implement.

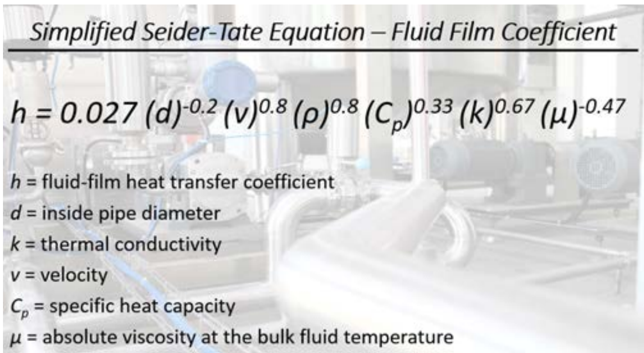

Figure 2. Simplified Seider-Tate equation for comparing HTF efficiency.

Heat transfer efficiency

More efficient heat transfer means less energy usage and potential for lower process temperatures. Thermal efficiency is maximised with a combination of high specific heat, high thermal conductivity, high density and low viscosity. A comparison of efficiency between two or more fluids can be estimated using a simplified version of the Seider-Tate equation (Figure 2). Higher film coefficients equate to higher thermal efficiency.

Cost

As the adage goes, you get what you pay for, and it is well-advised that a fluid is not chosen on price alone. Choosing a lower cost product up front may lead to more costly fluid replacement down the road. Conversely, it is also possible to 'over-specify' a fluid for a given application wherein the upfront cost of a higher performing product may not be justified for the process temperatures.

Safety properties

Any connection in a heat transfer system can become a potential leak point. Therefore, when possible it is wise to select a fluid with a high boiling point, low vapour pressure and high autoignition temperature. Combining these properties helps to ensure that fire risk is minimised as much as possible in the event of a leak. High boiling point and low vapour pressure mean the system can be designed to operate at a lower pressure (often atmospheric). It is also important to consider the hazard profile of the candidate fluid. Many synthetics present handling and environmental concerns and can require dedicated waste streams for disposal. Conversely, most mineral oils are innocuous and used fluid can generally be disposed of with other non-hazardous lubricant oil waste.

Protect the investment

Even the most expensive, highest performing HTF can fall victim to rapid degradation if suitable controls are not in place. It is wise to routinely inspect the system for leaks or other abnormalities, and to regularly log system performance metrics (pressures and temperatures, etc). Most fluid manufacturers offer annual HTF analysis to monitor critical properties and prevent unwanted surprises. A well-designed system will also do well to protect the investment, and will include provisions such as:

- Nitrogen blanketing, buffer tanks or seal pots to minimise or eliminate oxidation.
- Pumps rated for the design temperature and flow rates required by the process.
- Gauges and controls to monitor performance and maximise safety and efficiency.
- Adequate expansion and drain structure to handle thermal expansion and discharge volume.

Final thoughts

Hydrocarbon based HTFs include many different chemistries, and understanding the chemistry helps the end user make an informed decision when selecting an appropriate HTF. A good candidate fluid will provide many years of continuous, efficient service on the initial charge, and routine fluid analysis can help catch mechanical system issues before they become catastrophic. Mineral oils are generally not used above 600˚F and synthetic fluids are seldom used under 500˚F. For everything else, the preceding discussion should be valuable to the heat transfer practitioner for making a wise decision for the most suitable fluid.

Notes

1. The scope of this article excludes silicones, glycols, and any other non-hydrocarbon-based HTFs.
2. Viscosity index is a unitless measure of the change of viscosity with temperature, commonly associated with lubricating oils.
3. Thermal property data includes density, viscosity, thermal conductivity, heat capacity, and vapour pressure over the recommended operating range.
4. A well-designed system is properly engineered to balance and monitor operational stresses and eliminates or mitigates fluid degradation pathways.