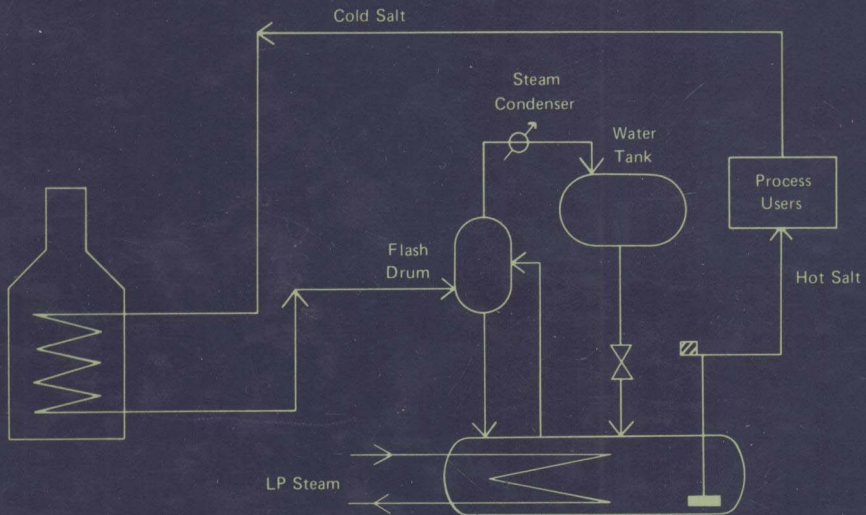


# HEAT TRANSFER FLUIDS AND SYSTEMS FOR PROCESS AND ENERGY APPLICATIONS



**JASBIR SINGH**

# Heat Transfer Fluids and Systems for Process and Energy Applications

JASBIR SINGH

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## Preface

There is a wealth of literature covering most theoretical aspects and design methods for heat transfer equipment. However, the step that precedes detailed design—the selection of the overall system—has largely been neglected. This aspect is becoming increasingly important with continued emphasis on energy conservation leading to the integration of heating, cooling, and power generation systems.

The overall system specification in terms of the hardware involved and performance obtained is dictated primarily by the heat transfer fluid(s) selected. The fluid choice defines to a large extent the design and performance of the system, and it is from this standpoint that the subject of heat transfer system selection and design has been approached in this text.

The overall objective of the book is to present the basic principles and engineering data governing the process design of indirect heat transfer systems. Included in the scope are systems using steam/water, combustion products and other gases, organic fluids, salts, and liquid metals, covering aspects of simple heating/cooling, power generation, and combined heating/power. The book is intended primarily for applications in the process and energy industries and is aimed at both professional engineers and students. The emphasis is on the selection of systems based on common engineering criteria such as performance, reliability, and cost but with particular focus on energy conservation and safety. For engineers new to the field, it is also intended to serve as an introduction, covering the basic principles, the hardware involved, and practical considerations and constraints.

Sample calculations are included either to help to illustrate important technical points or to explain the application of data/equations presented in the text.

The theoretical presentation, which has been kept to a minimum, is included to allow an appreciation of the basic laws governing system performance and the parameters that affect design. Where purely theoretical treatment is inadequate for process design, it is supplemented by empirical data. Detailed referencing is included in each chapter to allow more detailed study, particularly where space limitations have prevented a full discussion.

The system of units is essentially SI, particularly in calculations. In the presentation of some of the data, more "practical" units (such as bar, centipoise, °C) are used, especially if the equivalent SI unit is obvious.

The author wishes to thank the management of Badger for allowing the use of various facilities within the company, and particularly Mr. D. C. Ferrari for encouragement in the first instance. Thanks are also due to Mr. P. E. Minton and Dr. P. J. Heggs for reviewing the manuscript, and especially to Sandra Hodge for much practical help and valuable comments.

Jasbir Singh



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# 1

## General Aspects of Indirect Heat Transfer

### 1.1 INTRODUCTION

Heat transfer represents one of the most important steps in industrial processing, encompassing many widely differing industries and disciplines. The subject in its broadest sense can be divided into two categories. The first is transfer of heat at temperatures well below  $0^{\circ}\text{C}$ , such as in air liquefaction plants. The second category involves transfer of heat at temperatures near atmospheric up to  $1000^{\circ}\text{C}$  and above. Heat transfer at low temperatures is normally termed refrigeration or cryogenic technology and the fluids involved in such cases are therefore called refrigerants. The subject of this text is the second category, involving temperatures above ambient and the term heat transfer fluids is generally reserved for heat transfer media in this high-temperature range. The most common fluids applicable in this range include air, products of combustion (flue gases), and water; organic fluids comprise the next largest category; and in the final category, molten salts and molten metals serve a small but important sector of industry. The nature of the fluids involved, in particular combustion products and steam, and the urge to conserve energy, establish a strong link between simple indirect heat transfer and energy generation and conservation. This means that efficient heat transfer includes features of power generation and fuel conservation.

## 1.2 RANGE OF FLUIDS

Fluids used for heating and cooling in the process and power industries include gases (such as air, products of combustion, and helium), water and steam, organic mineral oils (manufactured and sold by the major oil companies), organic synthetic fluids (manufactured primarily by the major petrochemical companies), a limited number of silicone-based fluids, inorganic molten salts (principally nitrates and nitrites of sodium and potassium and chloride-bromide mixtures of aluminum), and molten metals (limited largely to sodium and potassium).

Water is the most common heat transfer medium; it can be used as a liquid or as a condensing vapor, is readily available and cheap, and offers the highest rates of heat transfer. The technology for using water (or steam) is well understood, and equipment is readily available and fairly inexpensive.

At temperatures between 0 and 100°C, water can be used without any decomposition or corrosion problems and very little fouling. Below 0°C, water freezes, so additives such as ethylene glycol must be added to depress the freezing point.

The drawbacks of water become serious when temperatures above 150 to 200°C are required. The thermodynamic properties of water are such that at these temperatures extremely high working pressures have to be maintained. For instance, to exchange heat by condensing water vapor at temperatures between 250 and 350°C, pressures between 40 and 148 bar are required. Similarly, if water is to be used over the same temperature range, saturation pressures of 41 to 169 bar are required. Hence the use of water (or steam) at elevated temperatures involves the operation of equipment at very high pressures, which is costly. Also, at temperatures above 200°C, the presence of air and salts dissolved in the water results in very high rates of corrosion; this effect becomes more pronounced with temperature rise. Therefore, in plants using high-temperature water (or steam), extensive purification facilities have to be installed, adding further to the cost.

The main advantage of gases as heat transfer media is that they can be used at very high temperatures without any thermal decomposition. However, there are disadvantages—nonuniformity of heating, difficulty in temperature control, and very low rate of heat exchange—features arising from the low thermal conductivity and heat capacity of gases compared with liquids.

The low heat transfer rate of gases is a particularly serious drawback in that very large and costly heat exchangers are needed. As a result, heating via gases is economically feasible only if hot gases are present as a by-product or are products of combustion (flue gases). As for cooling, air plays an important role in the process and power industries. The exception is in the nuclear industry, where helium and CO<sub>2</sub> are used in gas-cooled reactors.

Organic compounds form a large category of fluids which is rapidly replacing water in the high-temperature range. This includes substances that have freezing points as low as  $-50^{\circ}\text{C}$  and others that are chemically stable up to temperatures of about  $420^{\circ}\text{C}$ . Included are synthetic hydrocarbons formulated from ester-based compounds or various aromatic mixtures, all of which are available under a variety of trade names. The primary advantages offered by these fluids are:

- Noncorrosiveness to most common metals
- High thermal stability (within the recommended operating limits)
- Little or no pressurization needed even at high temperature, in most cases

Degradation of these substances results from ingress of air, ingress of contaminant material, and overheating. Air can enter the system through joints and the expansion tank. The contaminant may be process material that leaks in through heat exchanger tubes, or residue and breakdown products of material left in the system prior to filling with heat transfer fluid.

Under normal operating conditions, organic fluids can be used for many years, but once degradation starts, the breakdown material can produce poor circulation, reduce the heat transfer coefficient, and even cause carbon formation inside the tubes (or the shell). The carbon deposits encourage still more thermal degradation, eventually rendering the heat transfer medium useless.

Use of organic fluids requires stringent leakage and joint failure control since they are all flammable, most are irritating to the eyes and/or skin, and some are quite toxic. Most of these fluids freeze at about  $0^{\circ}\text{C}$  or above, and those that have subzero freezing points can be employed only up to temperatures of approximately  $250$  to  $300^{\circ}\text{C}$ .

One widely used organic fluid is the eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl, sometimes referred to as Dowtherm (strictly, Dowtherm A\*), and sold by a number of companies under various names. This fluid can be used at temperatures of up to  $400^{\circ}\text{C}$  as a vapor or as a liquid, under a pressure of about 11 bar.

A possible substitute for this mixture is a hydrogenated terphenyl known as Santotherm 66<sup>†</sup>, which is usable at a lower temperature and can be circulated at virtually atmospheric pressure. A synthetic hydrocarbon material, Santotherm 88<sup>†</sup>, which is solid at room temperature (melting

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\* Dowtherm A and Dowtherm J (discussed below) are trade names of the Dow Chemical Company.

† Santotherm 66 and Santotherm 88 are trade names of the Monsanto Company.

point 145°C) can be used up to temperatures of 400°C, requiring an over-pressure of only about 2 bar.

Fluids that exhibit subzero freezing points include mineral oils (e.g., Essotherm 500\*), mixtures of alkylated aromatics (such as Dowtherm J), and several others. Their main advantage over the higher-temperature ones, apart from low freezing point, is their very low vapor pressures, enabling fairly low pressure equipment to be used.

The choice of organics has been widened even further by the introduction into the general heat transfer field of fluids that were originally used for cooling electrical components. Recently, compounds (called Midel fluids†) formed by reacting tri and tetra esters of a glyceride (pentaerythritol) with natural fatty acids, originally used as liquid dielectrics, have been introduced. These fluids have very low toxicity, a freezing point of -50°C, stability up to about 300°C, and low vapor pressure. They are likely to present a serious challenge to the mineral oil fluids mentioned above. Until a few years ago, chlorinated diphenyls (such as Aroclor 1248) were readily available and had the distinction of being nonflammable. Unfortunately, they were also nonbiodegradable and regarded as environmentally undesirable and are no longer used.

Many metal chlorides and bromides can be used as heat transfer media, their chief limitation being high melting point. Most of the attention has been focused on the eutectic mixture of approximately 25%  $\text{AlCl}_3$  and 75%  $\text{AlBr}_3$ . This has a melting point of 68°C and can be used as a liquid up to about 200°C and as a vapor or a liquid above 200°C.

Many combinations of nitrite-nitrate salt mixtures are possible, but the one most frequently used and commercially available is the triple eutectic 40%  $\text{NaNO}_2$ , 7%  $\text{NaNO}_3$ , and 53%  $\text{KNO}_3$ . This salt mixture has a melting point of 143°C, a boiling point in excess of 1000°C, and very low corrosivity to common metals. It is used only in the liquid phase, at temperatures below 550°C, and has a very low vapor pressure.

Although metals such as tin, bismuth, cadmium, and lead have all been considered as possible heat transfer media, only sodium, sodium-potassium alloys, and mercury have actually been used. They can be used at temperatures of 1000°C or above, at virtually atmospheric pressure, and without fear of decomposition. However, they do have a number of undesirable properties; they are all toxic and very expensive. In addition, sodium can dissolve certain metals at high temperatures, reacts violently with water, and burns in air.

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\* Essotherm is a trade name of the Esso Petroleum Company.

† Midel is a trade name of the Micanite and Insulator Co. Ltd.

### 1.3 INDUSTRIAL PROCESS HEAT DEMAND

The present applications of heat transfer fluids and probable future developments may be established from the distribution of heat demand in industry. Two major reports [1,2] published in 1977 analyzed the trends in energy consumption in the United States based on standard industrial classifications. Of the  $16 \times 10^{18}$  J ( $21 \times 10^{15}$  Btu) of energy consumed by industry in 1976, 68% is estimated to have been used for process heating, covering temperatures from below 100°C to above 1100°C [3].

Industrial process heating applications can be divided into three categories: low temperature (below 290°C), medium temperature (between 290 and 590°C), and high temperature (above 590°C). Rather surprisingly, the high-temperature category is the largest, accounting for about 50% of the energy consumed for heating, while the low-temperature category comprises about 28% of the total heat used by industry.

The high-temperature heat consumers are concentrated in a few industries and include primary metals, stone, clay and glass products, and chemicals. The number of facilities in this category is also quite small, the number of iron and steel plants in the United States, for example, totaled only 43 in 1973 [3].

The medium-temperature-range consumption is even easier to identify, over 95% of it being in the petroleum refining industry. The number of U.S. refineries at present is about 300 and their consumption amounts to about 4% of total U.S. energy requirements. A typical refinery consumes about 5 to 10% of the energy content of the crude oil processed and approximately 80% of this energy is used to provide process heat at temperatures above 370°C.

In contrast to the medium- and high-temperature energy consumers, low-temperature consumers are extremely varied and very large in number. The plants in this range are much less energy intensive and widely spread. They include such varied establishments as textiles and dairy foods. These two industries alone comprise nearly 5500 sites in the United States.

If the available heat transfer fluids are considered in the light of the foregoing trends in industrial heat consumption, it is clear that excluding molten metals and gases, the fluids can cover less than 50% of heat requirements. When it is recalled that even applications down to about 350°C often use direct-fired heating (such as crude oil preheating furnaces), indirect heating probably accounts for about 30% of industrial heat consumption.

### 1.4 SELECTION CRITERIA FOR HEAT TRANSFER SYSTEMS

The main parameters to consider in the selection of heat transfer fluids are:



- Temperature limitations
- Heat transfer coefficient
- Cost of fluid
- Limitations on materials of construction
- Fluid treatment or degradation
- Operating pressure
- Hazards associated with fluid
- Ease of operation
- Energy conservation/power generation possibilities

The first consideration must be whether or not the fluid in question can withstand the process operating temperature. This will usually cut down the choice if the temperature is high, say over 300°C, where the number of suitable fluids is limited. The next four items—heat transfer rate, initial fluid cost, degradation rate (or treatment costs), and materials of construction—are basically all related to installation and operating costs. For example, a low heat transfer coefficient implies large heat exchangers and thus involves large initial investment. Operating pressure also has an effect on investment, since high pressure requires thicker vessels and piping and possibly more sophisticated controls. High pressure also has an impact on the hazard potential. Boiler explosions, for example, can have devastating effects due to the enormous pressure released as a result of catastrophic failure. Fluids used at lower pressure may pose other hazards—they are often flammable, many are toxic, and they can be irritating to the eyes and skin.

The simplicity of a heating or cooling system, which is a function of many process and engineering variables, including the fluid used, can have a large influence on its reliability. Systems with complex operating procedures and involving large numbers of delicate process items will be unpopular with operating staff and may add to the frequency of failures and result in poor temperature control. One example of operating complexity is the dewatering facilities that may be required. Mineral oils have a freezing point well below 0°C, the diphenyl-diphenyl oxide mixture has a freezing point of about 12°C, and commercial molten salt mixtures freeze at nearly 150°C—indicating clearly that whereas mineral oils would need no dewatering facilities (such as steam or electric tracing) in any climate, molten salts would require extensive facilities as standard. The ease with which a system may be operated is an important consideration and can certainly determine its success or failure.

The importance of any one parameter over another depends to a large extent on the application. For small-scale laboratory projects or pilot plant studies, considerations of heat transfer coefficient, flammability, and fluid cost may be relatively unimportant in view of the small amounts of fluid that are likely to be used. The principal criterion is likely to be accurate control coupled with simplicity. In the case of a petrochemical plant requiring a large fluid inventory, the heat transfer rate, fluid