Sublimation

A non-fluid thermal separation process

Dr. G. Raouzeos, Dr. W. Schwenk

The most common application of sublimation is separation of volatile solids and purification of substances. This paper explains the p-T diagram of a pure substance, and discusses existing processes and their operation. The particular advantages of Discotherm sublimers, and examples of continuous and batch sublimation and desublimation under vacuum, are highlighted.

Figure 1 illustrates the p-T diagram (also known as phase diagram) of a pure substance. Points S→D show a sublimation process. Sublimation occurs at the sublimation point, T_S, at which the vapour pressure of the solid, P_S, equals the total pressure of the gas phase in contact with it.
In practice, there are two methods applied to promote sublimation:

- control the total system pressure, vacuum is usually applied, and
- reduce the partial pressure of the solid by introducing a high-vapour-pressure gas into the system (entrainer sublimation, see later).

Sublimation is enhanced applying heating temperatures T_H well above the triple point TP. The difference $\Delta\vartheta s$ (= $T_H - T_S$) is the driving temperature difference.

Point S corresponds to the conditions in the sublimer (vaporiser). Line SM represents the pressure drop experienced by the vapour between the sublimer vapour exit and desublimer (condenser) inlet. Line MN represents the effect of cooling and reduction of partial pressure in the desublimer. Line ND represents external surface cooling at constant partial pressure. The sublimate vapour desublimes at point D, the snow point, which corresponds to the equilibrium conditions T_D, P_D. Desublimation is promoted applying cooling temperatures T_K lower than T_D. The difference $\Delta\vartheta_D$ (= T_D-T_K) is the driving temperature difference.

A distillation or vaporisation with subsequent solidification of the vapours is known as pseudo sublimation. All it has in common with sublimation process is that the end product is a solid. Points L→D′ illustrate a pseudo sublimation process.

In common with distillation, sublimation is an operation for the thermal separation of substances. Materials are, however, solids at operating conditions. Industrially it is applied to separate volatile solids and to purify substances.

Conventional sublimation processes and methods

There will always be two operating chambers in a sublimation process, for sublimation and desublimation respectively. There are three types of process [1, 3, 4]:

- entrainer (sweep gas) sublimation,
- simple (or vacuum) sublimation,
- fractional sublimation.

Both continuous and batch operation can be employed for either process.

Entrainer (sweep gas) sublimation usually works at atmospheric pressure. The partial pressure of the product is generally between 0,1 and 0,01, that of the entrainer gas. For this reason the quantity of entrainer gas circulated per unit weight of sublimate is high, as is consequently the energy consumed for repetitive cooling and reheating of the system. Passage of sublimate to the desublimation chamber can occur by diffusion or convection, whether natural or forced.

Only part of the heat is transferred by conduction, mainly through contact of the proc-

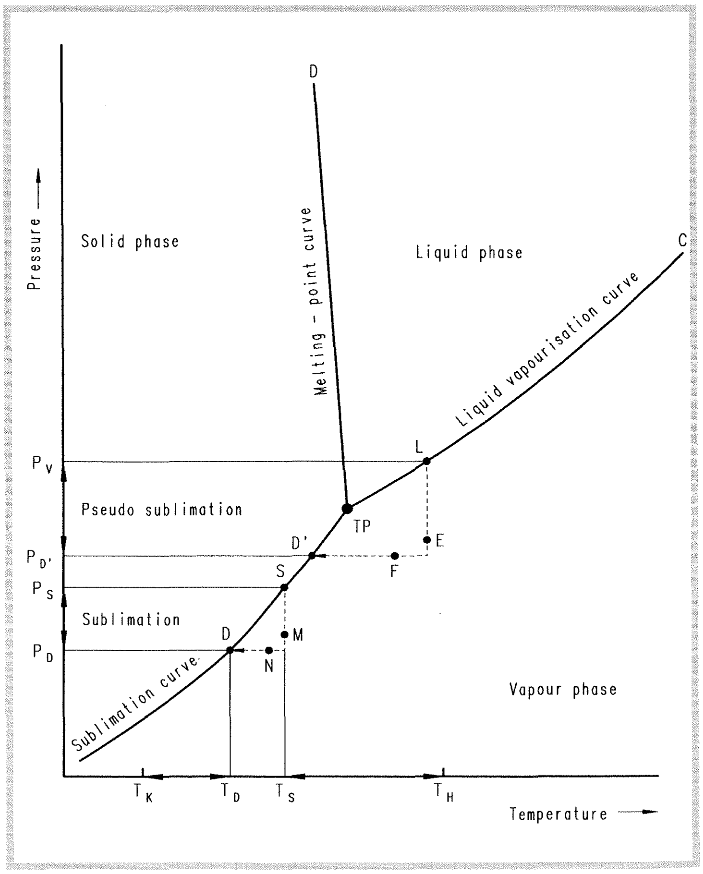

Fig. 1 The p–T (phase) diagram of a pure substance

essed material with entrainer gas which has been reheated in returning from the desublimer. Sublimate is frequently obtained in the form of loose needle shapes. As large quantities of gas are involved, with low specific heats and mass transfer rates, entrainer sublimation plants are large and require considerable space.

In the simple (vacuum) sublimation the vapour phase consists essentially of the sublimate. There will be a small fraction of gas through leakage, but this will be drawn off through the vacuum pump. The energy consumption for heating and cooling is low, as no entrainer gas is recycled. The sublimation enthalpy is the sum of the heats of melting and vapourisation. The sublimate obtained tends to be more compact with a higher bulk density.

A conventional batch-type plant consists of a sublimer (evaporator) which is usually a flat heated pan with agitator [1, 2, 3, 4]. Vapours pass to the desublimer, which is usually a large horizontal cylinder with cooling surfaces on which the product solidifies. Emptying this type of desublimation chamber is labour intensive, which runs against current needs for economic and efficient operation, and clean working conditions. A filter and vacuum pump are installed down-stream of the desublimer.

A similar arrangement can be operated with a sweep gas at atmospheric pressure, circulation being achieved with a fan or by natural convection [1, 3, 4]. To date, simple (vacuum) sublimation has been run as a batch operation, although continuous plant exists for entrainer sublimation. Fluidised bed systems, heated screws and vertical systems similar to plate dryers are in commercial use too [1, 2].

From an equipment point of view, continuous direct descublimation under vacuum presents a considerable challenge as the sublimate product has to be continuously removed from the cooling surfaces and discharged. Most attempted solutions using hammers and brushes, cooling rolls with scrapers and alternately melting condensers, have failed to prove commercially viable. An economic and operator-friendly system, based on the Discotherm B Conti, or batch kneader sublimer, is now available and is described later in this article.

Discharging sublimate from the cooling surfaces in conventional systems is problematic, either employing expensive, and often hazardous, manual labour in the case of static sublimation chambers, or by using entrainer sublimation resulting in low density, loose needle-shaped particles. The large quantity of entrainer gas used in this case greatly reduces rates of heat and mass transfer on heating and cooling surfaces. Furthermore, the steady sublimate build-up in a static desublimation chamber reduces the specific desublimation capacity of the equipment.

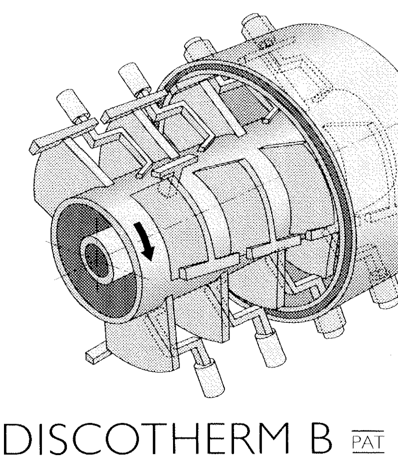

Fig. 2 The Discotherm B – operating principle

Advantages of Discotherm B sublimers

Several years of development on industrial, as well as pilot-scale vacuum sublimation units have demonstrated that Discotherm B kneader sublimers/desublimers are highly suited to the sublimation process. Discotherm B units are totally enclosed, directly heated or cooled systems with extensive self-cleanded heat exchange surfaces.

The Discotherm B is a contact processor. It comprises a horizontal, cylindrical shell housing with a coaxial agitator shaft carrying disk elements set at right angles to the shaft and peripheral kneading/mixing bars (Fig. 2). Stationary hook-shaped bars mounted in the shell interact to clean the shaft and disk elements as they rotate. The shell, agitator shaft and disk elements can all be directly heated or cooled, resulting in an extremely large heat transfer surface to equipment volume ratio. The combined effect of the intensive mixing and kneading action and self-cleaning of the heat exchange surfaces results in very high sublimation and desublimation rates (improvement of limiting factors 1, 2 and 3). For continuous operation, axial conveying is effected by the spiral configuration of the mixer bars. The Discotherm B is easily adapted to changing feed rates or material composition.

A fill level of 60 to 80% is utilised in the sublimer to allow sufficient free volume for disengagement of the sublimate vapour. The average fill level is controlled by an adjustable weir plate at the discharge. Unlike screw flight systems, axial conveying rates are not proportional to agitator rotational speed, which allows speed to be adjusted for optimal heat transfer (improvement of limiting factors 1 to 4). The disk elements, which themselves take no part in the conveying of material prevent backmixing as well as providing heat transfer surface area. Typical residence times in continuous operating units range from 0.5 to 3 hours, depending on scale. Whether or

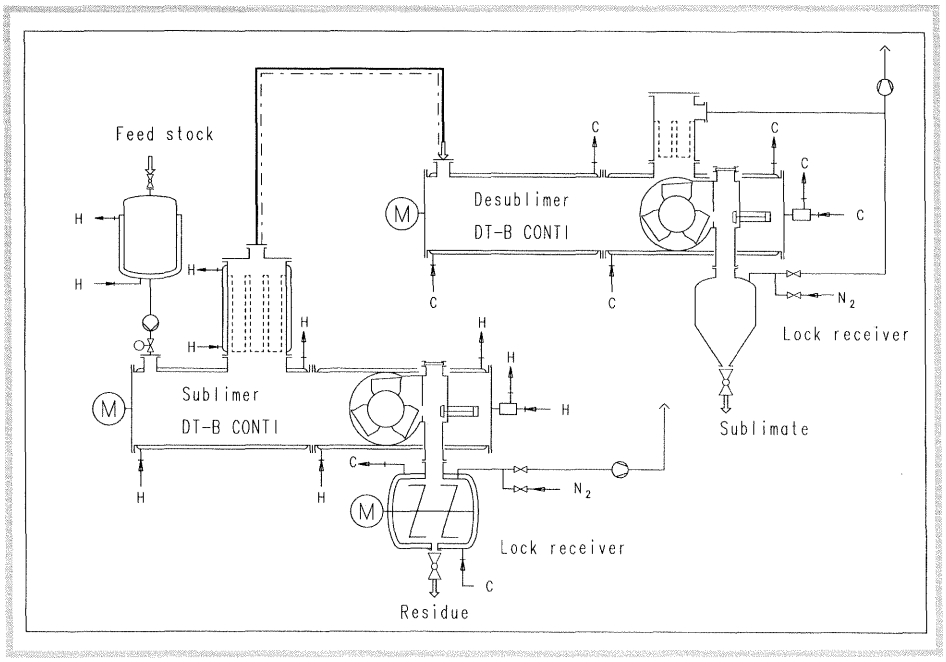

Fig. 3 Continuous vacuum sublimation

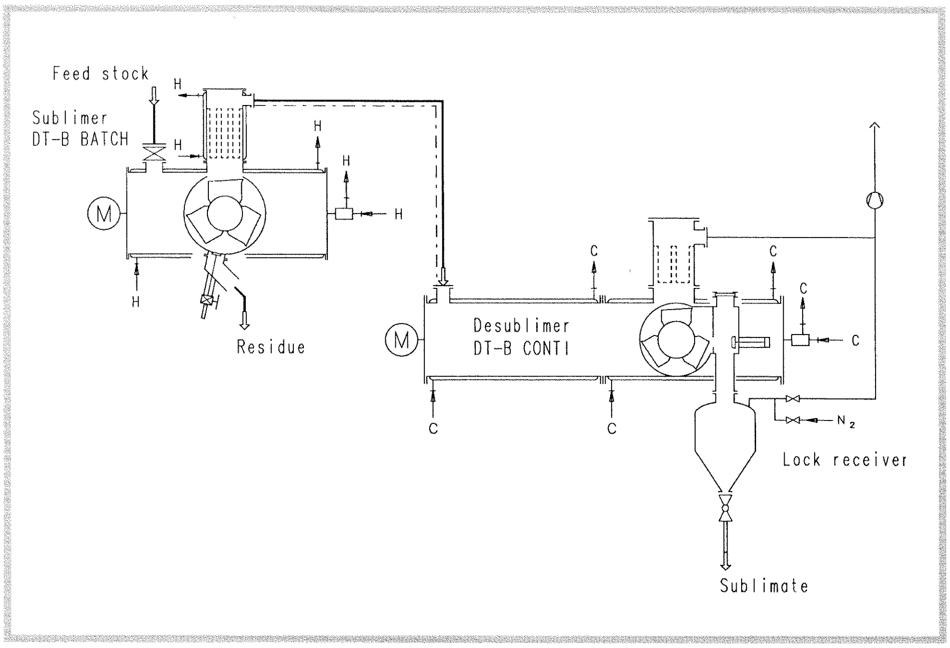

Fig. 4 Batch vacuum sublimation

not batch or continuous processing should be employed depends on the material handled and the specific process constraints of each application.

Typical applications

Figure 3 shows two Discotherm B Conti units set up for continuous sublimation/desublimation of an organic intermediate. In this instance the feed is a pumpable melt. Feed to the heated Discotherm B Conti sublimer is by means of a metering pump.

The sublimer under vacuum, at an equilibrium temperature below the melting point, causes the product to solidify with spontaneous vaporisation of the sublimate.

With the sublimer filled to approximately 2/3 of its normal volume, the sublimate is vaporised progressively from the mixture of product and residue impurity. The non-volatile, free-flowing residue is intermittently discharged through a vacuum-tight lock receiver. The vapours of the sublimate pass through a heated and jet cleaned filter and a large diameter heated vapour pipe into the cooled Discotherm B Conti desublimer. Condensation takes place, both on the cooled surfaces of the unit and the cool solid sublimate which occupies about half the machine volume. The fact that the agitated bed of sublimate contributes to the condensation process enhances the transfer of heat of sublimation to the cooling surfaces, effectively extending the condendsation area (improvement of limiting factor 4). Pure sublimate leaves the desublimator through a lock system, which discharges it intermittently ba means of alternately opening and closing two vacuum-tight valves.

A dust filter prevents sublimate fines from being entrained into the vacuum pump. Retained sublimate fines drop back into the system and are discharged.

Batch vacuum sublimation

For lower throughput rates, or for operation in conjunction with batch upstream equipment, batch or semi-continuous sublimation may be more economical. Batch processing may also be advantageous for frequent product changes or very low impurity levels. Figure 4 shows a set-up employing a heated Discotherm B Batch unit as the sublimer.

The heated sublimer is charged with raw product through a large diameter vacuum tight valve. The product is heated through contact with the heat transfer surfaces and the pure component sublimates as soon as vacuum is applied. The sublimate vapour passes through a heated filter and large diameter vapour pipe to the cooled desublimer. Non-volatile residue accumulates in the sublimer and is discharged, as required, through a bottom discharge valve. If the residue by-product fraction is small, emptying is performed only after several batches. A second, equally large, Discotherm B batch unit can be used as desublimer to contain the complete batch. In this case emptying takes place after every batch.

The desublimer may need a smaller cooling area than the sublimer's heating surface because of the greater temperature difference between condensation and coolant temperatures. Under these circumstances it would be more economical to use a smaller continuous Discotherm B desublimer and to collect the larger sublimate quantity produced by a batch in a vacuum-tight receiver. This can then be replaced of emptied at the end of each batch when the installation is vented with inert gas.

Design calculations and scale-up

Preliminary design calculation procedures for simple, entrainer and fractional sublimation are given in the literature [3, 4]. As a "rule of thumb" most applications give the following specific sublimation capacities:

- sublimation: 5 to 20 kg sublimate/m^2/h,
- desublimation: 10 to 40 kg sublimate/m^2/h.

As properties of materials and scale of operation is so variable, the appropriate equipment and process conditions need to be established by pilot plant testing, following careful consideration of process alternatives.

Sophisticated pilot plant facilities are available. Proven scale-up procedures ensure effective translation of pilot scale experience to the required commercial installation.

Further information **cpp 242**

Literature

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