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REVIEW

# Purification by Sublimation

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## Summary

Sublimation is a unit operation that could receive much greater attention in the future as a purification method. From a frequent batch process used for simple separation of a desired volatile constituent from a nonvolatile impurity, sublimation can progress to continuous, multistage methods for fractionating materials of differing volatility on a large industrial scale. This will be particularly important for materials that decompose at temperatures below the melting point and that have low solubilities in common solvents. More experimental information, particularly as regards the factors influencing the condensation of solids from the vapor, would be of value in design of equipment.

## INTRODUCTION

Sublimation is of particular interest as a future large-scale purification method. Sublimation is normally used when the material to be purified is unstable, i.e., temperature- or oxidation-sensitive at temperatures near to or below the triple point (*1*) or when the more conventional separation methods of distillation, solvent extraction, adsorption, etc., are either impossible or highly expensive. As a general rule, it is understood that a substance may be considered for sublimation purification if it is normally solid and has a reasonably high vapor pressure at moderate temperatures (economics are strongly influenced by vapor pressure as discussed below). Certain compounds listed in the literature as amenable to purification by sublimation are listed in Table 1.

A definition of terms is useful because the word *sublimation* has been used to describe the vaporization process alone as well as the entire

**TABLE 1**

Materials Mentioned in Patent Literature on Purification by Sublimation[a]

Aluminum chloride (*20*)
Anthracene (*21, 22*)
Anthranilic acid
Anthraquinone (*23, 24*)
Benzanthrone (*25*)
Benzoic acid (*26, 27*)
Calcium (*28, 29*)
Camphor (*30*)
Chromium chloride (*31*)
Ferric chloride (*20*)
Iodine (*32, 33*)
Magnesium (*34*)
Naphthalene (*35*)
β-Naphthol
Phthalic anhydride (*11, 36*)
o-Phthalimide (*37*)
Pyrogallol
Salicylic acid (*38, 39*)
Sulfur (*40–42*)
Terephthalic acid
Titanium tetrachloride (*20, 43*)
Thymol
Uranium hexafluoride (*44*)
Zirconium tetrachloride (*45, 46*)

[a] Literature references in parentheses.

operation of both vaporization and condensation (*2*). In the following discussion, the terms *solids vaporization* and *solids condensation* will be used to avoid confusion. Equally acceptable would be use of *sublimation* and *desublimation* for vaporization and condensation, respectively.

The term *entrainer* is used for the inert gas that, through dilution, lowers partial pressure of the vaporized solids at some distance from the vaporizing surface and hence increases vaporization rates and transports the vapor. The term *cooling diluent* is used for the inert gas or liquid added for condensation of the vaporized solids.

In addition to purification situations, various parts of the solids vaporization and condensation operations can also be of interest in:

1. Meteorological applications (solids condensation).
2. Vapor deposition of metals (solids condensation). A related application is fluid coking in the petroleum industry.
3. Freeze drying where ice is sublimed from a desired food or antibiotics product (solids vaporization).
4. Engineering research where the vaporization of solids offers a convenient means of measuring mass-transfer rates (*3, 4*). The object can be prediction of heat transfer or fluid friction by analogy (solids vaporization).
5. Carrying out chemical reactions not feasible in the solid state (solids vaporization and condensation).

This list is probably not complete but is illustrative of the diversified applications of this technology.

The present review involves an examination of the conditions under which sublimation can be used as a process for purification. Attention will be focused on what a sublimation process looks like and the variations in choices of engineering designs. An attempt will be made to emphasize those areas in which more fundamental information is needed if this purification process is to become more useful in the future.

## THE PURIFICATION PROCESS

There are several types of purification situations that may be amenable to sublimation methods. The sequence of operations and the general complexity of the process and plant will vary among the three situations described below.

The first is the removal of a nonvolatile impurity from the desired volatile product. Operations were usually batch and without entrainer, and the nonvolatile impurity would be either removed as a residual ash from the vaporizer or filtered from the vaporized solid. Condensation, generally also a batch operation, would be a total condensation. Most early patent references are for this process.

The second condition involves the removal of an impurity that may be more or less volatile than the volatile solid that is the desired product. This would require a fractional condensation of solids, often in the presence of a cooling diluent. The major industrial example here is the continuous purification of salicyclic acid by removing the more volatile phenol impurity.

The third purification method, which is the general situation, includes the removal of three or more separate impurities that are nonvolatile, less volatile, or more volatile than the desired solid volatile product. No industrial examples of this type are known but this method can become of interest in the future. This is the situation to be discussed here and is the one for which a general flow sheet is shown in Fig. 1. One stage of sublimation purification is shown in Fig. 1, but a specific purification process may require one or more such stages. In addition to the two major operations of solids vaporization and condensation, a number of other operations such as gas-phase filtration, vacuum generation, off-gas scrubbing, etc., may be involved. Attention in this discussion will be limited to the vaporization and condensation operations. The temperature history of the solid to be purified is shown in Fig. 2 for an operation of the type shown in Fig. 1 using both entrainer and cooling diluent streams.

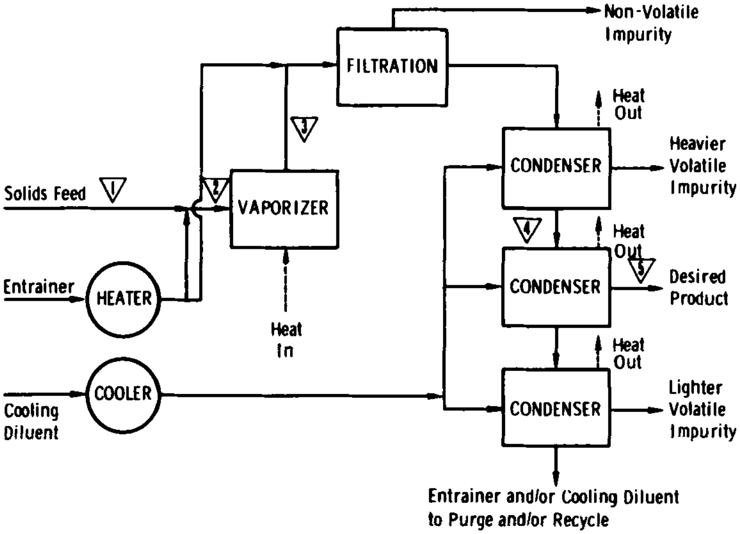

**FIG. 1.** Sublimation purification—general block flow diagram.

## THE VAPORIZATION OF SOLIDS

The first operation in a sublimation-purification process is the total or partial vaporization of the impure solids fed to the process. For design of the vaporization equipment several basic decisions are required concerning the temperatures and pressures at which vaporization will take place and the type of equipment to be used.

### The Vaporization Temperature

Vaporization temperature, i.e., solids vapor pressure, can strongly affect the economics of a sublimation-purification facility. If a high temperature is required to achieve reasonable vapor pressures, capital and operating costs also increase.

### The Vaporization Pressure

Vapor pressure is another important factor in the success of purification by sublimation. Low vapor pressures in the vaporizer must be compensated for by using higher vacuum or larger entrainer gas rates to increase the vaporization rate and transport the vapor molecules to the condenser at a reasonable rate. The choice between the use of vacuum or of entrainer gas must consider the relative advantages of each:

**Advantages of an Entrainer:**

1. Avoids equipment for production of a vacuum, avoids in-leakage and sealing problems; permits simpler vessel design.

2. More amenable to continuous operation.

3. All or part of the heat required for vaporization can be added as sensible heat of the incoming entrainer gas.

4. The entrainer gas can, in continuous operations, be used as a carrier gas to transport solids to, or through, the vaporization equipment.

5. If a particular atmosphere is necessary to avoid decomposition during vaporization, carrier-gas composition can be selected to provide the mass-action effect desired. If, for example, the decomposition problem were dehydration of the solids feed, then the entrainer gas could contain sufficient water vapor for prevention.

6. Dispersion in an entrainer gas (dense or dilute phase) during vaporization can provide closer temperature control. This is particularly important when the vaporizing solids are heat sensitive.

7. The entrainer gas can constitute all or part of the dilution sometimes necessary during fractional condensation to achieve the stage purification desired (*5*).

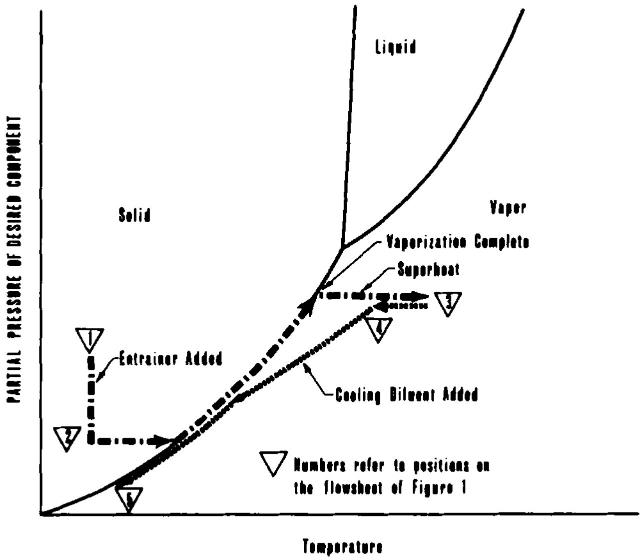

**FIG. 2.** Typical temperature profile for a sublimation-purification process.

**Advantages of Vacuum:**

1. Avoids need for another flow stream and other compounds in the system.
2. Reduces cooling duties in condensation; no entrainer gas to be cooled or condensed.
3. Avoids dilution of vapors entering the condenser. Dilution due to presence of entrainer gas can adversely affect condensation rates and size and shape of the condensed solids.
4. Total recovery of product is often higher. The fraction of desired product uncondensed per pass through the solids condenser will be greater in entrainer vaporization. Hence, recirculation of entrainer is usually necessary to minimize product losses.

### Vaporization Equipment

The type of vaporization equipment to be used must take into account that solids may be continuously vaporized in a variety of ways:

1. A bed of dry solids, without entrainer gas. This is the simplest arrangement.
2. Dry solids suspended in a nonvolatile heavy liquid.
3. Solids suspended in a boiling (entrainer) liquid. Entrainer gas is formed in situ.
4. Entrainer gas flowing through a fixed bed of the solids to be vaporized.
5. Entrainer gas bubbling through the melted solids. A situation where vaporization takes place above the triple point.
6. Entrainer gas flowing through a dense phase of the solid to be vaporized, e.g., fluidized bed or spouting bed.
7. Entrainer gas flowing through a dilute phase of the solid to be vaporized, e.g., a transfer-line vaporizer where both solid and gaseous phases are in cocurrent flow or a raining solids unit where the solids and entrainer may be in countercurrent flow.

## THE CONDENSATION OF SOLIDS

The condensation operation is particularly important since the conditions affect not only condensation rates, and hence equipment size, but also physical properties and ease of collection of the final product (*6*). The condensation operation can be affected by the method of cooling, the conditions of temperature and pressure, etc., and by the nature of the condensate, e.g., whether a solid solution or mechanical mixture of desired product and impurities.

### The Method of Cooling

In general, cooling for solids may be achieved in the following three ways (*7*):

1. Cooling through a surface is often the simplest but can involve provision for mechanically cleaning the surface to maintain heat-transfer rates and to remove product.
2. Cooling by dilution may be achieved when the coolant is a vaporizable liquid or a lower-temperature liquid or noncondensible gas. In the case of a liquid, the product would be removed from the condenser as a slurry. If a vaporizable liquid or noncondensible gas is used, the product could be removed in the dry state.
3. Cooling by expansion through a nozzle has the disadvantage of requiring either higher pressure in the vaporization operation (which must be compensated for by higher temperature or dilution) or a lower pressure in the condenser (requiring a vacuum) in order to obtain sufficient cooling by expansion.

### General Conditions

Concerning conditions for the condensation operation, the rate of crystal formation depends on properties of the condensing compound, the presence of nuclei at the condensing surface, pressure, and temperature (*8*). The condensation of solids from the vapor can be considered to involve the following three processes (*9*):

1. Formation of new solids particles from the vapor—nucleation.
2. Deposition of condensing solids into existing solids—particle growth.
3. Collision or coalescence of two particles to form a larger particle—agglomeration.

The number and shape of the crystals of condensed solids depends on the rate of nucleus formation (nucleation) relative to that of crystal growth (particle growth), and on total condensation rates per unit volume of condenser (agglomeration).

The first two processes listed above can occur in succession but more

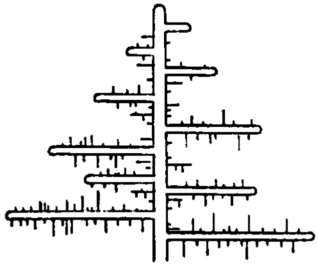

FIG. 3. Dendritic growth of a crystal.

often take place simultaneously and are thus frequently in competition. The particle-growth process is preferred in most cases, since it leads to larger particles (generally 30 $\mu$ or larger) which are easier to collect, convey, etc. A slow growth is conducive to perfection of shape. Crystallization from vapors frequently follows the dendritic pattern shown in Fig. 3 (*10*). The main stem grows quite rapidly in supercooled systems, followed first by primary branches at a slower rate and then by the secondary branches. In later stages of growth, branching ceases and the spaces between branches fill in, eventually tending toward the spherical shape. The holding of condensed solids at temperature for longer periods of time can promote the revaporization from high-curvature surfaces of higher fugacity, together with condensation on surfaces of lower curvature. The larger particles thus grow at the expense of the smaller ones, which eventually disappear, and the remaining particles tend toward increased sphericity. This treatment has been cited in the condensation of phthalic anhydride from the vapor (*11*).

The pattern of cooling for condensation, particularly initial cooling, is important because it affects the relative rates of nucleation and particle growth mentioned above. Several types of cooling curve are shown in Fig. 4. These curves are all for a simple condensation in which all heat would be removed through condenser walls and no dilution would take place. If a cooling diluent were used, the curves would be directed downward and to the left as in Fig. 2. In Fig. 4, curve AB represents a thermodynamically reversible process in which the various phases are in equilibrium at all times. Curve AC of Fig. 4 shows more rapid condensation, which would involve some degree of supersaturation. Curve AC can result in a final product in "sintered" form (*12*). This occurs because the liquid phase first formed in this cooling path aggregates a number of the solid particles subsequently formed. The liquid subsequently solidifies, giving the solid form. If this sintering is undesirable, it can often be avoided by diluting the incoming vapors with a hot fluid before the cooling diluent is added (*13*). This has the effect of moving the curve downward (and possibly to the right) from point A in Fig. 4 so that subsequent cooling can be below the triple point. On the other hand, the sintering effect can be desirable, since it reduces the number of small particles. Supersaturation (as in Curve AC) tends to create many small particles.

It is generally desirable to vaporize the solids at as high a temperature as possible and particularly at temperatures above the triple point (as in Curve AC) because:

1. Entrainer-gas requirements are reduced, because of the higher vapor pressure.

2. The melting that occurs during vaporization can be beneficial to heat transfer in vaporization.

3. The melting that occurs during condensation can be beneficial to particle size of condensed solids due to "sintering."

Often, however, it is necessary to vaporize below the triple-point temperature (as shown in Fig. 2). Examples are cases in which the triple point is very high or does not exist, i.e., decomposition takes place below the triple point.

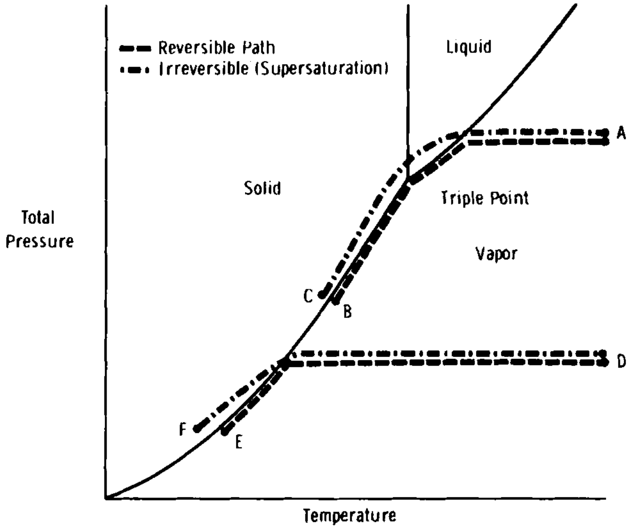

**FIG. 4.** Cooling curves for solids condensation without dilution.

### Nature of Solids Condensate

The nature of the solids condensate affects the type of crystals formed and denotes the difference between a solid solution or a mere mixture of pure crystals. The former is to be preferred, since it permits control of crystal composition. Usually a simple experiment will suffice to determine which situation exists. If solid solutions are formed, vapor-solid equilibria data can be obtained by common methods.

## EQUIPMENT DESIGN

The U.S. patent literature shows many examples of simple equipment devised for sublimation purification. References to a number of these patents are given in Table 1. Most were patented in the period 1890–1935, involved only the simplest engineering principles, and antedated much knowledge of fluidization or of two-phase flow and associated heat transfer. Solids condensation was particularly unsophisticated, consisting of batch vessels, batch removal of product, often by manual labor and often with poor recoveries of product.

The factors favoring continuous operation here are those of the chemical industry in general, viz., the need for large-scale operations, for the best control of product quality and processing conditions, and for minimum total cost of purification.

One type of solids-vaporization equipment is available commercially (*1*), but solids condensation equipment is usually designed for a particular application. This equipment often consists of field-fabricated tanks.

In a continuous process, vaporization can be continuous and condensation semicontinuous or cyclical, i.e., condensers are alternately filled and emptied of condensed solids, and gas ex vaporizer is alternately switched from one condenser to another. However, a truly continuous overall operation is desirable.

Choice between the two condensation methods of either condensing solids on cold walls by heat removal through the wall or condensing in the bulk stream by addition of cold gas often depends on the nature of the solids crystal and of the entire solids layer and of the strength of adherence to the cooler surface. The cooled-surface method is understood to be practiced in the purification of salicyclic acid from phenol impurity, in which case the condensed salicyclic-acid product collects on the wall as whisker-shaped crystals that are easily discharged by gravity fall or wall vibration. Cooled surfaces are also used for

TABLE 2

Research and Engineering Needs of Sublimation-Purification Technology

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1. Effect of cooling curve (distance from triple point) on particle shape and size of condensed solids.
2. Effect of supersaturation on particle shape and size of condensed solids.
3. Effects of other conditions (residence time, dilution, temperature level) on particle shape and size of condensed solids.
4. Methods of staging vaporization and condensation operations for minimum capital cost.
5. Translation of results to and from other scientific disciplines, e.g., meteorology.
6. Nature of the solids condensate (solid solution or crystal mixture) for specific systems of interest.
7. Condensation by expansion through nozzles.

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collection of products in $ZrCl_4$ and $TiCl_4$ purification; these are scraped from the walls by a continuously rotating chain assembly. There are a few situations, such as phthalic anhydride collection (from manufacture or from purification), in which condensed solids are melted and drained away (*14*) (cyclical operation of two or more condensers).

## FUTURE NEEDS FOR SUBLIMATION PURIFICATION

Application of the unit operations of solids vaporization and condensation to purification and separation could become of increasing interest in the future, particularly for compounds that decompose at temperatures below the melting point. In the case of monomers and certain pharmaceuticals, purification operations could be large-scale and could require multistage processing. For close design of such sublimation purification equipment, more knowledge is required in the areas of:

1. Factors affecting rates of condensation of solids from the vapor and resulting solids physical properties.
2. Multistage solids vaporization and fractional condensation.

A general survey of the literature reveals considerable work on nucleation phenomena in condensation of solids (or liquids) from the vapor (*9, 15–19*); but very few of the investigations reported studied more than one or two variables, and thus a generalized quantitative model does not appear possible at this time.

If sublimation purification is to enjoy widespread large-scale use, the development of multistage systems would be desirable. Obviously, clusters of vaporizers and condensers with various auxiliaries could be repeated, but the economic advantage would be rather limited. Some method of utilizing the advantages of staging in other separation operations, such as distillation, would be desirable. Such advantages are gravity flow of nonvapor streams between stages, inclusion of two or more stages in a single equipment shell, etc.

Table 2 lists several areas in which increased fundamental understanding could be of assistance to increased use of sublimation purification. The object of work in these areas would be more accurate engineering design methods.

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