CRYSTALLIZATION OF SUBLIMABLE SUBSTANCES FROM THE BULK VAPOUR PHASE COOLED BY EVAPORATING SPRAY OF LIQUID

J.Vítovec, J.Smolík and J.Kugler

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

A new method is described in the paper of the crystallization from the bulk vapour phase. Crystallization is effected by cooling the vapour phase by water spray in the space confined by porous walls. In order to prevent crystallization on the walls proper an inert gas is forced through these walls. A necessary minimum velocity of the inert gas through the porous walls was found as well as its minimum temperature in dependence on the vapour pressure of the sublimed substance.

Crystallization from vapour phase is applied for preparation of substances at higher temperatures such as *e.g.* production of anthraquinone by oxidation of anthracene or for isolation from mixture with nonvolatile substances by sublimation or for separation of substances exhibiting different volatility. Mostly it is worked with the vapour of the substance in mixture with an inert gas at atmospheric pressure or lowered pressure.

Crystallization from vapour phase is particularly well suited when the aim is to obtain high-grade purity substances.

Crystallization of substances from vapour phase in industrial processes takes place mostly within a few seconds because the small velocity of the gas phase would call for a large capacity equipment and long residence time in the space at high temperature might cause thermal decomposition particularly of organic substances. Cooling of the vapour mixture through a heat exchanging surface is not suitable for crystallization of thermally instable substances as it necessitates mechanical removal of the product from the cooling surface in order to preserve sufficient rate of heat transfer. This, of course, extends the residence time of the product in the space exposed to high temperature. For this reason the mixture is preferably cooled by contact with cooler liquids. Here too, though we find the undesirable partial crystallization on the walls of the equipment. This phenomenon can be avoided by *e.g.* heating the walls to a temperature above the dew point of the mixture[1]. Unfortunately, this also increases the residence in the space exposed to high temperature. Another way of avoiding crystallization on the walls is the irrigation of the

walls by cooling liquid[2]. The product is then obtained in the form of suspension which may be practical if the suspension can be directly processed in the subsequent operation.

This paper describes a new method of crystallization of substances from the bulk vapour phase by direct contact with cooler liquids[3]. The method is based on cooling the vapour phase in a volume confined by permeable walls through which an inert gas is being introduced into the cooled space creating on the interior side of the space a layer advancing toward the center of the cooled space into the bulk vapour phase containing the sublimed substance. The layer of inert gas prevents the contact of the vapour mixture with the walls and hence no crystallization on the walls can occur. The crystallization takes place in the bulk of the vapour phase by direct contact with the coolant supplied at the center of the equipment. As a coolant may serve dispersed water or other liquids or a cool gas.

EXPERIMENTAL

The apparatus is shown schematically in Fig. 1. The porous wall is formed by a glass gauze mounted to a wire frame. The wall is contained in a jacket 2 equipped with taps for supplying inert gas 3 into the space between the jacket and the porous wall. This space is divided about in the middle of its height into two parts by sealing rings made of silicon rubber. Each part is supplied with inert gas of different temperature penetrating through the porous wall into the cooled space consisting
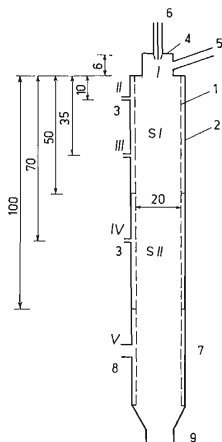

Fig. 1

Scheme of Apparatus

1 Porous wall, 2 jacket, 3 inlets of inert gas, 4 head, 5 inlet of gas mixture, 6 nozzle, 7 filter, 8 gas outlet, 9 storage of product. Distances indicated in cm.

thus from two sections SI and SII. In the head *4* of the apparatus there is a tap for supplying gas mixture *5* and a nozzle *6* for cooling liquid. At the bottom of the jacket there is a filter *7* to separate the product from the inert gas. The gas is withdrawn through an outlet *8* and the product is collected in the storage vessel *9*.

The jacket *2* is heated electrically by several heating sections to a temperature given by the condition of crystallization and the filter *7* is heated to a temperature above the dew point of water in the effluent gas mixture.

The experiments were carried out at the atmospheric pressure. The gas mixture was cooled by water spray dispersed in nitrogen in the nozzle *6*. The head of the apparatus *4* was heated to a temperature about 10 K above that of the dew point of the sublimed substance in the gas mixture. The inert gas was heated before entering the inlet taps *3* to a variable temperature depending on the type of experiment. The gas pressure was also measured in these taps. In the course of experiments the temperature was measured at the locations II—V by thermocouples. The temperature of the gas mixture at the location I was measured by a movable thermometer.

It may be assumed that crystallization of a sublimable substance in the vapour phase cooled by evaporation of injected spray of liquid in the space confined by porous walls takes place mostly in the bulk of the phase. The concentration of the crystallizing substance in the carrier gas near the walls is then relatively low. The necessary amount of inert gas penetrating through the walls in order to prevent crystallization on the walls can thus be kept low. It is not permissible that the droplets of the liquid dispersed in the nozzle hit the wall. In the opposite case the protective layer of the inert gas would be disturbed and the wall cooled by evaporation of the liquid spray would be exposed to crystallization. The maximum diameter of the cone of the liquid spray was 100 to 150 mm depending on the intensity of cooling. Accordingly, the minimum diameter of the cooled space confined by the porous walls was 200 mm.

The substance used for the model experiments was benzoic acid chosen due to its strong adhesion to cooled surfaces. This substance was thus used for fundamental experiments intended to find a minimum flow rate and minimum temperature of the inert gas penetrating through the porous walls which would completely eliminate crystallization on the walls. It was required that the efficiency of this continuous crystallization be high and that the obtained product be dry. The concentration of benzoic acid in nitrogen was varied between 2·2 and 10% by volume (0·16—1 kg/hour). This concentration was calculated from the known amount of acid evaporated per unit time and the flow rate of the carrier gas (nitrogen). The temperature of the gas mixture entering the cooled space was at least 10 K above its dew point. The gas mixture was cooled by the spray prepared by dispersing water by a stream of nitrogen in the nozzle. The amount of water supplied was adjusted according to the concentration of the crystallizing substance, flow rate and temperature of the gas mixture and experimentally found correction on heat losses (evaporation of a part of water in the head of the apparatus). The crystallization took place at atmospheric pressure. From the experiments we evaluated practical efficiency defined as

$$\eta = \Delta m / \Delta M , \qquad (1)$$

where Δm is the mass of isolated dry substance and ΔM is the mass of sublimed substance in the entering vapour mixture.

We also checked the humidity of the product caused mostly by malfunction of the nozzle. (At a proper function of the nozzle and an adequate amount of water the product was practically dry). Also we determined the mean size of the crystalls of the product.

The gas mixture of the sublimed substance and the carrier gas was continuously prepared in a laboratory sublimer consisting of a fluidized bed of inert particles[4]. The temperatures mea-

sured during experiments were those of the sublimation (position I, Fig. 1), of the inert gas in the proximity of the porous wall (positions II—IV) and of the effluent gas from the filter (position V).

The internal surface of the apparatus and particularly that of the porous wall was examined visually after each experiment.

The main portion of the substance crystallizes in the cone of the jet of water spray in the upper section. As satisfactory we took experiments when the surface of the upper part of the porous wall (section I) remained free of the crystals of the sublimed substance and only isolated aggregates of crystals adherred to the wall in the bottom half (II-nd section) after falling from the section I. Slight tapping on the apparatus caused these aggregates to break away; in some cases they fell spontaneously by its weight. Insatisfactory results were those when crystals grew on the surface of the porous wall in one or both sections.

It was established that a satisfactory course of the crystallization required a minimum temperature of the inert gas near the porous wall this being virtually independent of the concentration of benzoic acid in the mixture entering the cooled space in the studied concentration range between 2·2 and 10% by vol. (the amount of water spray though was increased with the concentration and the temperature of the mixture). This minimum temperature has a certain corresponding minimum flow rate of the inert gas forced through the porous wall. Increasing flow rate of the inert gas does not permit the minimum temperature to be decreased; on the contrary, at a substantially greater flow rate the intensity turbulence near the wall intensifies with subsequent crystallization of the substance on the wall. This necessarily calls for increased temperature of the gas in order to prevent crystallization on the walls.

The average velocity of the gas mixture entering the cooled space (not including the added water) ranged between 2 and 3 cm/s, the mean velocity of the mixture emerging from the I-st section of the porous wall was 4—8 cm/s and the mean velocity of the mixture emerging from the II-nd section amounted to 5 to 10 cm/s. The mean velocity of the inert gas through the porous wall ranged between 0·10 and 0·36 cm/s. The pressure drop at 1 m^3 of nitrogen/hour forced through the porous wall was 0·15 Torr.

The found minimum temperature of the inert gas near the wall at the location III (Fig. 1) for crystallization of benzoic acid was 105°C. The corresponding vapour pressure above solid benzoic acid is 1·7 Torr. The temperature of the inert gas (nitrogen) at this location was maintained at 105°C. The bottom section of the porous wall at the location IV was fed by nitrogen at 2 m^3/hour and the room temperature. The courses of the temperature of the inert gas near the outer surface of the porous wall at the concentration of benzoic acid 4·4 and 10% by vol. are shown in Fig. 2 and 3 (curve *1*).

The approximate course of the temperature along the axis of the cooled space was measured by movable thermometer. The knowledge of these temperatures is important for the control of the crystallization process. The mean temperature of the gas mixture entering the cooled space (location I, Fig. 1) always equaled the temperature of the head. During the cooling of the gas mixture by water spray the thermometer in the section between the inlet up to about 10 cm away indicated a rapid decrease of temperature down to about 80°C and then again a fast increase up to 100°C about 40 cm from the inlet. From here on the temperature steadily decreases. In this position probably the process of crystallization is mostly over and the state of the porous wall is characterized by the temperature of the location III (350 mm from the head). The erroneous reading of the thermometer is caused by evaporation of the water spray on its bulb. The minimum possible temperature in this region can be estimated from the data on critical supersaturation.

During rapid cooling of the mixture of the vapours and the inert we may encounter the problem of formation of the fog of the sublimed substance given rise to when critical supersaturation of the substance in the inert is reached. If the formation of the fog is to be avoided the crystallization must take place under conditions when the supersaturation is below the critical value. The critical supersaturation can be estimated from the simplified equation[5]

$$S_{crit} = \exp\left\{0\cdot57(M/d)\,(\sigma/T)^{3/2}\right\} = P/P_e \qquad (2)$$

where S_{crit} stands for the critical supersaturation, M is molecular weight, d density (g cm^{-3}), σ surface energy (dyn cm^{-1}), T temperature (K), Pe equilibrium vapour pressure and P is the actual vapour pressure.

Using Eq. (2) we can estimate for a given inlet composition of the vapour mixture the temperature at which the mixture would reach critical supersaturation. Because in our experiments we did not observe formation of fog (the fog cannot be trapped by currently available filters) it may be assumed that the mean temperature of the cooled mixture was above the temperature estimated from Eq. (2).

The calculated values of critical supersaturation and vapour pressure P for benzoic acid between 100 and 150°C are shown in Table I. In the calculations it was assumed that benzoic acid condensed in the above temperature region from the supersaturated phase in the form of undercooled liquid[6].

Probable course of temperature along the axis of the cooled space during crystallization of benzoic acid at the inlet concentration 4·4% by vol. is shown in Fig. 2 as curve 2; curve 3 in Fig. 3 represents the course corresponding to the inlet concentration of 10% by vol. The solid line indicates the measured values, broken line the probable course of temperature in region not accessible to measurement and therefore estimated from Eq. (2). The approximate mean temperature of the mix-

TABLE I

Values of Critical Supersaturation, S_{crit}, and Vapour Pressure, P, at Various Temperatures (°C) Calculated from Eq. (2)

| Values | Benzoic acid | | | | | |
	100°	110°	120°	130°	140°	150°
S_{crit}	5·6	4·9	4·3	3·8	3·4	3·1
Pe, Torr	1·8	3·2	5·5	9·3	15·4	23·9
P, Torr	10·0	15·7	23·7	35·3	52·4	74·1

| Values | Anthraquinone | | | | |
	210°	220°	230°	240°	259°
S_{crit}	5·2	4·5	4·0	3·6	3·2
Pe, Torr	2·9	5·0	8·4	14·0	22·9
P, Torr	15·1	22·5	33·6	50·4	73·3

ture at 4·4% of the inlet concentration entering the region of evaporation of water calculated from Eq. (2) amounts to 128°C and for 10% by vol. of the inlet concentration it is greater than 151°C. Thus it is unlikely that in region of contact of gas

FIG. 2

Temperature Course during Crystallization of Benzoic Acid at 4·4% by Vol. of Inlet Concentration

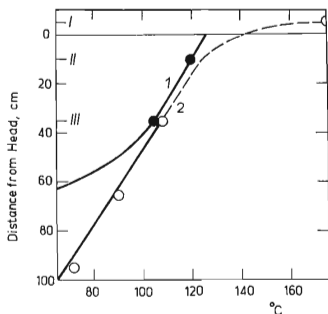Curve 1 temperature of inert gas near porous wall, 2 temperature along the axis of cooled volume.
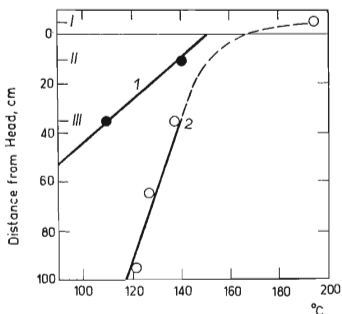

FIG. 3

Temperature Course during Crystallization of Benzoic Acid at 10% by Vol. of Inlet Concentration

Curve 1 temperature of inert gas near porous wall, 2 temperature along the axis of cooled volume.

mixture with the water spray the temperature should drop below 80°C without producing the fog of benzoic acid.

The results of experiments with benzoic acid are given summarily in Table II. The table gives the averages of repeated measurements at the same experimental conditions when no crystallization on the porous wall occured. The locations of the temperature probes I – V are shown in Fig. 1. The flow rate of gases was measured at the room temperature. The flow rate of inert was 0·09 cm/s at 20°C. The results indicate that the effectiveness of the crystallization decreases with increasing concentration of benzoic acid in the carrier gas. The temperature of the effluent gas rises with concentration up to 100°C and the gas entrains part of the sublimed substance in the form of vapour. The velocity of gas mixture in the cooled space increases with the concentration of the sublimed substance. It turns out that the height of the crystallization space of 1 m is not sufficient for concentrations in excess of 5%. With properly adjusted parameters and a proper function of the nozzle the product was dry. The average lenght of crystals was between 60 and 300 μm, the diameter between 10 and 40 μm.

The applicability of the method and the function of the equipment for long-term continuous process was tested by a series of 15 one- to two-hour experiments with the total time of operation 22 hours and the feed concentration of benzoic acid in the mixture 2·2% vol. Between the experiments the apparatus was not cleaned. No crystals were observed on the porous wall throughout the time of these experiments.

To test the crystallization at higher temperatures we used anthraquinone and terephthalic acid. The concentration of anthraquinone in the carrier gas (nitrogen)

TABLE II

Experimental Conditions and Efficiency of Crystallization of Benzoic Acid in Dependence on Concentration in Vapour Phase

gas mixture m^3/h	Benzoic acid % Vol.	water in nozzle ml/h	gas in porous wall I-st section m^3/h	I	II	III	IV	V	Efficiency % mass
		Flow rate				Temperature, °C			
1·3	2·2	260	1·0	160	120	105	40	46	98·5
1·4	4·4	280	1·0	175	120	105	46	50	98·0
1·5	6·4	300	1·5	180	120	105	56	65	97·0
1·6	7·3	330	2·0	185	125	105	62	80	93·0
1·7	8·2	380	2·0	190	125	105	65	90	90·0
1·8	10·0	400	3·0	195	140	110	70	100	86·0

was 3·5% vol. at 300°C. The experimentally found minimum temperature of the inert gas at the location III was 195°C at its mean velocity through the porous wall was 0·3 cm/s. The equilibrium vapour pressure of anthraquinone at this temperature was approximately 1·5 Torr, *i.e.* very close to the vapour pressure of benzoic acid at the minimum temperature at the location III. The porous wall during this experiment was perfectly clean and the efficiency of the crystallization was 99·3%; the product contained no moisture. The approximate course of temperature near the outer surface of the porous wall (curve *1*) and along the axis of the cooled space (curve *2*) are shown in Fig. 4. The values of the critical supersaturation and the vapour pressure of anthraquinone calculated from Eq. (*2*) for temperatures between 210 and 250°C are shown in Table I. The calculated minimum temperature of the mixture entering the space cooled by water evaporation is 224°C. The measured value was 237°C. Further course of measured temperatures is in good agreement with the course estimated from Eq. (*2*).

The concentration of terephthalic acid in the carrier nitrogen was also 3·5% by vol., the temperature at the location III was 250°C. The equilibrium vapour pressure of terephthalic acid at this temperature is approximately 1 Torr. The porous wall remained perfectly clean throughout the experiment. The efficiency of crystallization was 99% and the product was dry.

The crystallization of benzoic acid and anthraquinone from the bulk vapour phase by the described method has shown that in order to prevent crystallization on the porous wall the inert gas passing through the wall must have at the outer surface of the wall at the location III the temperature for which the corresponding equilibrium vapour pressure of the sublimed substance is approximately 1·6 Torr. This suggests that the admissible concentration of the sublimed substance in the proximity of the wall at the atmospheric pressure was in both cases about 0·2% by vol.
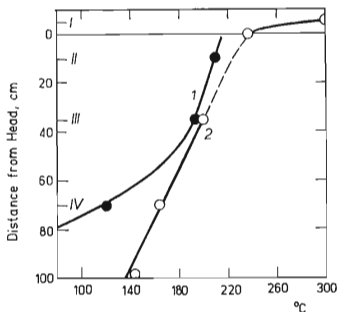

FIG. 4

Temperature Course during Crystallization of Anthraquinone at 3·5% by Vol. of Inlet Concentration

Curve *1* temperature of inert gas near porous wall, *2* temperatures along axis of cooled volume.

In order to find out whether this finding can be generalized a series of substances of various volatility was measured. In all cases the average concentration of the substance in the feed gas mixture was 3·5% vol., the velocity of the mixture entering the cooled space was in all cases 2 cm/s and the mean velocity of the inert gas through the porous wall was always 0·25 cm/s. The temperature of the mixture and the flow rate of water spray were varied according to the vapour pressure of the sublimed substance. Experimentally was sought the value of the temperature of inert gas at the location III at which no crystallization occurred at the porous wall. The results of these experiments are presented in Table III. It was established that for the majority of measured substances this minimum temperature of the inert gas at the location III corresponded to the vapour pressure of the substance below 3 Torr (for naphthalene (75°C)) and hexachlorethane (65°C) 6 Torr).

Thus this method enables continuous crystallization of sublimable substances from the bulk of the vapour phase cooled by evaporation of injected spray of water at temperature below 100°C while the obtained product remains dry. Using the results of this work the operating conditions of the process of crystallization of various organic substances can be approximately estimated.

The temperature and concentration distribution in the apparatus and the rate of crystallization with changing flow rates are subject to further study.

TABLE III

Summary of Temperatures in the Apparatus and Approximate Values of Equilibrium Vapour Pressure at the Temperature in Location III during Crystallization of Some Organic Substances

Concentrations of substances in inlet gas mixture are 3·5% Vol., flow rate of inert gas in each section of porous wall 2 m³/h.

Substance	Flow rate of water in nozzle ml/h	Temperature, °C				Equilibrium vapour pressure at III Torr
		I	II	III	IV	
Terephthalic acid	360	310	300	250	205	1·0
Anthraquinone	300	300	210	195	110	1·5
Hydroquinone	280	200	190	150	70	3·0
Pyrogallol	280	200	170	140	70	1·8
Salicylic acid	260	175	165	130	65	3·0
Pyrocatechine	230	150	110	95	48	3·0
Naphthalene	150	110	80	75	40	6·0
Hexachlorethane	130	100	75	65	35	6·0

REFERENCES

1. McMakin L. E., Bryant H. S. (Mobil Oil Corp.): U. S. 3 362 989; Chem. Abstr. *68*, 88596 (1968).
2. Vítovec J., Smolík J.: Chem. Prům. *25*, 84 (1975).
3. Vítovec J., Bažant V., Lucek F.: Czech. *157* 883 (1974); Czech. 161 505 (1974); Brit. 1 381 892 (1975).
4. Vítovec J., Hančil V.: Chem. Prům. *22*, 448 (1972).
5. Steinmeyer D. E.: Chem. Eng. Prog. *68*, 64 (1972).
6. Smolík J., Vítovec J.: This Journal *41*, 1471 (1976).

Translated by V. Staněk.