

SEPARATION OF SOLID SUBLIMABLE COMPOUNDS BY PARTIAL CRYSTALLISATION FROM THEIR VAPOUR MIXTURES

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Separation of solid sublimable compounds was measured by partial crystallisation from their mixtures with the carrier gas in a crystalliser with gas transpirable walls. The concentration of naphthalene in phthalic anhydride was decreased in one separation stage from 10% to 0.1% (mass) and from 1% to 0.03% at the yield 99%. The over-all concentration of volatile impurities in the distilled benzoic acid prepared by oxidation of toluene was decreased in two separation stages from 1.8% to 0.0015% and so the benzoic acid of edible grade quality has been obtained. In the following separation stage the impurities were completely removed. In this way six operations in the wet process can be substituted by two sublimation stages at a considerably higher efficiency.

Sublimation is known as a simple process used mostly for separation of solid organic volatile compounds from non-volatile inorganic matters. Its use is often inevitable for separation of low soluble or insoluble compounds in usual solvents and in cases where the usual separation methods such as distillation, extraction *etc.* are not suitable or are too expensive. The survey of patents on purification of compounds by sublimation is given in literature¹.

Though sublimation is a very effective separation process, it is not widespread in industry obviously due to general complexity of the process and the lack of suitable continuous processing plants. In a large scale, sublimation was applied for purification of terephthalic acid in the production of polyester fibres².

Separation of volatile compounds by sublimation is frequently performed in one stage. If the required effect is not attained, the operation is repeated. Recently, several continuous procedures have been proposed with multistage sublimation in one apparatus. Goldberg³ proposed a continuous sublimation by use of a bed of solid particles called "Thin-Film Fractional Sublimation". In principle a bed of solid inert particles, covered by condensation with the volatile solid compound, descends downward the column. By use of the temperature gradient or by use of the carrier gas, the counter-current flow of the vapour phase is obtained. Sevrjugova and others⁴ also perform continuous countercurrent sublimation on the principle of rectification. The solid condensed compound is continuously scraped off in the cooler and is falling

downward in opposition to the ascending vapours. Industrial application of the mentioned procedures is not known.

The continuous crystalliser with gas transpirable walls^{5,6} was used in this study for separation of solid sublimable compounds by partial crystallisation from the mixture of their vapours with the carrier gas. The mixture of vapours with the carrier gas is cooled by evaporation of the dispersed water in the cooling space formed by porous gas permeable walls through which the inert gas which protects the internal walls from solid deposits is transpiring into the cooling space. The crystallisation takes place in the bulk of vapour-gas mixture by direct contact with the dispersed water.

Separation of a mixture of phthalic anhydride with naphthalene in nitrogen in one stage and separation of benzoic acid produced by oxidation of toluene was studied.

EXPERIMENTAL

The experimental apparatus is schematically given in Fig. 1. Its detailed description and operating procedure is given in the preceding study⁶. The space between the inserted porous cylinder and the jacket is separated into 3 sections and inert gas is introduced into individual sections at different temperatures. Around the whole circumference, gas for removal of the remaining moist noncondensed mixture of vapours with the gas from the product is introduced through inlet 10 into the storage of product 9. The experiments were performed at atmospheric pressure. Temperatures of inlet and outlet gaseous streams were measured by thermocouples. The amount of water needed for cooling of the gas-vapour mixture and for partial crystallisation in individual experiments was calculated according to the concentration of compounds, the amount and temperature of the gas-vapour mixture, and according to experimentally determined corrections of thermal losses (part of water is evaporated already in the head of the column). The inert

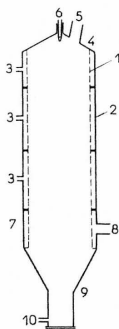


FIG. 1

Diagram of Crystalliser

1 Inserted porous cylinder, 2 jacket, 3 inlet of inert gas, 4 head, 5 inlet of vapour-gas mixture, 6 jet, 7 filter, 8 outlet of gases, 9 storage tank of product, 10 inlet of washing gas.

gas for transpiration through the porous wall was heated to the corresponding temperature prior to the inlet into individual sections of the space between the walls and the inserted porous cylinder.

The mixtures of solid compounds for purification were continuously, completely evaporated in the sublimator with the fluidized bed formed by inert particles of corundum ceramics and particles of purified compound⁷. The fluidizing gas was either nitrogen or air.

RESULTS AND DISCUSSION

Separation of the Mixture Phthalic Anhydride-Naphthalene

Four solid mixtures were prepared of phthalic anhydride with 1, 2, 5 and 10% by weight of naphthalene. The mixtures were evaporated completely in the continuous fluidized bed sublimator at the rate of 80 to 120 g of mixture/h. The fluidizing gas was nitrogen at the flow rate 0.9 m³/h, the inert gas was air and its transpiration flow rate 3 to 5 m³/h. Diameter of the inserted porous cylinder was 100 mm, height 1 m. The practical efficiency (yield) of crystallisation was determined as

$$\eta = \Delta m / \Delta M,$$

where Δm is the mass of separated dry solid compound and ΔM the mass of solid mixture supplied into the sublimator. Concentration of naphthalene in the final product was also measured. Conditions of the experiment at the inlet of the vapour-gas mixtures into the crystalliser are given in Table I, survey of conditions at the outlet and of calculated data is given in Table II.

TABLE I

Inlet Conditions and Experimental Data at Separation of the Mixture Phthalic Anhydride-Naphthalene

Flow rate of fluidizing nitrogen 0.9 m³/h, flow rate of water through the jet 150 to 170 ml/h.

Experiment	Sublimation rate g/h	Conc. N ^a in solid mixture mass %	Concentration gaseous mixture		Temperature		Inert gas	
			vol. %		inlet	outlet	m ³ /h	°C
			F	N	°C			
1	120	10	1.39	0.18	172	65	3	120
2	120	1	1.54	0.02	172	65	3	120
3	120	2	1.51	0.04	172	65	3	122
4	100	5	1.23	0.08	171	60	3	122
5	80	10	0.94	0.12	175	62	5	120

^a N is naphthalene, F is phthalic anhydride.

The inert gas was distributed uniformly over the whole height of the inserted porous cylinder at the velocity 0.3 to 0.5 cm/s. The Reynolds number of the vapour-gas mixture at the inlet into the crystalliser was in average 213. The sprayed aqueous dispersion has partially disturbed the laminar flow of the gas-vapour mixture but its mixing with the layer of inert at the wall practically did not take place. The inert gas has been mixed with the noncondensed part of the vapour-gas mixture in fact at the inlet of the filter. There it was passed over the layer of the product so that it could affect composition of the product and possibly increase the losses.

Concentration of naphthalene in the mixture entering the crystalliser was always less than the equilibrium concentration corresponding to the temperature of the mixture leaving the filter (at 65°C is the equilibrium concentration of naphthalene 0.34% vol, at 60°C it is 0.23% vol.). In the first experiment the concentration of vapour of naphthalene in the entering mixture was 0.18% vol. and after recalculation to the total gas flow rate at the outlet (the inert gas transpiring through the porous wall inclusive) would be 0.05 vol. %. In the fifth experiment the concentration of naphthalene in the inlet mixture was 0.12% and after recalculation to the total flow rate 0.023 vol. %, *i.e.* about half of the concentration in comparison with the experiment No 1. Nevertheless the concentration of naphthalene in the final product from both experiments was practically equal 0.09 and 0.08%. Increase in the flow rate of inert gas for 70% has obviously at these small concentrations no effect on composition of the product. Crystallisation takes place in the bulk of the vapour-gas mixture which is intensively cooled by evaporation of the finely dispersed water. The Reynolds number of the mixture passing from the crystalliser into the filter was in average 920 and in the 5th experiment 1360.

TABLE II

Outlet Conditions and Calculated Data at Separation of the Mixture Phthalic Anhydride-Naphthalene

Experiment	Yield of crystallisation mass %	Conc. N in product mass %	Yield based on F mass %	Flow rate outlet gas m ³ /h	Equil. vapour pressure at the outlet		Concentration of F in outlet gas	
					N Torr	F Torr	equil. vol. %	actual vol. %
1	90.8	0.09	99.0	4.18	2.57	0.033	0.004	0.016
2	98.0	0.03	98.8	4.15	2.57	0.033	0.004	0.005
3	97.0	0.05	98.6	4.15	2.57	0.033	0.004	0.006
4	94.2	0.09	99.2	4.15	1.76	0.022	0.003	0.003
5	88.7	0.08	98.6	6.15	2.05	0.027	0.0035	0.002

Purification of Benzoic Acid

Production of benzoic acid by catalytic oxidation of toluene is very profitable. But if it has to be used in food industry its purification is very demanding. It must be odourless and the acceptable concentration of volatile compounds is about 150 ppm.

The remaining toluene is removed from the reaction mixture by distillation and the resulting mixture is rectified at lowered pressure. Concentration of additional compounds in the product is 0.5 to 2%. These are then separated successively by a number of separation operations such as extraction, stripping by water vapour, adsorption, filtration, crystallisation with centrifugation and washing and fluidized bed drying. The crystallised benzoic acid obtained by this procedure is not edible grade because of its unpleasant though slight smell. Compounds causing this smell cannot be removed by drying neither at temperatures up to 70°C.

Distilled benzoic acid was purified by a repeated total fluidized bed sublimation and by partial crystallisation from the vapour phase in the transpiration crystalliser⁸. Its mean composition and summary of measured and calculated data are given in Table III. Vapour pressures were calculated according to relations given in literature^{9,10}. Diameter of the inserted porous cylinder was 200 mm, its height 1.5 m. Flow rate of the fluidizing gas—nitrogen was 1.4 m³/h. The sublimation rate was 250 g/h. Temperature of the vapour—gas mixture entering the crystalliser was 180°C, temperature of the outlet mixture was 55°C. Air was used as inert gas at the rates of

TABLE III
Experimental, Calculated and Literature Data for Purification of Benzoic Acid

Compound	Conc. in feed mass %	Conc. in inlet mixture 10 ⁴ , C vol. %	Vapour pressure		Equilibrium conc. at 55°C 10 ⁴ , C vol. %	Concentration of impurities ppm, (crystallisation, No)		
			180°C	55°C		I	II	III
Benzyl acetate	0.0164	3	295	1.273	1 700	5	2.6	—
Benzyl butyrate	0.0250	4	137 ^a	0.51 ^a	700	30	3.4	—
<i>m</i> -Methyldiphenyl	0.530	100	68 ^a	0.27 ^a	400	15	—	—
Benzyl benzoate	0.270	40	12.9	0.001	1	111	6	—
Benzaldehyde	0.0044	1	760	6.36	8 400	2	—	—
<i>o</i> -Methyldiphenyl	0.412	80	86 ^a	0.34 ^a	450	2	3	—
Diphenyl	0.527	110	105.4	0.18	235	1	—	—
Benzoic acid	98.215	26 300	83.16	0.0335	44	—	—	—

^a Vapour pressures estimated according to the Cox–Othmer rule.

3, 2 and 1 m³/h fed into individual sections (inlet 3 in Fig. 1) and 1.5 m³/h for removal of the remaining moist noncondensed mixture from the product in the tank.

Concentrations of 7 impurities in the distilled benzoic acid are given in Table III. Actually several others, mostly unidentified compounds are present in concentrations with the order of magnitude 10⁻²% which were already removed by the first partial crystallisation so that their concentration could not be determined. Time of operation of individual purification steps was 3 hours. Concentration of vapours of benzoic acid in the inlet mixture entering the crystalliser was 2.63 vol.% and concentration of individual impurities was smaller than 0.01 vol.% *i.e.* lower than the concentration corresponding to the equilibrium vapour pressure at temperature leaving the filter (55°C). Only concentration of benzyl benzoate was higher. Flow rate of the mixture entering the crystalliser (water vapour and nitrogen from the jet inclusive) was 1.74 m³/h, flow rate from the crystalliser into the filter 7.7 m³/h. The Reynolds number at the inlet was 139, at the outlet 785.

After first crystallisation 96% of dry product has been obtained. Its moisture was 0.07%. Practically all impurities were removed (1.77%) so that the lost benzoic acid accounted for 2.2%. With the gas leaving the filter (9.2 m³/h) leaves 0.9% of benzoic acid at the assumption of equilibrium concentration at the outlet temperature 55°C. The losses amounting to 1.3% can be the result of sticking of the raw material in the dosing system and of sticking of the product in the inserted porous cylinder.

The product obtained by first crystallisation did not meet the edible grade requirements. Thus it was sublimed and crystallised at the same conditions as in the first stage and concentration of impurities has decreased to 15 ppm. Such benzoic acid met the requirements of edible grade standards. In the third stage all the impurities were practically removed.

TABLE IV

Conditions and Results at Sublimation Purification of Crystallised Benzoic Acid

Sublimation rate kg/h	Flow rate fluidizing gas m ³ /h	Concentration benzoic acid in inlet mixture vol. %	Temperature outlet mixture °C	Transpiring gas m ³ /h	Losses in outlet gas mass %	Concentration of impurities in product ppm
0.5	1.5	4.3	60	3	0.48	15
1.0	1.8	6.9	65	4	0.50	23
2.0	2.0	11.6	70	5	0.42	17

In separation of the mixture phthalic anhydride-naphthalene it was determined that efficiency of separation at small concentrations is practically independent of the volume of the inert gas transpiring through the porous wall as its mixing with the gas-vapour mixture takes place in the filter when the crystallisation is already completed. Large flow rate of inert gas increases loss of product (it leaves in vapour from the filter). Thus it is suitable to decrease the flow rate of inert gas to minimum which is necessary for protection of the porous wall from formation of solid deposits.

In the next experiments the sublimation rate was 0.5 to 2 kg/h and the flow rate of inert gas was 3 to 5 m³/h. Air was introduced again at the flow rate 1.5 m³/h into the tank for removal of rests of moist gaseous mixture from the product. The temperature of the mixture entering the crystalliser was from 200 to 240°C at the sublimation rates 1 kg/h and higher, with the aim to observe the possibility of side reactions at larger temperatures. At the height of porous wall 1.5 m the mixture was insufficiently cooled and its temperature at the outlet has reached 60 to 70°C at which the equilibrium vapour pressure of benzoic acid vapours was 0.053 to 0.128 Torr.

The crystallised benzoic acid was used at the feed which had not satisfied the edible grade requirements, due to its unpleasant smell. The total concentration of impurities was 223 ppm, out of which were 20 ppm benzyl benzoate, 50 ppm *m*-methyl diphenyl and 5 undefined compounds determined chromatographically. Concentration of vapours of benzoic acid in the mixture entering the crystalliser was 4.3 to 11.6 vol.%. The maximum Reynolds number at the outlet from the crystalliser was 1000.

Summary of conditions and results of experiments is given in Table IV. The final product of all three experiments has met the requirements of edible grade standards. Relatively high losses were due to high temperature of the outlet gases. Side reactions obviously did not take place at high temperatures. Also it results that even at relatively high concentration of vapours of benzoic acid entering the crystalliser a very good separation effect has been reached. At the concentration of vapours of benzoic acid in the mixture 11.6% in one stage of partial crystallisation in the apparatus with the porous wall the concentration of impurities has decreased from 223 to 17 ppm. Such effect has not been reached by any usual separation method.

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