CRYSTAL SIZE DISTRIBUTION OF BENZOIC ACID AT ITS CRYSTALLIZATION FROM THE BULK OF VAPOUR PHASE

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Crystal size and their distribution were measured in the crystalliser with gas-permeable walls, at crystallisation of benzoic acid vapours from the bulk of vapour phase in the mixture with nitrogen in dependence on concentration (in the range from 1·1 to 23 vol.%), temperature (401 to 473 K) and velocity of mixture (0·5 to 6·6 cm/s). At small cooling rate of the mixture the vapours of benzoic acid are condensing in the form of droplets which at continuing cooling solidify. At cooling of the mixture by water dispersion create the needle-shaped crystals. The effect of concentration, temperature and velocity is not profound obviously because by evaporation of water is the mixture rapidly cooled and supersaturated. This results in creation of a large amount of crystal nuclei and thus also of small crystals.

Crystallisation of compounds from the bulk of vapour phase is advantageous especially as it is possible to perform it continuously. We meet it especially in sublimation of compounds with the carrier gas or at the production of compounds at higher temperatures in the vapour phase. The crystallisation process takes place mostly in the bulk vapour phase by direct contact of the gas–vapour mixture with the cooler fluid distributed in the whole volume of the mixture. The walls of the unit are heated to a temperature higher than is the dew point of the mixture, containing the vapours of the sublimable compound[1] or the internal walls of the crystalliser are gas-permeable and the inert gas is transpiring through them[2]. In both cases is prevented the condensation of vapours and sedimentation of solid deposits on walls. This enables continuous performance of the operation at the passage of the vapour–gas mixture through the apparatus.

One of the important criteria in industrial application of this operation is the size of crystals and their distribution. The growth rate and shape of crystals is mainly the function of supersaturation, temperature, saturation rate and relative velocity between the mixture and crystals. The size of crystals is also a function of the residence time of the solution in the unit. At large supersaturation there originate crystals with a simple shape. Small crystals have a small bulk mass which is disadvantageous at transport and storage of the product and from the analogy with crystallisation in the liquid phase they can be less pure than large crystals[3]. Large residence time necessary for production of larger crystals requires units of larger dimensions.

The gas–vapour mixture can be cooled by a cooler gas. Cooling takes place at a small velocity so that large crystals can originate, but with regard to large sublimation heat (*e.g.* benzoic acid 744 kJ/kg) and small specific heat of gases it is necessary to use several times larger amount of cooling gas. Very effective is crystallisation at cooling of the gas–vapour mixture by evaporation of a finely dispersed liquid, mostly water in the bulk of the mixture. Due to large supersaturation there originate only very small crystals.

Here is studied experimentally the effect of initial concentration, temperature and velocity of the mixture on size and shape of crystals of benzoic acid at crystallisation from the mixture of its vapours with nitrogen.

EXPERIMENTAL

The mixture of vapours of benzoic acid with nitrogen has been prepared in three in series connected saturation vessels made of stainless steel. The vessels were heated from outside by resistance heaters. Nitrogen has been bubbled through the molten benzoic acid. It has been introduced through a tube to the bottom of the vessel where it was uniformly distributed through a perforated plate. Temperature of the molten compound was measured by thermocouples. For reaching the equilibrium concentration in the vapour phase corresponding to the temperature of the molten compound in the last saturator the temperature of the molten compound in the last but one saturator was kept for 2 K higher. For the possible correction of the equilibrium concentration of the vapour–gas mixture was the inlet of pure nitrogen situated behind the last saturator. The inlet piping into the crystalliser was filled by small ceramic particles, at the outlet was situated a thermocouple for measurement of temperature of the mixture entering the head of the crystalliser.

Crystalliser (Fig. 1) had a rectangular cross sectional area 0·1 × × 0·075 m and was 0·5 m high. Its two walls were of porous glass and two of transparent glass plates heated from outside by a resistance wire. The wire was of insulated metal frame situated in slots of the supporting structure.

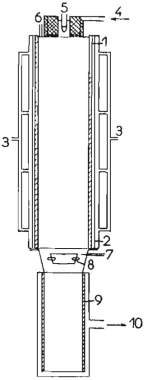

FIG. 1

Crystalliser

1 Porous walls, *2* resistance heating wire, *3* inlet of inert, *4* inlet of vapour–gas mixture, *5* jet, *6*, *7* thermocouples, *8* sampling hole, *9* receptacle of product, *10* gas outlet.

The upper support of the frame was stretched by stainless steel springs for compensation of thermal dilatations of the heated wire. Through the heated space between the glass plates was blown a small amount of air (1 m^3/h) for maintaining a uniform temperature. On the external glass plate was sticked a frame of laminated plastic and on it a plate of acrylate glass. Through the space between the both plates was also blown air with the aim to keep constant temperature. So were the heated glass walls thermally insulated from surrounding. The porous walls were heated in a similar way. On the back side of their frame was fixed a metal plate with gas inlet. The walls were heated by safe voltage 24 V. The inlet of the gas–vapour mixture was situated from the side of the head of the crystalliser. The gas–vapour mixture entered into the internal space of the head through holes on the upper circumference. Their distribution was non-uniform, greater number was on the oposite side of the inlet. On the perforated annular bottom was situated the packing of metal elements for uniform distribution of the mixture and keeping of its constant temperature measured by a thermocouple before the inlet into the cooled space of the crystalliser. In the centre of the head was situated the jet for inlet of the cooling fluid. At the circumference of the head were holes for thermocouples for measurement of temperature on the internal wall of the crystalliser. The head was heated from outside. In the lower, narrower part of the crystalliser was situated the device for sampling during the experiments and a thermocouple. The crystalline product has been accumulated in the receptacle made of metal basket covered with a glass thread. This functioned as a filter for separation of solid product from noncondensing vapour–gas mixture. It was situated in the jacket with holes for exit of the gas. The jacket was heated and gas--tightly connected to the crystalliser.

Procedure. The crystallisation operation was studied in the described equipment *a*) at cooling of the vapour–gas mixture by only convection with the inlet of cooler inert through porous walls and *b*) at cooling of the mixture by evaporation of the injected water finely dispersed in the jet by nitrogen. Transparent walls were heated to the required temperature so that condensation of benzoic acid was prevented and the operation could be observed visually. Through porous walls was transpired nitrogen heated according to the conditions of the experiment to a considerably lower temperature. At suitable fixed velocities and temperatures of the vapour–gas mixture and transpired inert gas the crystallisation took place only in the bulk of the mixture and around porous walls has formed crystal free layer of inert gas. The measurements were performed at atmospheric pressure.

Analysis. From the products of individual experiments were taken mean samples and in them 200 or more solid particles were measured by the microscope. In some cases they were solidified droplets, in others aglomerates of droplets. At cooling to a lower temperature and especially at cooling by evaporation of the dispersed water, crystals in the form of needles have formed with differing length and thickness. As these crystals have broken even at carefull manipulation it was practically impossible to determine their original length and thus the thickness of all particles was measured (in solidified particles the diameter).

Distribution of crystal sizes (or of spherical particles) was expressed graphically so that against the thickness of crystals (diameter of particles) has been plotted their corresponding sum expressed in percentages. The obtained curves have a maximum whose position corresponds to the most frequent appearing size of crystals. The slope of the curve characterizes the uniformity of granulation. This method of evaluation is in our case suitable for comparison of different effects on the growth rate of crystals. Evaluation of data in the form of the cumulative screen--analysis curve which is usual in crystallisation in liquids[3] has not been performed, as the crystals cannot be distributed on the sieve and so enough representative data could not have been obtained.

RESULTS

Cooling of the Vapour–Gas Mixture by Convection

The measurement has been performed at temperatures of the inlet vapour–gas mixture 423 and 438 K, of the outlet mixture from the crystalliser 353 and 373 K, concentrations in the range from 1 to 6·2 vol.% of benzoic acid in nitrogen and velocities in the cross-sectional area of the crystalliser (inclusive the transpiring gas and the conditions of the experiment) 2 to 4 cm/s. Particles of benzoic acid could have been observed practically already at the inlet of the gas–vapour mixture into the crystalliser. As cooling of the mixture at the passage through the apparatus has been insufficient only small amount of benzoic acid has crystallised or condensed.

At the inlet temperature of the mixture 438 K and at the outlet 373 K the benzoic acid condensed in the form of droplets which then solidified in the bottom part of the crystalliser. The equilibrium concentration of benzoic acid in nitrogen at temperature 438 K is 6·2 vol.%. The mixture has been diluted before its inlet into the crystalliser by nitrogen in the ratio 1 : 1 so that the resulting concentration was 3·1 vol.%. The mean temperature of nitrogen transpiring through the porous walls was 377 K (390 – 363 K) its flow rate 200 l/h. Volumetric flow rate of the mixture was 400 l/h. Particle size distribution according to the population is graphically plotted in Fig. 2, curve 2. The data represent averages of three measurements. The diameter of condensed droplets was within the range 35 to 55 μm.

At temperature of the vapour–gas mixture 423 K was the equilibrium concentration of benzoic acid in nitrogen 3·2 vol.%. After dilution by nitrogen in the ratio 1 : 1 was the inlet concentration 1·6 vol.%. The mean temperature of the transpiring inert was 358 K (368 – 348 K), the volumetric flow rates were the same as in the first example. The outlet temperature of the mixture from the crystalliser was 353 K.

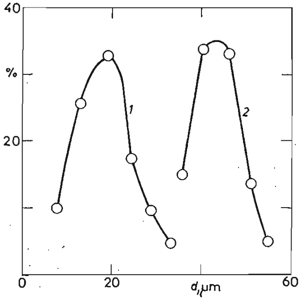

FIG. 2

Particle Size Distribution at Cooling by Convection

Curve *1* thickness of crystals at inlet temperature 423 K, *2* diameter of condensed particles at inlet temperature 438 K.

The products were mostly needle-shaped crystals with about 15% of condensed droplets. Dependence of distribution of the crystal thickness according to the population frequency (again average of three measurements at the same conditions) is given in Fig. 2, curve *1*. The thickness of needle-shaped crystals was within the range 8 to 33 μm.

Distribution of diameters of condensed droplets in dependence on concentration of the inlet mixture is graphically plotted in Fig. 3. Temperature of the mixture entering the crystalliser was 438 K and concentration of benzoic acid has varied in the range from 1 to 4 vol.%. From Fig. 3 results, that the size of particles is practically independent of concentration. The maximum on frequency curves are within the range of particle sizes from 37 to 44 μm at the greatest frequency from 32 to 38%.

The dependence of particle sizes and their distribution on velocity of the mixture form 2 to 4 cm/s in the cross sectional area of the apparatus is similar to the dependence on concentration. With increasing velocity slightly increases the frequency of greatest particles obviously due to the greater relative velocity between the mixture and particles.

Cooling of the Vapour–Gas Mixture by Evaporation of the Injected Water

At cooling of the vapour–gas mixture by evaporation of the injected water dispersion needle-shaped crystals of benzoic acid have formed. Crystallisation took place practically immediatelly in the cone of water dispersion sprayed by a jet in parallel into the vapour–gas mixture. The quantity of water for individual experiments was calculated so that its content in the dry product was smaller than 1%. The equilibrium mixture of vapours of benzoic acid with nitrogen leaving the last saturator was according to the needs diluted by pure nitrogen heated to the temperature of the mixture. Perfect

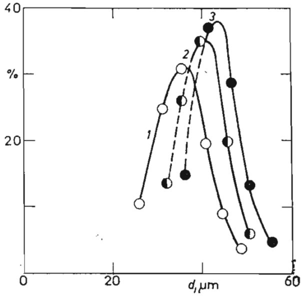

FIG. 3

Distribution of Diameters of Condensed Particles in Dependence on Concentration

Curve *1* 4%, *2* 2%, *3* 1% vol. benzoic acid in nitrogen.

mixing of the mixture was obtained by passage through the packing in the pipe before the inlet into the packing at the head of the crystalliser.

During the experiments samples were taken at the inlet of the product into the receptacle. Crystallisation was in the majority of cases practically total. The practical efficiency has been between 96 and 99%. The efficiency is here understood the mass fraction of separated dry compound and its mass entering in the vapours of the mixture into the crystalliser.

At this cooling method of the vapour–gas mixture was again studied the effect of velocity, temperatuie and concentration of the mixture on the magnitude and shape of crystals. The effect of velocity was studied in the range from 0·5 to 2·0 cm/s at concentration of benzoic acid in nitrogen 6·8 vol.% and temperature of the mixture entering the crystalliser 440 K. Temperature of the mixture leaving the crystalliser has varied between 343 and 353 K. The dependence of distribution of crystal thickness according to the frequency on velocity of the gaseous mixture is given in Fig. 4. The maximum of frequency curves is reaching 34 to 38% and the thickness of crystals is within the range 3 to 60 μm. With decreasing velocity is the slope of the curve greater but the differences are not significant.

The effect of concentration of the vapour–gas mixture was studied in the range from 1·1 to 5·5 vol.% of benzoic acid in nitrogen at 440 K and velocity 2·2 cm/s. The distribution of crystal thickness in dependence on their frequency has been evaluated similarly as in the last case but the differences are not significant. With decreasing concentration increases the maximum of frequency, the largest value of the maximum is at the lowest concentration.

The effect of temperature and concentration was studied at the velocity of the mixture 1·1 cm/s. At the inlet temperature 401 K, the equilibrium concentration 1·2 vol.% and the outlet temperature 339 K was the maximum of the frequency

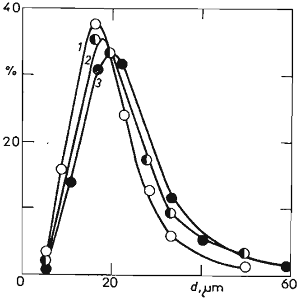

FIG. 4

Distribution of Crystal Thickness in Dependence on Velocity of Gas Mixture

Curve *1* velocity 0·5 cm/s, *2* 1·0 cm/s, *3* 2·0 cm/s.

curve 38% and thickness of crystals in the range from 3 to 35 µm. At the inlet temperature 473 K, corresponding equilibrium concentration 23 vol.% and outlet temperature 376 K was the value of maximum on the frequency curve 28% and thickness of crystals in the range from 8 to 50 µm. The low concentration has again a greater slope and the dependence is given in Fig. 5. With regard to the large difference in concentrations and temperatures is the difference in the thickness of crystals and its distribution also here relatively small.

Finally was studied the effect of velocity and concentration so that to the equilibrium vapour–gas mixture was added one, two and five times more nitrogen before the inlet into the crystalliser. The mixtures with concentrations 1·1 to 3·4 vol. % were so obtained at the velocities 2·2 and 6·6 cm/s. The dependences of distribution of crystal thickness according to frequency are given in Fig. 6. The curves have the maximum at 33 and 39% at the thickness of crystals from 12 to 17 µm, the thickness of crystals in the whole range is within 3 to 40 µm. With increasing velocity decreases the value of the maximum on the frequency curve.

DISCUSSION

The dependences in Figs 4 to 6 demonstrate a relatively small effect of velocity, concentration and temperature on the velocity of crystal growth of benzoic acid at cooling of the vapour–gas mixture by the water dispersion. Though, the mixture

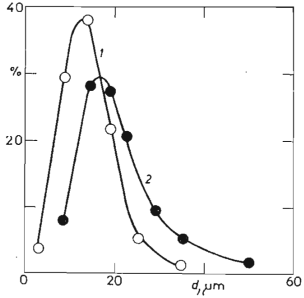

FIG. 5

Distribution of Crystal Thickness in Dependence on Temperature and Concentration

Curve *1* temperature 401 K, conc. 1·2%; *2* 473 K, 23% vol.

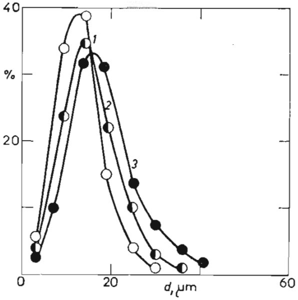

FIG. 6

Distribution of Crystal Thickness in Dependence on Velocity and Concentration

Curve *1* velocity 2·2 cm/s, conc. 3·4%; *2* 4·4 cm/s, 1·7%; *3* 6·6 cm/s, 1·1% vol.

is at this procedure intensively stirred in comparison with crystallisation at cooling by convection only, are the crystal sizes and their distribution in both cases comparable. This fact can be explained so that at cooling by convection is the vapour–gas mixture only slightly mixed and with regard to the short residence time (at max 100 s) small crystals grow. This opinion can be proved on basis of our observation so that the crystals catched at the top of the crystalliser have grown during 1 hr to long needles 500 μm thick. At cooling of the vapour–gas mixture by water dispersion then beside the direct intensive mixing of the mixture by the stream of water dispersion, its rapid cooling takes place accompanied by a very high supersaturation. This results in origination of a large quantity of crystal nuclei and thus also in small crystals.

By decreasing the flow rate of the water dispersion to 50% of the original value the practical crystallisation efficiency would decrease to 65% but the rate of crystal growth would not change substantially. This is probably due to a small cross sectional area of the crystalliser. The dispersion must be distributed over the whole cross sectional area even at minimum flow rates. The vapour–gas mixture is in any case quickly cooled in the bulk immediatelly after the inlet into the crystalliser. At larger excess of water is exceeded the critical supersaturation and only a fog forms which is passing through the filter.

Limitation of the metastable region of crystallisation which is suitable for control of its rate would require much slower cooling of the mixture which will probably require its circulation together with crystals.

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