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Impact of Fluid Flow Patterns on Metastable Zone Width of Borax in Dual Radial Impeller Crystallizer at Different Impeller Spacings

A. Čelan, M. Ćosić, D. Rušić, N. Kuzmanić

Abstract**—**Conducting crystallization in an agitated vessel requires a proper selection of mixing parameters that would result in a production of crystals of specific properties. In dual impeller systems, which are characterized by a more complex hydrodynamics due to the possible fluid flow interactions, revealing a clear link between mixing parameters and crystallization kinetics is still an open issue. The aim of this work is to establish this connection by investigating how fluid flow patterns, generated by two impellers mounted on the same shaft, reflect on metastable zone width of borax decahydrate, one of the most important parameters of the crystallization process. Investigation was carried out in a 15-dm^3 bench scale batch cooling crystallizer with an aspect ratio (H/T) equal to 1.3. For this reason, two radial straight blade turbines (4-SBT) were used for agitation. Experiments were conducted at different impeller spacings at the state of complete suspension. During the process of an unseeded batch cooling crystallization, solution temperature and supersaturation were continuously monitored what enabled a determination of the metastable zone width. Hydrodynamic conditions in the vessel achieved at different impeller spacings investigated were analyzed in detail. This was done firstly by measuring the mixing time required to attain the desired level of homogeneity. Secondly, fluid flow patterns generated in a described dual impeller system were both photographed and simulated by VisiMix Turbulent software. Also, a comparison of these two visualization methods was performed. Experimentally obtained results showed that metastable zone width is definitely affected by the hydrodynamics in the crystallizer. This means that this crystallization parameter can be controlled not only by adjusting the saturation temperature or cooling rate, as is usually done, but also by choosing a suitable impeller spacing that will result in a formation of crystals of wanted size distribution.

Keywords**—**Dual impeller crystallizer, fluid flow pattern, metastable zone width, mixing time, radial impeller.

I. Introduction

THE rise of popularity of crystallization in the process industries can mostly be thanked to the advantages that this separation technique has, such as its ability to purify while producing a solid with the desired physical properties [1]. Another advantage of this process is lower energy consumption considering that it can be conducted at relatively low temperatures [2], [3]. In pharmaceutical industry, the needs for an increased purity and product consistency are placing new demands on this process. This need requires extensive research on the matter.

Generally, the quality of the product of crystallization is determined by the crystal size distribution, the mean crystal size, and the product purity. The decisive step of this process is nucleation, which may occur uncontrollably. Therefore, controlling nucleation as well as knowing the value of metastable zone width is a crucial step in guaranteeing a constant product quality.

One of the most common definitions of metastable zone width, when the solution temperature is lowered at a constant rate, is the one where it is described as the difference between saturation and nucleation temperature, at which the mass fraction of crystals can be detected.

Metastable zone width can be considered as a characteristic property of each system which determines the range of operation conditions in which the crystallization process should be conducted [4]. Additionally, regarding the fact that it affects the kinetics of nucleation and crystal growth, the characteristics of the product obtained can be analyzed through the prism of metastable zone width.

Various factors can affect metastable zone width. Among those are the physical properties of the solvent, initial composition of a solution [5]-[10] cooling rate [11], [12], presence of impurities and crystalline seeds, mechanical action [13]-[16], etc. Knowing the value of metastable zone width is important on both scientific and industrial levels. On scientific level, knowing the value of metastable zone width is important for revealing the nucleation kinetics of the crystallization process. Industrially, the value of metastable zone width under various conditions is an essential requirement for the crystallization process if surface nucleation and particle aggregation is to be avoided. This is important in order to obtain the product of high purity, optimum particle size distribution and crystal shape.

In industry, the most commonly used equipment for cooling crystallization is an agitated vessel. Unfortunately, in that type of equipment, crystallization is often carried out without more precise optimization of the hydrodynamic conditions. This is the case even if sometimes these mechanisms are the controlling steps for an efficient separation of the crystals from the liquor and for a suitable morphology of the final product [17].

Mixing can have a dramatic effect on the properties of the product, including crystal size distribution, purity, morphology

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and polymorphic form. Regardless of the size, each crystallizer requires a proper selection of the mixing characteristics. Although it has been empirically known that the geometrical configuration in the crystallizer has a considerable effect on the product crystal size distribution, this problem has rarely been quantitatively investigated [18]-[20]

Recently, some authors investigated influence of hydrodynamic conditions caused by different impeller speeds on crystallization kinetic but in a batch crystallizer with one impeller [21], [22].

The aim of this research was to investigate the influence of fluid flow pattern in a dual radial impeller batch cooling crystallizer on the metastable zone width, which is one of the most important parameters of crystallization kinetics.

A more complete insight into the hydrodynamics of the crystallizer was gained by determining mixing time as well as visualizing the flow pattern by means of digital photography and by simulation using the VisiMix Turbulent software.

The effect of hydrodynamic conditions achieved at different impeller spacings on the metastable zone width of borax decahydrate in the process of batch cooling crystallization was examined in detail.

II. Experimental Procedures

A bench scale batch crystallizer (15 dm^3) was used in this investigation (Fig. 1). It was a flat bottom vessel whose internal diameter equaled 0.24 m. Vessels aspect ratio (liquid height to tank diameter ratio, H/d_T, equaled 1.3. Since aspect ratio exceeded the value of 1.0, it was necessary to introduce a second impeller in the system to ensure adequate mixing. Impellers used here were two radial 4-straight blade turbines (SBT), which were mounted on the same shaft. Also, the crystallizer was equipped with four baffles, with its bottom part cut to 45°.

The first part of the research dealt with a determination of impeller speed at which experiments will be performed since the process of crystallization is conducted in suspension. In batch cooling crystallization, the state of complete off-bottom suspension ensures optimum conditions for heat and mass transfer that occurs during the process [23], [24]. For this reason, critical impeller speed which ensures this was determined by Einenkel and Mersmann [25]. By their method, critical impeller speed which ensures the state of complete suspension is achieved when the cloud of suspension is lifted to 90% of the total liquid height. This is especially important in dual impeller systems with higher aspect ratios, where, even though the off-bottom suspension is ensured, the cloud of suspension remains concentrated in the vicinity of the impellers, while the rest of the vessel is occupied by a clear solution. The advantage of this method is that it focuses not only on the vessel bottom, but it also takes a column of liquid into account. By this method, the state of complete suspension is achieved at that critical impeller speed (N_{JS}) at which all particles are lifted up from the bottom and the cloud of suspension is elevated to 0.9H.

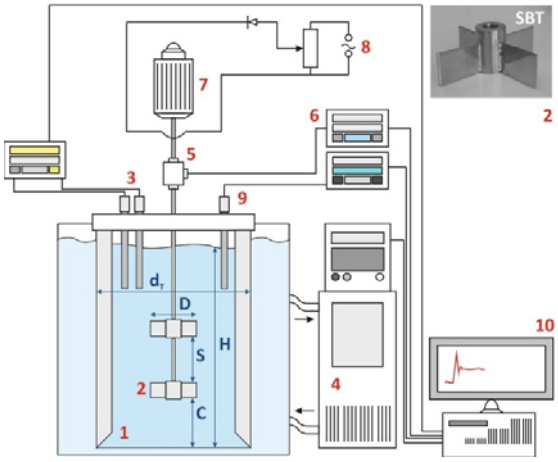

Fig. 1 Schematic illustration of the apparatus (1: crystallizer, 2: SBT impeller, 3: Na-ISE concentration measurement system, 4: thermostat, 5: torque sensor, 6: torque measurement system, 7: electromotor, 8: impeller speed regulation system, 9: temperature measurement system, 10: computer)

An insight into the hydrodynamics of the crystallizer was obtained by determining mixing time and by both simulating and digital imaging, that is by photographing of the fluid flows generated in the vessel. Mixing time was determined at the state of complete suspension in order to estimate the level of homogeneity of the mother liquor in the crystallizer. It was measured potentiometrically by using a tracer (sodium chloride solution, V_t=10 cm^3, c_t=2 mol dm^{-3}) which was injected into the continuous phase (distilled water). In this research, mixing time - t_{95} was defined as the time needed for a tracer concentration to reach and remain within 5% of the final concentration value [26]. Details on this measurement method are given in a previously published paper [27].

Fluid flow patterns generated in the vessel were analyzed by two different approaches – by using computer simulation software VisiMix Turbulent and by photographing the flow by the method proposed by Ibrahim and Nienow [28]. Photographs were taken in a dark room. A 5-mm wide column of liquid was illuminated by a 1500-W halogen lamp while the rest of the vessel was shaded. In this case, borax crystals of approximate size of 250 μm were used as tracers suspended in a continuous phase which, in this experiment, was saturated solution of borax.

Batch cooling crystallization was conducted in a described crystallizer. Saturated solution was prepared at 30 °C and it was cooled at the rate of 6 °C h^{-1}. Linear cooling of the solution was accomplished by *Medingen TC 250* programmable thermostat. Two most important variables monitored during process time were solution temperature and concentration. The first one was measured by a *Pt-100 probe* while the latter was determined from the solution potential data acquired by the *Na*-ion selective electrode. Both variables were measured continuously. Potentiometric measurements of the solution concentration gave access to supersaturation profile and at the same time, the metastable zone width.

The aim of this research was to investigate how the spacing

between the two impellers (*S*/*D*) and consequently the fluid flow pattern generated at those spacings influence the kinetic parameters of batch crystallization of borax decahydrate, i.e. how they reflect on the values of the metastable zone width.

III. Results and Discussion

Prior to conducting crystallization, it was necessary to determine the speed at which those experiments would be performed. This critical impeller speed had to ensure the state of complete suspension at all examined impeller spacings. It was determined by criterion 0.9*H* and results of those measurements are given in Fig. 2. In the same figure, the values of dimensionless mixing time are presented as well. As it can be seen from Fig. 2, critical impeller speed increases as the impellers are spaced further apart. This result implies that, if impeller spacing is increased, the desired state of complete suspension will be achieved only at somewhat higher impeller speeds. Determination of these speeds was the prerequisite for the research continuance.

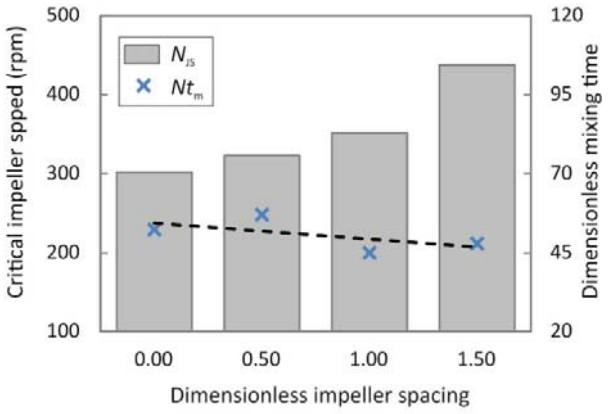

Fig. 2 Critical impeller speed (N_{JS}) and dimensionless mixing time (Nt_m) vs. dimensionless impeller spacing

Some researchers have shown that impeller position in the mixing vessel influences the hydrodynamic image of the system greatly [29]-[31]. Generally, investigation on impeller spacing gives an insight into the possible interaction of fluid flows generated by each impeller. This interaction can result either in strengthening or weakening of the overall convective flow. The value which gives information on this matter is dimensionless mixing time. In this research, mixing time was defined as the time needed for the system to reach the wanted level of homogeneity. It was determined by previously described method at the state of complete suspension. The dependence of mixing time, expressed in terms of dimensionless mixing time - Nt_m, on dimensionless impeller spacing is shown in Fig. 2. The figure shows an overall decrease of the value of dimensionless mixing time in the system as the impeller spacing is increased. These results will be commented in detail below.

As was mentioned earlier, during the process of batch cooling crystallization of borax decahydrate, both temperature and solution potential (i.e. concentration) were continuously measured. Combining these data with solution solubility, which was previously determined [32], it was possible to calculate supersaturation, which is the driving force of the process, at any point in process time [1], [33]. Supersaturation was calculated by:

$$\Delta c = c - c^* \quad (1)$$

where c is the concentration of the mother liquor, and c^* is the equilibrium concentration determined from the solubility data. In this research, supersaturation profile was determined for four different impeller spacings ranging from 0.0 to 1.5. During investigation, impeller diameters, off-bottom clearance as well as the impeller speed were kept constant (D/T=0.33, C/D=1.0, N/N_{JS} =1.0). Results of these measurements are given in Fig. 3.

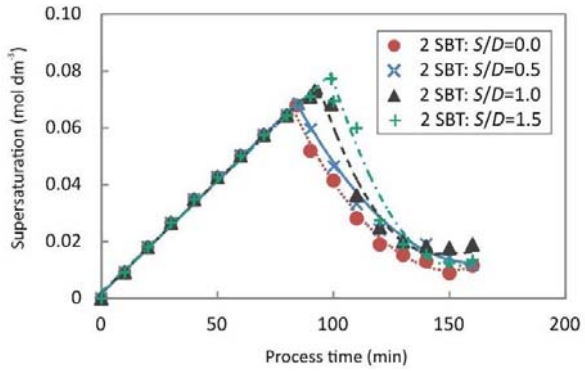

Fig. 3 Supersaturation profile in dual SBT impeller crystallizer at different impeller spacings

Fig. 3 shows that supersaturation profile has similar shape in all cases. At first it grows linearly, reaches its peak after which it decreases. It is also obvious that the first part of the supersaturation curve is identical in all experiments indicating that an increase of supersaturation is independent on the mixing parameters employed. It actually depends on the cooling rate and the salt solubility [34], both of which were kept constant in this research. However, as Fig. 3 shows, the supersaturation maximum and subsequent decreases depend on mixing parameters applied. In addition, the maximum supersaturation, Δc_{max}, indicates that the conditions for the onset of spontaneous nucleation have fulfilled. The stated value gives information on the metastable zone width expressed in terms of concentration.

The values of metastable zone width obtained at different impeller spacings examined in this investigation are shown in Fig. 4. Since this parameter is highly influenced by the level of turbulence in the system, it is presented along with the values of Reynolds number. It can be found in the literature that the rise in the level of turbulence results in an earlier onset of nucleation [2], [35]. While this may be true in most cases, results obtained in this investigation show that metastable zone width is widening with an increase of impeller spacing despite an increase of Reynolds number.

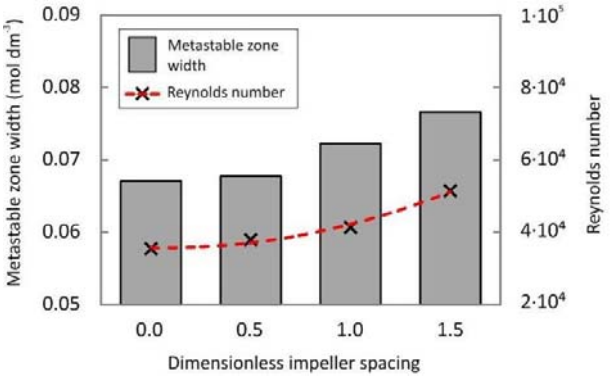

Fig. 4 Metastable zone width and Reynolds number in dual SBT impeller crystallizer at different impeller spacings

To be able to answer why this is happening, hydrodynamics in the vessel should be analyzed in detail. Obviously, the result obtained in this investigation implies that the metastable zone width has to be a consequence of not only the Reynolds number but also a consequence of the flow pattern, that is, a consequence of the intensity of the overall convective flow as well as the shear stress in the crystallizer caused by the impellers.

As stated earlier, the intensity of the overall convective flow is represented by the dimensionless mixing time, which is shown in Fig. 2. Values shown in the figure indicate that the intensity of the overall convective flow slightly weakens as impellers are set further apart on the shaft. Weakening of the flow suggests a decrease in the level of mixedness in this system.

To study the properties of the flow pattern, both visualization techniques presented here (VisiMix Turbulent and digital imaging) had to be applied. Simulations and photographs of the flow pattern are given in Figs. 5-8.

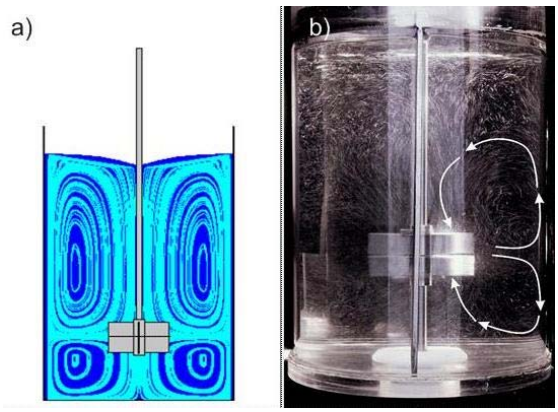

Fig. 5 Fluid flow pattern at *S*/*D*=0.0 visualized by a) VisiMix Turbulent software and b) digital imaging

If the lowest examined spacing is taken into account, it can be seen from Fig. 5 that impellers actually act as one but with modified geometry (impeller blade width/impeller diameter = 0.4). This is the reason why the classical radial fluid flow pattern can be observed here.

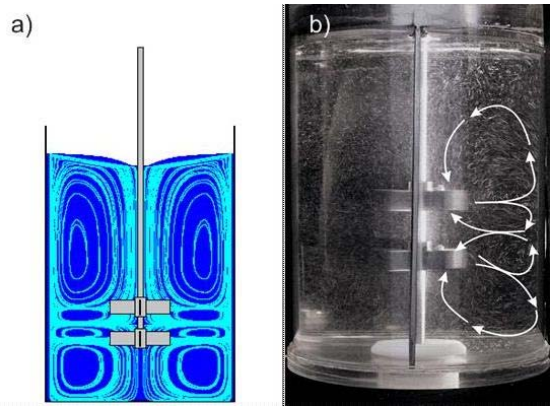

Fig. 6 Fluid flow pattern at *S*/*D*=0.5 visualized by a) VisiMix Turbulent software and b) digital imaging

If impeller spacing is increased, both SBT impellers will direct the fluid flow radially, as can be seen from Figs. 6-8. In all cases, four loops will be created, two of which will be located between the two impellers. At the position of *S*/*D*=0.5, a strong interaction of those two circulation loops is visible, both in simulation and in the digital image of the flow (Fig. 6).

At the standard impeller position of *S*/*D*=1.0, the listed interaction is still present but it is less intense, while at the highest examined impeller spacing of *S*/*D*=1.5, the two loops act almost independently. This is especially visible in the digital image of the flow pattern which also shows an area of lower mixedness in between of those two circulation loops.

In addition, if the values of mixing times for impeller spacings *S*/*D*=0.5 and *S*/*D*=1.5 are closely inspected, it can be seen that their values are slightly increased in comparison to the other two investigated positions. Obviously, an interaction of two circulation loops located in between the two impellers acted negatively and somewhat lowered the level of mixedness. The lowest value of mixing time was obtained at the standard impeller position suggesting a synergistic action of the two inner circulation loops.

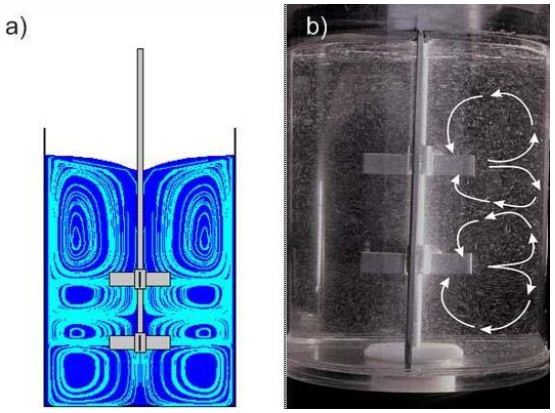

Fig. 7 Fluid flow pattern at *S*/*D*=1.0 visualized by a) VisiMix Turbulent software and b) digital imaging

The other aspect of the flow pattern is the shear stress imposed by the impellers. Generally, radial fluid flow is

characterized by strong shear stress. As stated earlier, the flow pattern in dual impeller systems is dependent on impeller spacing. An increase in impeller spacing results in a complete formation of four circulation loops. Having that in mind, there is a possibility that shear stress will increase as well.

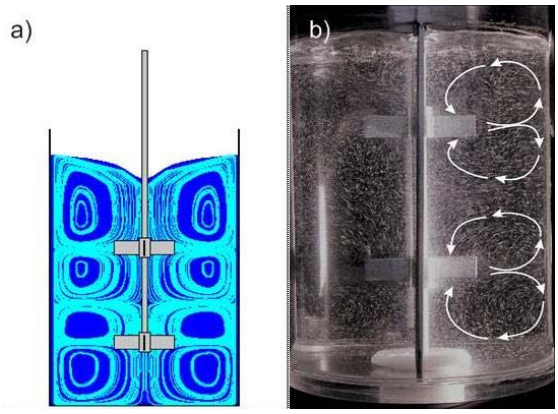

Fig. 8 Fluid flow pattern at S/D=1.5 visualized by a) VisiMix Turbulent software and b) digital imaging

One of the possible consequences of an increased shear stress is an interference with the formation of stable critical nuclei that could cause a delay of the onset of nucleation.

That the strengthening of the shear stress near impeller blade occurred was confirmed by VisiMix Turbulent. Those values are listed in Table I. The results suggest that the metastable zone width widens as a consequence of an increased shear stress which did not allow a formation of a stable critical nucleus despite the fact that the level of mixedness was increased.

TABLE I
SHEAR STRESS NEAR IMPELLER BLADE (BY VISIMIX TURBULENT)

Dimensionless impeller spacing		σ (N/m^2)
S*/*D (at D/T=0.33, N/N_{JS}=1.0, C/D=1.0)	0.0	5.04
	0.5	5.58
	1.0	6.35
	1.5	8.82

This observation implies that the flow pattern, i.e. the resulting intensity of the overall fluid flow as well as the shear stress near the impeller blade had a more pronounced effect on the start of nucleation rather than the level of turbulence, expressed in terms of Reynolds number, did.

IV. CONCLUSIONS

In this paper, a dependence of metastable zone width on impeller spacing in a dual impeller crystallizer was investigated in detail. Since different impeller positions result in different hydrodynamic conditions in the vessel, in order to be able to interpret the obtained results, they had to be taken into consideration as well.

Hydrodynamics of dual impeller crystallizer was analyzed based on the data on Reynolds number, dimensionless mixing time and by the flow pattern which was both simulated and photographed.

The results showed that an increase of supersaturation, i.e. the driving force of the process is independent on impeller spacing and is only a consequence of the physical characteristics of borax as well as the cooling rate which was kept constant in this research. Maximum supersaturation, i.e. the metastable zone width as well as the decrease of supersaturation, was obviously affected by impeller spacing.

As results showed, metastable zone width was affected by the value of shear stress in the system. An increase of shear stress in the system, which accompanied an increase of impeller spacing, obviously acted negatively on the formation of a critical stable nucleus. Since metastable zone width reflects on the properties of the final product, in order to obtain the crystals of wanted shape and size, mixing parameters such as impeller spacing should be taken into consideration as well.

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