Korean J. Chem. Eng., **27**(2), 619-623 (2010)
DOI: 10.1007/s11814-010-0069-y

Purification of naphthalene from eutectic mixture by continuous column crystallization

Qunsheng Li, Zhengming Yi†, Xufeng Sun, and Minggao Su

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100021, China
(*Received 11 May 2009 • accepted 3 August 2009*)

Abstract−To obtain highly purified naphthalene, a column crystallizer was employed and operated in the continuous multistage countercurrent fractional mode. The principles and characteristics of the process are introduced. A large amount of experimental work has been done on the crystallization process in a D=50 mm×1,350 mm column. The effects of operation conditions including the composition of feed, reflux ratio, stirring speed and the bed height of crystal on crystallization were systematically studied. The experiments showed that over 99.0% of the purity of product can be easily achieved in such conditions: feed composition among w=85.462-95.894%, reflux ratio among 1.42-4.04, the crystal bed height among 400-900 mm. The purity of product even reaches 99.996% in experiment.

Key words: Crystallization, Fractional, Continuous, Mass Transfer, Purification

INTRODUCTION

Recently, many types of column crystallizers have been applied in order to separate and purify organic compounds in the chemical industry. The process has been continuous multistage countercurrent fractional crystallization. That is a new and potential technique for separation and purification, and the evolution of its use in foreign countries has been rather active in recent years [1-3]. The principle of column crystallization is based on the use of a tower crystal container operated in a continuous multistage countercurrent mode, which makes effective contacting and mass transport between the crystals and melt possible [4]. Currently, a number of large scale processes involve countercurrent crystallization (wash) columns of different (mechanical, hydraulic, gravity) types and scales (with an annual capacity of up to 10^5 t). Australia [5] developed the Brodie crystallizer to purify 4-nitrochlorobenzene and 2-nitrochlorobenzene. Funakoshi et al. [6] used an inclined column crystallizer to separate and purify organic compounds such as acrylic acid. Quite recently, Li et al. [11] presented new experimental results on the separation of an o-dichlorobenzene and p-dichlorobenzene mixture in a continuous moving crystal bed crystallization column under the top-fed operation mode. Myasnikov et al. [7] studied the mass transfer in separation of ternary organic mixtures of two types and different compositions in a countercurrent crystallization column.

The mass transfer between a binary (or pseudobinary) melt and crystals in countercurrent columns has been studied in a rather large number of works. Most of them are devoted to the separation of mixtures with a simple eutectic, i.e., considering the purification of crystals of the main component for removing (washing away) eutectic-forming impurities trapped with the mother melt. In countercurrent flows of the phases, it is easier to wash away the adhering mother melt from the crystal surface. It is more difficult to remove impurities trapped with the mother melt in pores of crystals. From open pores, impurities are removed by liquid-phase diffusion as a result of the so-called diffusion washing, and from closed pores, impurities are removed because of migration of liquid inclusions in the presence of temperature gradients [8-12].

Wilcox critically reviewed and discussed the removal of inclusions by gradient methods by applying temperature gradients as large as 100 °C/cm or pressure gradients in an ultra centrifugal field of 210,000 G and showed the possibility of the removal. Practical applications of these gradients, however, seem impossible and these methods must be restricted to specific materials. Removal of inclusions by heating up to as high as the melting point of the crude crystals has been used in purifying a number of organics and metals [13]. This operation is, as described below, based on the solid-liquid phase equilibrium and is sometimes called "sweating." In the present paper the term "sweating" is used with the definition as a process of partial melting of crude crystalline materials by heating followed by drainage of the resulting melts.

Unfortunately, mechanism analyses of these operations are not sufficient, and understanding of the washing away phenomenon itself is so far very poor. The present study aims at using operation parameters to analyze the process systematically.

We conducted separation experiments in a top-fed column and purified industrial naphthalene in the column crystallizer by the continuous multistage countercurrent fractional crystallization mode. The raw material of industrial naphthalene used in the experiment is a binary mixture of naphthalene/benzothiophene (m.p.80.2 °C), which have an eutectic point.

PRELIMINARY CONSIDERATION

Consider a simple binary eutectic forming system as shown in Fig. 1. Crystalline products from a crystallizer, of which apparent composition is given as w_s at given temperature t_0, are mixtures of pure crystals and impure melts. The composition of the melt varies with the temperature; during crystallization it would be close to the bulk melt composition $w_{l,0}$ or its equilibrium composition $w^*_{l,0}$ while

†To whom correspondence should be addressed.
E-mail: easy857@hotmail.com

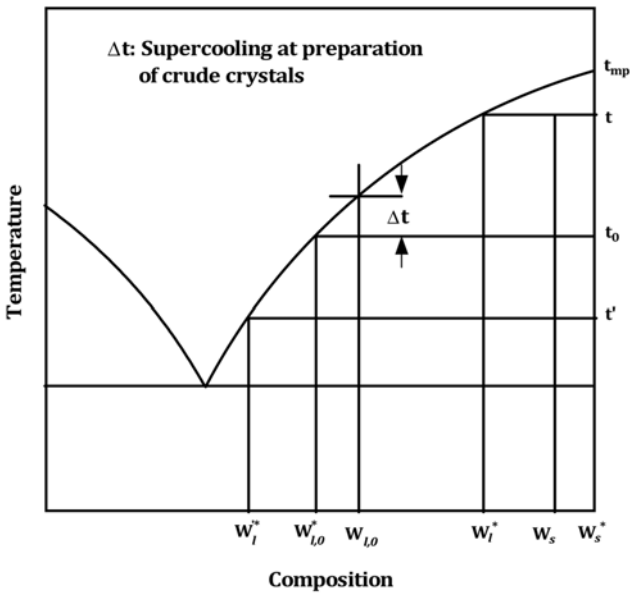

Fig. 1. Phase diagram of a simple eutectic system [14].

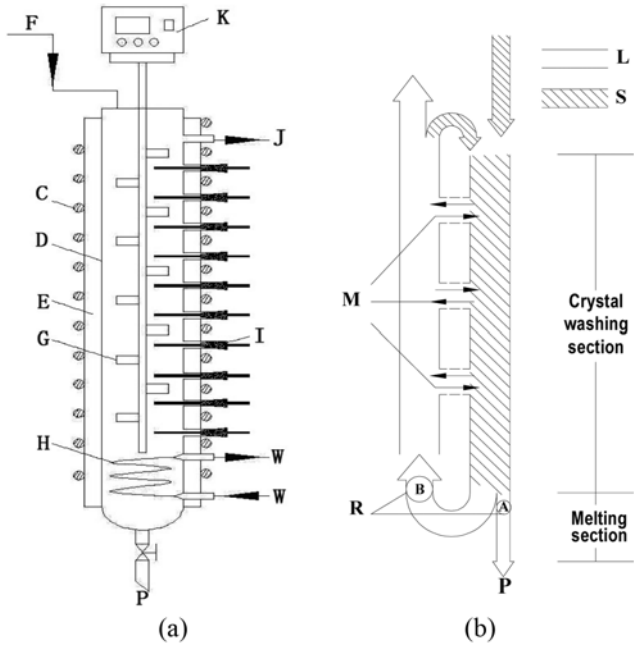

Fig. 2. (a) Schematic diagram of experiment setup. (b) Schematic of stream flow in the crystallization column.

F. Feed	K. Electromotor
C. Thermistor	P. Product
D. Inner column	R. Internal reflux ratio: B/(A+B)
E. Air jacket	L. Liquid
G. Stirring shaft	S. Solid
H. Coil pipe	M. Transfer between ascending solution and solution clinging to crystals
W. Hot water	
I. Sampling tap	
J. Residual outlet	

it may be $w'^{*}_{l,0}$. During the storage at a temperature t′. In addition, it will be w^{*}_{l} during the sweating at a temperature of/if equilibrium is assumed. Generally at higher sweating temperatures up to the liquidus point of the mixture, the amount of the melt is larger in accordance with the phase diagram and the lever rule. Therefore, the rate of purification must be connected with the rate of generation of the melt. Obviously, the rate of generation of the melt is dependent on the operation parameters such as the composition of feed, reflux ratio, stirring speed and the bed height of crystal.

For the present system, the solid-liquid equilibrium equations [15] are as follows:

$$T_{Le}=23.907+67.935x_A-5.024x_A^2-6.583x_A^3,$$
$$T_{Se}=16.911+36.438x_A-22.093x_A^2+48.714x_A^3$$

In the above equations, x_A is the mole fraction of naphthalene and $0.3707<x_A<1$. All experiments were conducted beyond the eutectic point.

EXPERIMENTAL

1. Apparatus

A schematic diagram of a column crystallizer is illustrated in Fig. 2. The column is constructed from a 50 mm i.d. Pyrex tube with a total length of 1,350 mm. In the column, there is a stirring shaft and a coiled pipe heater. The stirring shaft is used to provide gentle agitation of the crystal bed and also to partially support the crystal bed. The shaft was rotated to prevent encrustation on the column wall in the crystallization section and to enhance the counter-current contacts between crystalline particles and reflux melt in the purification section.

The heater serves to maintain a melt section at the bottom of the column. The column is insulated by a heated glass jacket that is equipped with accompanied heating, and hence it can be operated in an adiabatic mode. Feed materials are added to the top of the column by a screw feeder. A loading hopper is positioned just above the screw. Experiments were carried out in the manner of continuous operation.

2. Procedure

In the experiments, the column was firstly preheated by running the thermostat which was kept at a temperature of 60 °C. Then, 1,500 mL melt of the feed material was charged into the column. After that, the loading hopper and the screw feeder were started working to provide and pack crystals to the column to a desired height. Depending on the feed compositions, several hours were needed to establish a steady state operation, i.e., to achieve the overall balance between the feed and the two terminal streams, the residual melt flow and product flow.

In the column crystals nucleated on the wall and grew until they were scraped off by the action of the rotating spiral. The crystals then moved by gravity and countercurrent to the ascending mother liquor toward the bottom or "washing" section (as shown in Fig. 2(b)). These crystals descended through an insulated central section to be melted at the bottom of the column. The solution that the descending crystals displace was enriched in the crystallizing component and a countercurrent washing action was established, leading to the accumulation of high purity product at the bottom of the column.

Ten sample taps at fixed intervals of 100 mm were positioned along the column wall (as shown in Fig. 2(a)). Local concentration profiles were measured by sampling through each tap around 2-3 mL of the melt. The effluent residual melt flow at the top of the

Table 1. Summary of the conditions used in the reported runs

Run no.	x_F (wt%)	R	H (mm)	F (g·min^{-1})	p (g·min^{-1})
2	95.894	1.44	400	12.47	5.12
3	95.894	1.42	400	18.64	7.69
4	95.894	1.43	400	28.03	11.54
5	95.894	2.28	400	27.45	8.36
6	95.894	2.27	900	27.6	8.45
7	95.894	3.30	900	41.61	9.68
9	90.272	2.29	400	21.28	6.47
10	90.272	4.02	400	38.81	7.73
12	90.272	4.04	900	51.49	10.22
14	85.462	2.33	500	36.16	10.87
16	85.462	2.38	900	52.36	15.47

column was also sampled. A VISTA6000 gas chromatograph (Varian, USA) was used to analyze the sample concentrations with a resolution of 10 ppm.

RESULTS AND DISCUSSION

Experimental data were analyzed in an attempt to determine the factors which play important roles in bringing about and limiting the separation. The conditions used in the reported runs are summarized in Table 1.

To characterize the capability of the column, we defined the separation efficiency k and recovery efficiency ϕ as in the following equations:

$$\phi = \frac{x_p - x_w}{x_p} \quad (1)$$

$$k = \frac{y_p p}{y_w w} \quad (2)$$

In the above equations, x_p and x_w are the mass fraction of crystallizing component (naphthalene) in the product and residual melt, respectively. y_p and y_w are the mass fraction of non-crystallizable component (benzothiophene) in the product and the residual melt, respectively. In the eutectic mixture of naphthalene and benzothiophene, the theoretical limit value of ϕ is equal to 0.63, which is determined from a solid-liquid phase diagram of the binary system, and the higher the better. The theoretical value of k is 0.0, and the smaller the better.

1. Role of the Crystal Bed

Experiments were conducted to investigate the role played by the crystal bed and the first sampling tap was (near the top end) defined as the start point (z=0). At a steady-state operation, sufficient heating was provided by the heating system so that there was no crystal bed formed inside the column other than the melt. The measured concentration profiles are shown in Fig. 3.

It is noted that negligible concentration gradients existed along the column in these cases, and the corresponding product and residual melt compositions are nearly the same as that of the feeds. This means that a certain crystal bed exist in column is a necessary condition to achieve effective separation of the crystallization component.

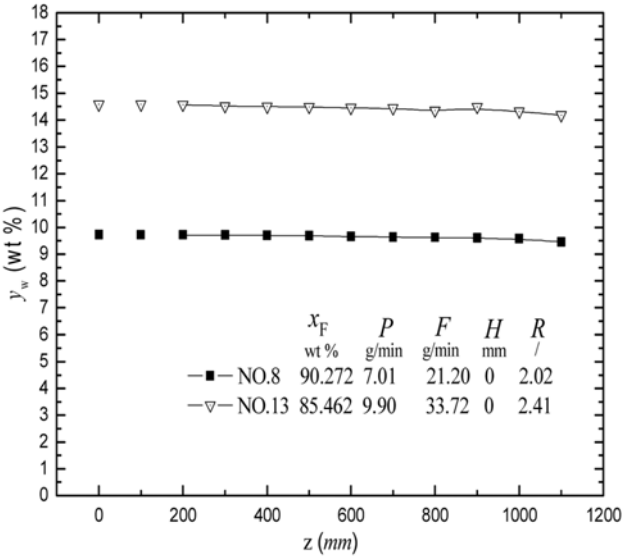

Fig. 3. Concentration profiles without formation of crystal bed inside of the column.

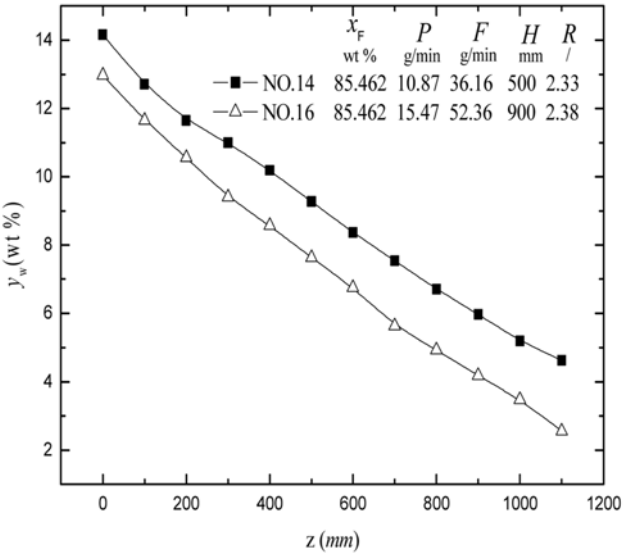

Fig. 4. Effect of the crystal bed height on concentration distribution along the column.

Fig. 4 shows the measured concentration profiles in the cases of identical operation conditions other than the heights of the crystal beds.

From Fig. 4, one can see the increase of concentration of key component along with the height of crystal bed. It is noted that, from an overall performance point of view, the height of the crystal bed has effect on the separation and purification of product and it will get

Table 2. Values of the separation indices corresponding to operating conditions in Fig. 3

Run no.	x_p (wt%)	x_w (wt%)	ϕ	k×10^2
14	95.38	85.84	0.099	14.0
16	97.44	87.03	0.107	8.29

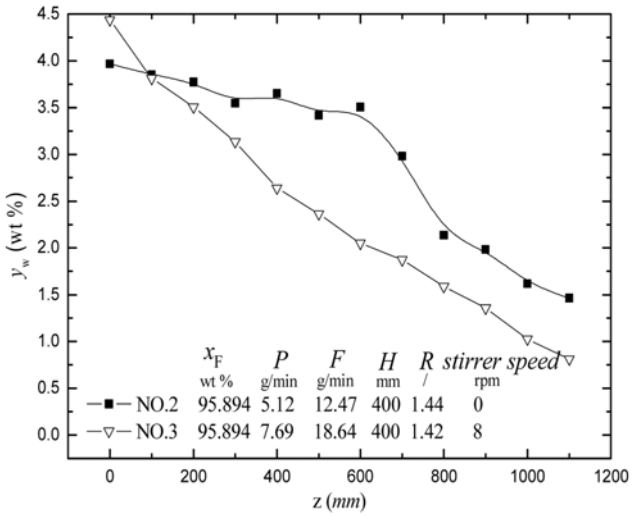

Fig. 5. Effect of the stirring speed on concentration distribution along the column.

the same conclusion from Table 2. But higher bed height of crystals means higher investment of equipment, which should be determined on the base of the actual situation.

2. Role of Stirring

As shown in Fig. 5, in the presence of stirring, significant change in concentration distribution was observed when compared with the extreme case of no stirring. It is noticeable that there is little change in concentration along the first-half column (from the top of column to the middle) in the case with no stirring. Compared to the other profile of Fig. 5, the measured concentration has a regular change along the full column. Obviously, this trend can be attributed to the action of the stirring shaft that provides the crystal bed with gentle agitation, thereby avoiding formation of dead zones or preferential flows within the bed. This leads to significant improvements in enhancing the mass transfer between the crystal and the melt. From

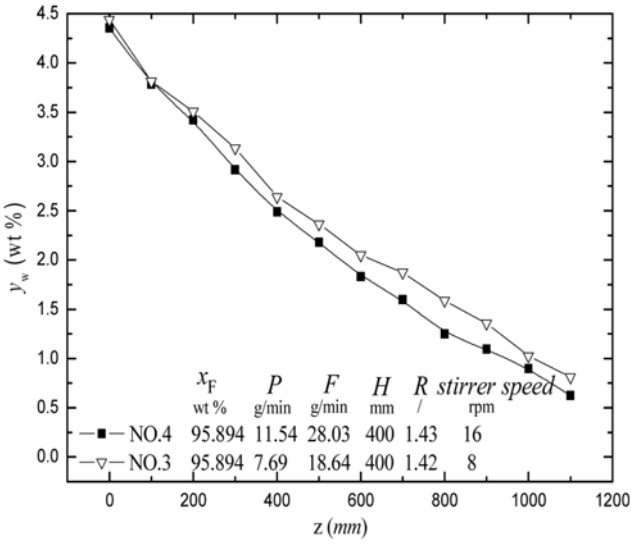

Fig. 6. Concentration profiles under the condition of with or without stirring of the beds.

Table 3. Values of the separation indices corresponding to operating conditions in Fig. 4 and Fig. 5

Run no.	x_p (wt%)	x_w (wt%)	ϕ	k×10^2
2	98.54	96.03	0.0254	25.7
3	99.19	95.56	0.0366	12.8
4	99.38	95.64	0.0376	10.0

Fig. 6 it is observed that a great variation in residual component concentration occurred near the bottom melt section and high purity product cannot be obtained with no stirring speed.

As shown in Fig. 6, on the other hand, further increase in stirring speed had no noticeable effect on the concentration distributions.

For the cases shown in Fig. 6, the results suggest that stirring speed beyond a certain value is not necessary for high-purity separation as the product purity is high under the low stirring speed and one can get more clear vision about the results from Table 3.

3. Effect of the Reflux Ratio

Fig. 7 shows the measured concentration dates in the cases of identical operating conditions other than the reflux ratios. From these concentration profiles, one can see the noticeable effect of reflux ratios on concentration distribution of benzathiophene, in particular near the bottom of the column.

This trend implies that contacting and mass transfer conditions of the crystal and melt is highly dependent on this parameter. It is noted that, from an overall performance point of view, the reflux ratio mainly affects the recovery capability of the column over the range of the conditions investigated, while high purity products are

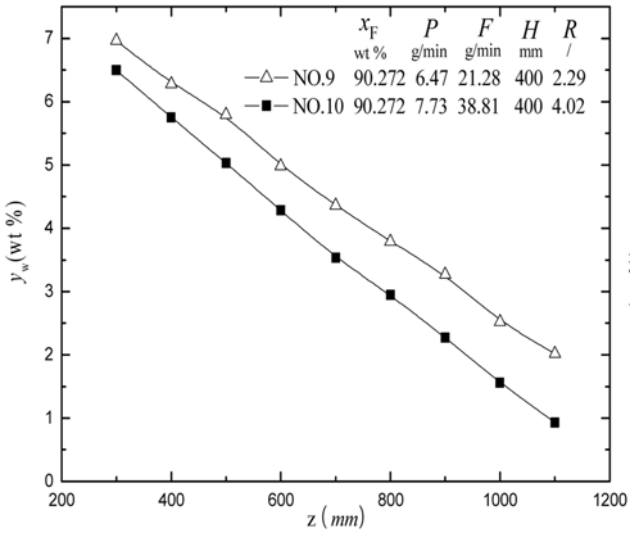

Fig. 7. Effect of the reflux ratios on concentration distribution along the column.

Table 4. Values of the separation indices corresponding to operating conditions in higher purities

Run no.	R	x_p (wt%)	x_w (wt%)	ϕ	k×10^2
12	4.04	99.98	91.88	0.0812	0.0641
7	3.30	99.99	96.16	0.0384	0.0315
6	2.27	99.93	95.89	0.0403	0.795

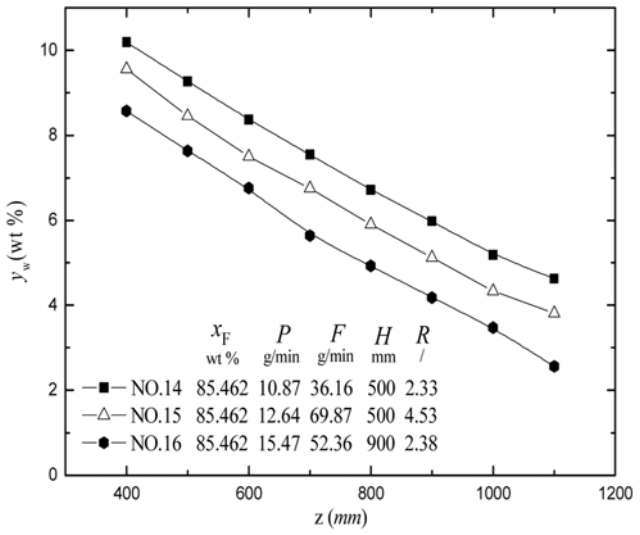

Fig. 8. Comparison of the effect of the reflux ratios with that of the heights of crystal bed.

obtainable under the conditions investigated. Obviously, at a large reflux ratio, more fresh liquors are provided by the reflux stream and enhanced the efficiency of contacting and mass transfer between crystals and melts in the column.

Combining with Table 1 and Table 4, one can see that increase reflux ratio can increase product purity, but it does not mean reflux ratio can always be the dominant parameter and it has its limit level. From the Fig. 8 one can see that an increase in bed heights of crystals can greatly reduce the effect of increasing the reflux ratio under similar operating conditions. It means that higher bed height of crystals can supply more adhering liquid washed away by the ascending mother liquid from the bottom and dilute impurities which are contained in the reflux; the effective mass transfer area and time were also increased and hence improved the purification efficiency.

CONCLUSIONS

The possibility of high purity separation of naphthalene and benzathiophene, in continuous moving crystal bed column crystallization, has been investigated experimentally. Local concentration of distributions for the particular separation of naphthalene and benzathiophene mixtures was measured as a function of feed composition, reflux ratio, height of the crystal bed, and internal stirring speed. A detailed examination of the design parameters of the crystallization demonstrated that, for a given feed stock with compositions beyond the eutectic point, the separation capability to achieve a demanding purity is not dependent on one individual parameter of interest and the same conclusion can be drawn from Table 4. It is concluded that the reflux ratio and height of the crystal bed have a pronounced effect on the product purities and hence the overall performance of the separation column. Taking the investment of equipment into account and the reflux ratio may be more easy to control by adjusting the heating power of the thermostat. An analysis based on the overall performance indices characterizing the separation efficiency revealed the potential of the process to achieve high purity of products exceeding 99.0%.

NOMENCLATURE

D : inner diameter of column [m]
F : feed stock flow rate [g·min^{-1}]
H : height of a column [mm]
P : terminal product liquid flow rate [g·min^{-1}]
R : reflux ratio
k : separation efficiency defined by Eq. (2)
ϕ : recovery efficiency defined by Eq. (1)
x : weight fraction wt% of naphthalene
y : weight fraction wt% of benzathiophene

Subscripts

F : feed stock
P : terminal product
W : terminal residual liquid

REFERENCES

1. G. J. Arkenbout, A. Van Kuijk and W. M. Smit, Progress in continuous fractional crystallization, Industrial crystallization, Plenum Press, NY, 431 (1976).
2. Q. Li and Y. Zhang, *Journal of Beijing University of Chemical Technology*, **24**(1), 1 (1997).
3. Q. Li and Y. Zhang, *Journal of Chemical Industry and Engineering (China)*, 44(4), 472 (1993).
4. P. M. Arnold, *Continuous fractional crystallization process*, US Patent 2,540,977 (1951).
5. Moyers, Charles Guthrie, jr. (Union Carbide Australia), Ltd. Crystallization apparatus [P]. Ger. Offen.2207814. 1972-8-31.
6. M. Matsuoka, K. Funakoshi, H. Uchida and H. Takiyama, *Journal of Crystal Growth*, **237**, 2251 (2002).
7. S. K. Myasnikov, A. D. Uteshinsky and N. N. Kulov, *Theoretical Foundations of Chemical Engineering*, **41**(2), 124 (2007).
8. G. J. Arkenbout and W. M. Smit, *Separation Science*, **3**(6), 501 (1968).
9. P. J. Jansens, R. Ham, O. S. L. Bruinsma, G. M. Rosmalen and M. Matsuoka, *Chem. Eng. Sci*., **50**(17) 2717 (1995).
10. R. Scholz and R. Ruemekorf, *Industrial wash column technology*, Proc. of the 11th Int. Workshop on Industrial Crystallization (BIWIC2004), September 15-17, Gyeongju, Korea, 116 (2004).
11. Q. Li, H. Liu, B. Wang and Y. Zhang, *Trans. IchemE*, **81A**, 1373 (2003).
12. S. K. Myasnikov, *Teor. Osn. Khim*., 37(2), 153 (2003).
13. M. Zief and W. R. Wilcox, *Fractional solidification*, Marcel Dekker Inc., New York (1967).
14. M. Matsuoka, M. Ohishi and S. Kasama, *J. Chem. Eng. (Japan)*, **10**(3), 181 (1986).
15. K. J. Kim, J. W. Kim, J. S. Chae and S. K. Ryu, *Sep. Sci. and Tech*., **38**(11), 2407 (2003).