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Purification of ε-caprolactam by means of a new dry-sweating technique

A. Chianese*, P. Cipriani, M. Parisi

Department of Chemical Engineering, University of Rome "La Sapienza", via Eudossiana 18, 00184 Rome, Italy

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Abstract

A new dry-sweating technique, based on the use of a centrifuge was applied to purify solid particles of ε-caprolactam. It allows elimination of up to 80% of the organic impurities with a relatively low molten mass, between 20 and 30%. Experimental runs were carried out on specifically produced solid pastilles and solid particles of industrial material. On the basis of the achieved results, a mechanism of the dry-sweating process is proposed.

Keywords: ε-Caprolactam; Dry-sweating technique; Centrifuge

1. Introduction

Sweating is a unit operation which consists of a partial melting of a solid particle to exude the impurities, which are present in the entrapped melt droplets. The effect of such a treatment is the improvement of the purity grade of the solid product. This operation is known as wet sweating or dry sweating if the solid is put in contact with a purer warm melt or a hot gas, respectively.

Wet sweating is more often applied by using a column, where a purer melt stream is put in countercurrent contact with the solid to be purified. The final product is a melt of a high purity grade. The process requires the overall melting of the fed solid particles and its stable operation is difficult.

The application of the dry-sweating operation is easier than the wet sweating one and less energy consuming, but the achieved purification is limited by the difficulty of detaching the melt generated from the solid [1].

This work reports the results of the experiments done on ε-caprolactam (CLP) containing both the water and organic impurities by using a new dry-sweating technique, based on the use of a centrifuge [2]. Caprolactam is an organic compound of industrial interest, its physical properties are well known and it exhibits a simple eutectic system with water. On the basis of the achieved results, an interpretation of the dry-sweating process is attempted.

2. Experimental

The equipment set up is shown in Fig. 1. The apparatus consists of a centrifuge with a 250 ml capacity-120 mm diameter basket, in which the purification took place, and of a hot gas stream circuit. Nitrogen was used as a heat carrier in order to prevent both the oxidation of the crystal and introduction of moisture: it was fed directly into the top of the centrifuge and it entered the heating system at a flowrate of approximately $5 \times 10^{-4}\,\mathrm{m^3\,s^{-1}}$; its temperature was manipulated in order to control the temperature in the inner side of the basket. The temperature outside the basket was continuously monitored. An ejector fitted to the centrifuge evacuated the nitrogen during the run.

Two kinds of solid CPL were used in the experiments: pastilles produced from a molten CPL–water mixture and solid crude caprolactam from an industrial plant. In the latter case, the CPL was crushed and the produced particles were sieved. Two classes of particles, in the size range 1–4 and 4–6.3 mm, respectively, were then submitted to the treatment.

The CPL pastilles, 3 mm in diameter and 1 mm in height in average, contain water and Sudan Red dye as impurities. They were produced by the cooling belt technique from Sandvik Process System [3]: this technique allows the production of regular-shaped pastilles that can be easily treated in washing columns [4]. The pastilles were produced with a different content of water and Sudan Red: the content of water ranged between 0.23 and 0.50% b.w., and that of the dye was between 10 and 20 ppm.

The Sudan Red content was used to estimate the sweating extent: in fact, this dye is soluble in water, it is present

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[*] Corresponding author. Tel.: +39-6-445-85-928; fax: +39-6-482-74-53.
E-mail address: chianese@ingchim.ing.uniroma1.it (A. Chianese).

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Nomenclature

a	acceleration field (m/s^2)
g	gravitational acceleration (m/s^2)
G	"G" number (dimensionless)
k, k'	fitting parameters
k_{imp}	impurity content ratio (dimensionless)
m	inverse of the liquidus curve (°C^{-1})
M	mass (kg)
M_{loss}	molten mass removed from the solid (kg)
N_{d}	number of droplets that leave the pastilles (dimensionless)
T	temperature (°C)
T_{M}	melting point of pure CPL (°C)
V	volume (m^3)
w	weight fraction (dimensionless)

Greek letters

β	liquid compressibility (Pa^{-1})
γ	surface tension (N/m)
ρ	density (kg/m^3)

Subscripts

CPL	caprolactam
d	droplet
e	external
i	internal
imp	impurity
s	solid
w	water
0	initial

Superscripts

m	melt
s	solid product
ss	start of the sweating process
$*$	equilibrium
0	initial

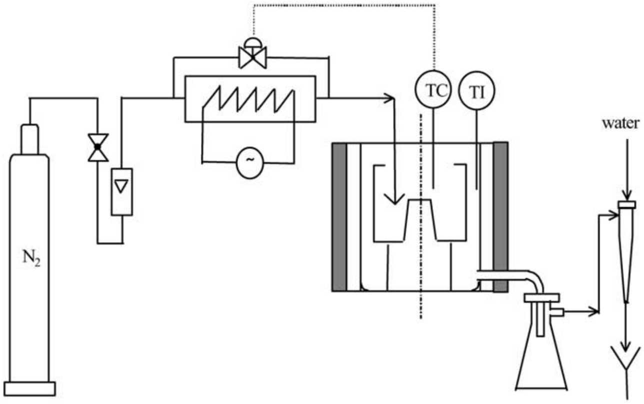

Fig. 1. The dry-sweating experimental apparatus.

in the aqueous melt droplets entrapped in the solid and it can be expelled from the solid only by the sweating process. This is not the case for water. In fact, when the melt droplets reach the solid surface, during the sweating, water can leave the solid either together with the droplets or by drying/evaporation.

For these reasons, the water content was only measured for some preliminary runs. The dye simulates the effect of some organic impurities like aniline and nitrobenzene, whose content in the industrial crude CPL is a few tenths of parts per million.

At the beginning of each run, the inner side of the basket centrifuge was heated up to the fixed temperature of the experiment, then the solid particles were fed into the rotating basket, which resulted in an almost uniform distribution of particles on the inner wall of the basket.

Most of the runs were carried out in a number of successive stages with the temperature of the gas being increased at each transition. The difference between the values of the temperatures inside, T_{i}, and outside, T_{e}, the basket was approximately 5 °C. When the run was completed the gas stream was stopped and a rapid cooling of the apparatus took place due to its rotation. When the internal temperature fell below 50 °C, the centrifuge's engine was switched off. The residual solids were weighed to determine the mass loss percentage and a small sample was then analysed.

The purity grade with respect to the organic compound—i.e. Sudan Red for the pastilles, aniline, nitrobenzene and traces of other compounds for the industrial crude CPL—was estimated on the basis of spectrophotometric analyses. The solid was dissolved in distilled water to obtain a 50% by weight solution, then the absorption of the solution was measured at a wave length of 290 nm. The accuracy of the measured absorption index was ±3%. The reduction of the Sudan Red content in the pastilles because of the treatment was also qualitatively estimated on the basis of the pastilles colour, changing from red for the original material to white for the highly purified solid.

3. Results

Table 1 reports a series of runs on CPL pastilles, containing water and Sudan Red, operated at a rotation speed of 1000 rpm. The feed mass varied from 10 to 100 g and the temperature of the gas stream was varied in 1, 2 or 3 steps.

The efficiency of the purification process was expressed, according to Bulau and Ulrich [5], as the ratio between the impurity content in the purified solid and in the raw material, respectively:

$$k^{\mathrm{s}}_{\mathrm{imp}} = \frac{\text{impurity content of the purified product}}{\text{impurity content of the raw material}} \tag{1}$$

This ratio gives an immediate measure of the purification extent, since it represents the fraction of impurities that have not been removed by the purification process: it ranges from

Table 1
Experimental runs on CPL pastilles (rotational speed: 1000 rpm)

Run ID	Feed (g)	No. of stages	Operating conditions of the stages			M_{loss}/M_0 (%)	k_{d}	k_{res}
			Time (min)	$T_{\mathrm{i,av}}$ (°C)	$T_{\mathrm{e,max}}$ (°C)			
P1	10	2	10–10	67.9–70.0	64.7–66.5	15.5	0.585	3.26
P2	10	2	10–10	68.1–70.1	63.9–65.6	11.3	0.608	4.08
P3	10	2	10–10	68.1–71.9	64.1–66.5	12.8	0.543	4.11
P4	10	2	10–10	67.9–72.0	64.9–67.8	39.5	0.334	2.02
P5	10	2	10–10	68.0–72.9	64.7–67.5	25.8	0.387	2.76
P6	10	2	10–10	67.7–73.0	63.5–67.1	29.3	0.332	2.61
P7	10	2	10–10	68.0–74.0	63.9–67.7	27.3	0.343	2.75
P8	10	3	10–5–5	68.0–71.9–74.0	64.6–66.0–68.0	62.0	0.230	1.47
P9	10	2	10–10	68.0–75.0	63.5–67.9	54.3	0.242	1.64
P10	10	1	10	68.0	63.2	3.70	0.955	2.17
P11	30	2	10–10	68.0–70.0	63.5–65.3	7.87	0.755	3.87
P12	30	2	10–10	67.9–71.9	64.1–67.7	23.9	0.373	3.00
P13	30	2	10–10	68.0–74.0	64.1–67.7	33.7	0.290	2.40
P14	30	2	10–10	68.1–74.0	63.0–68.1	41.7	0.265	2.03
P15	60	2	10–10	68.0–74.0	65.2–69.3	42.8	0.273	1.97
P16	60	1	10	68.0	64.0	2.17	0.957	2.94
P17	100	2	10–10	68.0–74.0	63.1–68.0	15.8	0.512	3.60
P18	100	3	10–10–10	70.1–75.0–80.0	64.6–68.7–70.9	88.3	0.212	1.10
P19	100	3	10–10–8	70.0–75.0–77.0	62.9–66.8–68.7	33.8	0.258	2.45
P20	100	2	15–15	67.9–72.0	63.6–67.2	21.7	0.389	3.20

1—when no purification occurs—to 0 when all the impurities are removed from the product. Only the organic impurity was taken into account for the evaluation of the impurity content ratio for the reasons reported in the section above. Since the organic impurity content was proved to be proportional to the absorption index of the aqueous solutions of the pastilles, $k_{\mathrm{imp}}^{\mathrm{s}}$ was determined as the ratio between the absorption index of the purified products and the feed pastilles, respectively.

Similarly, the increase of the impurity content in the residue can be defined as follows:

$$k_{\mathrm{imp}}^{\mathrm{m}} = \frac{\text{impurity content of the removed melt}}{\text{impurity content of the raw material}} \tag{2}$$

The value of $k_{\mathrm{imp}}^{\mathrm{m}}$ was calculated from the impurity mass balance by means of the following equation:

$$k_{\mathrm{imp}}^{\mathrm{m}} = k_{\mathrm{imp}}^{\mathrm{s}} + \frac{M_0(1 - k_{\mathrm{imp}}^{\mathrm{s}})}{M_{\mathrm{loss}}} \tag{3}$$

where M_0 is the mass of the feed and M_{loss} the molten mass removed from the solid. The ratio between $k_{\mathrm{imp}}^{\mathrm{s}}$ and $k_{\mathrm{imp}}^{\mathrm{m}}$ is the total coefficient of distribution as defined by Saxer [14].

The achieved results lead to the following comments:

- The impurity content ratio $k_{\mathrm{imp}}^{\mathrm{s}}$ ranges between 0.96 and 0.21 and is strictly related to the molten mass percentage M_{loss}/M_0 (see also Fig. 2); this relation is not significantly affected by the applied operating conditions, i.e. the mass of the feed and the number of stages.
- The concentration of the impurity in the exuded molten mass is rather high for a small mass loss, whereas it decreases as the mass loss increases. In fact, $k_{\mathrm{imp}}^{\mathrm{m}}$ is around 4.1 for a partial melting of approximately 12% (see runs P2 and P3) and it falls to 1.10 when most of the solid is molten as occurs in run P18.
- The temperature of the pastilles surface is close to the temperature of the gas stream outside the basket: in fact, this temperature is generally lower than 69.2 °C, which is the melting point of pure CPL [6], while the temperature of the gas inside the basket is significantly higher.

A second series of runs was made to investigate the effect of the centrifuge's rotation speed. The results reported in Table 2 exhibit a small effect of the applied centrifugal acceleration in the range 67–6700*G* corresponding to rotation speeds from 1000 to 10000 rpm. Therefore, because of the energy saving, in all the subsequent runs a rotation speed of 1000 rpm was adopted.

A series of runs was made by using an industrial solid sample of crude CPL, whose 50% aqueous solution has an absorption index at 290 nm of 0.72 and a permanganate number of 900. The amount of water in the original sample was negligible.

The main operating conditions together with the results of these runs are reported in Table 3. It can be observed that the purification of the smaller particles is more effective: 84% of the original impurities are removed for a melt drainage between 20 and 30%.

For both the particle sizes, the impurity content ratio for the solids is well related to the percentage of the solid mass loss (see Fig. 3) which agrees well with the observations for the pastilles. The fitting curves are of the exponential decay type.

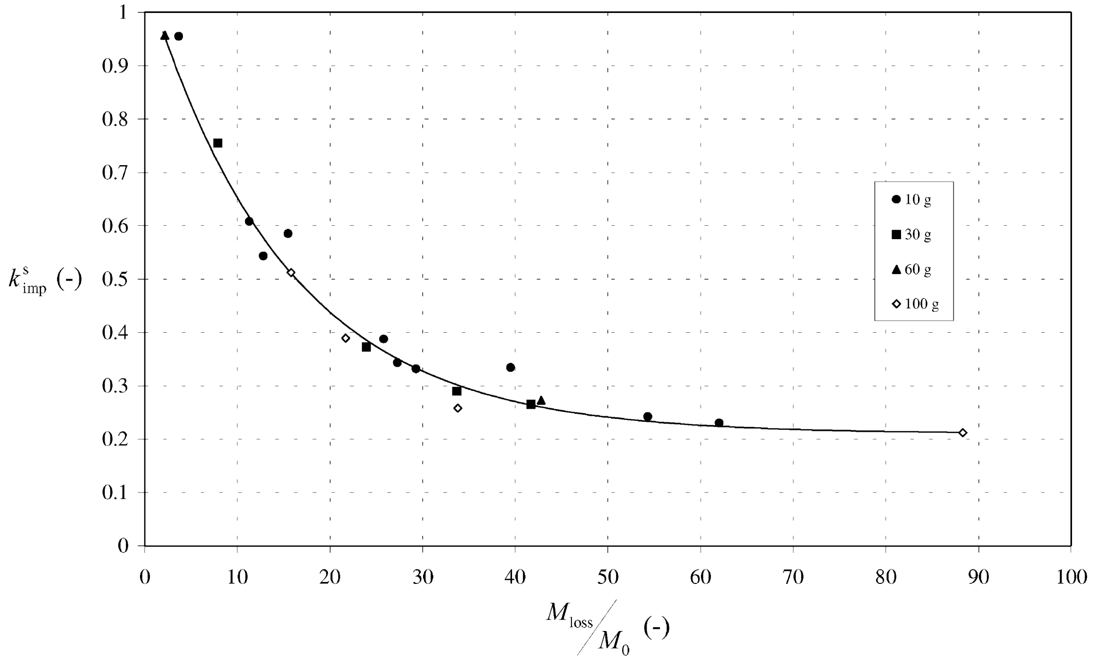

Fig. 2. Experimental runs on CPL pastilles: impurity content ratio versus mass loss.

Table 2
Experimental runs on CPL pastilles at different rotational speeds (two stages of 10 min each)

Run ID	Feed (g)	Rotation speed (rpm)	I step		II step		M_{loss}/M_0 (%)	k_d	k_{res}
			$T_{i,av}$ (°C)	$T_{e,max}$ (°C)	$T_{i,av}$ (°C)	$T_{e,max}$ (°C)			
P6	10	1000	67.7	63.5	73.0	67.1	29.3	0.332	2.61
P21	10	2500	68.0	64.7	72.0	67.0	27.9	0.426	2.48
P22	10	7500	68.0	66.6	69.9	68.5	43.7	0.232	1.99
P9	10	1000	68.0	63.5	75.0	67.9	54.3	0.242	1.64
P23	10	7500	67.9	65.8	72.0	68.4	52.6	0.244	1.68
P12	30	1000	67.9	64.1	71.9	67.7	23.9	0.373	3.00
P24	30	5000	68.0	65.4	72.0	67.8	16.7	0.319	4.40
P25	30	7500	67.9	65.5	69.9	67.7	18.9	0.363	3.73
P26	30	10000	68.0	66.2	70.0	68.1	20.0	0.281	3.88

Table 3
Experimental runs on crude CPL particles

Run ID	Size (mm)	Run time (min)	T_i (°C)	M_{loss}/M_0 (%)	$k_{d,org}$
R1	1–4	1 × 10	69	1.7	0.85
R2	1–4	2 × 10	69/71	4.1	0.72
R3	1–4	1 × 10	71	10.8	0.38
R4	1–4	1 × 15	71	10.8	0.37
R5	1–4	1 × 20	71	20.2	0.16
R6	1–4	1 × 30	71	29.7	0.16
R7	4–6.3	1 × 10	69	1.4	0.89
R8	4–6.3	2 × 10	71/73	4.6	0.73
R9	4–6.3	2 × 10	69/71	4.6	0.67
R10	4–6.3	2 × 10	71/74	7.5	0.55
R11	4–6.3	2 × 10	71/76	14.2	0.45
R12	4–6.3	1 × 30	71	13.9	0.47
R13	4–6.3	2 × 10	71/74	20.0	0.39

The deviation between the results for the crude CPL and those for the pastilles are justified on the basis of the different nature and particle shape of the crude CPL material.

4. Discussion

In this work, the purification of ε-caprolactam with respect to water and organic impurity was investigated. The phase diagram of the binary system CPL/water exhibits a eutectic point at −19.3 °C for a CPL concentration of 60.3% b.w., while the melting temperature of pure CPL is 69.2 °C [6]. It was verified by means of DSC analyses that the Sudan Red does not significantly change the melting temperature of the system.

The results obtained in this work show that the use of a rotating unit to accomplish a dry-sweating process results

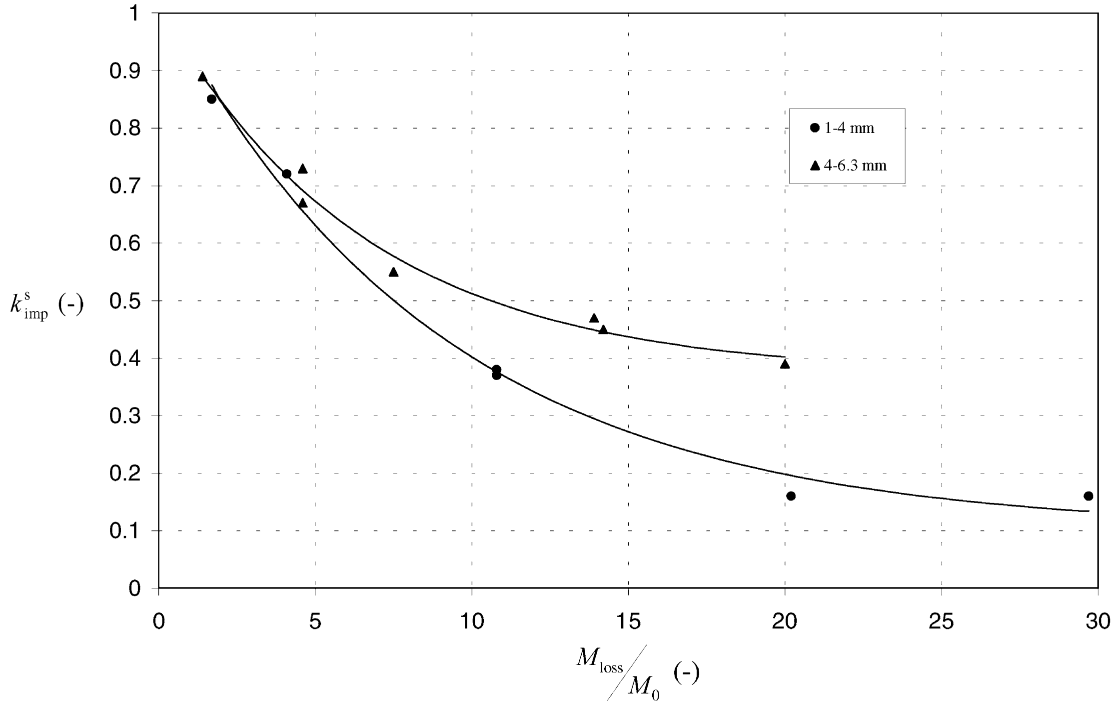

Fig. 3. Experimental runs on CPL particles: impurity content ratio versus mass loss.

in a good purification of the solid product. This separation process only requires a short process time, i.e. 10–20 min, and a low heat consumption, that is the heat required to melt 30% or less of the solid mass. These good performances were mainly achieved because the centrifugal force enables the complete detachment of the exuded molten drops which reach the solid surface.

If the dry-sweating is performed in a static unit, however, the separation of the molten drops from the solid is a difficult task. In fact, a static dry-sweating process was applied to the CPL pastilles in preliminary runs and an unsatisfactory purification was achieved regardless of the solid mass loss. For up to 20% of drained melt, the k^{s}_{imp} calculated with respect to water was higher than 0.65, while the purification with respect to Sudan Red was always negligible: because the Sudan Red is dissolved in the water this difference indicates that the purification for water is caused by evaporation/drying and not by the detachment of the drops. Similar results were obtained by Bulau and Ulrich [5] for CPL pastilles: operating at 64 °C the purification was less than 30% with respect to the initial content of water.

The low efficiency of the static dry-sweating is due to the difficulty of draining away the molten exuded drops as soon as they reach the solid surface. The reason is the rather high mass of the single drop required for falling down from the solid surface. In fact, the balance between adhesion and mechanical forces acting on the droplet leads to the following relationship between the detachable drop mass M_d and the applied acceleration [13]:

$$M_d = 11 \times \left(\frac{\gamma}{a}\right)^{1.5} \rho_d^{-0.5} \tag{4}$$

where γ is the surface tension and ρ_d the drop density.

In the case of caprolactam and under normal gravity force, the minimum weight of the droplets prone to detachment equals 80 mg. This value is much larger than the weight of a single pastille, which equals 5.2 mg. Therefore, the detachment of droplets cannot take place under the gravitational force. When a pastille is exposed to an acceleration field of 70*G*, which is in the range of the centrifugal accelerations applied in this work, the weight of the minimum drop size that can be detached is smaller than 0.2 mg. Thus the acceleration field attained in the centrifuge allows the drainage of the molten drop from the particle surface, whereas the gravity acceleration does not.

On the basis of the achieved results, an interpretation of the process can be attempted. As stated earlier, the presence of Sudan Red does not significantly affect the melting temperature of the pastilles, thus it can be assumed that the behaviour of the solid–melt system is that of the binary eutectic system CPL–water.

In principle, the pastilles are predominantly composed of a solid phase that consists of pure CPL: the impurities are mainly located in the liquid inclusions. In fact, when a melt containing impurities is cooled during pastille formation a relatively pure solid phase will crystallize and some melt droplets with a relatively high impurity concentration will be trapped in the solid, thus the impurities concentrate in them [1]. During crystallization, the concentration of the impurities in the included droplets slowly increases, due to the crystallization of pure solid at the droplet boundary, until the equilibrium condition is attained. A further location of impurities is in the grain boundaries because the impurity molecules tend to be expelled as the single crystal grain grows.

The dry-sweating process causes some physical changes in the solid particle. First of all the temperature increase gives rise to lower values of the water equilibrium concentration at the solid–melt boundary in the included droplets. As a consequence, the solid CPL at the solid–melt interface melts and a mass transfer flux between the droplet boundary and its bulk occurs till the new equilibrium condition is attained. This process leads to a volume increase of the melt droplet.

Since the specific volume of the molten CPL is approximately 6% higher than that of the solid CPL, the increase of the droplet volume, ΔV, is accompanied by a pressure increase given by

$$\Delta P = \frac{1}{\beta}\frac{\Delta V}{V_0}\left(1 - \frac{\rho_L}{\rho_S}\right) \tag{5}$$

where β is the CPL's liquid compressibility. When the stress in the solid, due to the droplet inner pressure, overcomes the maximum resistance of the solid material, fracturing may result as noted by many authors [14,15]. Then, according to Knight [16], the molten inclusions work their way towards the surface by repeatedly cracking the solid and flowing into fractures. This appears to be the only realistic hypothesis for movement of the inclusion within the pastilles. In fact, the thermomigration of the droplets [15] is negligible due to the almost uniform temperature field within each pastille.

When the migration of the droplets penetrate the surface of the pastilles the sweating process starts and the expelled mass is given by

$$M_{\text{loss}} = N_d M_d \tag{6}$$

where N_d is the number of the droplets leaving the solid mass due to sweating.

Since the droplet enlargement is due to the melting of pure CPL, the amount of impurity in each droplet is constant. Thus the mass of the droplet, M_d, is related to the initial droplet mass M_d^0 on the basis of the constancy of the water content in the droplet, i.e.

$$M_d = \frac{M_d^0 w_{w,d}^0}{w_{w,d}} \tag{7}$$

where $w_{w,d}^0$ and $w_{w,d}$ are the initial and the current water weight fraction in the included droplet, respectively.

The water content which is attained throughout the sweating process is equal to the equilibrium value if the process is carried out very slowly or can be considered in first approximation proportional to it if the sweating proceeds quite quickly. For the examined case, where the content of water never exceeds 2% b.w., the following equilibrium equation holds:

$$w_{w,d}^* = 1 - w_{\text{CPL},d}^* = m(T_M - T) \tag{8}$$

where $w_{w,d}^*$ and $w_{\text{CPL},d}^*$ are the water and the CPL weight fraction in the droplet at equilibrium condition, T_M the pure CPL melting temperature, T the effective temperature and m the inverse of the slope of the liquidus curve, which is equal to $2.93 \times 10^{-3}\,^\circ\text{C}^{-1}$.

By assuming the proportionality between $w_{w,d}$ and $w_{w,d}^*$ and by substituting M_d in Eq. (6) with the expression at the right-hand side of Eq. (7) the following proportionality can be assessed:

$$M_{\text{loss}} \propto \frac{M_d^0 w_{w,d}^0}{m(T_M - T)} \tag{9}$$

The plot in Fig. 4 of the experimental data for the CPL pastilles confirms the inverse proportionality between the mass loss and the term $(T_M - T)$ expressed by Eq. (9), thus validating the adopted hypotheses. Therefore, the following expression was used for the data interpolation:

$$\frac{M_{\text{loss}}}{M_0} = k\left(\frac{1}{T_M - T} - \frac{1}{T_M - T^{\text{ss}}}\right) \tag{10}$$

The best fit of the experimental data by Eq. (10) leads to a value of k equal to 0.699 °C and of $T^{\text{ss}} = 63\,^\circ\text{C}$. T^{ss} may be considered as the temperature at which sweating occurs. In particular, we can assume that the volume and the internal pressure in the droplet increase at this temperature and the solid fracturing takes place. The impurity content ratio $k_{\text{imp}}^{\text{s}}$ can also be related to $1/(T_M - T)$.

From the mass balance of the organic impurity Sudan Red

$$w_{\text{imp},s}(M_0 - M_{\text{loss}}) = w_{\text{imp},s}^0 M_0 - w_{\text{imp},d} M_{\text{loss}} \tag{11}$$

it follows that:

$$k_{\text{imp}}^{\text{s}} = \frac{1 - (M_{\text{loss}}/M_0)(w_{\text{imp},d}/w_{\text{imp},s}^0)}{1 - (M_{\text{loss}}/M_0)} \tag{12}$$

moreover, because the impurity content in the droplet is constant, it holds that

$$M_d = \frac{M_d^0 w_{\text{imp},d}^0}{w_{\text{imp},d}} \tag{13}$$

Comparing Eq. (13) with Eq. (7), learns that

$$\frac{w_{\text{imp},d}}{w_{\text{imp},d}^0} = \frac{w_{w,d}}{w_{w,d}^0} \tag{14}$$

and for the direct proportionality between $w_{w,d}$ and $w_{w,d}^*$, we have

$$\frac{w_{\text{imp},d}}{w_{\text{imp},s}^0} \propto \frac{w_{\text{imp},d}^0}{w_{\text{imp},s}^0}\frac{m(T_M - T)}{w_{\text{imp},d}^0} \tag{15}$$

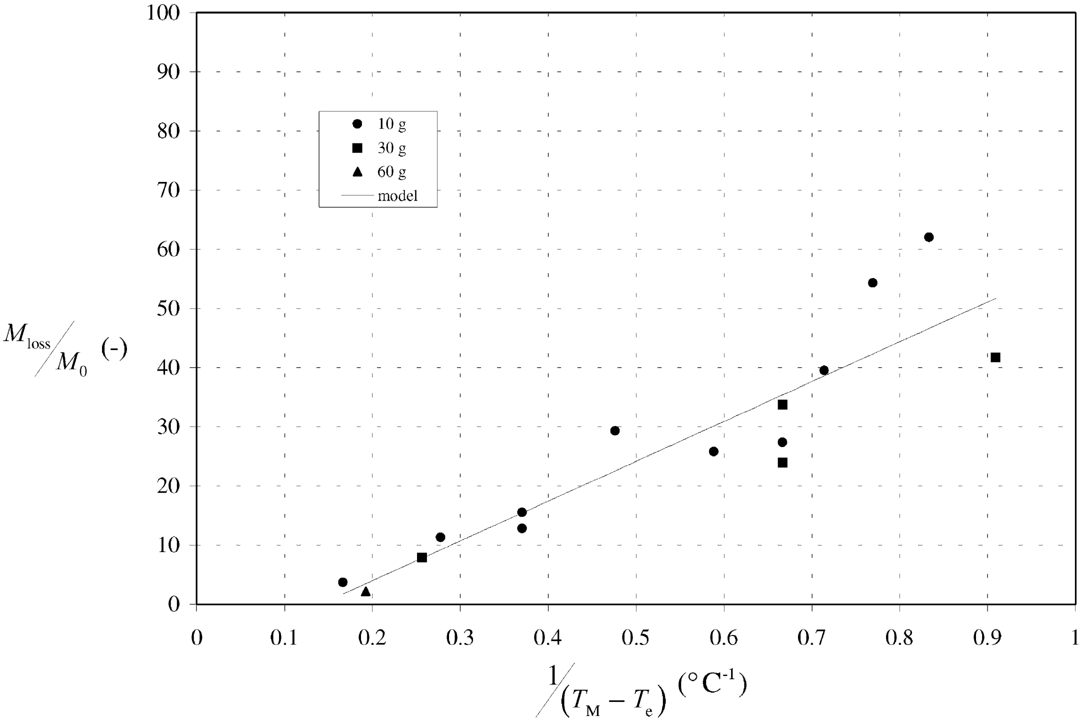

Fig. 4. Experimental runs on CPL pastilles: effect of the temperature on the mass loss.

Finally, substituting M_{loss}/M_0 given by Eq. (10) and $w_{\text{imp,d}}/w^0_{\text{imp,s}}$ given by Eq. (15) in Eq. (12), the following relation to evaluate $k^{\text{s}}_{\text{imp}}$ can be attempted:

$$k^{\text{s}}_{\text{imp}} = \frac{1 - k'[1 - (T_{\text{M}} - T)/(T_{\text{M}} - T^{\text{ss}})]}{1 - k[(1/(T_{\text{M}} - T)) - (1/(T_{\text{M}} - T^{\text{ss}}))]} \quad (16)$$

In Fig. 5, the impurity content ratio $k^{\text{s}}_{\text{imp}}$ determined from the experimental runs on the CPL pastilles are plotted versus the factor $1/(T_{\text{M}} - T)$. The data are well interpolated by Eq. (16) with $k' = 1.04$ as only additional parameter. It has to be noted that the three constants T^{ss}, k and k' are required to fit the two

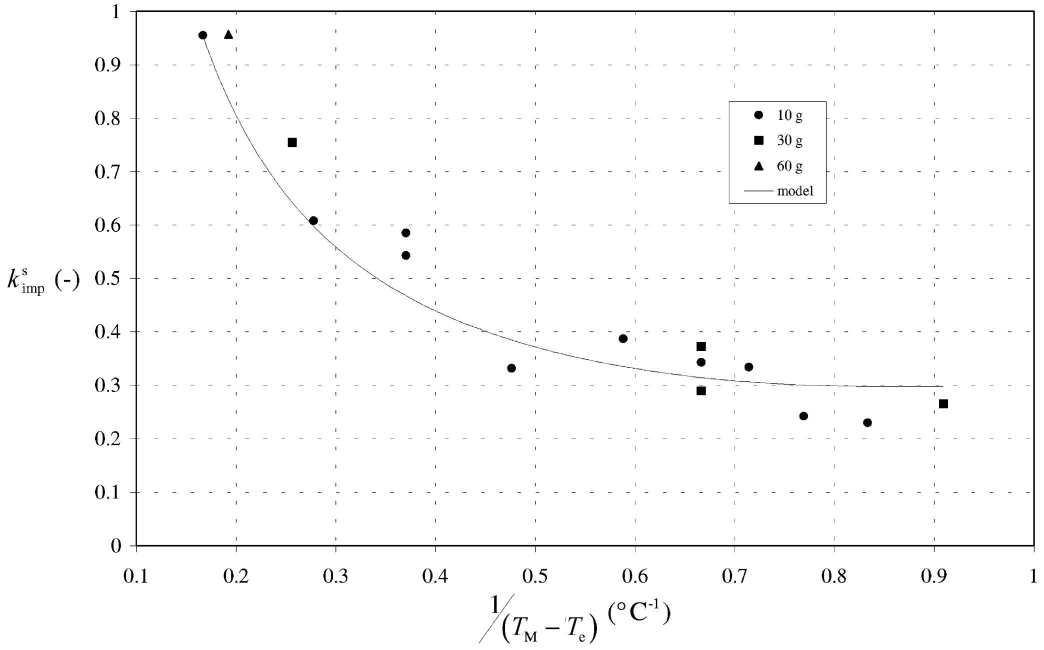

Fig. 5. Experimental runs on CPL pastilles: effect of the temperature on the impurity content ratio.

experimental series of data $M_{\text{loss}}/M_0(T)$ and $k^{\text{s}}_{\text{imp}}(T)$ versus $1/(T_{\text{M}} - T)$.

The adopted model, despite of the approximations made, allows a good interpretation of the dry-sweating phenomena. The sweating starts at a specific temperature T^{ss}, equal to 63 °C in the examined case. The sweating leads to an overpressure within the droplets such that fractures in the solid pastilles are generated. Purification takes place by the expulsion of the melt droplets originally included in the pastilles, which reach the external surface of the particles by repeatedly cracking the solid and flowing to the fractures. When the sweating temperature is low, droplets of small mass and with a relatively high concentration of impurities are expelled. The mass of the original solid is then only slightly reduced and the impurity is highly concentrated in the expelled sweat droplets. On the contrary, if an operating temperature quite close to the melting temperature is adopted, the expelled droplets have a higher mass and a lower impurity concentration and the overall mass loss of the solid increases.

The importance of the solid particles shape/dimension in the proposed mechanism must be stressed: the expulsion of the inclusions located close to the boundary of the particle is rather easy, since a small increase of their internal pressure—thus a small increase of their volume—is able to produce a crack that reach the solid surface. On the contrary, the deeper included droplets are able to reach the solid surface when their pressure increase is quite high. Thus the surface/volume ratio of the particle, which determine the mean distance between the liquid inclusions and the solid particle wall, affect the purification achieved. The experimental evidence on the crude CPL particles supports this interpretation: the comparison between the two $k^{\text{s}}_{\text{imp}}(M_{\text{loss}}/M_0)$ curves in Fig. 3 clearly show that the purification of the smaller particle requires a lower mass loss, since the included droplets reach the solid surface when their volume increase is low.

It is interesting to compare the present work with the dry sweating of aromatic compounds published by Matsuoka et al. [17]. The authors reported a two stages purification process: in the first, the solid was partially melt and second the solid–melt separation was carried out by means of a centrifuge. It has to be pointed out that, after the treatment reported here, the particles are compact and exhibit a smooth surface, while the particles treated in the experiments of Matsuoka et al. [17] have a ragged profile. This means that the solid undergoes a recrystallization throughout the operation, the cracks are welded and the particles maintain their mechanical resistance when the removal of the melt droplets and the heating of the solid occur simultaneously.

A number of works in the literature report experimental results concerning the purification of CPL by melt crystallization by using different and more sophisticated technologies with respect to the one of the present work. Most of the work concerns the removal of the impurity water [5,7–11]. Verdoes and Nienoord [12] studied the removal of Sudan Red from CPL pastilles similar to those used in the present work. They obtained a removal of the Sudan Red dye up to 88% by using a stirred batch crystallizer with a residence time equal to 1 h and up to 99.4% by adding a further purification step with a washing column. The results obtained by the proposed dry-sweating technique are then comparable to those reported by Verdoes for the stirred batch crystallizer.

5. Conclusion

The main aim of the work was to show the effectiveness of a new dry-sweating technique based on the use of a centrifuge. The experimental work was focussed on the purification of solid particles of crude ε-caprolactam. The major advantage of the adopted technique is that the applied centrifugal force removes the melt droplets as they reach the surface of the solid particles. Consequently, the results obtained in this work are significantly better than what can be achieved with static dry sweating.

The driving force of the process is the inverse of the difference between the melting point of the pure product and the operating temperature. The effect of this driving force on the solid mass fraction loss and the removal of the impurity can be described by a simplified model based on the behaviour of the melt droplets included in the solid and their expulsion from the solid.

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