FRACTIONAL SUSPENSION CRYSTALLIZATION
OF ORGANIC COMPOUNDS
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OF ORGANIC COMPOUNDS

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Pieter Johannes JANSENS
scheikundig ingenieur
geboren te Roosendaal
Dit proefschrift is goedgekeurd door de promotoren:
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Voor Rian

Aan mijn ouders
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chapter 1

INTRODUCTION TO
FRACTIONAL CRYSTALLIZATION

P.J. Jansens and G.M. van Rosmalen

Handbook of Crystal Growth, Ed. D.T.J. Hurle
1.1 INTRODUCTION

Fractional crystallization (FC) is a general term for separation processes which can be used for large scale separation and ultrapurification of organic compounds from multicomponent mixtures in an economically favourable and environmentally safe way. The driving force for crystallization is either cooling or pressurization (fig. 1.1). The vast majority of the FC processes is based on cooling crystallization but in Japan the relatively new and promising high pressure crystallization is already applied on an industrial scale. In a cooling crystallization process crystals are grown either freely suspended or as a fixed layer on a cooled surface. In Europe mainly layer growth processes are applied whereas in Japan suspension growth processes are dominant. Worldwide both crystal growth techniques seem to be equally represented.

Figure 1.1: techniques applied in fractional crystallization processes

FC processes can be characterized as a multistep operation which usually involves a countercurrent contact between crystals and mother liquor in such a way that the crystals are grown and/or washed in mother liquor of increasing purity at ascending
temperatures (fig. 1.2). Layer growth and pressure crystallization processes are usually operated batchwise whereas suspension crystallization processes mostly feature a continuous operation.

\[ T_1 < T_2 < T_3 \]

**Figure 1.2:** general set-up of fractional crystallization processes

Advantages of FC in comparison to conventional separation techniques like distillation and extraction are its superior selectivity, lower energy consumption (providing the operating temperature exceeds 273 K) and moderate operating conditions whereas addition of toxic or explosive solvents can usually be avoided. The superior selectivity stems from the fact that the molecular mobility is very restricted in the crystal lattice due to strong molecular bonds and a regular arrangement which makes it difficult for impurities to enter the lattice. The energy consumption of FC is relatively low because of its high selectivity which allows low reflux ratios and, when compared to distillation, because the latent heat of fusion of organic compounds is often two to four times smaller than their latent heat of evaporation. Reservations have to be made for FC processes which require deep cooling to crystallize a low melting point compound and for the so-called dynamic layer growth processes which involve repeated crystallization operations. The operating conditions for cooling crystallization processes lie close
to the melting point of the pure component at atmospheric pressure. Figure 1.3 [1] demonstrates that almost 90 % of the organic compounds have a melting point above 273 K at atmospheric pressure. In cases where the melting point of an organic compound is considerably lower than 273 K, pressure crystallization can be considered which allows separation above room temperature at low energy demands. Addition of a solvent may be used to reduce the viscosity of the mother liquor, to enhance the growth rate of the crystals, to improve the selectivity, to lower the operating temperature and to facilitate solid/liquid separation. If possible solvent addition has to be avoided for safety, environmental and economic reasons.

![Graph showing melting points of organic compounds](image)

**Figure 1.3:** melting points of organic components at atmospheric pressure [1]

A disadvantage of FC processes is the inherent slowness of a crystallization process resulting in low **specific** production capacities, which results in rather large equipment and relatively high investment cost.
Evaluating the merits and drawbacks of FC it can be said that application of FC is most interesting as a tool in ultrapurification where the feedstock is already 70-80% pure and a product purity of 99.99% is strived for. Such stringent purity demands are frequently needed for advanced polymer and pharmaceutical applications. Another important field of application lies in the purification of thermally unstable components which have to be treated in modern food industry. Table 1 summarizes a number of organic (bulk) compounds which can be purified with FC and their estimated world wide production capacities.

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Estimated world wide production capacity</th>
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<tr>
<td>p-xylene</td>
<td>4.5*10^6 t/y (1992)</td>
</tr>
<tr>
<td>acetic acid</td>
<td>4.0*10^5 t/y (1989)</td>
</tr>
<tr>
<td>phenol</td>
<td>3.7*10^6 t/y (1989)</td>
</tr>
<tr>
<td>dimethylterephthalate</td>
<td>4.6*10^6 t/y (1992)</td>
</tr>
<tr>
<td>caprolactam</td>
<td>3.6*10^6 t/y (1992)</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.6-1.0*10^6 t/y (1992)</td>
</tr>
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</table>

Table 1: organic compounds suited for purification with fractional crystallization and their estimated world wide production capacities
1.2 BASIC CONCEPTS

1.2.1 phase diagrams
Phase diagrams are the graphical expression of phase equilibria and can be used to obtain a first indication of the separability of the components of a mixture. The complexity of phase diagrams rapidly increases with the number of components. Binary phase diagrams are simple and well documented, whereas ternary phase diagrams are very complicated and rarely described in literature. Data on phase equilibria of systems with four components or more are almost never available. In practice, however, multicomponent systems are usually of great interest and these systems are simply treated as combinations of separate binary systems. This simplification is only valid in the absence of ternary and higher order interactions and when each impurity behaves independent of the others in its relationship to the main component. In this section only binary phase diagrams will be discussed.

Binary solid-liquid phase diagrams were divided by Roozeboom [2] in two categories: eutectics which show no solid solubility and solid solutions which exhibit limited or complete solid solubility.

Solid solution may involve either the inclusion of guest molecules in the interstitial voids of the host lattice or the isomorphous substitution of host molecules by guest molecules. In case of organic systems only the substitutional mode is known [3]. Criteria for the formation of solid solutions are extensively described by Kitaigorodskii [4]. It is obvious that similarity in size and shape between the host and the guest molecules is essential for the formation of solid solutions. Introduction of look alike guest molecules will not lead to major changes in the crystal lattice of the host molecules. In this respect Kitaigorodskii argues that host molecules are replaced more easily by smaller molecules than by larger ones. Furthermore, for solid solution to be continuous throughout the full range of compositions the structure of the components must have identical space-groups,
the same number of molecules per unit cell and similar molecular packing. Matsuoka [1] showed that according to the data he reviewed 85.9 % of the binary organic mixtures belong to the eutectic category of which the "simple eutectic" is the most important representative (54.3 %). Complete solid solubility occurs in about 1 % of the investigated binary mixtures (fig. 1.4).

Figure 1.4: statistic probability of binary phase diagrams of organic compounds [1]

The composition changes of the liquid and the solid phase during a crystallization process, at infinitely slow growth rates under ideal mixing conditions in both phases, can be read from a phase diagram as is illustrated for the cooling crystallization of an eutectic mixture and for the pressure crystallization of a solid solution mixture in figure 1.5. The recovery of these crystallization processes at temperature $T_2$ or pressure $P_2$ can be calculated using the lever-rule:

$$R_{T_2/P_2} = \frac{(X_0 - X_2)}{(Y_2 - X_2)}$$

(1.1)
Figure 1.5: equilibrium crystallization process by (a) cooling of a eutectic and (b) pressurization of a complete solid solution system

1.2.2 incorporation of impurities

The incorporation of impurities in the crystal lattice under equilibrium conditions can be quantified as the equilibrium distribution coefficient \( (K_0) \) which is defined as the ratio of the impurity concentration in the crystal phase \( (C_s) \) to the impurity concentration in the mother liquor \( (C_L) \).

\[
K_0 = \frac{C_s}{C_L} \tag{1.2}
\]

For the binary mixtures illustrated in figure 1.5 the equilibrium distribution coefficient \( K_0 \) at temperature \( T_2 \) or pressure \( P_2 \) can be expressed as:

\[
K_{0,T_2,P_2} = \frac{(1-Y_2)}{(1-X_2)} \tag{1.3}
\]

For eutectic mixtures \( K_0 = 0 \) and for solid solution systems in practice \( K_0 > 0 \). For
multicomponent mixtures a multi-dimensional equilibrium distribution matrix is described by Tiller [5].

![Diagram of crystal and mother liquor with label $\delta_m$]

**Figure 1.6: impurity concentration gradient at the interface of the crystal and the mother liquor**

During a non-equilibrium crystallization process the balance between crystal growth, which involves selective rejection of impurities from the growing crystal surface, and mass transfer of impurities away from the crystal surface results in an impurity concentration gradient in front of the growing crystal surface as is illustrated in figure 1.6. It is assumed here that mass transfer within the stagnant liquid boundary layer $\delta_m$ adhering to the crystal surface is governed exclusively by diffusion. The thickness of the boundary layer depends on the hydrodynamic conditions and approaches a minimum value as mixing improves ($\delta_m = 10^{-5}$-$10^{-4}$ m). Because crystal growth occurs from the impurity rich boundary layer and not from the purer bulk of the mother liquor Burton, Prim and Slichter [6] defined an **effective distribution coefficient** ($K_{\text{eff}}$):

$$K_{\text{eff}} = \frac{C_{S,i}}{C_{L,b}} = \frac{K_0}{K_0 + (1 - K_0) \cdot \exp\left(\frac{-G \cdot \delta_m}{D}\right)}\quad(1.4)$$

Here $C_{S,i}$ represents the impurity concentration in a crystal just behind the interface.
and \( C_{l,b} \) is the impurity concentration in the bulk of the mother liquor, both under non-equilibrium growth conditions. Equation (1.4) neglects the difference in specific weight between the crystal phase and the mother liquor but this omission can easily be repaired by substituting \( G' \) for \( G \) [5].

\[
G' = \left( \frac{\rho_s}{\rho_L} \right) \cdot G
\]  

(1.5)

Tiller [5] argues that a delay in mass transfer caused by surface integration and adsorption effects should be accounted for in the calculation of the effective distribution coefficient \( K_{\text{eff}} \). When surface integration becomes the rate determining step of a crystal growth process, the equilibrium distribution coefficient \( K_0 \) is to be replaced by an interface distribution coefficient \( K_i \) in equation (1.4).

Wintermantel [7] developed a practical correlation for \( K_{\text{eff}} \), based on the BPS-relation (eq. 1.4), which includes the impurity concentration gradient in a laminar boundary layer at the solid/liquid interface.

1.2.3 inclusion of impurities due to unstable growth morphologies

Inclusion of impure mother liquor in the crystal matrix reduces the average crystal purity and consequently the selectivity of the crystallization process. Inclusion of mother liquor can hardly be avoided in bulk crystallization processes of highly concentrated solutions or near melts. It creates a major problem in large scale ultrapurification of organic compounds and is the main reason why the design and operation of FC equipment differs significantly from the conventional industrial crystallization processes [8].

An inclusion is formed when a small portion of mother liquor gets entrapped between irregular growth patterns on the crystal surface and becomes eventually
enclosed by the crystal matrix. The irregular patterns, usually referred to as **unstable growth morphologies**, occur most easily at high growth rates and poor mixing conditions in the mother liquor.

Crystal growth can not proceed without heat and mass transfer. Heat transfer was shown to be the rate determining step when crystallization occurs from a melt by De Goede et al. [9,10] and Matsuoka & Garside [11]. Since heat release is proportional to the heat exchanging area, a growing crystal has a tendency to increase its surface area. There are two ways available to oppose this tendency. First, there is an intrinsic stabilising effect of a crystal striving for minimization of its surface tension and consequently a reduction of its surface. Secondly, an externally applied temperature gradient may reduce the driving force in a direction from the crystal interface into the mother liquor. The stabilising surface tension effect increases with stronger curvature of the crystal surface [12]. At low growth rates the effect of surface tension is dominant and well faceted crystals can be produced but at high growth rates the effect of heat transfer is dominant and cellular or dendritic morphologies will appear on the crystal surface [13].

An intrinsically unstable growth situation can occur when the supersaturation (undercooling or overpressure) of the mother liquor increases in the direction from the crystal surface towards the bulk of the mother liquor. The presence of an impurity gradient in front of the crystal surface (fig. 1.6) lowers the equilibrium temperature near the crystal surface. Consequently the presence of the impurity gradient enhances the probability of the occurrence of a zone of increasing supersaturation adjacent to the crystal surface. This condition is usually referred to as **constitutional supersaturation** [12,14,15]. In the presence of constitutional supersaturation, an accidental protrusion on a flat crystal surface will enter a region of higher supersaturation and tends to outgrow the surrounding surface (fig. 1.7). Likewise small dips in the crystal surface tend to become retarded even more.
From figure 1.7e it is easy to see how portions of mother liquor can get entrapped between the branches of the dendritic structures.

Figure 1.7: macroscale roughening of a crystal surface [10]

The concept of constitutional supersaturation and other stability criteria which are necessary to predict stable growth morphologies are more extensively described by Tiller [16] and by Sekerka [13]. The level of constitutional supersaturation and therefore the stability of a crystal morphology under practical crystallization conditions is to a large extent dependent on the applied crystallization technique as will be discussed in the next section.
1.3 CRYSTAL GROWTH TECHNIQUES

The layer growth technique is based on the formation of a crystal layer on a cooled heat exchanger surface. The main growth direction is perpendicular to the cooled surface into the bulk of the mother liquor. The heat of crystallization is removed through the cooled surface via the crystal layer and consequently the bulk of the mother liquor is undersaturated. By keeping the growth rates low and providing good mixing conditions constitutional supersaturation can in principle be avoided in layer growth processes as is illustrated in figure 1.8a.

![Diagram of layer growth conditions](image)

**Figure 1.8:** stable (a) and unstable (b) growth conditions in layer growth
Unfortunately, the growth rates applied in industrial layer crystallizers have to be high ($\pm 10^6$-$10^5$ m/s) to meet the specified production capacity and the mixing conditions in some equipment designs are moderate to poor. The production capacity is defined here as the product of the average linear growth rate and the surface area available for crystal growth. Since the available crystal growth area in layer crystallizers is relatively small because it is limited to the installed heat exchanger surface ($\leq 100$ m²/m³), high growth rates are necessary to compensate for it. As a result significant constitutional supersaturation is always present in industrial layer growth processes (fig. 1.8b). According to the Mullins-Sekerka stability criterion the stabilising effect of surface tension on the flat surface of a crystal layer is weak [12]. Consequently, unstable growth morphologies easily occur and the purity of the crystal layer is reduced significantly due to inclusions of mother liquor.

In conclusion, the selectivity of most industrial layer growth processes is moderate because of the high growth rates and poor mixing conditions which promote both incorporation and inclusion of impurities.

Figure 1.9: intrinsically unstable growth conditions in suspension growth
In **suspension growth** processes crystals grow freely suspended in their undercooled mother liquor. A suspension growth situation is intrinsically unstable because some degree of constitutional supersaturation cannot be avoided (fig. 1.9). Fortunately, the growth rates applied in suspension crystallization equipment can be kept low ($\pm 10^{-9}$-$10^{-7}$ m/s) and the mixing conditions are usually good. Since the area available for crystal growth is equal to the total crystal surface area, which can measure up to 10,000 m$^2$/m$^3$, fairly high specific production capacities can already be accomplished at low growth rates. As a result the degree of constitutional supersaturation in suspension growth processes is small. Furthermore the stabilizing effect of surface tension in case of suspension growth is strong because of the strong curvature of the surface of individual crystals. Consequently, unstable growth morphologies can usually be avoided in industrial suspension crystallizers. In conclusion, the selectivity of most suspension growth processes is very good because of the low growth rates and good mixing conditions.

![Diagram](image)

**Figure 1.10**: intrinsically unstable growth conditions in pressure crystallization

In a **pressure crystallization** process crystals grow in an unstimred compressed compartment at extremely high growth rates ($\pm 10^{-4}$-$10^{-3}$ m/s). The crystals grow from a supersaturated melt and this situation is intrinsically unstable (fig. 1.10).
Even though the applied pressure distributes instantaneously and homogeneously through the crystallizing mixture, considerable constitutional supersaturation is inevitable in pressure crystallizers. At the extremely high growth rates, the stabilising effect of surface tension is not strong enough to prevent unstable growth morphologies. Industrial practice shows that the selectivity of a single pressure crystallization step is moderate mainly due to inclusion of mother liquor in the product crystal cake.

1.4 PURIFICATION MECHANISMS

Crystal purity is hampered by impurities, which are incorporated in the crystal lattice, included in the crystal matrix, and/or adhered to the crystal surface. Several purification mechanisms can be applied to upgrade the crystal purity and thus to improve the overall separation efficiency of a fractional crystallization process. Usually four purification mechanisms are distinguished: washing, sweating, recrystallization and solid state diffusion.

Washing or rinsing involves the displacement of impure mother liquor, which adheres to the crystal surface, by wash liquid. In fractional crystallization preferably pure(r) molten product is used as the wash liquid. The efficiency of washing can be improved, in suspension growth processes, by establishing a countercurrent transport between the crystal phase and the wash liquid. Washing has only a small effect on included and no effect on incorporated impurities.

Sweating is a technical term which originates from the wax purification industry. Raw wax containing water and oils is heated slowly until droplets of the low melting components appear on the surface, resembling sweat droplets. By removing the
droplets from the surface, the purity of the remaining wax is increased. In fractional crystallization processes sweating is applied for the removal of included impurities from the crystal matrix. Sweating takes place by increasing the temperature or by reducing the pressure in order to partially melt the impure portions of the crystals thus forming an impurity rich liquid phase on the crystal surface which is then separated. For a sweating operation to be effective, it is essential that the impurities are locally dispersed as inclusions of mother liquor in the crystal phase [17]. The inclusions, which have solidified during the progress of the crystallization, will melt first upon gradual heating because of their lower melting point while the surrounding (purer) crystal structure remains solid. Exactly what forces cause the melt to move towards the crystal surface is still unknown but thermal gradients [18], difference in expansion coefficient between the solid and the liquid phase, capillary forces and gravity are expected to play a role. The pathways for the transportation of the melt to the crystal surface may be pores resulting from a recrystallization process or thermal cracks [19]. Ulrich & Özoğuz [20] argue that the efficiency of the sweating step in a layer crystallization process is (i) nearly independent of the heating rate, (ii) higher when the crystal layer has a higher impurity content and (iii) higher when the crystal layer is thicker. Research on sweating of crystal layers and separate crystals was performed extensively by Ulrich and co-workers [20,21,83], Matsuoka [17,22-24] and Toyokura et al. [25].

Recrystallization can be used to purify crystals that contain incorporated impurities. In a complete recrystallization operation crystals are separated from impure mother liquor, next the crystals are molten and a portion of this melt is again crystallized. In practice this operation is carried out batchwise in layer growth and pressure crystallizers. In suspension crystallizers continuous in situ partial recrystallization is strived for by contacting a hot and purer liquid phase with colder and impurer crystals. During this encounter an impure crystal will partially melt because of its lower melting point but only at the expense of a certain enthalpy
change. Since suspension crystallization on microscale occurs almost adiabatically, this enthalpy change is the driving force for the crystallization of a portion of the surrounding purer liquid either on the surface of existing crystals or via the formation of new crystals.

**Solid state diffusion** is best described as the migration of molecules through the crystal structure. The driving force for solid state diffusion is a concentration gradient inside the crystal structure. The purifying effect of solid state diffusion may be considered negligible in industrial practice because of the low diffusion coefficients (< $1 \times 10^{-14}$ m$^2$/s) of impurities in organic crystals.

### 1.5 INDUSTRIAL LAYER GROWTH EQUIPMENT

Industrial layer growth crystallization processes can in principle be operated **continuously** but the vast majority is operated **batchwise**. Two types of batchwise layer growth processes can be distinguished: static and dynamic. In **static** equipment crystal growth occurs from a stagnant mother liquor. In **dynamic** equipment crystal growth occurs from a mother liquor in motion. The movement of the mother liquor can be achieved by **internal mixing** or by **external circulation** (see fig. 1.11).

A rotary-drum crystallizer [26,27] consists of a horizontally mounted internally cooled drum which is partially immersed in a liquid feedstock. Upon rotation of the drum the crystal layer which is formed on the immersed part of the drum emerges from the liquid feedstock. The crystal layer is removed from the rotating drum with a knife. Extra mixing devices can be installed in the liquid feedstock to enhance mass and heat transfer. High growth rates are applied and thick crystal layers need
to be grown to meet production capacities. Hence the single step separation efficiency of the rotary drums is rather poor and nowadays these devices are mainly used as product flakers.

![Layer Growth Equipment Diagram](image)

**Figure 1.11:** layer growth equipment and processes

Another recent attempt to develop a continuous process based on layer growth is the Brembelt [28,29]. In this design a conveyor belt is positioned at an angle to the horizontal (fig. 1.12). A coolant is sprayed in different compartments at the bottom of the belt and a liquid feedstock is supplied on top of the belt. The belt transports a growing crystal layer upwards while the mother liquor flows downwards as a film. The temperature of the coolant in every compartment is adjusted to achieve an ascending temperature profile along the belt in the direction of the crystal layer transport. The temperature rise will induce sweating and possibly recrystallization.
The Brembelt is at present tested on pilot plant scale for its ability to combine a good separation efficiency with an acceptable specific production capacity.

![Flow scheme of the Brembelt](image)

**Figure 1.12:** flow scheme of the Brembelt [28,29]

The Proabd refiner of the French BEFS-technologies is the most applied representative of the **batchwise static** layer growth processes [30,31]. The original design features a rectangular closed vessel equipped with finned heat exchange tubes. The heat exchange medium flows along the inside and crystallization occurs on the outside of the heat exchange tubes. Other static designs differ slightly from the Proabd refiner in the shape of the heat exchange elements and the geometry of the crystallizer. The largest static crystallizer manufactured by Sulzer measures...
a length of 6.1 m, a width of 2.0 m and a height of 2.4 m [33]. One static operation cycle comprises five phases. First the vessel is filled with liquid feedstock. The temperature of the heat exchange medium is then carefully lowered and part of the feed is crystallized. Next, an outlet valve is opened and the residual mother liquor is allowed to drain away. In the fourth phase, the temperature of the heat exchange medium is gradually increased to induce sweating. Drainage continues during the sweating phase. Finally, the remaining crystal cake is molten completely and the product is withdrawn.

In the stagnant melt, mass and heat transfer are diffusion controlled and despite the fact that the growth rates are kept only at ± 10^{-6} m/s constitutional supersaturation is inevitable and unstable growth morphologies are bound to occur. In industrial practice networks of dendrite structures fill up the available space between the heat exchange tubes during the crystallization process and cause entrapment of large quantities of impure residual mother liquor in the crystal layer. Long drainage and sweating times are necessary to release the entrapped mother liquor. Due to the slow crystallization and the long sweating period, a typical operation cycle may take about 1 day.

Sulzer is market leader with its batchwise dynamic falling film system which features an external transport loop for the feedstock and the heat exchange medium [34,35]. The principle of this system is explained from the simplified scheme in figure 1.13. A liquid feedstock is supplied to a collecting vessel. When the filling of the collecting vessel is completed, the product and the coolant pump are activated at the same time, producing cocurrent falling films on both sides of the vertical tubes. The tubes are 0.07 m in diameter and 12 m long. The maximum number of tubes in one crystallizer shell is 1250. Like in the static systems, one operation cycle consists of five phases: filling, crystallization, drainage of residual mother liquor, sweating and product melt-off [36].
Figure 1.13: Sulzer dynamic falling film system

The turbulent flow regime in the falling film enhances heat and mass transfer which facilitates high growth rates \(10^6-10^5\) m/s and reduces the degree of constitutional supersaturation. Consequently, unstable growth morphologies do not occur as easily as in static layer crystallizers. Some typical values: crystallization of a portion of the feedstock takes about 45 minutes and in this period a 0.015 m thick crystal layer is produced. Drainage of the residual mother liquor needs only 1-5 minutes, sweating takes about 15-20 minutes and product removal is completed in 5-10 minutes. Thus one operation cycle is completed in about 1.5 hours [36].
The short operation cycle time makes the dynamic system well suited for repeated processing of an ever purer feedstock. Sulzer adopted the **sequential countercurrent staging** method illustrated in figure 1.14.

![Diagram](image)

\[ T_1 < T_2 < T_3 \]

**Figure 1.14: sequential countercurrent staging**

The residual mother liquor from an arbitrary stage 2 operated at temperature \( T_2 \) is transported to an earlier stage 1 to be processed at a lower temperature \( T_1 \). The sweat obtained in stage 2 can be mixed with a new feedstock for stage 2 or with the drained residue from stage 3. The molten product from stage 2 is transferred to consecutive stage 3 and will be processed again at a higher temperature \( T_3 \). Sequential countercurrent staging can be performed **intermittent** in one crystallizer providing that sufficient intermediate storage tanks are available.

Figure 1.15 displays the increase in crystal purity per stage for an unspecified substance obtained with a (sequential countercurrent) multistage falling film system and with a single step static crystallizer [35]. The separation achieved in the single stage static unit is equivalent to about two and a half dynamic stages of the
dynamic multistep system. However, the static operation took about 20 hours while the same separation effect was achieved with the dynamic system in only 2-3 hours.

![Graph showing comparison of purification results obtained with static and dynamic layer growth systems.](image)

**Figure 1.15:** comparison of purification results obtained with static and dynamic layer growth systems [35]

In the dynamic systems from ICI [37] and BASF [38] the mother liquor and the coolant are supplied as fully developed tubular flows. The falling film principle has distinct advantages over the fully developed flow principle: (i) lower energy consumption for transport of the flows and (ii) easy monitoring of the progression of the crystallization via a measurement of the liquid level in the collecting vessel [39]. Sulzer [33] claims the applicability of their static system for production capacities up to 15,000 tonnes per year and product purities up to 99.7 %. Their dynamic falling film system is recommended for higher purities and production capacities. A
dynamic multistage plant has been constructed with a capacity of 150,000 tonnes per year for the purification of bisphenol-A.

In recent years research has been focused on the development of **dynamic crystallizers with internal mixing**. Rütgerswerke [40] developed a bubble-column. In this design bubbles of inert gas are blown through the crystallizer to enhance mass transfer in the mother liquor. However, during operation crystal deposition via sublimation occurs in the circulation circuit of the inert gas and also unwanted nucleation in the bulk of the mother liquor is initiated by the gas bubbles in the crystallizer. A more successful design seems to be the pulsed column [41, 42]. In this column mass transfer in the mother liquor is promoted by pulsation which is effected by means of an external moving piston unit.

Layer crystallizers have difficulty in purifying relatively impure feedstocks. At higher impurity levels in the liquid phase, constitutional supersaturation becomes more pronounced and unstable growth morphologies occur more easily. Another phenomenon which is not yet well described in literature concerns the attachment of a crystal layer to the cooling surface which seems to decrease when growth occurs from a more impure mother liquor.
1.6 INDUSTRIAL SUSPENSION GROWTH EQUIPMENT

Industrial suspension crystallization processes are generally operated continuously and feature a cascade of crystallizers followed by a solid/liquid separation unit (see Table 2).

<table>
<thead>
<tr>
<th>Process</th>
<th>Cascade</th>
<th>Solid/Liquid separation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phillips Petroleum</td>
<td>cocurrent</td>
<td>wash column, mechanical bed transport (I)</td>
<td>60,62</td>
</tr>
<tr>
<td>(I and II)</td>
<td></td>
<td>wash column, hydraulic bed transport (II)</td>
<td>61,62</td>
</tr>
<tr>
<td>Brodie Purifier</td>
<td>countercurrent</td>
<td>wash column, gravity bed transport</td>
<td>46,47</td>
</tr>
<tr>
<td>Niro [Greenco]</td>
<td>countercurrent</td>
<td>wash column, mechanical bed transport</td>
<td>56,57</td>
</tr>
<tr>
<td>GMF-Gouda (CDC)</td>
<td>cocurrent</td>
<td>centrifuge</td>
<td>43,44</td>
</tr>
<tr>
<td>Kureha (KCCP)</td>
<td>cocurrent</td>
<td>beltfilter + sweat column</td>
<td>63,64</td>
</tr>
<tr>
<td>Newton Chambers</td>
<td>countercurrent</td>
<td>centrifuge</td>
<td>65,66</td>
</tr>
<tr>
<td>Nippon Steel (BMC)</td>
<td>single step</td>
<td>wash column, gravity bed transport</td>
<td>67,68</td>
</tr>
<tr>
<td>TNO-Thijssen</td>
<td>cocurrent</td>
<td>wash column, hydraulic bed transport</td>
<td>51,52</td>
</tr>
<tr>
<td>Tsukish. Kikai (4C)</td>
<td>countercurrent</td>
<td>wash column, gravity bed transport</td>
<td>48,49</td>
</tr>
</tbody>
</table>

Table 2: suspension growth processes

The selectivity of a suspension crystallization process is usually good but the overall separation efficiency strongly depends on the way slurry handling and solid/liquid separation are performed. The slurry handling in the cascade is aimed at either a cocurrent or a countercurrent contact pattern between the crystals and the mother liquor. With a cocurrent contact pattern, crystals and mother liquor are transported in the same direction and crystals are grown from a mother liquor of decreasing purity at descending temperatures. With a countercurrent contact pattern, crystals and mother liquor are transported in opposite directions and crystals are grown from a mother liquor of increasing purity at ascending temperatures.
Figure 1.16: GMF Cooling Disc Crystallizer with a detail of a cooling element

A good example of a **cocurrent** cascade is the Cooling Disc Crystallizer (CDC) of the Gouda machine factory [43,44]. The CDC consists of a horizontal trough which is divided by fixed cooling elements into separate compartments, which are comparable to separate crystallizers (fig. 1.16). In each compartment a disc rotates which is equipped with teflon wipers and mixing blades. The discs are mounted on a longitudinal axis which rotates with 5-45 rpm. Internal slurry transport facilities are absent in a CDC since both crystals and mother liquor flow freely from one crystallizer to the next via openings at the bottom of the cooling elements. The crystal content increases in the successive compartments and may amount up to 45 v% in the last compartment. Since the temperature difference between the slurry and the coolant is kept approximately constant throughout the CDC and the
specific crystal surface area increases from inlet to outlet, the crystal growth rates are lowest in the last compartments where the impurity concentration in the mother liquor is highest. Consequently, in a CDC a good selectivity can be maintained at high production rates whereas the minimal slurry handling contributes to preserving a good crystal quality. The largest available CDC is 8 m long, has a volume of 20 m³, contains 19 cooling elements with a total cooling surface of 130 m² and has a maximum production capacity of about 30,000 tonnes per year [45].

The first industrial countercurrent cascade was designed by Brodie [46,47]. This ingenious design features two or three horizontally positioned crystallizers in which crystal transport is promoted by helix-shaped steel scrapers. The horizontal crystallizers are mounted on top of each other with a direct open connection between them. This open connection on the one hand provides a continuous countercurrent contact between crystals and mother liquor which has a favourable effect on crystal shape and purity, but on the other hand it reduces, because of thermal convection, the maximum temperature difference between the cold and the hot end of the cascade and consequently the maximum recovery. The complex precision design of the scrapers caused major scale-up problems and limited the capacity of an industrial Brodie purification process to approximately 10,000 tonnes per year. Industrial Brodie crystallizers are 10-15 m long and have a maximum diameter of about 1 m.

Based on their experience with the Brodie purification process, Tsukishima Kikai (TSK) developed the Continuous Counter Current Crystallization (4C) system [48,49]. The TSK-4C process features separated crystallizers resulting in a discontinuous contact between the crystals and the mother liquor (fig. 1.17a). The crystallizers are equipped with an external cooling jacket and steel scrapers which are mounted on a rotating draft tube (fig. 1.17b). Slurry transport outside the crystallizers is effected by pumps followed by concentration in cyclones. Meanwhile

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the residual mother liquor is withdrawn from a crystallizer via an overflow. The height and diameter of the industrial crystallizers amount to 5 m. The draft tube rotates at about 25 rpm and in the crystallizers the suspension density amounts about 25 v%. Relatively large temperature difference of 15-20 K per stage can easily be obtained which provides a good recovery.

TSK has built a cascade comprising three crystallizers with a design capacity of 70,000 tonnes per year for the purification of p-xylene [50].

To summarize, **cocurrent** cascades are simple designs, easy to operate and require limited auxiliary equipment. These cascades are designed to produce a pure and easily filterable crystal product by maintaining low growth rates and minimization of slurry handling.

**Countercurrent** cascades feature more complex designs and usually need more auxiliary equipment. These cascades are designed to introduce extra purification by allowing washing, sweating and recrystallization already to occur in the crystallization section of a FC plant. So far, significant extra purification due to a countercurrent contact pattern has not been positively demonstrated on an industrial scale. A major advantage of countercurrent cascades is the fact that the product slurry is discharged from the hot end at the highest temperature. This "hot" **product discharge** can lead to savings in the downstream solid/liquid separation section as will be discussed in following the paragraphs.
Figure 1.17: (a) principle of the countercurrent TSK-4C system and (b) detail of a TSK-crystallizer
Solid/liquid separation may be achieved by using well known equipment such as centrifuges, beltfilters and cyclones but more and more the so-called wash columns are applied. These wash columns combine a virtually complete solid/liquid separation with a highly efficient crystal washing action. Basically three types of wash columns can be distinguished after the different mechanisms for crystal bed transport (see fig. 1.18).

![Diagram of wash columns](image)

**Figure 1.18:** (1) gravity wash column, (2) hydraulic wash column and (3) mechanical wash column

In the first type a crystal bed is transported by gravity. The feed slurry is entered at the top of the wash column. The crystals settle under the influence of gravity into a loosely packed downward moving bed and the mother liquor leaves the column via an overflow. At the bottom of the column the crystal bed is melted. In industrial gravity wash columns the melter is simply positioned inside the wash column. Though heat transfer is poor in these almost stagnant melting sections, it is sufficient to meet the low production capacities of this type of wash column. A portion of the molten product is withdrawn from the bottom section and the remainder ascends in the column thus providing a countercurrent washing action.
A sharp wash front, as can be detected in the other two types of wash columns, does not appear because of the loose packing and the disturbance of the bed by the agitator. The agitator covers the total height of the column and serves to prevent agglomeration and/or channelling in the crystal bed.

The heat input, required to overcome the difference in temperature between the slurry feed and the molten product, is produced mainly by the crystallization of the wash liquid. This temperature difference between top and bottom of the column should not exceed 15-20 K, because crystallization of large amounts of wash liquid will lead to serious agglomeration problems. When larger temperature differences have to be overcome, another type of separator (e.g. a centrifuge) has to be used as a pre-separation step. In view of this, the advantage of a **hot product discharge** from the crystallization section, as is the case in a countercurrent cascade, becomes obvious.

An industrial TSK-4C gravity wash column is 8 m high, has a maximum diameter of 2.2 m and is filled for about 6 m with a crystal bed. The revolution rate of the agitator is low (≤ 1.5 rpm). The capacity of gravity wash columns of course depends on physical properties of the solid and the liquid phase, the crystal size distribution and the wall friction but it does not exceed 1500 kg/m²h for organic compounds [48,49,50].

In the second type of wash column a dense crystal bed is transported by means of **hydraulic force**. A slurry is fed under pressure at the top of the column. After a short zone of rapid thickening, the crystals are caught in a densely packed downward moving bed. The residual mother liquor leaves the column via filters which are positioned either in separate filter tubes [51,52] or in the wall of the column [53]. From a scale-up point of view the version with separate filter tubes, which is known as the TNO-Thijssen column, is favourable. In this version the ratio of the total surface area of the filters to the cross-sectional surface area of the column can be kept constant and the radial distance which has to be overcome by the mother liquor before it reaches the filter surface can be minimized by installing
more filter tubes as the column diameter increases. At the bottom of the column
the crystals are scraped off, suspended in the wash liquid and melted in an
external melter. The wash liquid (refluxed molten product) flows upwards in the
column due to the overpressure in the reslurry-chamber below the scraper and thus
provides a countercurrent washing action. The ascending wash liquid does not
leave the column through the filters but crystallizes on the cold crystal bed. The
perfect plug flow of the wash liquid through the packed bed results in a sharp wash
front. The wash front marks a steep temperature gradient and a sharp decrease in
the porosity and permeability of the bed which are caused by the crystallization of
the wash liquid. The permeability decrease underneath the wash front improves the
washing efficiency and is essential for a stable washing action [54]. The maximum
temperature difference which can be overcome between the slurry feed and the
molten product is 10-15 K. A larger temperature difference will make the
permeability underneath the wash front extremely low. Consequently, the
production capacity will be reduced drastically and/or the washing action will be
hampered.

At present the TNO-Thijsse wash column has been tested extensively on a pilot
plant scale and the positive results encourage further scale-up. The maximum
production capacity of hydraulic wash columns will probably be 5000-10,000 kg/m²h
[55].

In the third type of wash column a dense crystal bed is transported by mechanical
force created by a moving piston or a screw. The mother liquor leaves the column
via pores in the mechanical aid. Otherwise this type of wash column is operated
identically to the hydraulic wash column. An industrial Niro (Grenco) mechanical
wash column is about 1.5 m high and has a maximum diameter of 1.2 m. The
capacity of mechanical wash columns is limited to 10,000 kg/m²h [56,57].
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A comparison of the three types of wash columns shows that gravity columns have significantly smaller capacities than hydraulic and mechanical columns. Gravity columns require as a rule of thumb an average crystal size larger than ±500 µm to achieve an economically viable operation [50,58] whereas the mechanical and hydraulic columns can already be successfully operated with much smaller crystals (100-200 µm) [55,58]. The requirement of a larger average crystal size for the gravity column has an important impact on the design of the preceding cascade of the crystallizers: the residence times need to be longer, equipment volume will become larger and investment cost will increase.

The residence times of crystals in gravity columns may amount several hours which allows extra purification by sweating and recrystallization to occur. The residence times of crystals in columns with hydraulic or mechanical bed transport is about 10 minutes which is too short for extra purification effects in addition to the washing action.

Finally, the compressive stresses exerted on the crystal bed during operation are negligible with gravity bed transport but are relatively high (2-10 bar) with hydraulic or mechanical bed transport. The level of these compressive stresses is a relevant parameter in the choice of a particular type of wash column in a fractional crystallization process because various organic compounds (e.g. cyclohexane) form mechanically weak crystals.
1.7 INDUSTRIAL PRESSURE CRYSTALLIZATION EQUIPMENT

In pressure crystallization the driving force for crystallization is created by an increase of pressure. A pressure crystallization process under near equilibrium conditions is illustrated in figure 1.5b.

![Phase Diagram](image)

**Figure 1.19:** phase diagram of p- and m-cresol

The most lucrative aspect of pressure crystallization might be the fact that phase equilibria can often be manipulated through pressure variations. This makes it possible to process compounds with melting points well below 273 K at 1 bar at about room temperature at elevated pressures or to increase the maximum
recovery by shifting the eutectic composition just by raising the pressure. Figure 1.19 represents the binary phase diagram of p- and m-cresol at various pressures. From the phase diagram at 1 bar, it follows that p-cresol crystals can only be recovered from feedstocks containing at least 58 wt% p-cresol corresponding with the composition at the eutectic. Moritoki [69] observed that this eutectic shifts to lower p-cresol mass percentages at higher pressures. p-Cresol crystals can still be recovered from feedstocks containing 40 wt% p-cresol at 3000 bar. This demonstrates that the maximum recovery for some organic mixtures depends on the pressure level and for the case of m- and p-cresol can be increased through pressurization. Figure 1.19 also shows higher melting points for p- and m-cresol at increased pressures.

![Flow scheme of the adiabatic Kobe Steel high pressure process](image)

**Figure 1.20:** flow scheme of the adiabatic Kobe Steel high pressure process [72]

The pressure crystallization process was developed by Kobe Steel [69-75] to the large scale adiabatically operated plant design illustrated in figure 1.20. The pressure variations in the crystallizer during one operation cycle are presented in figure 1.21. The plant is operated as follows: A liquid feedstock is supplied to a
chiller vessel, where it is kept at a fixed temperature and some seed crystals are formed or added. The feed is transferred to the crystallizer by means of a slurry pump. When the filling is completed, the piston moves stepwise into the crystallizer thus building up pressure and triggering crystallization. The pressure in the crystallizer is gradually increased to a predetermined level ($P_0$) to obtain the desired recovery. The residual mother liquor is drained from the crystallizer by opening the valve on the right. The remaining crystal cake is squeezed out during this drainage by the continuing inward motion of the piston. Eventually, the liquid pressure gradually decreases and sweating occurs. Nitrogen gas is supplied at the top of the crystallizer to remove the residual mother liquor remaining in the dead spaces of the crystallizer. Finally the piston and the wall of the crystallizer are lifted and the remaining crystal cake is discharged. Contrary to the cooling crystallization processes the product is obtained as **solid** material.

![Graph showing pressure variations during a pressure crystallization cycle](image)

**Figure 1.21:** pressure variations during a pressure crystallization cycle

In 1984 the first commercial Kobe Steel high pressure crystallizer was taken into operation at Sumitomo Chemical Co. in Japan to purify $p$-cresol. In one operation
Introduction to fractional crystallization

cycle 15 kg feedstock (80 wt% p-cresol) is treated and 5 kg product (99.5 wt% p-cresol) is obtained. This operation cycle is completed in 2 to 4 minutes. The maximum operation pressure is about 2000 bar. The production capacity of this plant does not exceed 1000 tonnes per year [76-78].

A practical problem in pressure crystallization is the removal of residual mother liquor and sweat from the product crystal cake. Experimentally it was found [79] that the centre part of the product cake is the most impure due to entrapped mother liquor which can not be squeezed out. The commercial plant of Kobe Steel is equipped with filters in the wall of the crystallizer to improve the efficiency of the solid/liquid separation.

Advantages of the pressure crystallization process are:
- the easy and accurate control of crystallization and melting rates due to the instantaneous and homogeneous distribution of the driving force (pressure),
- the absence of auxiliary solid/liquid separators, stirring and scraping devices,
- low energy consumption since only mechanical energy for compression of 10-20 % of the volume is required.

The major disadvantages of this process are the high investment and maintenance costs relative to its low production capacity [77,78].
1.8 EVALUATION

All three crystallization techniques described in the above being: layer growth, suspension growth and (high) pressure crystallization, can be successfully applied for ultrapurification of organic compounds on an industrial scale. Each technique has, however, its own advantages and disadvantages which must be taken into consideration when designing a purification plant.

The layer growth technique is a proven technology which is usually applied batchwise. Scale-up of layer growth processes is very easy to perform. Operation is simple and flexible for limited variations in the feed conditions and purity demands. Slurry handling can be avoided and there is no need for auxiliary solid/liquid separation units. However, the single step separation efficiency and the specific production capacity are moderate in comparison to suspension growth processes. The investment costs and energy demands for the dynamic systems are relatively high because in most cases a multistage operation is needed. The maintenance costs, on the other hand, are low. Finally, this technique is well suited for ultrapurification purposes but it is less well applicable for separation of more impure feedstocks.

The suspension growth technique is also a proven technology and is usually operated continuously. The single step separation efficiency is excellent and the specific production capacity is high. Slurry handling is, however, inevitable and the overall separation efficiency of a suspension growth process is to a large extent determined by the efficiency of the downstream solid/liquid separation unit. Investment and maintenance costs are moderate and the energy demands of suspension processes are low. Scale-up requires extensive testing on laboratory and pilot plant scale. The suspension growth technique is applicable for ultrapurification of rather pure feedstocks but also for separation of impure feedstocks. The presence of impurities in the feedstock often has a positive side effect because
it reduces encrustation problems that might occur.

The **pressure crystallization** technique must be considered as a technology in development. Pressure crystallization is always performed batchwise. Scale-up beyond productions of 1000 tonnes per year will be difficult. The single step separation efficiency is moderate but one operation cycle is very short which makes the technique well suited for multistage operation. This technique is particularly well suited to treat low melting point compounds at about room temperature. Furthermore, the recovery of a crystallization step may improve at higher operating pressures. Energy consumption is low. Slurry handling is avoided and there is no need for auxiliary solid/liquid separation equipment. Investment and maintenance cost are at present still high.

Reviews on fractional crystallization and/or comparisons between the three crystal growth techniques are presented in references [80-85]. In near future a book will be presented on this topic by Arkenbout [86].
### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$C_L$</td>
<td>impurity concentration in the liquid phase</td>
<td>[wt%]</td>
</tr>
<tr>
<td>$C_S$</td>
<td>impurity concentration in the solid phase</td>
<td>[wt%]</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
<td>[m$^2$/s]</td>
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<td>$K_d$</td>
<td>equilibrium distribution coefficient</td>
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<tr>
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<td>[N/m$^2$]</td>
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<tr>
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<td>saturation pressure under equilibrium conditions</td>
<td>[N/m$^2$]</td>
</tr>
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<td>[N/m$^2$]</td>
</tr>
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<td>$R$</td>
<td>recovery of the main component</td>
<td>[-]</td>
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<tr>
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<td>actual temperature</td>
<td>[K]</td>
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<tr>
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<td>[K]</td>
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<td>temperature at time i or stage i</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_M$</td>
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</tr>
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<td>$G$</td>
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<td>[wt%]</td>
</tr>
<tr>
<td>$Y_i$</td>
<td>composition of the crystals at $T_i$ or $P_i$</td>
<td>[wt%]</td>
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### Greek

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<td>[m]</td>
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<tr>
<td>$\delta_{th}$</td>
<td>thickness of stagnant heat transfer boundary layer at the crystal surface</td>
<td>[m]</td>
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<td>$\rho_L$</td>
<td>specific weight or density of the liquid phase</td>
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<td>$\rho_S$</td>
<td>specific weight or density of the solid phase</td>
<td>[kg/m$^3$]</td>
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References


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[77] Private communication to Dr. S. Arakawa, Dr. F. Horiuchi, Dr. N. Kanda and Dr. T. Umemura of Sumitomo Chemical (Ohita Works) (1991).


introduction to fractional crystallization
OBJECTIVES AND SCOPE OF THIS THESIS
2.1 OBJECTIVES

This thesis is focused on the development and optimization of the operation of equipment for fractional suspension crystallization (FSC) processes. The advantages of the suspension growth technique in comparison to layer growth and pressure crystallization, as elucidated forward in chapter 1, are numerous: (i) superior selectivity, (ii) high specific production capacities, (iii) continuous operation and (iv) low energy requirements (relative to multi-stage layer growth processes). World-wide large scale application of this technique, however, has been hampered by a lack of fundamental knowledge, traditional difficulties with slurry-handling and solid/liquid separation and the lack of reliable engineering models for feasibility studies and scale-up procedures. By dealing with a number of these problems, this thesis may help FSC to grow to maturity.

FSC processes consist of a cascade of crystallizers followed by a solid/liquid separation unit. In the design of an FSC process two essential choices must be made: (i) cocurrent or countercurrent transport of the crystals and the mother liquor in the cascade and (ii) selection of the solid/liquid separator. The new FSC process proposed here, comprises a GMF Cooling Disc Crystallizer followed by a TNO-Thijssen hydraulic wash column. The GMF Cooling Disc Crystallizer (CDC) must be regarded as an integrated cascade of crystallizers with a cocurrent transport of crystals and mother liquor (see fig. 1-16, chpt. 1). The CDC was selected for this project because the complete absence of slurry transport equipment in this cascade and its ability to operate at a high crystal content are expected to have a beneficial effect on the purity and the filterability of the produced crystals. Furthermore, its easy accessible design and flexible operation made it ideal for the experimental program.

The TNO-Thijssen hydraulic wash column (see fig. 1-18) combines a virtually complete solid/liquid separation with a high product throughput (up to
10,000 kg/m²h). The major advantage of this hydraulic wash column over other high performance solid/liquid separators (e.g. mechanical wash columns, centrifuges) is its simple design without complex expensive moving parts because only hydraulic pressure is applied to transport crystals.

Two organic mixtures were selected for the experimental programs.

In the experiments with the pilot plant at the T.U. Delft, which comprises a CDC and a TNO-Thijssen wash column (see chpt. 3), \textit{\varepsilon-caprolactam} was crystallized and separated from a binary mixture with water. Caprolactam is used almost exclusively for polymerization of nylon-6. The main impurity in crude caprolactam is water, which must be removed because the anionic polymerization of caprolactam allows a maximum water content of only 0.01 wt\% water. At present removal of the final 0.5-1.5 wt\% water from the crude caprolactam occurs in falling film evaporators under deep vacuum. This separation process is highly energy consuming and therefore FSC is studied as an alternative. Solid/liquid separation was anticipated to be difficult with this test material because (i) the viscosity of the mother liquor is rather high (> 12 mPa.s) and (ii) caprolactam crystals can be relatively thin and needle-like dependent on the crystallization conditions.

In a series of experiments with a pilot plant at TNO-IMET in Apeldoorn, which comprises a single stage crystallizer and a TNO-Thijssen wash column, \textit{p-xylene} was crystallized and separated from a C8-aromatic mixture. This mixture contained o-xylene, m-xylene, ethylbenzene and toluene as impurities. P-xylene is the basic material for the production of the polyester PET (polyethylene terephthalate). FSC is already applied for p-xylene purification on an industrial scale. Solid/liquid separation is relatively easy with this test material because (i) the viscosity of the mother liquor is low (< 1 mPa.s) and (ii) p-xylene crystals are usually block-like. The experiments with TNO-IMET's pilot plant concentrated on the performance of the TNO-Thijssen wash column with this test material. Extensive research on the crystallization of p-xylene has been performed at the T.U. Delft by De Goede [1].
objectives & scope

General objectives of the whole research project were:

1. To review and evaluate the different fractional crystallization techniques and processes (chapter 1).

2. To optimize the operating conditions for a cocurrent cascade of crystallizers (the CDC) with respect to the filterability of the produced crystals, because this parameter determines the separation efficiency and the production capacity of the downstream solid/liquid separator(s).

3. To analyze transport forces, purification mechanism and fluid dynamics in a TNO-Thijsen wash column in order to provide a sound basis for technical feasibility studies and future scale-up of this apparatus.

4. To investigate the technical feasibility of caprolactam purification with a FSC process comprising a CDC and a TNO-Thijsen wash column.

2.2 SCOPE

with respect to general objective 2

The filterability of caprolactam crystals depends not only on their size distribution but also on their morphology. Van der Heijden et al. [2] discovered that the morphology of caprolactam crystals depends strongly on the crystallization conditions. Under certain conditions relatively thin and needle-like crystals are formed whereas in other cases more three-dimensional crystals grew. The former morphology is unlikely to have a good filterability and must be avoided if possible.

In chapter 4 the results are reported of a joined research project, conducted in cooperation with the group of Prof. dr. P. Bennema at the University of Nijmegen, which was aimed at the effect of crystallization conditions on the morphology of caprolactam crystals. Experiments were performed in a single crystal growth cell, a
lab scale batch crystallizer and the pilot CDC.

Chapter 5 describes the optimization of the operating conditions of the CDC to produce crystals with an optimum filterability. Also integral model for the crystallization process in a (cocurrent) Cascade of Crystallizers with Backmixing (CCB) is presented. The CCB model integrates mathematical descriptions of the hydrodynamics, mass and heat transfer, crystallization kinetics and population density in the cascade and allows for prediction of the crystal size distribution and the filterability of the product.

*with respect to general objective 3*

An analytical model has been developed, which enables prediction of the compressive stresses exerted on crystals and equipment during the operation of a hydraulic wash column. The model can be used in feasibility studies to estimate the hydraulic pressures required for crystal bed transport. The model and supporting experimental results, obtained with the C8-aromatic feed stock, are presented in chapter 6.

The purification mechanism in the TNO-Thijssen wash column has been investigated experimentally using the C8-aromatic feed mixture. Based on the experimental observations a model has been developed, which yields axial concentration, temperature and porosity profiles and can be used to correlate the product purity to the wash front height. Experimental and simulation results are presented in chapter 7.

The parameters most suited to control the levels of the top of the crystal bed and the wash front (independently of one another) are identified in chapter 8. Optimum settings of both levels have been determined using the transport force model (chapter 6), the purification model (chapter 7) and computational fluid dynamics. Finally, the control strategy was applied to automate the column operation.
objectives & scope

with respect to general objective 4

The results of the crystallization experiments with the caprolactam/water mixture are reported in the chapters 4 and 5. An evaluation of the technical applicability of the TNO-Thijssen wash column to the purification of caprolactam is presented in chapter 8.

References


chapter 3

DESCRIPTION OF THE PILOT PLANT
AT THE T.U. DELFT
pilot plant description

In this chapter only the pilot scale fractional suspension crystallization plant, designed and built at the Laboratory for Process Equipment of the Delft University of Technology, is described. Other experimental units used in this Ph.D. project are described in relevant detail in the experimental part of each chapter.

The pilot plant at the T.U. Delft comprises a GMF Cooling Disc Crystallizer (CDC), a TNO Thijssen hydraulic wash column and a gravity wash column. The design and operation, including the merits and drawbacks, of the CDC and both wash columns are treated in the first chapter of this thesis. Reasons for the selection of these pieces of equipment are given in chapter 2. The flow sheet of the pilot plant, shown in figure 3.1, will first be discussed. Next, dimensions and some particularities of the crystallizer and the wash columns will be given.

3.1 FLOW SHEET OF THE PILOT PLANT

A liquid feed mixture is kept just above its melting point in storage vessel V1. By pump P1 the feed stock is circulated from V1 to the dosing vessel (V2) and back to V1. Two filters with different pore sizes are incorporated in this circulation loop to remove solid impurities (e.g. pieces of stator material). From the dosing vessel, P2 supplies the feedstock to the first compartment of the CDC. A crystal slurry leaves the CDC via an overflow in the last compartment. At this point there are three possibilities: (i) the product slurry is transferred to V1 by P3, (ii) the product slurry is pumped into the hydraulic wash column (C1) by P4 or (iii) the product slurry is supplied to the gravity wash column (C2) by P7.

The residual mother liquor, which leaves the hydraulic wash column (C1) via filters, can be recycled to the inlet by P5, which will be referred to as the steering pump, or can flow to the residue storage vessel (V3). The product crystals form a densely packed bed in C1, which is transported downward under the hydraulic pressure exerted by P4. At the bottom of C1 the crystal bed is scraped of by a rotating knife (M3) and the crystals enter a melting circuit.
Figure 3.1: Flow sheet of the pilot plant at the T.U. Delft

<table>
<thead>
<tr>
<th>code</th>
<th>description</th>
<th>code</th>
<th>description</th>
<th>code</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC1</td>
<td>GMF Cooling Disc Crystallizer</td>
<td>P1</td>
<td>screw pump (max. 500 l/h)</td>
<td>M1</td>
<td>agitator (max. 150 rpm)</td>
</tr>
<tr>
<td>C1</td>
<td>TNO-Thijssen hydraulic wash column</td>
<td>P2</td>
<td>piston pump (max. 113 l/h)</td>
<td>M2</td>
<td>agitator (max. 45 rpm)</td>
</tr>
<tr>
<td>C2</td>
<td>gravity wash column (24 l)</td>
<td>P3</td>
<td>diaphragm pump (max. 500 l/h)</td>
<td>M3</td>
<td>scraper (max. 80 rpm)</td>
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<tr>
<td>V1</td>
<td>feed vessel (1500 l)</td>
<td>P4</td>
<td>screw pump (max. 50 l/h)</td>
<td>M4</td>
<td>agitator (max. 20 rpm)</td>
</tr>
<tr>
<td>V2</td>
<td>dosing vessel (25 l)</td>
<td>P5</td>
<td>screw pump (max. 50 l/h)</td>
<td>M5</td>
<td>scraper (max. 60 rpm)</td>
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<tr>
<td>V3</td>
<td>residue vessel (1500 l)</td>
<td>P6</td>
<td>screw pump (max. 500 l/h)</td>
<td>M6</td>
<td>agitator (max. 150 rpm)</td>
</tr>
<tr>
<td>V4</td>
<td>product vessel (1500 l)</td>
<td>P7</td>
<td>screw pump (max. 50 l/h)</td>
<td>M7</td>
<td>agitator (max. 150 rpm)</td>
</tr>
<tr>
<td>E1</td>
<td>cooler (max. 6 kW)</td>
<td>P8</td>
<td>screw pump (max. 200 l/h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>heater (max. 1 kW)</td>
<td>P9</td>
<td>diaphragm pump (max. 500 l/h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>heater (max. 1 kW)</td>
<td></td>
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</tbody>
</table>
pilot plant description

P6 provides a circulation flow in this circuit where the crystals are melted in E2. Via a control valve, which will be referred to as the product valve, the liquified product flows to product vessel V4. The residual mother liquor, which leaves the gravity wash column (C2) via an overflow, is transported to V3 by P9. In C2 a loosely packed crystal bed is transported downward under the influence of gravity. The product removal and melting section is constructed similar to the hydraulic wash column. Both wash columns can be operated at the same time.

Figure 3.2 shows a picture of the hart of the pilot plant: the CDC on the left hand side, the tall glass gravity column on the right hand side and the smaller glass hydraulic wash column in the middle at the back.

Figure 3.2: overview of the pilot plant at the T.U. Delft featuring: the GMF-Cooling Disc Crystallizer (left), the TNO-Thijssen hydraulic wash column (middle) and the gravity wash column (right)
3.2 EQUIPMENT DIMENSIONS AND PARTICULARITIES

*GMF Cooling Disc Crystallizer*

The CDC is a 100 l. trough (U-profile), which is divided into eight compartments by seven cooling elements. The cooling elements, which are connected in series, have a total wiped surface area of 0.91 m². The coolant flows countercurrent to the feed/product slurry in the CDC. Seven flat bottom valves, for sampling purposes, are placed in the bottom of the CDC directly underneath the opening in the cooling elements. Temperature sensors (Pt100 elements) are installed in each compartment of the CDC and in the inlet and the outlet of the cooling elements. The GMF Cooling Disc Crystallizer and a detail of a cooling element is schematically shown in figure 1.16 (chapter 1). Figure 3.3 presents a picture of the top view of the CDC (when the lid is removed). The eight compartments with rotating discs and the seven cooling elements are clearly visible.

![Figure 3.3: top view of the pilot GMF Cooling Disc Crystallizer, which shows: 8 compartments, 8 discs and 7 cooling elements](image)
**TNO-Thijssen hydraulic wash column**

The glass column wall is 0.64 m high and has an internal diameter of 0.06 m. A single filter tube is installed with an outer diameter of 0.02 m. A filter tube consists of three parts: a stainless steel hollow tube, a porous filter and a massive teflon bar at the bottom end. Six thermocouples are incorporated in the teflon part of the filter tube and can be used to detect the wash front level. Pressure indicators and temperature sensors (Pt100) are installed in the feed line and in the melting circuit of the wash column. Product samples can be taken from the melting circuit or from the product line, right after the product valve. The TNO-Thijssen wash column is schematically shown in figure 1.18. Figure 3.4a presents a close-up of the pilot hydraulic column, which is surrounded by a glass isolation jacket. Figure 3.4b gives a detail of the bottom section of the column, which features the filter tube (porous filter and teflon bottom end) and the knife at the bottom.

*Figure 3.4a: close-up of the pilot TNO-Thijssen wash column*
Figure 3.4b: detail of the bottom section of the pilot
TNO-Thijssen hydraulic wash column

gravity wash column
The glass column is 1.45 m high and has an internal diameter of 0.15 m. The feed inlet is positioned 0.15 m below the overflow to guarantee a crystal free residual mother liquor flow. Furthermore, the level of inlet and overflow and consequently the effective column height can be varied (overflow at 1.3 m, 1.05 m or 0.75 m). The column is equipped with a pen-type agitator driven by M4. The number and the position of the pens on the axis of the agitator can be changed. Liquid samples can be taken (via a septum using a syringe) and the temperature is measured (Pt100 elements) at seven equidistant positions along the column axis. Pressure indicators and temperature sensors (Pt100) are installed in the feed line and in the
melting circuit of the wash column. Product samples can be taken from the melting circuit or from the product line/tube, right after the product valve. A gravity wash column is schematically shown in figure 1.18. Figure 3.5 presents a close-up of the pilot gravity column.

Figure 3.5: close-up of the pilot gravity wash column
chapter 4

MORPHOLOGY OF $\varepsilon$-CAPROLACTAM CRYSTALS DEPENDENT ON THE CRYSTALLIZATION CONDITIONS

Abstract

The morphology of caprolactam crystals is an important property because it can affect their filterability. This study shows that the morphology of caprolactam crystals depends on the water content of the mother liquor and on the applied growth kinetics. Needle-like crystals were formed during single crystal experiments under two sets of conditions: (1) at high growth rates in a water rich mother liquor and (2) at low growth rates in the absence of water. Experiments were also performed in a lab-scale batch crystallizer and in a pilot-scale continuous crystallizer but did not yield needle-like crystals.

P.J. Jansens, Y. Langen

&

E.P.G. van den Berg, R.M. Geertman

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morphology of \( \varepsilon \)-caprolactam crystals

4.1 INTRODUCTION

\( \varepsilon \)-Caprolactam is used almost exclusively as the basic material for the polymerization of nylon-6, which is applied a.o. in the textile industry and for tyre manufacturing. The properties of nylon-6 depend strongly on the purity of the basic material and, consequently, caprolactam must meet stringent purity demands [1,2,3]. The main impurity in caprolactam is water, which enters the production process at the Beckmann rearrangement of cyclohexanone oxime to caprolactam and at the extraction of the crude lactam oil. Water must be removed because the anionic polymerization of caprolactam allows a maximum water content of only 0.01 wt%. The separation of the final 0.5-1.5 wt% water from the caprolactam occurs in falling film evaporators under deep vacuum because caprolactam is unstable at elevated temperatures. This separation technique is highly energy consuming and therefore fractional suspension crystallization is investigated as an alternative.

Fractional suspension crystallization processes generally consist of a crystallization section and a downstream solid/liquid separation unit [4]. The over-all separation efficiency and the production capacity of these processes are determined to a large extent by the filterability of the crystals produced in the crystallization section. The permeability of a bed of crystals, which is a quantitative measure for their filterability, depends on the crystal size distribution and on the crystal morphology.

Van der Heijden et al. [5] grew single caprolactam crystals from various solvents and at different growth rates and the different morphologies are summarized in figure 4.1. It was found that caprolactam has the tendency to develop in the presence of water (\( \pm 15 \) wt%) thin and needle-like crystals if high growth rates (\( \pm 10^{-6} \) m/s) are imposed. Needle-like (elongated) crystals usually have a poor permeability in comparison to more block-like (three dimensional) crystals.
Figure 4.1: Morphologies of caprolactam crystals grown in different solutions [5].

(a) alkanes, (b) alcohols (slow growth), (c) alcohols (fast growth),
(d) acetone (e) water (fast growth) and (f) water (slow growth)

The aim of this joint research project was to study the effects of the water content of the feed stock, the growth rate and the design of the crystallization process on the morphology of caprolactam crystals. For this purpose experiments have been performed in a micro scale single crystal growth cell, a lab scale batch crystallizer and a semi-industrial scale continuous GMF Cooling Disc Crystallizer. The feedstock in most experiments was a binary mixture of caprolactam and water (0-8 wt%). A multi-component sample taken from an industrial plant, which contained water and traces of organic impurities was used in some single crystal growth experiments. The correlation between the morphology and the permeability of caprolactam crystals was also investigated.
4.2 THEORY

4.2.1 structure and equilibrium morphology of caprolactam

The crystal structure of caprolactam was determined by Winkler et al. [6]. The structure is monoclinic and centrosymmetric (space group C2/c) with eight molecules in the unit cell. The lattice parameters are \(a=19.28\text{Å}, \ b=7.78\text{Å}, \ c=9.57\text{Å}\) and \(\beta=112.37^\circ\). All molecules were found as dimers in the crystal structure connected by two strong hydrogen bonds. Therefore in the Periodic Bond Chain (PBC) analysis, carried out by Geertman and Van der Heijden [7], the possibility of caprolactam growing from the melt with dimers as growth units was also considered. It turned out that the PBC analysis and an Ising model analysis based on the dimer growth, agreed best with the experimentally found morphology. Geertman and Van der Heijden found three different faces in their analyses: \((200), (110)\) and \((11\bar{1})\) and their prediction of the equilibrium morphology, based on the sequence in roughening temperature of these forms in case of dimer growth, is shown in figure 4.2.

![Crystal structure diagram](image)

Figure 4.2: predicted equilibrium morphology of caprolactam, assuming that growth occurs via dimer growth units
4.2.2 non-equilibrium morphology of caprolactam

The driving force for crystallization is a deviation from equilibrium conditions:

$$
\Delta \mu = R T \ln \frac{a(p,T,X)}{a^*(p,T,X^*)}
$$

(4.1)

where the asterisk denotes the equilibrium value. If the liquid phase behaves ideally or when the activity coefficient is approximately constant between X and X*, eq. (4.1) may be rewritten as:

$$
\beta = \frac{\Delta \mu}{R T} = \ln \frac{X}{X^*}
$$

(4.2)

where \( \beta \) is called the supersaturation. For low values of \( \beta \), eq. (4.2) may be simplified into:

$$
\beta = \frac{X - X^*}{X^*}
$$

(4.3)

In cooling crystallization processes, \( \beta \) is usually defined in terms of supercooling:

$$
\beta = \frac{\Delta H_m}{R T^2} \Delta T
$$

(4.4)

Crystal growth involves three processes: volume diffusion, surface integration and heat transfer. The correlation between the growth rate \( G \) and the supercooling \( \beta \) depends on which of these three process is limiting. De Goede and Van Rosmalen [9] derived eq. (4.5), which gives the ratio of the resistances to heat transfer and volume diffusion.

$$
q = \frac{X_b}{1 - X_b} \frac{\rho L}{M} \frac{k_D}{\alpha} \frac{\Delta H_m^2}{R T_b^2}
$$

(4.5)

where the subscript b denotes the value in the bulk of the liquid phase. The value of \( k_D/\alpha \) depends on the flow regime. In a stagnant liquid phase, the Nusselt and the Sherwood numbers are equal (Nu=Sh=2) and therefore:

67
\[ \frac{k_D}{\alpha} = \frac{D}{\lambda_L} \] (4.6)

In figure 4.3 the relative contribution of the resistance to heat transfer is plotted versus the weight fraction of caprolactam in a caprolactam/water system for \( \Delta H_m = 16046 \ \text{J/mol}, \ \lambda_L = 0.16 \ \text{W/mK}, \ \rho_L = 1022 \ \text{kg/m}^3, \ M = 113.2 \ \text{g/mol}, \ T_b = 342 \ \text{K}, \ R = 8.31 \ \text{J/molK} \) and two diffusion coefficients. The diffusion coefficient in a caprolactam/water system is not reported in literature but according to the Wilke-Chang correlation [10]: \( D = 10^{-10} \ \text{m}^2/\text{s} \). Figure 4.3 clearly demonstrates that only for \( W_b > 0.99 \), the resistance to heat transfer is larger than the resistance to volume diffusion \( (q/(1+q) > 0.5) \).

![Graph](image)

**Figure 4.3:** relative contribution of the resistance to heat transfer as a function of the weight fraction caprolactam \((W_b)\)

The dependence of both the diffusion coefficient and the operating temperature on
the water content of a mixture was not accounted for in the calculations but these
effects counteract each other and do not significantly change the general view of
figure 4.3 (D \propto T/\eta).
Caprolactam crystals grown from a mixture with water (15 wt\%) are well faceted
and strongly anisotropic [5], which indicates that surface integration rather than
volume diffusion is the rate determining step at the applied supercoolings. Well
known surface integration models are the Burton-Cabrera-Frank (BCF) and the
Birth and Spread (B+S) models.
The BCF or spiral growth model describes the outgrowth of screw dislocations in
the crystal lattice. The BCF correlation is given by eq. (4.7):

\[ G = A_1 \cdot \beta^2 \cdot \tanh \left( \frac{A_2}{\beta} \right) \]  \hspace{1cm} (4.7)

where \( A_1 \) and \( A_2 \) are complex temperature dependent constants. At low \( \beta \) the BCF
equation approximates to \( G \propto \beta^2 \) and at high \( \beta \) to \( G \propto \beta \).
The B+S model is based on two dimensional nucleation on a smooth crystal
surface followed by spread of the monolayer over the surface. The B+S correlation
is given by eq. (4.8):

\[ G = A_3 \cdot \beta^5 \exp \left( \frac{A_4}{\beta} \right) \] \hspace{1cm} (4.8)

Growth of caprolactam crystals is not likely to proceed via the B+S mechanism
because recent work done by Van der Heijden and Geertman [11] revealed that
always a large number of dislocations emerge at the surface of caprolactam
crystals.
The morphology of crystals is not determined by the absolute values of the growth
rates of the individual faces but rather by the ratio of these growth rates. Since the
\( G-\beta \) relation can be different for each individual face, the ratio of the growth rates
may vary considerably depending on the supersaturation as is shown in figure 4.4.
Caprolactam crystals grown from a mixture with water feature three different faces
(200), (110) and (11\bar{1}). The G-\( \beta \) relation of each face depends on the orientation
morphology of $\varepsilon$-caprolactam crystals

and number density of the molecules in the growth layer and on molecular interactions at the solid/liquid interface.

Figure 4.4: dependence of the growth rates of two faces ($G_A$ & $G_B$) and their ratio ($G_A/G_B$) on the supercooling $\beta$

Van der Heijden et al. [5] argue that water molecules break up the caprolactam dimers, as is shown in figure 4.6. They found that the growth of the (200) face is hampered most and the growth of the (11T) face is hampered least by the presence of water in the mother liquor. It seems that this difference in blocking efficiency of the three faces is related to the orientation of the caprolactam dimers in the faces. Figures 4.5a-c present the side views of the three faces, which are rotated in such a way that the faces are horizontal and perpendicular to the paper.
Figure 4.5a: side view of the (200) face of caprolactam crystals

Figure 4.5b: side view of the (110) face of caprolactam crystals
The side view of the (11\overline{1}) face, presented by Van der Heijden et al. [5], has been corrected. Figure 4.5a shows that all hydrogen bonds between the dimers are positioned upright and therefore (nearly) perpendicular to (200) face. Figure 4.5b shows that only in every other half layer the hydrogen bonds are positioned perpendicular to the (110) face. Figure 4.5c shows upright and horizontal hydrogen bonds within one half layer in the (11\overline{1}) face. Assuming that the blocking efficiency of water is most effective on hydrogen bonds oriented perpendicular to the faces, the following sequence of decreasing efficiency can be given: (200)> (110)> (11\overline{1}).
4.2.3 characterization of caprolactam crystals

Here, the produced crystals are characterized by their length/width (l/w) ratio, which is a measure for their needle-likeness, and by their length/thickness (l/t) ratio, which is a measure for their three dimensionality or block-likeness. The dimensions of a crystal are indicated in figure 4.7.
The thickness \( t \) was calculated via the Steno law:

\[
t = 2 \times \tan(\omega) \times \delta = 2.44 \times \delta
\]  \hspace{1cm} (4.9)

where \( \omega \) is the fixed angle between the (200) and the (110) face and amounts 67.72 \(^\circ\).

The permeability of a bed of crystals, which is a measure for their filterability, is defined by Darcy's law [12]:

\[
B = \frac{-U_L \cdot \eta \cdot h}{\Delta p}
\]  \hspace{1cm} (4.10)

### 4.3 EXPERIMENTAL PROCEDURE

Experiments were performed in three units: a 14 ml single crystal growth cell, a 1.5 l batch crystallizer and a 100 l continuous GMF Cooling Disc Crystallizer. Caprolactam was obtained from DSM.

#### 4.3.1 single crystal growth experiments

A 14 ml sealed glass ampoule (cell), filled with a mixture of the desired composition, was placed in a thermostated cell (see fig. 4.8a). At the start of an experiment the (liquid) feed mixture was thoroughly shaken and completely crystallized. Next the crystal mass was melted until one isolated crystal seed remained. The seed was kept at its melting point for twenty minutes. Then the coolant temperature was lowered to a level needed to achieve the desired, virtually constant, linear growth rate. Here, the linear growth rate is defined as the increase of the crystal length \( l \) as a function of time. Crystal growth was observed with a microscope which was coupled to a video camera. From these recordings, using digital image processing, photographs were made, which were used to measure...
the length (l), the width (w) and the thickness (t) of the crystals at different times during the experiments. During the experiments the linear growth rate was kept at $10^8$ m/s, $10^7$ m/s or $10^6$ m/s. The water content of the binary feed mixtures amounted 0 wt%, 1.3 wt%, 2.4 wt% or 8.5 wt% and remained virtually constant during the experiments because only a minor portion of the mixture was solidified. The industrial sample contained ± 1 wt% water and traces of organic impurities such as toluene, cyclohexanone and cyclohexanone-oxime.

Figure 8a: experimental unit: single crystal growth cell

4.3.2 batch experiments

A 1.5 l glass batch crystallizer, equipped with a cooling jacket and a teflon scraper, was used (see fig. 4.8b). The temperature difference between the coolant and the crystallizing mixture ($\Delta T_c$) was kept constant during the experiments by means of a P.I.D. controller. The temperatures of the mixture and the coolant and the revolution rate of the scraper were monitored continuously during the experiments. At the beginning of the experiments the feed mixture was melted completely. The melting point was determined by lowering the temperature until spontaneous nucleation occurred followed by gradual remelting of the formed crystals. During
morphology of ε-caprolactam crystals

the actual experiments ± 100 mg seed crystals was added when the temperature of the feed mixture came below the melting point. The crystal production (yield) was varied by altering the time span of the experiments. The experimental conditions were varied as follows:

- **water content feed:** 0 to 8 [wt%]
- **temperature difference:** 2 to 5 [°C]
- **revolution rate:** 50 or 100 [rpm]
- **yield:** 5 to 14 [wt%]
- **batch time:** 15 to 30 [min]

At the end of an experiment part of the content of the crystallizer was centrifuged and washed with a saturated n-decane solution whereas the remainder was used for a constant pressure filtration experiment. The size distribution of the centrifuged crystals was determined by sieving and/or by using a forward light scattering technique (Malvern). The filtration experiment was used to determine the yield and the permeability.

![Experimental unit: batch crystallizer](image)

**Figure 8b:** experimental unit: batch crystallizer
4.3.3 GMF Cooling Disc Crystallizer (CDC)

The Cooling Disc Crystallizer (CDC) of GMF-Gouda may be regarded as an integrated cascade featuring a cocurrent contact between the crystals and the mother liquor. A CDC (fig. 8c) consists of a U-shaped horizontal trough which is divided into compartments by fixed cooling elements. In each compartment a disc, equipped with wipers and mixing blades, slowly rotates. The product slurry flows freely from one compartment to the next through small openings at the bottom of the cooling elements and leaves the CDC via an overflow in the last compartment. The trough of the pilot plant CDC, used for the experiments, has a volume of 100 l and it is divided into eight compartments. Seven cooling elements are connected in series and have a total wiped surface area of 0.91 m². The coolant flows countercurrent to the product from the seventh to the first cooling element. In the start-up phase of an experiment the inlet temperature of the coolant was gradually lowered until the crystal content in the overflow (yield) of the CDC reached the desired value. The inlet temperature of the feed was kept just above its melting point temperature. The experimental conditions were varied as follows:

<table>
<thead>
<tr>
<th>Water content feed:</th>
<th>1 to 8 [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant flow:</td>
<td>125 or 500 [l/h]</td>
</tr>
<tr>
<td>Revolution rate:</td>
<td>15 [rpm]</td>
</tr>
<tr>
<td>Yield:</td>
<td>10 to 40 [wt%]</td>
</tr>
<tr>
<td>Residence time:</td>
<td>55 or 110 [min]</td>
</tr>
</tbody>
</table>

To assure a steady state operation before sampling took place, the crystallizer was operated for at least seven times the mean residence time at given operating conditions after nucleation had occurred. Slurry samples were taken from the overflow and from seven sampling points positioned at the bottom of the trough underneath the openings in the cooling elements. The size distribution, yield and permeability of the crystals were determined by the same procedures as for the batch experiments.
4.4 RESULTS AND DISCUSSION

4.4.1 single crystal growth

In all experiments well faceted and strongly anisotropic crystals were formed indicating that crystal growth is limited by surface integration rather than by heat transfer or volume diffusion. The β-values reported in this section were calculated via eq. (4.4) using the temperature difference between the melting point and the coolant. This is a rough assumption because this temperature difference is not identical to the temperature difference at the crystal surface.

In figure 4.9a-c the growth rate of the three faces is plotted as a function of the supercooling for different water contents of the feed mixture. Data obtained by Van den Berg [8], who measured $G_{(110)}$ and $G_{(110)}$ as a function of β in a pure melt, are included.
Figure 4.9a: growth rate versus supercooling of the (1\{1\bar{1}\}) face at different water contents

Figure 4.9b: growth rate versus supercooling of the (110) face at different water contents
morphology of ε-caprolactam crystals

Figure 4.9c: growth rate versus supercooling of the (200) face at different water contents

Regression analysis yielded the following G-β relations (S.I. units):

\[
g_{(11\bar{1})} = (0.018 \pm 0.005) \cdot \beta^{(1.93 \pm 0.10)} \quad (\text{in pure melt}) \tag{4.11}
\]

\[
g_{(110)} = (0.027 \pm 0.009) \cdot \beta^{(2.03 \pm 0.17)} \quad (\text{in pure melt}) \tag{4.12}
\]

Not enough data were available to obtain an accurate G-β relation for the (200) face. The growth order (r) to the supercooling equals approximately 2, which indicates that growth proceeds via the spiral growth mechanism. Not enough data are available to calculate accurately the kinetic coefficient (k_i) and growth order (r) for the water containing mixtures.

In figure 4.10, the measured l/w ratios are plotted versus the order of magnitude of the linear growth rate and the water content of the feed mixtures. It can be seen that elongated crystals are not only formed in case of growth from a water rich feed stock at fast growth rates [5], but also during growth from the pure melt at low growth rates. For intermediate circumstances the crystals were more block-like.
The trends in the I/w ratio are caused by changes in the ratio of the growth rate of the (11T) and the (110) faces ($G_{(11T)}/G_{(110)}$).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure410.png}
\caption{I/w ratio dependent on the linear growth rate and on the water content}
\label{fig:410}
\end{figure}

\textbf{Remark:} values for the industrial sample are underlined.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure411.png}
\caption{$G_{(11T)}/G_{(110)}$ versus $\beta$ with different water contents}
\label{fig:411}
\end{figure}
Figure 4.11 demonstrates how $G_{(11\bar{1})}/G_{(110)}$ depends on the applied supercooling and on the water content of the mixture. Surprisingly, the ratio sharply decreases with $\beta$ in the absence of water (pure melt), gradually decreases with $\beta$ at 2.4 wt% water and gradually increases with $\beta$ at 8.5 wt% water.

In figure 4.12 the data obtained by Van den Berg and the results from this study are combined and reveal that a maximum occurs in the $G_{(11\bar{1})}/G_{(110)}$ ratio at $0.004<\beta<0.008$. The figures 4.10 and 4.12 prove that the formation of elongated crystals is not exclusively caused by the presence of water.

In figure 4.13, the measured I/t ratios are plotted versus the order of magnitude of the linear growth rate and the water content of the feed mixtures. Figure 4.13 shows how the I/t ratio increases with increasing growth rate during crystallization from the pure melt. Most striking, however, is the production of relatively thick crystals (small I/t ratio) in the presence of 8.5 wt% water.

The I/t ratio of the crystals is determined by the $G_{(11\bar{1})}/G_{(200)}$ ratio, which is plotted versus the supercooling in figure 4.14. All plotted curves feature an increase of the $G_{(11\bar{1})}/G_{(200)}$ ratio with increasing supersaturation.

Figures 4.9a-c show that with an increase of the water content from 0 wt% to 2.4 wt%, the growth rates of all three faces are reduced at constant $\beta$. However, a further increase of the water content from 2.4 wt% to 8.5 wt% has virtually no effect on $G_{(200)}$ but does reduce $G_{(11\bar{1})}$ and $G_{(110)}$. Apparently, the blocking effect on the (200) face is already maximal at 2.4 wt%.

The industrial mixture shows normal behaviour with respect to the I/w ratio but has significantly lower I/t ratios than could be expected from its water content. This indicates that the impurities present in the industrial sample specifically block the (11\bar{1}) and the (110) faces but not or to a lesser extent the (200) face. Possible candidates for this behaviour could be oxidation products and/or small caprolactam polymers.
Figure 4.12: $G_{(111)}/G_{(110)}$ versus $\beta$ in a pure melt including results obtained by Van den Berg [8]

Figure 4.13: I/t ratio dependent on the linear growth rate and on the water content

Remark: Values for the industrial sample are underlined.
4.4.2 **lab scale batch crystallization**

It proved to be difficult to determine the effect of the experimental conditions on the morphology of caprolactam crystals produced in batch experiments because, surprisingly, crystals from the same batch sometimes featured a variety of morphologies. This is illustrated by figure 4.15, which shows an elongated crystal next to nearly square crystals. Furthermore, attrition, agglomeration and even crystal breakage of the crystals could be observed.

An unambiguous trend, however, was the formation of elongated and relatively large crystals upon crystallization from a *pure melt*, as could be anticipated from the single crystal growth experiments. Figure 4.16 displays these needle-like crystals with a l/w ratio of 5 to 10. The thickness of the crystals could not be measured accurately but the narrow dark margins at the edges of the (200) faces, which represent the (110) faces, and the good transparency of the crystals suggest relatively thin crystals. The mass based mean size of the needle-like crystals amounted 620 μm. Crystals produced from a *water containing feedstock* were
generally smaller \( (d_{p,m} = 400-500 \ \mu m) \), featured a \( l/w \) ratio ranging roughly from 1.5 to 5 and appear to be thicker (see fig. 4.17).

Unlike the single crystal growth experiments, the batch experiments with a water rich feed mixture (8 wt% water) and large \( \Delta T_c \) (5°C) did not yield elongated crystals. This indicates that in the batch crystallizer, the \textit{actual} supercooling \( \beta \) (at the crystal surface) was not high enough to make \( G_{(117)}/G_{(110)} \) deviate significantly from unity (see fig. 4.11). In general the supercoolings achieved in a \textit{well mixed} batch crystallization are significantly lower than those in a \textit{stagnant} single crystal growth experiment. The operating conditions during batch crystallization, apart from the experiment with a pure melt, apparently correspond to the intermediate region in figure 4.10.

Although the operating conditions, apart from the water content, had no visible effect on the morphology of the caprolactam crystals produced in the batch experiments, they did affect the permeability and the size distribution of the crystals. The relation between morphology, size distribution and permeability will be discussed below.

![Image of crystals](image)

\textbf{Figure 4.15: different crystal morphologies occurred in the same batch}

\begin{itemize}
\item \textit{experimental conditions:} 2.5 wt\% water, 50 rpm, \( \Delta T = 1.7 \, ^\circ C\), 6 wt\% yield.
\item \textit{scale picture:} 1 cm = 330 \( \mu m \)
\item \textit{sieve fraction:} 0.71 - 0.85 mm
\end{itemize}
Figure 4.16: needle-like crystals formed in a pure melt (batch)

experimental conditions: 0 wt% water, 50 rpm, $\Delta T = 2.0 \, ^\circ C$, 11 wt% yield
scale picture: 1 cm = 330 $\mu$m
sieve fraction: unsieved

Figure 4.17: three dimensional crystals formed in a melt containing water (batch)

experimental conditions: 2.5 wt% water, 50 rpm, $\Delta T = 1.7 \, ^\circ C$, 6 wt% yield
scale picture: 1 cm = 220 $\mu$m
sieve fraction: unsieved
4.4.3 *pilot scale continuous crystallization (CDC)*

In general, the crystalline product from the Cooling Disc Crystallizer (CDC) was of poor quality in comparison to that from the batch crystallizer. The crystals formed in the CDC were relatively small ($d_{p,m}=350-400 \mu m$). Under a microscope, large numbers of fines could be detected which either stuck to the surface of larger crystals or formed agglomerates (see fig. 4.18).

Similar to the batch experiments but unlike the single crystals growth experiments, the CDC runs with a water rich feedstock (8 wt\%) did not yield needle-like crystals. Apparently, the operating conditions during the CDC experiments also correspond to the intermediate region in figure 4.10. Using an integral model, which describes the crystallization process in cascades of crystallizers with backmixing [13,14], the growth rate in the CDC was calculated as a function of the operating conditions in each compartment. In all cases, the model predicts moderately low values for the over-all growth rate ($G=10^{-9}-10^{-7}$ m/s). The single crystal growth experiments showed that needle-like crystals are not formed at such low growth rates.

Figure 4.18: larger crystal with fines stuck to its surface, formed in the CDC

*experimental conditions:* 2.2 wt\% water, $\Delta T = 5 ^\circ C$, $\tau=110$ min, 33 wt\% yield  
*sieve fraction:* unsieved
morphology of ε-caprolactam crystals

Unfortunately, due to logistic problems, no experiments could be performed with a pure melt, which could verify the formation of elongated crystals in a pure melt. On the other hand, crystallization from a pure melt is not very relevant from a practical point of view.

The CDC crystals, similar to the batch crystals, showed a significant spread in the l/w ratio within one sample (roughly 1.5 < l/w < 5). Although, the operating conditions did not have a detectable effect on the l/w ratio, they did affect the number of fines and consequently the permeability of the crystalline product as will be discussed below.

4.4.4 permeability in relation to morphology

In the batch experiments most experimental conditions, except the water concentration, had no significant effect on the morphology but did affect the permeability of the produced crystals. The highest permeability ($B = 10^{-9}$ $m^2$) was achieved at: a low revolution rate (50 rpm), a small temperature difference ($\Delta T_c = 1.7^\circ C$), an intermediate water content (2 wt%), a short batch time (15 min) and consequently a low yield (6 wt%). Under these conditions, the number of fines in the product is low and the mean size of the product is relatively high $d_{p,m} = 500 \mu m$, which has a positive effect on the permeability. The relevance of morphology control, however, is demonstrated by the fact that the very large needle-like crystals produced in pure melt ($d_{p,m} = 620 \mu m$) only had a moderate permeability of $4 \times 10^{-10} m^2$. In this respect it could be argued that CSD measurements of needle-like crystals using a light scattering technique are inaccurate but these techniques are likely to predict too small rather than too large mass based mean sizes of elongated crystals. In summary, the permeability of batch crystals proved to be primarily determined by their mean size and the number of fines but the effect of morphology is not negligible and needle-like crystals should be avoided.

In the continuous CDC experiments the operating conditions had no effect on the morphology but did effect the permeability of the produced crystals [14].
permeability of the CDC crystals ranged from $1 \times 10^{-11}$ m² to $5 \times 10^{-11}$ m², which is very poor in comparison to that of the batch crystals. The poor permeability is caused by the smaller dimensions of the crystals ($d_{p,m} = 350-400$ μm) and the large number of fines, but could not be related to changes in morphology.

4.5 CONCLUSIONS

The morphology of caprolactam crystals was shown to depend on the supercooling and the water content of the mother liquor. Needle-like crystals are formed in two cases: (i) from a pure melt at low growth rates and (ii) from a water rich feed stock at high growth rates. The formation of needle-like crystals in a water rich mixture is probably related by blocking of the (200) and the (110) faces by water molecules. The crystals grew thicker upon an increase of the water content from 2.4 wt% to 8.5 wt%, which may be caused by the fact that blocking of the (200) face is already maximal with 2.4 wt% water whereas blocking of the (111) and (110) faces becomes more and more effective with increasing water content.

The permeability of caprolactam crystals is hampered by the formation of needle-like crystals but primarily depends on the size distribution of the product (mean size and fines fraction). Under industrially relevant operating conditions (water content ≥ 1 wt% and high yield), the morphology of caprolactam crystals is approximately constant and therefore does not determine the filterability of the product.
morbology of $\varepsilon$-caprolactam crystals

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>permeability of a bed of crystals</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$d_{pm}$</td>
<td>mass based mean size</td>
<td>[m]</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient (in liquid phase)</td>
<td>[m$^2$/s]</td>
</tr>
<tr>
<td>$G$</td>
<td>growth rate</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$h$</td>
<td>height of a crystal bed</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta H_m$</td>
<td>heat of fusion</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$k_0$</td>
<td>volume diffusion or mass transfer constant</td>
<td>[m/$s$]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>kinetic coefficient ($G = k_i \cdot \beta'$)</td>
<td>[m/$s$]</td>
</tr>
<tr>
<td>$l$</td>
<td>crystal length</td>
<td>[m]</td>
</tr>
<tr>
<td>$M$</td>
<td>molar weight</td>
<td>[g/mol]</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
<td>[-]</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>pressure drop over a crystal bed</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$q$</td>
<td>ratio of resistances</td>
<td>[-]</td>
</tr>
<tr>
<td>$r$</td>
<td>growth order ($G = k_i \cdot \beta'$)</td>
<td>[-]</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>[J/mol$K$]</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
<td>[-]</td>
</tr>
<tr>
<td>$t$</td>
<td>crystal thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta T_c$</td>
<td>temperature difference between the mixture and the coolant</td>
<td>[K]</td>
</tr>
<tr>
<td>$U_L$</td>
<td>superficial liquid velocity through a crystal bed</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$w$</td>
<td>crystal width</td>
<td>[m]</td>
</tr>
<tr>
<td>$W$</td>
<td>weight fraction caprolactam</td>
<td>[g/g]</td>
</tr>
<tr>
<td>$X$</td>
<td>mole fraction caprolactam</td>
<td>[mol/mol]</td>
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</tbody>
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Greek

<table>
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<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>heat transfer coefficient</td>
<td>[W/m$^2$K]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>supercooling or supersaturation</td>
<td>[-]</td>
</tr>
<tr>
<td>$\delta$</td>
<td>measure for the crystal thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>thermal conductivity</td>
<td>[W/mK]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity</td>
<td>[Pa.s]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>specific weight</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$\Delta \mu$</td>
<td>difference in chemical potential, driving force</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angle between the (200) and the (110) face</td>
<td>[°]</td>
</tr>
</tbody>
</table>

Subscript/Superscript

- $b$       | bulk of the liquid phase                                                  |
- $L$       | liquid phase                                                               |
- *         | equilibrium condition                                                      |
References


[14] Chapter 5 of this thesis.
morphology of ε-caprolactam crystals
chapter 5

OPTIMIZATION AND MODELLING OF THE CRYSTALLIZATION PROCESS IN A CASCADE WITH BACKMIXING

Abstract
Cascades of crystallizers are applied in many industrial crystallization processes. This chapter deals with the optimization of the filterability of crystals produced in such a cascade, since a good filterability is often one of the main product specifications. An integral model description of the crystallization process was developed which allows for the prediction of the crystal size distribution and the filterability in each stage of the cascade and experiments were performed to support this model. The integral model can be used as a predictive tool in future filterability optimization studies.

P.J. Jansens, O.S.L. Bruinsma and G.M. van Rosmalen
Submitted to A.I.Ch.E. J.
5.1 INTRODUCTION

Fractional suspension crystallization processes are aimed at ultrapurification of organic compounds and are based on cooling crystallization [1]. These processes generally comprise a cascade of crystallizers and a downstream solid/liquid separation unit (Chapter 1). The over-all separation efficiency of these processes depends to a large extent on the filterability of the crystals produced in the cascade.

Research at the T.U. Delft is focused on optimization of the crystallization process in cascades of crystallizers, primarily with respect to the filterability of the product crystals. Optimization and control of the product filterability requires a good understanding of the hydrodynamics and the crystallization process in the cascade. Therefore this study is also aimed at the development of an integral model description of the crystallization process in cocurrent cascades which can be a useful tool in the filterability optimization process.

A series of experiments was conducted to determine the effect of practical process variables (i.e. throughput, feed temperature and composition and coolant flow and temperature) on the permeability of the crystals in the different compartments and in the product outlet in a pilot-scale cascade of crystallizers. The permeability of a bed of crystals is a quantitative measure of the filterability of these crystals. The experiments were performed with a so-called Cooling Disc Crystallizer (CDC), which can be regarded as an integrated cascade featuring a cocurrent contact between the crystals and the mother liquor with backmixing between the compartments. The pilot CDC (fig. 5.1) consists of a horizontal trough which is divided into eight compartments by seven fixed cooling elements. In each compartment a disc equipped with wipers and mixing blades slowly rotates. The product slurry flows from one compartment to the next via small openings at the bottom of the cooling elements and leaves the CDC via an overflow in the last compartment.
Figure 5.1: Cooling Disc Crystallizer (GMF-Gouda) with a detail of cooling element

The CDC was selected for this study because of two characteristics which were expected to have a beneficial impact on the filterability of the product crystals: (1) the complete absence of auxiliary slurry transport equipment and (2) its ability to operate with very high crystal contents (up to 45 v%).

Parallel to the experimental program, a mathematical description of the crystallization process in a cocurrent Cascade of Crystallizers with Backmixing has been developed. The CCB model integrates five aspects: (i) hydrodynamics, (ii) mass and heat transfer, (iii) thermodynamics and crystallization kinetics, (iv) crystal size distribution (CSD) and (v) bed porosity and permeability. Key-parameters in the model are a backmix ratio, a classification ratio, a nucleation constant and a nucleation exponent. The integral model description allows for the calculation of the CSD, the nucleation rate, the growth rate and the permeability of the crystals in every compartment and in the product outlet of a cascade of
optimization and modelling of the crystallization process in a cascade

crystallizers.

The importance of this contribution is that it links operating conditions to the most relevant properties of a crystalline product (CSD and filterability) by a combination of mass, heat and population balances. Further, this is the first example in which population densities of crystals slurries are directly translated into the porosity and permeability of a bed of these crystals. It is stressed here, that the model is of general importance and its use is not restricted to the CDC.

5.2 MODEL FORMULATION

5.2.1 hydrodynamics

The hydrodynamics of stirred tanks with backmixing has been investigated extensively [2-5]. Roemer and Durbin [5] presented the Backflow Cell (BC) model, which consists of N ideally mixed cells of equal volume with a constant net throughput $\Phi_i$ and with equal backmix flow $\Phi_{b}$ between neighbouring cells (see figure 5.2).

Figure 5.2: cascade with backmixing model (8 compartments)
The residence time distribution function $E(t)$ for a single phase flow through this cascade reads:

$$E(t) = \sum_{m=1}^{N} \frac{A_m}{\tau} \exp\left(\frac{s_m t}{\tau}\right)$$  \hspace{1cm} (5.1)

where $A_m$ and $S_m$ are complex functions depending on the backmix ratio $f$ and on the number of cells $N$ [5].

$$f = \frac{\Phi_b}{\Phi_f}$$  \hspace{1cm} (5.2)

The backmix ratio can be calculated from the mean residence time and the variance of an experimentally determined residence time distribution curve [2]:

$$\frac{\sigma^2}{\tau^2} = \frac{N(1-F^2)-2F(1-F^N)}{N^2(1-F^2)} \hspace{1cm} \text{and} \hspace{1cm} F = \frac{f}{1+f}$$  \hspace{1cm} (5.3)

Bell and Babb [3] argue that the BC model can be applied also to multi-phase flow cases provided that all phases are well mixed. In the case of crystallization of organics from the melt this condition is nearly always satisfied because the difference in specific weight between the crystals and their mother liquor is usually small. Hence, the BC model can be applied to describe the hydrodynamic behaviour of a cascade of crystallizers. Typical for the CDC is the removal of product via an overflow which may cause some classification in the last compartment. For this purpose a size independent classification ratio $h$ is included in the hydrodynamic model. From this assumption it follows:

$$h = \frac{W_{\text{overflow}}}{W_{\text{comp},N}}$$  \hspace{1cm} (5.4)

If the last compartment of a cascade is a mixed product removal type crystallizer, the value of $h$ amounts 1.
5.2.2 mass and heat transfer

The component balances over the compartments 1, i and N of a cascade of crystallizers, assuming that the formed solid phase is 100 % pure, can be reduced to eqs. (5.5), (5.6) and (5.7):

\[ x_i + f((1 + w_i)*x_i) - (1 + f)(w_i + (1 - w_i)*x_i) = 0 \]  \hspace{1cm} (5.5)

\[
(1 + f)((1 - w_{i-1} + (1 - w_{i-1})*x_{i-1}) + f((1 - w_{i-1})*x_{i-1}) - (1 + 2f)((1 - w_i)*x_i) = 0 \]  \hspace{1cm} (5.6)

\[
(1 + f)((1 - w_{N-1})*x_{N-1}) - f((1 - w_N)*x_N) - hw_N - (1 - hw_N)*x_N = 0 \]  \hspace{1cm} (5.7)

The heat of crystallization and the sensible heat are removed through the coolant.

A heat balance on the coolant side over compartment i yields:

\[ \Phi_c*C_p*c*(T_{c,i} - T_{c,i-1}) - K*A*(\Delta T)_{cp,i} = 0 \]  \hspace{1cm} (5.8)

For the cooling element i, which separates the compartment i and i+1, \((\Delta T)_{cp,i}\) is simply defined as:

\[ (\Delta T)_{cp,i} = \frac{1}{2}*(T_{p,i} - T_{c,i} - T_{c,i-1} + T_{c,i} + T_{c,i-1}) \]  \hspace{1cm} (5.9)

The numbering of \(T_p\) and \(T_c\) is illustrated by figure 5.3.

Heat balances on the product side over the compartments 1, i and N, assuming that heat transfer to the environment is negligible, can be reduced to eqs. (5.10), (5.11) and (5.12):
\[ H_{\text{feed}} + f \cdot H_{SL2} - (1 + f) \cdot H_{SL1} - \frac{K \cdot A}{\Phi_f} \cdot (\Delta T)_{pc1} = 0 \] (5.10)

\[ (1 + f) \cdot H_{SL,i-1} + f \cdot H_{SL,i-1} - (1 + 2f) \cdot H_{SLi} - \frac{K \cdot A}{\Phi_f} \cdot (\Delta T)_{pc,i} = 0 \] (5.11)

\[ (1 + f) \cdot H_{SL,N-1} - f \cdot H_{SL,N} - h \cdot w_N \cdot H_{S,N} - (1 - h \cdot w_N) \cdot H_{S,N} - \frac{K \cdot A}{\Phi_f} \cdot (\Delta T)_{pc,N} = 0 \] (5.12)

For compartment, \( i \) \((\Delta T)_{pc,i}\) is defined as:

\[ (\Delta T)_{pc,i} = \frac{1}{2} \left( T_{pi} - \frac{T_{ci} + T_{ci+1}}{2} \right) + \frac{1}{2} \left( T_{pi} - \frac{T_{ci} + T_{ci+1} + T_{ci+2}}{2} \right) \] (5.13)

**Figure 5.3:** definition/numbering of the temperature of the product slurry (\( T_p \)) and the coolant (\( T_c \)) in the pilot CDC with eight compartments
optimization and modelling of the crystallization process in a cascade

In conventional cascades consisting of separate vessels equipped with cooling jackets the terms \((\Delta T)_{cp,i}\) and \((\Delta T)_{pc,i}\), which represent the local temperature difference between the coolant and the product, are identical. In the CDC, however, N-1 cooling elements separate N compartments (see figs. 5.1 to 5.3). Obviously, the fact that in a CDC the first and the last compartment face only one side of a cooling element must be accounted for in the calculations.

The enthalpy of the liquid phase is assumed to be independent of its concentration and is defined to be zero at the melting point of the pure main component. The enthalpies of the slurry \((H_{s,i})\), the liquid phase \((H_{l,i})\) and the solid phase \((H_{s})\) are defined as:

\[
H_{s,i} = w_i \cdot H_{s,i} + (1 - w_i) \cdot H_{l,i}
\]

\[
H_{l,i} = C_{p,i} \cdot (T_{p,i} - T_m)
\]

\[
H_{s,i} = -\Delta H_m + C_{p,i} \cdot (T_{p,i} - T_m)
\]

(5.14)
(5.15)
(5.16)

5.2.3 **thermodynamics and kinetics**

Each compartment of the cascade is assumed to be a class II crystallizer, which means that the yield is independent on the throughput and the exit concentration of the liquid phase approaches the equilibrium concentration [6]. Thus the liquid concentration in each compartment can be calculated using a relation for the liquidus curve. Here, for the sake of simplicity, the liquidus is described as a straight line with slope \(q\):

\[
x_i = 1 - \frac{(T_m - T_{p,i})}{q}
\]

(5.17)
Randolph and Larson [6] suggest the following empirical correlation for the nucleation rate in mixed suspension crystallizers:

\[ B = k(T) \cdot \omega^x \cdot w^y \cdot s^z \]  \hspace{1cm} (5.18)

where \( \omega \) is a measure for the mechanical agitation, \( w \) is the crystal content or suspension density and \( s \) is the degree of supersaturation. The exponent \( y \) in eq. (5.18) is usually 1 [7]. In a class II system the supersaturation is conveniently substituted by the growth rate. With the assumptions that the degree of agitation is constant and that the effect of temperature changes on the nucleation constant are negligible, the nucleation rate in compartment \( i \) becomes:

\[ B_i = k_i \cdot w_i \cdot G_i^j \]  \hspace{1cm} (5.19)

Phenomena such as attrition, agglomeration, crystal breakage and size-dependent crystal growth, are neglected in this model for the sake of simplicity.

5.2.4 crystal size distribution - moments

In general form a balance for the moment \( k \) over the compartments 1, \( i \) and \( N \) of a cascade of crystallizers can be written as:

\[ S_{k1} + \frac{f \cdot m_{k2}}{\tau} - \frac{(1 + f) \cdot m_{k1}}{\tau} = 0 \]  \hspace{1cm} (5.20)

\[ S_{ki} + \frac{(1 + f) \cdot m_{k,i-1}}{\tau} + \frac{f \cdot m_{k,i+1}}{\tau} - \frac{(1 + 2f) \cdot m_{ki}}{\tau} = 0 \]  \hspace{1cm} (5.21)

\[ S_{kN} + \frac{(1 + f) \cdot m_{k,N-1}}{\tau} - \frac{(h + f) \cdot m_{kN}}{\tau} = 0 \]  \hspace{1cm} (5.22)

with boundary condition: \( m_{0,i} = w_i/k_w \).

For the zeroth moment \( m_{0,i} \), which indicates the number of crystals in compartment \( i \), the source term \( S_{k,i} \) is equal to the nucleation rate \( B_i \) (eq. 5.18). For the higher
moments \( S_{k,i} \) is given by eq. (5.23) [6]:

\[
S_{k,i} = k \cdot G_i \cdot m_{k-1,i}
\]  
(5.23)

The mean crystal size and the coefficient of variation of the crystal size distribution can be calculated from the moments of the crystal size distribution:

\[
L_n = \frac{m_1}{m_0} \quad \text{and} \quad L_m = \frac{m_4}{m_3} \quad \text{(5.24)}
\]

\[
CV_n = \left( \frac{m_2}{m_1^2} - 1 \right)^{\frac{1}{2}} \quad \text{and} \quad CV_m = \left( \frac{m_4}{m_3^2} - 1 \right)^{\frac{1}{2}} \quad \text{(5.25)}
\]

### 5.2.2.5 crystal size distribution - population density

The population balance for each compartment is, similar to the moment equations (eqs. 5.20-23), given by (#/m^3.m.s):

\[
G_i \cdot \frac{dn_i}{dl} + \frac{f \cdot n_2}{\tau} - \frac{(1 + f) \cdot n_2}{\tau} = 0 \quad \text{(5.26)}
\]

\[
G_i \cdot \frac{dn_i}{dl} + \frac{(1 + f) \cdot n_{i-1}}{\tau} + \frac{f \cdot n_{i-1}}{\tau} - \frac{(1 + 2f) \cdot n_i}{\tau} = 0 \quad \text{(5.27)}
\]

\[
G_i \cdot \frac{dn_i}{dl} + \frac{(1 + f) \cdot n_8}{\tau} - \frac{(h + f) \cdot n_8}{\tau} = 0 \quad \text{(5.28)}
\]

with boundary condition \( n_i(0) = B/G_i \) where \( B \) and \( G_i \) are obtained by solving the moment equations (5.20-23). The population densities in the eight compartments, \( n_i(L) \), are calculated by using the 4\textsuperscript{th} order Runge-Kutta method.
5.2.6 porosity and permeability of a crystal bed

To calculate the porosity of crystal bed constructed by random packing of particles with an arbitrary size distribution, the so-called geometrical method developed by Ouchiama and Tanaka [8,9] can be applied. This method is based on the coordination number, $C_n$, around each particle of size $L$. Input parameter to this porosity model are the size distribution and the porosity of a bed of uniform sized crystals, $\varepsilon_0$.

The numerical form of the geometrical porosity model is given by:

$$
\varepsilon = 1 - \frac{\sum_{k=1}^{\infty} L_k^3 n_{i,k}}{\sum_{k=1}^{K} (L_k - L_{n,i})^3 n_{i,k} + \frac{1}{C_n} \sum_{k=1}^{K} [(L_k + L_{n,i})^3 - (L_k - L_{n,i})^3] n_{i,k}} \tag{5.29}
$$

where:
- $n_{i,k}$ = number of particles in size class $k$ in compartment $i$ [#/m$^3$]
- $L_k$ = particle size in class $k$
- $L_{n,i}$ = number based mean size in compartment $i$
- $K$ = total number of size classes
- $L_k - L_{n,i}$ = 0 for $L_k \leq L_{n,i}$
- $L_k - L_{n,i}$ for $L_k > L_{n,i}$

$C_n$ is the averaged coordination number given by:

$$
C_n = 1 + \frac{4}{13} *(7 - 8*\varepsilon_0)*L_{n,i}^2 \left( \frac{\sum_{k=1}^{K} (L_k + L_{n,i})^2 + [1 - \frac{3}{8}(\frac{L_{n,i}}{L_k + L_{n,i}})] n_{i,k}}{\sum_{k=1}^{K} [L_k^3 - (L_k - L_{n,i})^3] n_{i,k}} \right) \tag{5.30}
$$

From eqs. (5.29) and (5.30) it is clear that the porosity $\varepsilon_i$ depends on the number based mean size $L_{n,i}$ as well as on the 1$^\text{st}$, 2$^\text{nd}$ and 3$^\text{rd}$ moment of the CSD. In this approach particles larger than $L_{n,i}$ are assumed not to effect the porosity.
optimization and modelling of the crystallization process in a cascade

The permeability of the crystal bed can now be calculated from the Kozeny-Carman equation:

\[ P_{kc} = \frac{1}{K_{kc}} \cdot \frac{e^3}{(1-e)^2} \cdot \frac{1}{S_0^2} \]  \hspace{1cm} (5.31)

where:
- \( K_{kc} \) = Kozeny-Carman constant \((K_{kc}=5 \text{ for spheres})\)
- \( S_0 \) = specific surface area of the particles \((m^2/m^3)\).

MacDonald et al. [10] suggested the following alternative:

\[ P_m = \frac{1}{K_m} \cdot \frac{e^3}{(1-e)^2} \cdot (L_{2,1})^2 \]  \hspace{1cm} (5.32)

where:
- \( K_m \) = MacDonald constant \((K_m=9\pi^2/2=44.4)\).
- \( L_{2,1} \) = length based mean size \((L_t)\)

5.2.7 set-up of the Cascade of Crystallizers with Backmixing model (CCB model)

A flow scheme of the CCB model is presented in figure 5.4. Input to the heat and mass balances are practical operation conditions, a relation for the liquidus, the backmix ratio \( f \) and the classification ratio \( h \). Both hydrodynamic parameters must be determined by fitting the calculated crystal content \((w_{i,calc})\) to experimental data \((w_{i,exp})\). Subsequently, the crystal content \((\text{via } m_{3,i} = w_i/k_i)\), the nucleation constant \( k_n \) and the nucleation exponent \( j \) are input data to the CSD moment balances. Both kinetic parameters must be determined by fitting calculated and experimental values for the mass based mean size \( L_m \) and coefficient of variation \( CV_m \). At this point the nucleation rate, the growth rate, the mean size and coefficient of variation can be calculated in each compartment. Via the population balances the full CSD can be calculated. Next, the porosity and the permeability of a bed of crystals can be calculated. Calculation time amounts approximately 4 minutes on a personal IBM compatible computer with a 486 processor.
Figure 5.4: flow scheme of the CCB model
5.3 EXPERIMENTAL PROCEDURE

The trough of the pilot plant CDC has a volume of 100 l and it is divided into eight compartments. The seven cooling elements are connected in series and have a total wiped surface area of 0.91 m². The coolant flows countercurrent to the product from the seventh to the first cooling element. A mixture of caprolactam and water, from which caprolactam crystallized upon cooling, was used as the feed stock during the experiments.

Crystallization experiments were performed within the following limits:

- **feed flow ($\Phi_1$)**: 56.5 - 113 [l/h]
- **water content feed stock**: 1.0 - 7.6 [wt%]
- **coolant flow ($\Phi_c$)**: 125 - 500 [l/h]
- **revolution rate discs**: 15 [rpm]

In the start-up phase of an experiment the inlet temperature of the coolant was gradually lowered until the crystal content in the overflow of the CDC reached the desired value (10 - 35 v%). To assure a steady state operation, the crystallizer was operated for at least seven times the mean residence time after nucleation had occurred. The inlet temperature of the feed was kept just above its melting point temperature. Slurry samples were taken from the overflow and seven sample points positioned at the bottom of the trough underneath the openings in cooling elements. Consequently a sample taken, for example, underneath the first cooling element is actually a mixture of the contents of the first and the second compartment.

The crystal size distribution was determined off-line using a laser diffraction technique. For this analysis, slurry samples were first centrifuged and next the obtained crystals were suspended in a saturated n-decane solution. The bed permeability and the crystal content of a slurry sample were determined through
filtration at a constant pressure difference [11]. The permeability of the bed proved to be dependent on the applied pressure drop indicating that the bed is compressible. The permeabilities reported in this chapter were obtained with a pressure drop of 0.2 bar was applied. The water content of liquid samples was determined through Karl-Fisher titration. The physical properties of the caprolactam/water feedstock, as used in the calculations are presented in table 5.1.

In addition to the crystallization experiments, a few tracer-pulse experiments were performed to verify the hydrodynamic model. The feed stock in these experiments was either a homogeneous water phase or a suspension of plastic particles (PVC) in water. A concentrated sodium chloride solution was used as tracer material.

<table>
<thead>
<tr>
<th>Heat of Crystallization ($\Delta H_m$)</th>
<th>142 kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point ($T_m$)</td>
<td>342 K</td>
</tr>
<tr>
<td>Specific Heat Liquid Phase ($C_{p,L}$)</td>
<td>2.13 kJ/kg.K</td>
</tr>
<tr>
<td>Specific Heat Solid Phase ($C_{p,s}$)</td>
<td>1.67 kJ/kg.K</td>
</tr>
<tr>
<td>Viscosity</td>
<td>14-18 mPa.s</td>
</tr>
<tr>
<td>Specific Weight ($\rho_L = \rho_p$)</td>
<td>1000 kg/m$^3$</td>
</tr>
<tr>
<td>Slope Liquidus ($q$)</td>
<td>345 K</td>
</tr>
</tbody>
</table>

Table 5.1: physical properties of the caprolactam/water mixture
(as used in the calculations)
5.4 RESULTS

This section is divided in two parts. The first part covers the experimental optimization study and describes the effects of different operating conditions on the permeability of the crystals produced in the CDC. The second part deals with the modelling of the crystallization process in the CDC and presents a comparison between model predictions and experimental results.

Throughout this section the results from experiment 18/03, which will be referred to as the standard experiment, are used to demonstrate observed trends, to fit the key parameters of the Cascade of Crystallizers with Backmixing (CCB) model and to compare model predictions with experimental findings.

5.4.1 optimization of the permeability

The operating conditions and the main results of some experiments are summarized in table 5.2.

<table>
<thead>
<tr>
<th>experiment code</th>
<th>( \Phi_i ) [l/h]</th>
<th>( \Phi_o ) [l/h]</th>
<th>Owater content feed [wt%]</th>
<th>crystal content comp. 8 [%]</th>
<th>( P_n ) ( 10^{12} ) m(^2)</th>
<th>remarks</th>
</tr>
</thead>
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<tr>
<td>18/03</td>
<td>56.5</td>
<td>500</td>
<td>2.2</td>
<td>26.5</td>
<td>36</td>
<td>standard experiment</td>
</tr>
<tr>
<td>19/01</td>
<td>56.5</td>
<td>125</td>
<td>2.3</td>
<td>20.2</td>
<td>27</td>
<td>effect coolant flow</td>
</tr>
<tr>
<td>02/02</td>
<td>56.5</td>
<td>500</td>
<td>2.2</td>
<td>22.1</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>11/03</td>
<td>56.5</td>
<td>500</td>
<td>2.3</td>
<td>11.6</td>
<td>17</td>
<td>effect residence time</td>
</tr>
<tr>
<td>16/03</td>
<td>113</td>
<td>500</td>
<td>2.4</td>
<td>11.8</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>09/08</td>
<td>56.5</td>
<td>500</td>
<td>2.5</td>
<td>27.9</td>
<td>44</td>
<td>effect water content</td>
</tr>
<tr>
<td>01/04</td>
<td>56.5</td>
<td>500</td>
<td>7.6</td>
<td>27.8</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: the effect of various process conditions on the product permeability
The crystal content and the permeability of the crystals in various compartments and in the overflow of the CDC during the standard experiment (18/03) are shown in figure 5.5. The values for the overflow are registered on the horizontal axis in figure 5.5 as compartment number 8.5.

![Graph](image)

**Figure 5.5:** permeability and crystal content in the CDC during the standard experiment (18/03)

Figure 5.5 shows a steady increase in the crystal content from the first to the last compartment followed by a small decrease in the overflow. This trend has been observed in all experiments. The permeability shows a gradual increase particularly in the second half of the CDC. In experiments with a lower crystal content in the CDC (i.e. ≤ 15 v% in comp. 8), the permeability did not change significantly in the CDC. The increase of the permeability in experiment 18/03 was not accompanied by a significant change in the mass based crystal size distributions (CSD) as can be seen in figure 5.6 ($L_m=370 \mu m$, $CV_m=0.48$).
optimization and modelling of the crystallization process in a cascade

![Graph](image)

**Figure 5.6:** mass based crystal size distributions of slurry samples taken from compartments 2, 5, 7 and from the overflow during experiment 18/03

The *crystal content* in the CDC was found to have a dominant effect on the permeability of the product crystals. In figure 5.7 the permeability of the crystals in the overflow is plotted as a function of the crystal content in the eighth compartment of the CDC for all experiments. An increase of the crystal content clearly has a positive effect on the permeability. The large variations in permeability between the different experiments could not be correlated to changes in the measured (mass based) CSD. In all experiments: $330 \, \mu m \leq L_{m,\text{product}} \leq 370 \, \mu m$ and $0.45 \leq CV_m \leq 0.55$ (the differences are within the range of reproducibility).

An increase of the *coolant flow* from 125 l/h to 500 l/h also had a positive impact on the product permeability as can be seen in table 5.2. The experiments 19/01 and 02/02 were performed under the same operating conditions except for the coolant flow ($\Phi_c$). Another benefit of the high coolant flow proved to be a reduction
of the degree of encrustation on the unwiped parts of the cooling elements.

Figure 5.7: product permeability versus crystal content in compartment 8

The *residence time*, which could be adjusted through the feed flow, proved to have only a minor effect on the product permeability (see table 5.2). Comparison of the experiments 11/03 and 16/03, both performed at a low crystal content, shows a small increase in permeability upon an increase of the residence time. An increase of the *water concentration* in the feed from 2.5 wt% to 7.6 wt% resulted in a significant reduction of the product permeability (see table 5.2, experiments 09/08 and 01/04). No significant effect of the water concentration was observed upon variation from 1 wt% to 2.5 wt%.

The effect of crystallization conditions on the *morphology* of caprolactam crystals has also been investigated and the results are presented in chapter 4. The morphology of the crystals formed in the CDC proved not to depend on the operating conditions (within the experimental limits) nor on the compartment
number and therefore the crystal morphology cannot explain for the observed changes in permeability.

5.4.2 modelling of the crystallization process
The Cascade of Crystallizers with Backmixing (CCB) model contains four key-parameters: the backmix ratio f, the classification ratio h, the nucleation constant $k_N$ and the nucleation exponent j. The hydrodynamic parameters (f, h) must be determined by fitting the calculated to the measured crystal content and the kinetic parameters ($k_N$ and j) must be determined by fitting the calculated to the predicted mass based mean size and coefficient of variation (see also fig. 5.4).

hydrodynamics and crystal production
The Backflow Cell (BC) model proved to describe well the residence time distribution of the sodium chloride tracer pulse in the CDC both with the homogeneous water phase and with the slurry of PVC particles and water.

![Diagram](image)

**Figure 5.8:** $E(t)$ curves for the CDC at 15 rpm and 60 l/h with a homogeneous water phase (f=2)
Figure 5.8 shows a comparison of an experimentally determined E(t) and the prediction of the BC model. The backmix ratio (f=2) was obtained using eq. (5.3). Figure 5.8 demonstrates that the BC model offers a good description of the hydrodynamic behaviour of a homogeneous liquid phase in the CDC. Other tracer-pulse experiments revealed that the backmix ratio increases with increasing revolution rate and decreasing flow rate.

To avoid pollution of the caprolactam/water feed stock, no tracer-pulse experiments were performed during the crystallization test runs. In this case the classification ratio h was determined via eq. (5.4) and the backmix ratio f was obtained by fitting the simulation result of the CCB model to the experimental data on the crystal content in the CDC.

![Graph showing crystal content vs. compartment number for different backmix ratios](image)

**Figure 5.9:** comparison of the measured and the simulated crystal content in the CDC for different backmix ratio's (f) for experiment 18/03

Figure 5.9 shows the data of the standard experiment (18/03) and simulation results for f=0 (no backmixing), f=1 and f=10 (nearly ideal mixing) where h=0.91.
The simulation result for f=1 shows good agreement with the experimental result particularly for the compartments 3 to 8. The experimental curve is somewhat flatter first compartments (1 to 3) than the simulation curve, which indicates larger backmixing on this side of the CDC. Probably the local backmix ratio in the CDC is dependent on the crystal content, which affects the apparent slurry viscosity, whereas the f is assumed to be a constant throughout the CDC in the CCB model.

In order to investigate this effect h and f are plotted as a function of the crystal content in the last compartment of the CDC (figure 5.10). The plot demonstrates that with increasing crystal content in the CDC, the classification in the last compartment becomes negligible and the degree of backmixing reduces.

**Figure 5.10:** dependence of the backmix ratio f and the classification ratio h on the crystal content in the overflow of the CDC (different experiments)

It is concluded that the CCB model, based on the Backflow Cell approach, provides a simple and satisfactory description of the hydrodynamic behaviour and the crystal
production in a cascade of crystallizers.

**crystallization kinetics and crystal size distribution (CSD)**

Different combinations of $k_N$ and $j$ result in a good match between the simulation results and the experimental mass based CSD’s i.e. $j=1.5$ with $k_N=2.5\times10^{19}$, $j=2$ with $k_N=1.3\times10^{23}$ and $j=3$ with $k_N=3.5\times10^{30}$. For the standard experiment (18/03), figure 5.11 presents the experimentally determined $L_m$ and $CV_m$ and their simulated values for $j=2$ (and $k_N=1.3\times10^{23}$).

![Graph showing Lm and CVm](image)

**Figure 5.11:** measured and calculated mass based mean size ($L_m$) and coefficient of variation ($CV_m$) for experiment 18/03

CCB parameters: $f=1$, $h=0.9$, $k_N=1.3\times10^{23}$, $j=2$

The differences between the simulated $L_m$ and $CV_m$ for different $j-k_N$ combinations are too small to be able to distinguish between these combinations. There are, however, distinct differences in the calculated $L_n$ and $CV_n$. The simulations with higher $j$-values result in a steeper increase of the number based mean diameter $L_n$.
throughout the CDC and a smaller value of CVn in the overflow of the CDC. Unfortunately, transformation of the measured mass based CSD's into number based CSD's is subject to large errors and does not provide accurate data on Ln or CVn. It is therefore at this stage impossible to positively discriminate between the different nucleation exponents. Below it will be shown that the CCB prediction of the permeability depends on the choice of j, which offers an opportunity to select the best j-value.

![Graph](image)

Figure 5.12: calculated growth rate (G), nucleation rate (B), number based mean size (Ln) and coefficient of variation in the CDC for experiment 18/03

CCB parameters: f=1, h=0.9, k_m=1.3*10^{13}, j=2

Figure 5.12 presents, for the operating conditions of the standard experiment, the growth rate G, the nucleation rate B, L_n, and CV_n in different compartments of the CDC as calculated with the CCB model for j=2. B_i and G_i show a strong increase from the first to the second compartment followed by a gradual decrease to the last
compartment. Note that the first compartment of the CDC is cooled only on one side and part of the available cooling power is used to cool the (slightly over heated) feedstock to its melting temperature. The choice of the nucleation exponent $j$ has only a minor effect on $G_j$. With increasing $j$-values, nucleation occurs more and more in the first compartments of the CDC. The increase in the number based mean size $L_n$ and the narrowing of the number based CSD ($CV_n$) with increasing compartment number indicate a reduction of the number of small crystals (fines), which explains the measured increase of the permeability along the CDC (fig. 5.5).

Figure 5.13 presents the CCB predictions for $L_n$ and $CV_n$ in the overflow versus the experimentally determined product permeability for different experiments. It is shown that the CCB model predicts a large value of $L_n$ and a small value of $CV_n$ for experiments which yielded a high product permeability. Therefore the calculated values of $L_n$ and $CV_n$ already provide a qualitative indication on the product permeability.

![Graph showing $L_n$ and $CV_n$ versus permeability](image)

**Figure 5.13:** calculated number based mean size ($L_n$) and coefficient of variation ($CV_n$) versus measured product (overflow) permeabilities for different experiments
optimization and modelling of the crystallization process in a cascade

CCB permeability predictions
In figure 5.14, the CCB permeability predictions based on the Kozeny-Carman relation (eq. 5.31) and on the MacDonald relation (eq. 5.32) are compared with the measured data for the standard experiment (18/03). Both model predictions show correct trends but the absolute values are either too high ($P_m$) or too low ($P_{kc}$). The values of the constant $K_{kc}$ and $K_m$ must be adjusted to get a better agreement between the absolute values ($K_{kc}$=3.3 and $K_m$=57.7). It is very difficult to decide on the best permeability prediction (Kozeny-Carman or MacDonald). Because the MacDonald equation is more sensitive to changes in the smaller size classes, it is used below.

![Graph showing permeability predictions and measured data](image)

Figure 5.14: CCB predictions ($P_{kc}$ & $P_m$) and measured permeabilities in different compartments of the CDC for the standard experiment (18/03)

CCB parameters: \( f=1 \), \( h=0.9 \), \( k_N=1.3 \times 10^{23} \), \( j=2 \), \( K_{kc}=5 \), \( K_m=44.4 \)
The effect of the choice of $j$ (and $k_n$) on the permeability prediction is clearly shown in figure 5.15. The permeability curves, obtained with $K_m=57.7$, are steeper at higher values of $j$. From figure 5.15 it can be concluded that the combination of $j=2$ with $k_n=1.3\times10^{23}$ yields the best agreement with the experimental data.

![Graph showing permeability prediction](image)

**Figure 5.15:** effect of the choice of the kinetic parameters ($k_n$ and $j$) on the permeability predictions of the CCB model

*($P_m$, experiment 18/03)*

CCB parameters: $f=1$, $h=0.9$, $K_m=57.7$ and:

- $k_n=2.5\times10^{19}$ with $j=1.5$;
- $k_n=1.3\times10^{23}$ with $j=2$;
- $k_n=3.5\times10^{30}$ with $j=3$

In figure 5.16 CCB predictions of the permeability of the product crystals in the overflow, based on the MacDonald relation using $K_m=57.7$, are plotted versus the values measured during different experiments. The agreement between the predicted and the measured values is not perfect but at this stage acceptable.
optimization and modelling of the crystallization process in a cascade

![Graph showing predicted vs. measured permeability values.](image)

**Figure 5.16:** Comparison between CCB prediction ($P_m$ with $K_m=57.7$) and measured permeabilities in the overflow of the CDC for different experiments.

CCB parameters: $K_m=57.7$, $k_N=1.3\times10^{23}$ with $j=2$

### 5.5 DISCUSSION

The mass based CSD did not change significantly throughout the CDC and proved to be almost independent on the residence time and other operating conditions which indicates that nucleation as well as backmixing play a dominant role with respect to crystal growth in the CDC. The nucleation rate (and the growth rate) decrease with higher crystal content, which explains for the positive effect of an increase of the crystal content on the product permeability. A positive side-effect of an increase of the crystal content is the reduction of the amount of backmixing, which results in a better approximation of a plug flow in the CDC and consequently in a narrowing of the CSD.
chapter 5

At a high coolant flow (500 l/h) the temperature difference between the coolant and the slurry decreases from the first to the last compartment. This "converging" temperature profile results in relatively low nucleation rates in the last compartments of the CDC, which explains for the positive effect of a high coolant flow on the product permeability. At 125 l/h coolant flow the temperature profile was almost parallel or even diverging, resulting in higher nucleation rate towards the exit of the CDC and lower permeabilities.

The raising of the water content from 2.5 wt% to 7.6 wt% resulted in an increase of the liquid viscosity from 14 mPa.s to 18 mPa.s due to the formation of hydrogen bonds. It is possible that the growth rate is hampered by the viscosity increase (see also chapter 4).

The permeability of a crystal bed appears to be governed by the number based rather than by the mass based CSD. The mass based CSD is insensitive to the presence of small crystal whereas these fines have a significant effect on the bed porosity. Besides nucleation, also crystal breakage and attrition contribute to the production of fines. It may be useful to incorporate source terms for these phenomena in the CSD equations but the introduction of extra constants, which must be determined, reduce the value of the model as an engineering tool.
5.6 CONCLUSIONS

The filterability/permeability of caprolactam crystals produced in the Cooling Disc Crystallizer (CDC) depends mainly on the crystal content. An increase of the crystal content decreases the degree of backmixing and reduces the nucleation rate, which both have a positive impact on the product filterability. Other operating conditions which proved to have an effect on the filterability are: the coolant flow, the water content and the residence time.

The developed Cascades of Crystallizers with Backmixing model (CCB model) provides a satisfactory prediction of the production, size distribution and permeability of the crystals produced in the CDC and can be used to optimize the operating conditions.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>cooling surface area</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$B_0$</td>
<td>nucleation rate</td>
<td>[#/m$^3$.s]</td>
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<tr>
<td>$K_n$</td>
<td>nucleation constant</td>
<td>[(m/s)$^j$/m$^3$.s]</td>
</tr>
<tr>
<td>$K_v$</td>
<td>volumetric shape factor</td>
<td>[-]</td>
</tr>
<tr>
<td>K</td>
<td>heat transfer coefficient</td>
<td>[kW/m$^2$K]</td>
</tr>
<tr>
<td>$K_{tc}$</td>
<td>Kozeny-Carman constant</td>
<td>[-]</td>
</tr>
</tbody>
</table>
$K_m$  MacDonald constant  
$l$  length  
$L$  mean size/length of CSD  
$m_k$  $k^{th}$ moment of CSD  
$n(L)$  population density (CSD)  
$N$  number of compartments/crystallizers  
$P_{kc}$  permeability based on Kozeny-Carman relation (eq. 5.31)  
$P_m$  permeability based on MacDonald relation (eq. 5.32)  
$q$  slope of the liquidus in a phase diagram  
$s$  supersaturation  
$t$  time  
$T_m$  melting point temperature  
$w$  crystal content of slurry  
$x$  fraction of the main component in liquid phase  

**Greek**

$\Delta H_m$  heat of crystallization  
$\Delta T$  temperature difference between bulk and coolant  
$\varepsilon$  porosity  
$\Phi$  flow rate  
$\rho$  specific weight  
$\tau$  mean residence time  
$\sigma$  variance of the residence time distribution  
$\omega$  revolution rate  

**Subscript**

$a$  surface area based  
b  backmix  
c  coolant  
f  feed  
i  compartment number i  
l  length based  
$L$  liquid phase  
m  mass based  
n  number based  
p  product  
$S$  solid phase  
$SL$  slurry
References


chapter 6

COMPRESSIVE STRESS & TRANSPORT FORCES
IN HYDRAULIC PACKED BED WASH COLUMNS

Abstract

Hydraulic packed bed wash columns are continuous solid/liquid separators, which combine a virtually complete crystal/mother liquor separation with a highly efficient washing action at high throughput. The applicability of this type of wash column i.e. for large scale ultrapurification of organic crystals depends amongst others on the compressive stresses that are exerted on these crystals upon processing in a hydraulic wash column. In this chapter an analytical model is presented which can be used in technical feasibility and scale-up studies to predict the compressive stress profiles that occur in a hydraulic wash column during operation. From calculations based on experimental data, rules were derived on how to minimize the compressive stresses during the operation of a hydraulic wash column.

P.J. Jansens, O.S.L. Bruinsma, G.M. van Rosmalen and R. de Goede

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6.1 INTRODUCTION

Fractional suspension crystallization processes which are aimed at large scale ultra-purification of organic compounds, generally consist of a cascade of crystallizers followed by so-called wash columns. Three types of wash columns may be distinguished after the different mechanism applied to transport of a packed crystal bed: mechanical, gravitational and hydraulic (chapter 1). In hydraulic wash columns a liquid pressure drop is the driving force for bed transport and this mechanism is utilized in several industrial designs a.o. Phillips Petroleum [1], Brennan-Koppers [2] and TNO-Thijssen [3]. Basically these industrial designs only differ in the position of the filtrate removal filters.

Figure 6.1: Principle of a hydraulic wash column (TNO-Thijssen type)
1 = column wall, 2 = settling zone, 3 = bed level, 4 = moving crystal bed,
5 = filter tube, 6 = porous filter, 7 = wash front level, 8 = steering pump,
9 = rotating knife, 10 = melter, 11 = product valve
The principle of a hydraulic wash column is illustrated by figure 6.1 (TNO-Thijssen type). A slurry is fed under hydraulic pressure at the top of the column. After a short zone of rapid thickening, the crystals are caught in a dense downward moving bed. The residual mother liquor flows through the crystal bed and leaves the column via filters which are positioned in filter tubes. In other hydraulic wash column designs the filters are positioned in the wall of the column which is unfavourable from a scale-up point of view. The drag of the mother liquor on the crystal bed effectuates the bed transport. A so-called steering pump can be used to recycle filtrate (residual mother liquor) into the feed line. In this way the hydraulic bed transport force can be influenced without alteration of the feed condition. At the bottom of the column a knife rotates which scrapes off the descending crystal bed. The product crystals are removed from the reslurry chamber underneath the knife by a liquid current and are subsequently molten in the melter. The main part of the melt is withdrawn as product and the rest is refluxed to the reslurry chamber as wash liquid. Due to a small overpressure in the reslurry chamber the wash liquid ascends in the column, thus providing a washing action countercurrent to the direction of bed movement. The wash liquid does not leave the column via the filters but recrystallizes beforehand on the colder crystal bed thus producing a sharp wash front beneath the filters. The released heat of crystallization heats the crystals to near their melting temperature. The wash front marks a steep temperature gradient and a sudden change in porosity and permeability of the crystal bed. The permeability decrease below the wash front improves and stabilizes the washing action [4].

In some applications a separate non-crystallizing liquid can be used as wash liquid instead of the pure molten product. A non-crystallizing wash liquid does leave the column via the filters and does not produce a sharp wash front. This type of operation will be referred to as a wash column without recrystallization, opposed to the operation depicted in figure 6.1, which will be referred to as a wash column with recrystallization.
compressive stress in hydraulic wash columns

A difficulty sometimes encountered in the processing of organic crystals in hydraulic wash columns is their poor mechanical strength. Crystal beds of e.g. cyclohexane crystals easily compress and deform under compressive stress. Compression of a crystal bed leads to a significant decrease of the bed permeability. As a result the pressure drop over the bottom section of the column, caused by the upward motion of the wash liquid, will increase and higher pressures will have to be applied on the feed side to transport the bed. Furthermore, serious sideways deformation of the crystal bed will cause the bed to get stuck in the wash column and will hamper the washing action.

In technical feasibility studies and scale-up procedures, it is important to be able to predict the compressive stress exerted on a crystal bed during processing in a wash column and to compare the predicted stresses with data on compressibility of a packed crystal bed of the specific material. Knowledge of the stress distribution in the solid phase is also important for construction purposes. Particularly relevant in this respect are the stresses exerted by the bed on the knife and on the column wall.

The first mathematical analysis of the compressive stress distribution in a hydraulic wash column was presented by Schneiders and Arkenbout [5]. Their model was based on the assumption that the compressive stress on the knife equals zero. This assumption, however, is not correct because the knife supports the crystal bed and production capacity and the bed height can be altered by changing the revolution rate of the knife (see also chapter 8). Furthermore, the model of Schneiders and Arkenbout does not account for recrystallization of wash liquid in the bottom section of the wash column.
The objective of this study was to develop a general model which can be used to predict the compressive stresses that are exerted on the crystal bed, the column wall and the knife during operation of a hydraulic packed bed wash column *without* (CASE I) and *with* (CASE II) recrystallization of the wash liquid.

The model is presented for CASE I and CASE II and it is illustrated using experimental data obtained with a model system *without* recrystallization and an industrial organic system *with* recrystallization of the wash liquid. Several methods of determining the friction coefficient \( K_f \), which is the key-parameter in the model, are discussed and \( K_f \) values have been determined for the model system and the industrial organic system.

Finally, based on the model predictions, recommendations are made on how to minimize the compressive stresses exerted on the crystal bed by manipulation of the operating conditions.

### 6.2 MODELLING

The stress distribution on an infinitesimally small axisymmetrical volume of a *dry* packed bed of solids moving under the influence of gravity at a constant velocity was presented by Delaplane [6]. Figure 6.2 shows three normal compressive stresses \( \sigma_n \), \( \sigma_r \) and \( \sigma_\theta \) acting perpendicular to the planes of the differential volume and six shear stresses \( \tau_{n\theta} \), \( \tau_{n\theta} \), \( \tau_{r\theta} \), \( \tau_{r\theta} \), \( \tau_{r\theta} \) and \( \tau_{r\theta} \) acting parallel to the planes in the direction of the second subscript.
compressive stress in hydraulic wash columns

Figure 6.2: Stress distribution on an infinitesimal small volume in cylindrical coordinates of a packed bed of solids

The corresponding force balances, denoted in the cylindrical coordinates $h$, $r$ and $\theta$, with gravity acting in the $h$-direction are:

$$\frac{\partial \sigma_h}{\partial h} = -\frac{\partial \tau_{rh}}{\partial r} - \frac{\partial \tau_{\theta h}}{r \partial \theta} - \frac{\tau_{rh}}{r} + (1 - e) \rho_s g$$  \hspace{1cm} (6.1)

$$\frac{\partial \sigma_r}{\partial r} = -\frac{\partial \tau_{hr}}{\partial h} - \frac{\partial \tau_{\theta r}}{r \partial \theta} - \frac{\sigma_r - \sigma_\theta}{r}$$  \hspace{1cm} (6.2)

$$\frac{\partial \sigma_\theta}{r \partial \theta} = -\frac{\partial \tau_{he}}{\partial h} - \frac{\partial \tau_{r \theta}}{\partial r} - \frac{\tau_{\theta r} + \tau_{r \theta}}{r}$$  \hspace{1cm} (6.3)

In hydraulic wash columns bed transport is effectuated by the mother liquor flowing through the crystal bed. The resulting liquid pressure drop over the bed and the
buoyancy may be included in the stress analysis as additional body forces [7-9]:

\[
\frac{\partial \sigma_h}{\partial h} = -\frac{\partial \tau_{rh}}{\partial r} - \frac{\partial \tau_{\theta h}}{r \partial \theta} - \frac{\tau_{rh}}{r} + (1 - e)(\rho_s - \rho_l) g - \frac{\partial P_L}{\partial h}
\]  

(6.4)

\[
\frac{\partial \sigma_r}{\partial r} = -\frac{\partial \tau_{hr}}{\partial h} - \frac{\partial \tau_{\theta r}}{r \partial \theta} - \frac{\sigma_r - \sigma_\theta}{r} - \frac{\partial P_L}{\partial r}
\]  

(6.5)

\[
\frac{\partial \sigma_\theta}{\partial \theta} = \frac{\partial \tau_{h\theta}}{\partial h} - \frac{\partial \tau_{r\theta}}{\partial r} - \frac{\tau_{\theta r} + \tau_{r\theta}}{r} - \frac{\partial P_L}{\partial \theta}
\]  

(6.6)

The mathematical analysis is simplified to an one-dimensional problem by assuming that radial and tangential liquid flow are negligible in comparison to the axial flow.

The stresses acting on a horizontal slab of the crystal bed in a hydraulic wash column now become as presented in Figure 6.3.

---

Figure 6.3: Stress distribution on a horizontal slab of the moving crystal bed in a hydraulic wash column
compressive stress in hydraulic wash columns

A vertical force balance over the slab, assuming that the compressive stresses and the liquid pressure are uniformly distributed over the cross-section of the column, yields:

\[
\frac{d\sigma_h}{dh} = \frac{-dP_L}{dh} + (1 - e)(\rho_s - \rho_l)g - (\tau_{rh})_w \frac{4}{D}
\]  

(6.7)

Using the theory developed by Janssen [10], the axial compressive stress \( \sigma_h \) can be related to the shear stress at the wall \( (\tau_{rh})_w \) via the friction factor \( K_f \):

\[
(\tau_{rh})_w = \mu \sigma_r = \frac{K_f \sigma_h}{H_{bed}}
\]  

(6.8)

Here \( K_f \) is assumed to be constant along the wall of the wash column. The validity of this assumption is discussed in the appendix.

In addition, the crystal bed is assumed to be incompressible and homogeneously packed which implies a linear liquid pressure gradient in the vertical direction.

\[
\frac{-dP_L}{dh} = \frac{\Delta P_L}{H_{bed}}
\]  

(6.9)

Substitution of eqs. (6.8) and (6.9) in eq. (6.7) yields:

\[
\frac{d\sigma_h}{dh} = \frac{\Delta P_L}{H_{bed}} + (1 - e)(\rho_s - \rho_l)g - \frac{4K_f}{D} \sigma_h
\]  

(6.10)
6.2.1 **CASE I: a wash column without recrystallization**

In this case the porosity \( \varepsilon \) remains constant in the whole wash column because no crystallization of wash liquid occurs. Model I divides the wash column in a top section (ts) and a bottom section (bs), which meet at the centre of the filter(s) (fig. 6.4).

Integration of eq. (6.10) over the height of the top section \( (H_{ts}) \) with \( \alpha_n=0 \) for \( h=0 \) leads to:

\[
\alpha_n = \left( \frac{A}{F} \right) (1 - \exp(-Fh))
\]

\[\text{where: } \quad A = (1 - \varepsilon)(\rho_s - \rho_L)g - \left( \frac{\Delta P_{L,ts}}{H_{ts}} \right) \quad (6.11)\]

\[F = \frac{4K_f}{D} \quad (6.12)\]

Figure 6.4: Dimensions in a hydraulic wash column without recrystallization
compressive stress in hydraulic wash columns

The liquid pressure drop over the top section of the bed \( \Delta P_{L,\text{top}} \) may be regarded as the main driving force for bed transport. Eq. (6.11) was experimentally verified by Hancher and Jury [7] and Brandt and Johnson [8]. Integration of eq. (6.10) over the height of the bottom section \( (H_{\text{bot}} - H_{\text{in}}) \) with \( \alpha_n = (\sigma_n)_{\text{Hin}} \) for \( h = H_{\text{in}} \), where \( (\sigma_n)_{\text{Hin}} \) is calculated with eq. (6.11), gives:

\[
\sigma_n = \frac{B}{F} - \left( \frac{A}{F} \right) \exp(-Fh) + \left( \frac{A-B}{F} \right) \exp(-F(h-H_{\text{in}}))
\]  

(6.14)

where:

\[ B = (1-e)(\rho_s-\rho_L)g - \frac{\Delta P_{L,\text{bot}}}{(H_{\text{bot}})} \]  

(6.15)

The liquid pressure drop over the bottom section of the bed \( \Delta P_{L,\text{bot}} \) results from the ascending wash liquid and counteracts the bed transport.

6.2.2 CASE II: a wash column with recrystallization

In this case the porosity above the wash front is assumed to be constant and equal to \( \varepsilon_{aw} \). Due to the crystallization of the wash liquid a sharp porosity drop occurs at the wash front. The porosity below the wash front \( \varepsilon_{bw} \) can be calculated from elementary mass and heat balances assuming that (i) the wash liquid crystallizes completely, (ii) the crystal bed moves at a constant velocity and (iii) the wash liquid enters and the crystal bed leaves the column at the melting point temperature \( T_m \).

\[
\varepsilon_{bw} = \varepsilon_{aw} - (1-\varepsilon_{aw}) \left( \frac{C_{PS}(T_m-T_{\text{feed}})}{\Delta H_m} \right)
\]  

(6.16)

It is assumed that crystallization of the wash liquid occurs entirely inside the crystal bed and that it does not affect the friction factor \( K_r \).

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Three sections are recognized in the wash column in this case: a top section (ts), a middle section (ms) and a bottom section (bs). The middle section meets the top section at the centre of the filter(s) and the bottom section at the wash front as is shown in figure 6.5.

Since the top sections in both cases are identical, eq. (6.11) also fits CASE II. Here, parameter A can be calculated from eq. (6.12) by substituting $\varepsilon$ by $\varepsilon_{aw}$.

Integration of eq. (6.10) over the height of the middle section ($H_{ms}=H_{wsh}-H_{mf}$) with $\sigma_h=(\sigma_h)_{H_{mf}}$ for $h=H_{mf}$, where $(\sigma_h)_{H_{mf}}$ is calculated from eq. (6.11), yields:

$$\sigma_h = \frac{C}{F} - \left( \frac{A}{F} \right) \exp(-Fh) + \left( \frac{A-C}{F} \right) \exp(-F(h-H_{mf}))$$ (6.17)

where: $$C = (1-\varepsilon_{aw})(\rho_s-\rho_L)g - \frac{\Delta P_{L,ms}}{(H_{ms})}$$ (6.18)
The pressure drop over the middle section $\Delta P_{L,ms}$ can be calculated via the Darcy law, assuming that the permeability of the top section is equal to that of the middle section (see eq. 6.22). However, since there is no nett transport of liquid through the middle section of the wash column, $\Delta P_{L,ms}$ is negligible in comparison to $\Delta P_{L,bs}$. Furthermore, due to the recrystallization of wash liquid on the cold crystal bed the permeability of the bottom section is significantly lower than the permeability of the top and the middle section ($B_{bs}=1.4*10^{-11}$ m$^2$ & $B_{bs}=2.0*10^{-12}$ m$^2$, chapter 8). Consequently, $\Delta P_{L,ms}$ is also small in comparison to $\Delta P_{L,bs}$ and eq. (6.18) may be simplified to:

$$C = (1 - e_{sw})(\rho_s - \rho_l)g$$  \hspace{1cm} (6.19)

Integration of eq. (6.10) over the height of the bottom section ($H_{bs}=H_{lot}-H_{wash}$) with $\alpha_h=(\alpha_h)_{wash}$ for $h=H_{wash}$, where $(\alpha_h)_{wash}$ is calculated from eq. (6.17), gives:

$$\sigma_h = \frac{D}{F} - \left(\frac{A}{F}\right)\exp(-Fh) + \left(\frac{A-C}{F}\right)\exp(-F(h-H_m)) + \left(\frac{C-D}{F}\right)\exp(-F(h-H_{wash}))$$  \hspace{1cm} (6.20)

where:  \hspace{1cm} $D = (1 - e_{bw})(\rho_s - \rho_l)g - \frac{\Delta P_{L,bs}}{(H_{bs})}$  \hspace{1cm} (6.21)

The presented model relates the compressive stresses in a hydraulic wash column with or without a wash front to the exerted hydraulic transport forces ($\Delta P_{L,ls}$ and $\Delta P_{L,sw}$), the column dimensions, physical properties, the porosity of the bed and the friction factor $K_f$. The key-parameter in the model is $K_f$ which must be determined experimentally.

For usage of the model in technical feasibility studies or scale-up procedures the hydraulic pressure drops over top and bottom section of the bed need to be estimated. For this purpose the Darcy law can be combined with simple over-all steady state mass balances, assuming a constant bed velocity:
\[
\frac{\Delta P_{L,bs}}{H_{bs}} = \left( \eta \varepsilon_{bw} \right) \left( 1 - \alpha \right) \Phi_F \left( \frac{\varepsilon_{bw}}{e_{bw}A_c} \frac{\Phi_F}{(1 - \varepsilon_{bw})A_c} \right)
\]

(6.22)

\[
\frac{\Delta P_{L,bs}}{H_{bs}} = \left( \eta \varepsilon_{bw} \right) \left( \frac{\Phi_W}{\varepsilon_{bw}A_c} \frac{\alpha \Phi_F}{(1 - \varepsilon_{bw})A_c} \right)
\]

(6.23)

In the case of a wash column without recrystallization the porosity \( \varepsilon \) and the permeability \( B \) of the crystal bed are assumed to be constant throughout the wash column (\( \varepsilon = \varepsilon_{aw} = \varepsilon_{bw} \) and \( B = B_{aw} = B_{bw} \)).

### 6.3 Determination of \( K_f \)

Experimental methods to determine \( K_f \) have been published by: Hancher and Jury [7], Brandt and Johnson [8] and by Schneiders and Arkenbout [5]. These methods require special equipment. Since this equipment was not available, a new strategy was developed to deduce \( K_f \) from regular experiments with a pilot plant wash column. This strategy starts with the calculation of an apparent friction factor (\( K_f \)) from eqs. (6.14) and (6.20) by supposing that the compressive stress at the bottom of the wash column (\( \sigma_{h,hot} \)) is equal to zero. Obviously, (\( \sigma_{h,hot} \)) is not equal to zero under all operating conditions but it approaches zero when the upward force caused by the ascending wash liquid and the wall friction exerted on the crystal bed are relatively large in comparison to the downward force caused by the descending mother liquor.

A dimensionless pressure ratio (\( P_f \)) is introduced, which features the upward hydraulic force \( \Delta P_{L,bs} \) and the total bed height \( H_{tot} \) in the numerator and the downward hydraulic force \( \Delta P_{L,bs} \) and the distance of the filter(s) to the knife \( (H_{tot} - H_{in}) \) in the denominator.
compressive stress in hydraulic wash columns

\[ P_r = \frac{(\Delta P_{L,bs} + H_{tot})}{(-\Delta P_{L,fs} + (H_{tot} - H_{mf}))} \quad (6.24) \]

The total bed height \( H_{tot} \) is incorporated in \( P_r \) because the wall friction is proportional to it. The distance \( H_{tot} - H_{mf} \) is a constant for a given wash column and it is merely incorporated in eq. (6.24) to make \( P_r \) dimensionless. At higher \( P_r \) values, \((\alpha_n)_{H_{tot}}\) approaches zero and \( K_r^* \) will approach the true value of \( K_r \). Therefore \( K_r \) can be obtained by plotting \( K_r^* \) versus \( P_r \), followed by extrapolation of \( K_r^* \) to high \( P_r \) values.

6.4 EXPERIMENTAL PROCEDURE

Experiments were performed with a PVC/water model system without wash liquid recrystallization in a wash column with an internal diameter of 0.06 m and with an industrial C8-aromatic system with recrystallization in a wash column with a diameter of 0.156 m.

6.4.1 PVC/water system without recrystallization

The 0.06 m wash column contained one filter tube with an outer diameter of 0.02 m. The porous part of the filter tube, the actual filter, was positioned 0.165 to 0.195 m above the knife. The experimental unit did not feature a steering pump. The flow rates of the filtrate and the product slurry were determined by weighing samples collected in a certain time span. The pressure at the feed inlet and in the reslurry chamber were measured continuously in-line. The pressure at the filtrate outlet was assumed to be atmospheric.

The feedstock consisted of PVC particles suspended in water. Water was also
used as the wash liquid. The PVC particles had a mass based mean diameter of 160 μm and a density of 1100 kg/m³. The average porosity and permeability of a dense bed of the PVC particles amounted to respectively 40 v% and 1.5*10⁻¹¹ m². To study the effect of the liquid viscosity some starch was added to the water in some experiments to increase the viscosity to 2.5 mPa.s.

The experimental settings were varied as follows:

- **Feed flow (Φₚ):** 20-40 [l/h]
- **Feed temperature (Tₚ):** 5-7 [°C]
- **Product flow (Φₚ):** 1-3 [l/h]
- **Total bed height (Hₚ):** 0.30-0.45 [m]
- **Revolution rate of the knife (N):** 8-64 [rpm]

Data from the experiments were only taken after the column operation had been stable for at least one hour, which was equal to five or six residence times of the PVC bed in the wash column.

**6.4.2 C8-aromatic system with recrystallization**

The 0.156 m wash column contains six filter tubes with an outer diameter of 0.02 m. The porous part in the filter tubes is positioned 0.265 to 0.295 m above the knife. A steering pump was used to recycle the filtrate (fig. 6.1). The pressure at the feed inlet, the filtrate outlet and in the reslurry chamber were measured continuously. The flow rates of feed slurry, filtrate and product were measured continuously with positive displacement meters.

The industrial C8-aromatic mixture consisted mainly of p-xylene (91 wt%), its isomers and ethylbenzene. The p-xylene crystals, which were produced in a 70 l scraped crystallizer, had a mass based dominant diameter of 500 μm and a density of 948 kg/m³. The porosity of the top section of the moving crystal bed was assumed to be equal to 40 v%. The average permeability of the top section of the bed, calculated via eq. (6.22), proved to be practically independent on the compressive stress exerted on the crystal bed during a steady state operation of
compressive stress in hydraulic wash columns

the column and amounted $1.4 \times 10^{-11}$ m² (see also chapter 8). A minor amount of red
dye was added to the mother liquor in order to visualize the wash front. Molten
pure p-xylene was refluxed as wash liquid. The mother liquor and the wash liquid
had approximately the same density: 861 kg/m³ and viscosity: 0.683 mPa.s.
The experimental settings were varied as follows:

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<thead>
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<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
<td>Feed flow ($\Phi_f$)</td>
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<td>l/h</td>
</tr>
<tr>
<td>Product flow ($\Phi_p$)</td>
<td>50-100</td>
<td>l/h</td>
</tr>
<tr>
<td>Steering flow ($\Phi_s$)</td>
<td>0-400</td>
<td>l/h</td>
</tr>
<tr>
<td>Total bed height ($H_{tot}$)</td>
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<td>m</td>
</tr>
<tr>
<td>Wash front height ($H_{wash}$)</td>
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<td>m</td>
</tr>
<tr>
<td>Revolution rate of the knife ($N$)</td>
<td>8-75</td>
<td>rpm</td>
</tr>
</tbody>
</table>

Data from the experiments were only taken after the column operation had been
stable for about one hour.

6.5 RESULTS AND DISCUSSION

6.5.1 Friction factor $K_f$

In figure 6.6 the apparent friction factor $K_f^*$ is plotted against the hydraulic pressure
ratio $P_r$ for the PVC/water system. The data for the pure water and the more
viscous water phase match very well. This implies that within the experimental
limits $K_f$ is independent of the viscosity of the mother liquor and the wash liquid.
The true average friction factor $K_f$ is obtained through extrapolation of $K_f^*$ to high $P_r$
values and amounts to $7.0 \times 10^{-2}$. The adjective average refers to the three surface
materials used in the wash column: the filter tubes are made of stainless steel and
teflon whereas the column wall consists of glass.
Figure 6.6: $K_r^*$ versus $P_r$ for the PVC/water system in the 0.06 m wash column containing one filter tube

In figure 6.7 the apparent friction factor $K_r^*$ is plotted against the hydraulic pressure ratio $P_r$ for the C8-aromatic system. The true average $K_r$, obtained by extrapolation, amounts to $4.7 \times 10^{-2}$ and is in good agreement with the value of $4.8 \times 10^{-2}$ which has been reported by Schneiders and Arkenbout [5]. The deviations of the $K_r^*$ values with respect to the plotted regression curve are somewhat larger with the C8-aromatic system than with the PVC/water system. The larger deviations probably originate from fluctuations in room temperature during the experiments which affect the wall temperature of the column. Column wall temperatures well above the melting point of the crystals will induce partial melting of the crystals in contact with the wall and consequently change the wall friction.

For technical feasibility studies, when data on $K_r$ are not available, $K_r$ is best estimated to be between 0.05 and 0.15.
compressive stress in hydraulic wash columns

Figure 6.7: $k'_f$ versus $P_r$ for the xylene system in the 0.15 m wash column containing six filter tubes

6.5.2 Compressive stress profiles

The compressive stress profiles presented in this section (6.5.2) were calculated via the presented model using the experimental data summarized in table 1. These data represent the steady state values of a number of process parameters under different operating conditions. Each operating condition is identified by an experimental code i.e. PVC-1 refers to the first experiment with the PVC/WATER system and XYL-2A refers to the first steady state (A) achieved during the second experiment (2) with the C8-aromatic system.
<table>
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<th>( \Phi_p ) [l/h]</th>
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<th>( H_{\text{tot}} ) [m]</th>
<th>( H_{\text{wash}} ) [m]</th>
<th>( N ) [rpm]</th>
<th>( \Delta P_{\text{ts}} ) [kPa]</th>
<th>( \Delta P_{\text{bs}} ) [kPa]</th>
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<td>0.50</td>
<td>0.12</td>
<td>60</td>
<td>-68</td>
<td>28</td>
</tr>
<tr>
<td>XYL-1B</td>
<td>432</td>
<td>52</td>
<td>202</td>
<td>0.45</td>
<td>0.12</td>
<td>60</td>
<td>-66</td>
<td>30</td>
</tr>
<tr>
<td>XYL-1C</td>
<td>429</td>
<td>52</td>
<td>307</td>
<td>0.41</td>
<td>0.12</td>
<td>60</td>
<td>-67</td>
<td>32</td>
</tr>
<tr>
<td>XYL-2A</td>
<td>442</td>
<td>57</td>
<td>402</td>
<td>0.51</td>
<td>0.14</td>
<td>60</td>
<td>-108</td>
<td>33</td>
</tr>
<tr>
<td>XYL-2B</td>
<td>462</td>
<td>62</td>
<td>400</td>
<td>0.39</td>
<td>0.06</td>
<td>60</td>
<td>-65</td>
<td>22</td>
</tr>
<tr>
<td>XYL-3A</td>
<td>468</td>
<td>91</td>
<td>485</td>
<td>0.49</td>
<td>0.12</td>
<td>75</td>
<td>-148</td>
<td>51</td>
</tr>
<tr>
<td>XYL-3B</td>
<td>402</td>
<td>68</td>
<td>457</td>
<td>0.53</td>
<td>0.12</td>
<td>10</td>
<td>-227</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 1: Steady state values of operating parameters during experiments with the PVC/water model system in the 0.06 m wash column (code PVC) and with the C8-aromatic system in the 0.156 m wash column (code XYL)

The compressive stress profiles in the 0.06 m wash column during the experiments PVC-1 and PVC-2 (CASE I) are shown in figure 6.8. The compressive stresses are by definition equal to zero at the top of the bed, reach a maximum value at the filter and differ positively from zero at the bottom of the wash column. The increase in the production capacity from 0.9 l/h in PVC-1 to 2.6 l/h in PVC-2 resulted in an increase of the maximum compressive stress from 42 kPa to 72 kPa. Similar results were obtained with the C8 aromatic system upon variation of the production capacity.
Figure 6.8: Compressive stress profiles in the 0.06 m wash column during the experiments PVC-1 and PVC-2 showing the effect of an increase of the production capacity from 0.9 l/h to 2.6 l/h

The compressive stress profiles in the 0.156 m wash column under the conditions of XYL-1A, XYL-1B and XYL-1C (CASE II) are shown in figure 6.9. The compressive stresses are zero at the top of the bed, reach a maximum value at the filter, gradually decrease from the filter to the wash front and then sharply decrease to a lower value at the knife. During the experiment XYL-1 the production capacity and the wash front height were kept constant but the steering flow was increased from 98 l/h in steady state A, via 201 l/h in state B to 307 l/h in state C. As a result the bed height decreased but the maximum compressive stress did not change significantly. The decrease of the bed height was not caused by consolidation or compression of the bed because the permeability of the top section of the bed, calculated using eq. (6.22), remained constant at 1.4*10⁻¹¹ m². A simple explanation is the following: a sudden increase of the steering flow leads to a higher pressure drop over the top section of the bed and consequently to an increase of the bed
transport rate. Since the supply rate of crystals is not affected by the steering flow variation, the bed height will start to reduce. The decreasing bed height will in its turn reduce the pressure drop over the top section and the bed transport rate will go down until it balances the supply rate of crystals again. In the new steady state the same throughput of crystals is accomplished in the wash column at approximately the same compressive stress level. It can be concluded that the maximum compressive stress in the wash column is independent of the amount of mother liquor flowing through the bed when the wash front height and the production capacity of mother liquor are kept constant.

![Graph showing compressive stress profiles](image)

**Figure 6.9:** Compressive stress profiles in the 0.156 m wash column during the experiments XYL-1A, 1B and 1C showing the effect of an increase of the steering flow from 98 l/h to 307 l/h

Figure 6.10 presents compressive stress profiles in the 0.156 m wash column during the experiments XYL-2A and 2B. It shows that a decrease of the wash front height from 0.14 m to 0.06 m leads to a significant decrease of the maximum compressive stress and of the bed height in the wash column. The reduction of the
wash front height is effectuated by a decrease of the pressure drop over the bottom section of the crystal bed. Since the pressure drop over this section counteracts the bed transport, a reduction of this parameter will result in larger bed transport rates. Analogous to the earlier argumentation the bed height will decrease until the bed transport rate balances the crystal supply rate. In the new steady state the same throughput is achieved but at a lower compressive stress level. Unfortunately, the capacity of the feed pump in the experimental unit was slightly dependent of the pressure at the top of the wash column. This explains why the feed and product flow are somewhat larger in steady state 2B. Similar results were obtained with the PVC/water system in the 0.06 m wash column upon variation of the wash liquid flow. It is therefore concluded that an increase of the wash front height and an increase of the wash liquid flow result in an increase of the compressive stress level in a hydraulic wash column.

Figure 6.10: Compressive stress profiles in the 0.156 m wash column during the experiments XYL-2A and 2B showing the effect of a decrease of the wash front height from 0.14 m to 0.06 m
Figure 6.11 presents compressive stress profiles in the 0.156 m wash column during the experiments XYL-3A and 3B. It shows that a decrease of the revolution rate of the knife from 75 rpm to 10 rpm resulted in a significant increase of the compressive stress, an increase of the bed height and a sharp decrease of the production capacity from 91 l/h to 68 l/h. The compressive stress exerted on the knife during XYL-3B was relatively high in comparison to the other reported experiments because only in steady state XYL-3B the throughput of the wash column was actually limited by the cutting capacity of the knife.

Figure 6.11: Compressive stress profiles in the 0.156 m wash column during the experiments XYL-3A and 3B showing the effect of a reduction of the revolution rate of the knife from 75 to 10 rpm
6.6 CONCLUSIONS

The presented model can be used to predict the compressive stresses in a hydraulic packed bed wash column under different operating conditions. In this study the compressive stresses were not actually measured to check the model predictions but the basic equation (eq. 6.11) was experimentally verified by several researchers [5,7,8].

In order to minimize the compressive stresses during the processing of a certain compound in a hydraulic wash column the following measures can be taken:

(i) reduce the production capacity,
(ii) lower the height of the wash front and reduce the amount of wash liquid,
(iii) increase the revolution rate of the knife,

These measures may have an effect on the separation efficiency, the controllability or the economy of the wash column operation but this is the subject of other studies. The steering flow can be used to adjust the bed height to a suitable level without having a significant effect on the maximum compressive stress in the wash column.
Notation

\( A_c \) cross-sectional area of a wash column  \([m^2]\)

\( B \) permeability of the packed bed  \([m^2]\)

\( C_{p,s} \) specific heat of the solid phase  \([\text{J/kg.K}]\)

\( D \) hydraulic diameter of the wash column  \([m]\)

\( g \) gravity constant  \([\text{m/s}^2]\)

\( h \) vertical coordinate  \([m]\)

\( H \) bed height  \([m]\)

\( \Delta H_m \) latent heat of fusion  \([\text{J/kg}]\)

\( k_s \) stress ratio  [-]

\( K_F \) friction factor  [-]

\( K_{*} \) apparent friction factor  [-]

\( P_L \) pressure in the liquid phase  \([\text{Pa}]\)

\( P_r \) pressure ratio  [-]

\( r \) radial coordinate  \([m]\)

Greek

\( \alpha \) solids content of the feed  \([\text{wt}\%]\)

\( \varepsilon \) porosity or void fraction of the packed bed  \([\text{wt}\%]\)

\( \Phi_F \) feed flow  \([\text{l/h}]\)

\( \Phi_p \) product flow  \([\text{l/h}]\)

\( \Phi_w \) wash liquid flow  \([\text{l/h}]\)

\( \eta \) viscosity of the liquid phase  \([\text{Pa.s}]\)

\( \rho_s \) density of the solid phase  \([\text{kg/m}^3]\)

\( \rho_L \) density of the liquid phase  \([\text{kg/m}^3]\)

\( \sigma_v \) vertical compressive stress  \([\text{Pa}]\)

\( \sigma_r \) radial compressive stress  \([\text{Pa}]\)

\( \sigma_0 \) tangential compressive stress  \([\text{Pa}]\)

\( \tau_{xy} \) shear stress on the x-plane in the y direction  \([\text{Pa}]\)

\( (\tau_n)_w \) shear stress at the wall  \([\text{Pa}]\)

\( \mu \) friction coefficient  [-]

Subscripts

\( \text{aw} \) above the wash front

\( \text{bw} \) below the wash front

\( \text{bs} \) bottom section of the crystal bed

\( \text{ms} \) middle section of the crystal bed

\( \text{ts} \) top section of the crystal bed

\( \text{tot} \) total crystal bed or position at the bottom of the bed

\( \text{fit} \) position at the filter(s)

\( \text{wsh} \) position at the wash front
compressive stress in hydraulic wash columns

References


Appendix: Dependence of the friction factor $K_r$ on flow direction, crystal size and bed depth

Data on the dependence of $K_r$ on the flow direction, the crystal size and the bed depth were presented by Brandt and Johnson [8]. They described a method to obtain values for the coefficient of friction $\mu$ and the stress ratio $k_a$. Their equipment consisted of a vertical column in which a packed bed of solids was transported at constant velocity by a piston. A liquid flow was established *cocurrent* and *countercurrent* to the direction of the bed movement. The radial compressive stress at the column wall was measured with differential pressure transducers and the average vertical compressive stress at the bottom was determined with a balance connected to the moving piston.

An equation similar to eq. (6.11) was used by Brandt and Johnson to calculate $\mu$ and $k_a$. Their results obtained with different sieve fractions of three bed materials (ion exchange resin A and B particles and glass beads) are summarized in table 2A for the cocurrent and in table 2B for the countercurrent movement experiments. The values for $K_r$, not reported by Brandt and Johnson, were obtained by multiplying $\mu$ with $k_a$ and vary from 0.05 to 0.36.

Brandt and Johnson concluded that with the *countercurrent* movement experiments $\mu$ and $k_a$ were essentially independent of the bed depth. For the 150-290 $\mu$m and the 840-1680 $\mu$m resin fractions in the *cocurrent* movement experiments they found that the values of $\mu$ and $k_a$ changed with bed depth but reached a constant value in deeper beds. Unfortunately not all values of $k_a$ in shallow beds were reported but from the available data it appears that an increase of $\mu$ with bed depth is compensated by a decrease in $k_a$ and vice versa. Hence also during the cocurrent experiments, $K_r$ was hardly dependent on the bed depth. The values of $\mu$ and $k_a$ presented in table 2 are the deep bed values. Brandt and Johnson found that $\mu$ was independent of the liquid velocity and showed only a weak dependency on the
compressive stress in hydraulic wash columns

moving bed velocity. From table 2 the conclusion is drawn that the value of $K_f$ during cocurrent and the countercurrent movement experiments are approximately equal. Thus the data reported by Brandt and Johnson support the assumption that $K_f$ may be considered constant throughout the wash column.

<table>
<thead>
<tr>
<th>2A</th>
<th>840-1680 μm</th>
<th>840-1680 μm</th>
<th>360-840 μm</th>
<th>150-290 μm</th>
<th>290-840 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>resin A</td>
<td>resin B</td>
<td>resin A</td>
<td>resin A</td>
<td>glass</td>
</tr>
<tr>
<td>$\mu$</td>
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<td>0.05</td>
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<td>0.22</td>
</tr>
<tr>
<td>$k_a$</td>
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<td>0.93</td>
<td>1.00</td>
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<tr>
<td>$K_f$</td>
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<td>0.11</td>
<td>0.05</td>
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<table>
<thead>
<tr>
<th>2B</th>
<th>840-1680 μm</th>
<th>840-1680 μm</th>
<th>360-840 μm</th>
<th>150-290 μm</th>
<th>290-840 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>resin A</td>
<td>resin B</td>
<td>resin A</td>
<td>resin A</td>
<td>glass</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.10</td>
<td>0.14</td>
<td>0.07</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>$k_a$</td>
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<td>0.70</td>
<td>0.76</td>
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</tr>
<tr>
<td>$K_f$</td>
<td>0.09</td>
<td>0.10</td>
<td>0.05</td>
<td>0.15</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 2: Values for $\mu$, $k_a$ and $K_f$ for the cocurrent movement (2A) and countercurrent movement experiments (2B) of Brandt and Johnson [8]
chapter 7

THE PURIFICATION PROCESS IN HYDRAULIC PACKED BED WASH COLUMNS

Abstract

Hydraulic packed bed wash columns are continuous solid/liquid separators, which can be applied as the final step in fractional suspension crystallization processes aimed at ultrapurification of organic compounds. In this paper an experimental study and a mathematical model of the purification process in packed bed wash columns are presented. The developed model can be used to calculate concentration, temperature and porosity profiles along the column axis and to predict the effect of practical operating conditions on the product purity.

P.J. Jansens, R. van der Ham, O.S.L. Bruinsma, G.M. van Rosmalen and M. Matsuoka
7.1 INTRODUCTION

The increasing demand for ultrapure organic compounds (≥ 99.9%) in, for example, the polymer, the pharmaceutical and the food industry encourages the development of high performance separation techniques. Fractional suspension crystallization is a general term for separation processes based on cooling crystallization, which comprise a crystallization section and a downstream solid/liquid separation [1]. The purity of the crystalline product from the crystallization section does not yet meet product specifications, mainly due to the presence of impure mother liquor, which adheres to the crystal surface or is included in the crystal phase. In order to meet the desired product purity an effective phase separation and possibly further purification of the crystal phase must be achieved in the downstream separation unit. For this purpose wash columns have been developed, which combine a virtually complete product/residue separation with an efficient countercurrent washing action. Additional purification of the crystal phase through sweating and recrystallization may also occur in wash columns, depending on the column design and the operating conditions.

Three types of industrial wash columns are distinguished by the different mechanisms applied to transport the crystals: gravity, hydraulic and mechanic columns (chapter 1). The three column types are illustrated in figure 7.1.

In the first type, which is applied e.g. in the TSK-4C process [2] and in the Brodie purification process [3], the crystals settle under gravity into a loosely packed downward moving bed and the mother liquor leaves the column via the overflow. A slowly rotating agitator (≤ 2 rpm) covers the whole length of the wash column and serves to prevent agglomeration and/or channelling in the bed. The production capacity of gravity wash columns does not exceed 1500 kg/m²h. The residence time of the crystals may amount several hours due the large column height (6-8 m).
Figure 7.1: (1) gravity, (2) hydraulic and (3) mechanical wash column type

In the second type, which is applied e.g. in the Koppers process [4] and in the TNO-Thijsse process [5], a *densely packed* crystal bed is transported by a hydraulic pressure. The mother liquor flows through the top section of the crystal bed and leaves the column via filters which are positioned either in separate filter tubes or in the column wall. From a scale-up point of view the version with separate filter tubes, known as the TNO-Thijsse column, is favourable. The product throughput can be as high as 10,000 kg/m²h. The residence time of the crystals in the compact equipment (height: 1-1.5 m) is in the order of 10-15 minutes.

In the third type, which is applied e.g. in the Philips Petroleum process [6] and the Niro (former Grenco) process [7], a *densely packed* crystal bed is transported by a mechanical force created by a moving piston or a rotating screw. The mother liquor leaves the column via pores in the mechanical device. Similar to the hydraulic type, the maximum throughput of mechanic wash columns is limited to 10,000 kg/m².h, the height amounts 1-1.5 m and the residence time of the crystals is about 10-15 minutes.
purification process in hydraulic wash columns

At the bottoms of all three column types the product crystals are molten. A portion of the molten product is withdrawn from the bottom section and the remainder ascends in the column thus providing a countercurrent washing action. The wash liquid does not leave the column but crystallizes on the descending cold crystals. In the densely packed hydraulic and mechanical wash columns the recrystallization of the wash liquid produces a sharp wash front. This wash front represents the border line between impure mother liquor and (nearly) pure wash liquid and it marks steep gradients in porosity, concentration and temperature.

The purity of the crude crystals descending in the wash columns is expected to increase due to (i) displacement of the mother liquor, (ii) washing of the liquid layer adhering to the crystals, (iii) crystallization of pure wash liquid on the cold crystals, (iv) sweating of the crystals in contact with the hot wash liquid and/or adiabatic recrystallization of the crystals. The contribution of the individual purification mechanisms depends on the contact time between the crystals and the wash liquid and on the morphology and composition of the crude crystals. In gravity wash columns with long contact times, recrystallization and sweating may result in the removal of incorporated impurities (solid solutions) and included impure mother liquor. In hydraulic and mechanic wash columns, however, the contact times are short and removal of impurities from the inside of the crystals is less likely to occur.

The objectives of this study were (i) to determine experimentally the effect of the operating conditions on the product purity, (ii) to identify the purification mechanisms which play a role and (iii) to analyze mathematically the purification process in hydraulic wash columns.

The developed purification model has been used to calculate axial temperature, concentration and porosity gradients in the bottom section of a hydraulic wash column, depending on the operating conditions. The model also predicts the effect of the wash front level on the product purity. Model predictions were verified by experiments in a pilot scale hydraulic wash column with a multicomponent
C8-aromatic mixture, consisting mainly of p-xylene. The purification model is applicable to both hydraulic and mechanic wash columns because the design of the bottom sections of these column types are basically the same.

### 7.2 REVIEW OF PURIFICATION MODELS

Mathematical models describing the purification processes in column type purifiers can be divided in two groups after the degree of packing of the crystal bed in the column: *loosely packed* (roughly $0.45 < \varepsilon < 0.65$) or *densely packed* (roughly $\varepsilon \leq 0.45$). The different models with their main features are summarized in table 7.1.

Purification models for *loosely packed* columns are often based on the assumption of constant solid and liquid flows throughout the column because significant axial dispersion is anticipated due to (intensive) mechanical agitation. The constant flow assumption simplifies the mathematical analysis because the heat balance can be neglected. Albertins and Powers [8] worked with a Schildknecht column crystallizer which is equipped with a rotating spiral conveyor to transport crystals upward. The column is operated with a bed porosity of approximately 0.65 and at high rotation rates (50-500 rpm). Albertins and Powers accounted for axial dispersion in the liquid phase but, like most other authors, assumed plug flow for the solid phase. They assumed that the individual crystals are surrounded by an adhering impure liquid layer and that exchange of impurities between the adhering layer and the bulk of the liquid (washing) contributes to the purification of the total crystal phase, which includes the adhering liquid. They determined the values of the mass transfer coefficient for the impurity exchange and the axial dispersion coefficient and concluded that the observed concentration profiles in their Schildknecht column were dominated by the axial dispersion. Gates
and Powers [9] and Henry and Powers [10] continued this experimental study and came to similar conclusions. Sakuma and Ikeda [11] presented experimental results obtained with an industrial gravity wash column. Since the revolution rate in this large scale column is kept \( \leq 2 \) rpm, axial dispersion is moderately low and the constant flow assumption must be rejected. Sakuma and Ikeda took the heat balance into account, included axial dispersion of the solid phase and proposed recrystallization of the crystals as a purification mechanism in their model.

Matsuoka and Kiyomura [12] used a column crystallizer with gravity bed transport and intensive agitation (180-280 rpm). They measured an upgrading of the crystal purity towards the hot bottom end of their column and proposed sweating as a purification mechanism. Matsuoka and Kiyomura assumed that the rate of purification through sweating is proportional to the deviation from the solid equilibrium concentration at a local temperature. They experimentally determined values for the sweating/purification coefficient and successfully analyzed the liquid and solid concentration profiles along their column for a solid solution system.

Hydraulic and mechanical wash columns are operated with a densely packed bed. The absence of mixing devices and the relative large compressive stresses, which are exerted on the moving crystal bed (chapter 6), result in low axial dispersion in the liquid phase whereas backmixing in the solid phase is negligible. Player [13] completely neglected axial dispersion in the liquid phase. He considered the cold crystals to be the heat sink for heat of crystallization and latent heat but could not estimate the value of the heat transfer coefficient. Using heat and mass balances, Player calculated concentration and temperature profiles along the column axis and reported the existence of a narrow zone, where very sharp gradients in temperature and concentration take place (the wash front). Players model predicts, for example, a temperature difference of 26 °C between the crystal and the liquid phase at this wash front, which suggests enormously high heat and mass fluxes.
between the phases and is hardly a realistic result. Moyers and Olson [14] extended Players model with axial dispersion in the liquid phase. They neglected heat transfer from the solid to the liquid phase by assuming thermal equilibrium but did account for sidewall heat losses. Weak points in their approach are the assumption of a constant bed porosity and the omission of a correlation for the dispersion coefficient. The porosity and the permeability decrease significantly at the wash front (Arkenbout et al. [15], chapter 8). In the model of Moyers and Olson the dispersion coefficient is a free parameter which can only be determined by fitting the experimental data and consequently this model cannot be used as a predictive tool.

The improved purification model, presented in this paper, comprises heat and mass balances. The contribution of resistance to heat transfer in the solid phase is investigated and the heat transfer coefficient in this phase is calculated. The dispersion coefficient is related to the operating conditions via the bed porosity and the Bodenstein number. The model can be used for eutectic and solid solution systems. The model yields axial porosity, temperature and concentration profiles and predicts the effect of the wash front level on the product purity.
Table 7.1: summary of purification models (+ = taken into account; - = ignored)

<table>
<thead>
<tr>
<th>1st author [ref]</th>
<th>packing of bed</th>
<th>column type</th>
<th>constant flows</th>
<th>complete displacement mother liquor</th>
<th>washing adhering layer</th>
<th>axial dispersion</th>
<th>sweating or recrystallization of crystals</th>
<th>system</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry [10]</td>
<td>loose</td>
<td>Schild-knecht</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>binary eutectic</td>
<td>no heat balance</td>
</tr>
<tr>
<td>Nakai [19]</td>
<td>loose</td>
<td>gravity column</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>binary eutectic</td>
<td>no heat balance</td>
</tr>
<tr>
<td>Matsuoka [12]</td>
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<td>gravity column</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>binary solid solution</td>
<td>no heat balance</td>
</tr>
<tr>
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<td>mechanic column</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>binary eutectic</td>
<td>no heat balance</td>
</tr>
<tr>
<td>Player [13]</td>
<td>dense</td>
<td>mechanic column</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>binary eutectic</td>
<td>crystals as heat sink</td>
</tr>
<tr>
<td>Moyers [14]</td>
<td>dense</td>
<td>mechanic column</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>binary eutectic</td>
<td>non-adiabatic porosity constant axial dispersion const.</td>
</tr>
<tr>
<td>Janssen (present study)</td>
<td>dense</td>
<td>hydraulic column</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>multi-comp. eutectic &amp; solid solution</td>
<td>crystals as heat sink bed velocity constant</td>
</tr>
</tbody>
</table>
7.3 FORMULATION OF A NEW PURIFICATION MODEL

Calculation of porosity, temperature and concentration profiles in the bottom section of a hydraulic wash column requires simultaneous solution of mass, component and heat balances. At the set-up of these balances the following assumptions were made:

1. Purification of the crystals occurs through displacement of the mother liquor by purer wash liquid and (re)crystallization of the wash liquid on the cold moving crystal bed. Sweating and recrystallization of the crystals may be neglected because of the short contact time between the crystals and the hot wash liquid (2-4 minutes) and because of the deposition of solidified wash liquid on the core crystals, which hampers the removal of impurities.

2. The solid flux is ideal plug flow, which is valid because of the high degree of compaction and the absence of mixing devices inside the crystal bed. Furthermore, the velocity of the moving bed is considered to be constant throughout the bottom section of the wash column.

3. The liquid flux is essentially plug flow modified with axial dispersion. The thermal and mass axial dispersion coefficients are assumed to be equal, which is reasonable for organic and aqueous mixtures with poor thermal conductivity (Moyers and Olson [14]).

4. The feed crystals contain some included or incorporated impurities.

5. The liquid phase is homogeneous in concentration and temperature and in equilibrium at each cross-section of the wash column. The liquidus curve is approximated by a straight line but this is not essential to the model.

6. The densities and specific heats of the liquid and the solid phase are independent of temperature and concentration, which is acceptable in view of the application of the wash columns for ultra-purification purposes. The maximum temperature difference between top and bottom, as a rule of thumb, is about 10-15 K.
Sidewall heat losses are negligible (adiabatic) and the resistance to heat transfer from the liquid to the solid phase is located in the solid phase.

![Diagram of purification process in hydraulic wash columns](image)

**Figure 7.2:** model for the bottom section of a hydraulic wash column, containing an infinitesimal horizontal slab $dz$

A differential mass balance over an infinitesimal horizontal slab $dz$ of the moving packed crystal bed in the bottom section of the wash column (fig. 7.2) yields:

$$\frac{d\Phi_S}{dz} = \frac{d\Phi_L}{dz} \quad (7.1)$$

Integration of eq. (7.1) from the filters at $z=0$ to $z$ gives:

$$\Phi_S - \Phi_L = \Phi_{S,0} - \Phi_{L,0} = C_1 \quad (7.2)$$
A differential component balance over the slab \(dz\) reads:

\[
\frac{d(\Phi_S \cdot X_S)}{dz} - \frac{d(\Phi_L \cdot X_L)}{dz} - \frac{d(\rho_L \cdot D_{ax} \cdot e \cdot \frac{dX_L}{dz})}{dz} = 0
\]  \(\text{(7.3)}\)

Integration of eq. \((7.3)\) from \(z=0\) to \(z\) produces:

\[
\Phi_S \cdot X_S - \Phi_L \cdot X_L - \rho_L \cdot D_{ax} \cdot e \cdot \frac{dX_L}{dz} = C_2
\]  \(\text{(7.4)}\)

\text{where:} \quad C_2 = \Phi_{s0} \cdot X_{s0} - \Phi_{l0} \cdot X_{l0} - \rho_L \cdot D_{ax,0} \cdot e_0 \cdot \left(\frac{dX_L}{dz}\right)_{z=0}

The crystallization of the wash liquid dilutes the impurity concentration of the crystal phase according to:

\[
\frac{d(\Phi_S \cdot X_S)}{dz} = K_{eq} \cdot X_L \cdot \frac{d\Phi_L}{dz}
\]  \(\text{(7.5)}\)

where \(K_{eq}\) is the equilibrium impurity distribution coefficient. For eutectic systems \(K_{eq}\) equals zero and the total amount of impurities in the solid phase remains constant throughout the column:

\[
\frac{d(\Phi_S \cdot X_S)}{dz} = 0 \quad \text{or} \quad \Phi_S \cdot X_S = \Phi_{s0} \cdot X_{s0}
\]  \(\text{(7.6)}\)

The set of equations, which make up this purification model, is solvable with eq. \((7.5)\) as well as with eq. \((7.6)\).
A heat balance over the slab $dz$ is derived similar to eq. (7.4):

$$\Phi_S*H_S - \Phi_L*H_L - \rho_L*C_{p,L}*D_{\text{ax}}*e* \frac{dT_L}{dz} = C_3$$  \hspace{1cm} (7.7)

where:  
$$C_3 = \Phi_{S,0}*H_{S,0} - \Phi_{L,0}*H_{L,0} - \rho_L*C_{p,L}*D_{\text{ax,0}}*e_0* \left( \frac{dT_L}{dz} \right)_{z=0}$$

$$H_S = C_{p,S}*(T_S - T_m)$$

$$H_L = \Delta H_m + C_{p,L}*(T_L - T_m)$$

The heat balance can be rewritten in terms of $X_L$ using a linear relation for the liquidus curve of the phase diagram:

$$T_L = T_m - q*X_L \quad \text{or} \quad \frac{dT_L}{dz} = -q* \frac{dX_L}{dz}$$  \hspace{1cm} (7.8)

In this analysis the cold moving crystal bed is treated as the heat sink and the heat transfer equation is:

$$\frac{\Phi_S*dH_S}{dz} = h*A_p*(T_L - T_S)$$  \hspace{1cm} (7.9)

$A_p$ is the specific surface area of the crystals ($m^2/m^3$) and $h$ is the heat transfer coefficient in the solid phase. The derivation of a relation for $h$ in a solid sphere is presented in the appendix. Using this correlation it can be shown that:

$$h*A_p = \frac{4\pi^2*\lambda*(1-e)}{(d_{p,s})^2}$$  \hspace{1cm} (7.10)

where $d_{p,s}$ is the surface based mean crystal diameter.
The axial dispersion coefficient for liquid flow through packed beds depends on the porosity and the Bodenstein number. Miller and King [16] showed that the product of the porosity and the Bodenstein number has a relatively constant value under laminar flow conditions:

$$Bo'\cdot e*Bo = \frac{e*V_{L,r}*d_{p,l}}{D_{ax}} = const \quad (Re \leq 20) \quad (7.11)$$

where $d_{p,l}$ is the length based mean crystal diameter and $V_{L,r}$ is the relative actual liquid velocity. Miller and King summarized literature data and showed that $Bo'$ is usually approximately equal to 0.2 in the laminar flow regime. They argued that there is no consensus concerning the absolute magnitude of $Bo'$ and that discrepancies may come from the use of particles with irregular shapes and/or with a non-uniform size. Since $V_{L,r}$ is the sum of the bed velocity and the countercurrent (upward) liquid velocity, the axial dispersion coefficient can be expressed as:

$$D_{ax} = \frac{1}{Bo'}*e*d_{p,l} \left( V_{bed} + \frac{\Phi_L}{\rho_L*e} \right) \quad (7.12)$$

The (constant) bed velocity can be related to the solid flux and the bed porosity:

$$V_{bed} = \frac{\Phi_S}{\rho_s*(1-e)} = \frac{\Phi_{S,0}}{\rho_s*(1-e_o)} \quad (7.13)$$

Via substitution of eq. (7.13) in eq. (7.12), it can be shown that $D_{ax}$ is nearly constant throughout the bottom section of the wash column, provided the difference between the specific densities of solid and liquid phase is small.

$$D_{ax} = \frac{1}{Bo'}*d_{p,l} \left( V_{bed} - \frac{\Phi_S}{\rho_s} + \frac{\Phi_L}{\rho_L} \right) = \frac{1}{Bo'}*d_{p,l} \left( V_{bed} - \frac{C_1}{\rho} \right) \quad (7.14)$$

$D_{ax}$, which is best calculated using eq. (7.12), depends strongly on the product throughput but features only a weak dependency on the axial position $z$. 
To obtain the desired temperature, concentration and porosity profiles along the column axis, a set of 8 equations (7.2, 7.4, 7.5, 7.7, 7.8, 7.9, 7.12, 7.13) with 8 variables (\(\Phi_s, \Phi_L, X_s, X_L, T_s, T_L, D_{ax}, \varepsilon\)) must be solved simultaneously. Input parameters to the model are: the initial conditions at the filters (\(\Phi_{S,0}, \Phi_{L,0}, X_{S,0}, X_{L,0}, \varepsilon_{0}, (dX_L/dz)_{z=0}\)), the particle diameters (\(d_{p,a}, d_{p,b}\)), the distribution coefficient \(K_{eq}\) and the relevant physical properties (\(\Delta H_m, T_m, C_{p,L}, \rho_L\)). The initial concentration gradient (\((dX_L/dz)_{z=0}\)) approaches to zero in the vicinity of the filters. Bo' is a key-parameter to the model and must be determined by fitting experimental data.

The product impurity \((X_p)\) can be calculated from an over-all component balance over the bottom section and the melting section of the wash column (fig. 7.2):

\[
X_p = \frac{\Phi_{S,0} * X_{S,0} - \Phi_{L,0} * X_{L,0} - \rho_L * D_{ax,0} * \varepsilon_0 * \left(\frac{dX_L}{dz}\right)_{z=0}}{\Phi_{S,0} - \Phi_{L,0}}
\]  

(7.15)

Since \(\Phi_{S,0} > \Phi_{L,0}\), assuming that \((dX_L/dz)_{z=0}=0\), \(X_p\) can be estimated from eq. (7.16):

\[
X_p = X_{S,0} - \frac{\Phi_{L,0}}{\Phi_{S,0}} * X_{L,0} = X_{S,0} - R * X_{L,0}
\]  

(7.16)

The optimum product purity (minimum product impurity) depends on the amount of wash liquid which can crystallize on the cold crystals. Via simplified over-all heat and mass balances, assuming an eutectic system, it can be shown that the minimum product impurity is reached roughly at \(R_{\text{max}}\):

\[
R_{\text{max}} = \frac{X_{S,0} * (1 - \beta)}{X_{L,0}} \quad \text{with} \quad \beta = \left(1 + \frac{C_{p,s} * (T_m - T_{S,0})}{\Delta H_m}\right)^{-1}
\]  

(7.17)
7.4 EXPERIMENTAL PROCEDURE

In a series of experiments, the temperature profiles at the wash front and the product purity were monitored in steady state operation under various operating conditions. The experiments were performed with a pilot plant, TNO-Thijssen type, hydraulic wash column. The height of the wash column is 1 m and it has an internal diameter of 0.156 m. The column contains six filter tubes with an outer diameter of 0.02 m. In some experiments three filter tubes were removed to study the effect of the filter geometry on the shape of the wash front. The column wall is made of glass. A filter tube consists of a stainless steel tube, a porous filter section and a massive teflon bottom end. The porous filters are positioned 0.265-0.295 m above the knife. Four thermocouples were installed at different axial and radial positions in the bottom section of the column (see fig. 7.3). It proved necessary to incorporate the thermocouples in smooth teflon bars which cover the whole length of the column to avoid disturbance of the wash front. The column is equipped with a so called steering pump which can be used to recycle residual filtrate into the feedline and thus to increase the available transport force (chapter 6).

The operating conditions were varied as follows:

| Feed flow: | 400-600 [l/h] |
| Product flow ($\Phi_p$): | 35-100 [l/h] |
| Steering flow (filtrate recycle): | 0-600 [l/h] |
| Bed height ($H_{bed}$): | 0.35-0.75 [m] |
| Wash front height ($H_{washing}$): | 0.025-0.25 [m] |

The original feed stock was a C8-aromatic system, containing p-xylene (89.2 wt%), m-xylene (7.0 wt%), o-xylene (2.0 wt%), ethylbenzene (1.5 wt%) and toluene (0.3 wt%), from which p-xylene was crystallized upon cooling at about 6 °C. The melting point of pure p-xylene equals 13.3°C. In some experiments the feed stock was enriched with 5 wt% toluene, because this compound shows limited solid solubility with p-xylene. A minor quantity of red dye was added to the mother liquor.
in order to visualize the wash front. The mean sizes of the feed crystals determined through sieving amounted 500 μm on mass base and 380 μm on length base. The temperature profiles at the wash front were determined by repeatedly gradually lowering and rising the visual wash front in such a manner that two thermocouples, positioned at the same height in the column, were passed by the front. The rate of the changing of the wash front level was kept low, i.e. one ascent or descent of the wash front took 25-45 minutes.

Product samples were analyzed with gas chromatography (column: 25 m, bonded phase, BP20-polar, film thickness 0.25 μm, inner diameter 0.22 mm). Two different analytical methods were applied, which will be referred to as GC-I and GC-II. In GC-I the product samples were diluted in hexane and analyzed at 50 °C, which resulted in a perfect separation of the component peaks but a rather high detection limit of 100 ppm. In GC-II the samples were injected without dilution at 35 °C. Using the GC-II method, the detection limit for ethylbenzene, o-xylene and toluene was lowered to 10 ppm but it proved impossible to separate m-xylene from p-xylene. GC-I was used to determine the product purity. The more accurate GC-II method was used a.o. to determine the inclusion factor, which is defined as the fraction of impure mother liquor included in the crystals [17], and the equilibrium distribution coefficient for toluene, which forms solid solutions with p-xylene.
Figure 7.3: positions of the four thermocouples (T1-T4) in the pilot wash column
7.5 EXPERIMENTAL RESULTS

7.5.1 temperature profiles at the wash front

The measurements of the temperature profiles in general were well reproducible. Lowering and rising of the wash front, visible through the (glass) column wall, yielded virtually the same result and the rate at which this visual wash front height \( H_{wsh,v} \) was changed did not affect the profiles.

Figure 7.4 shows temperature profiles for different product throughputs, registered by thermocouple 1 positioned 0.105 m above the knife and 0.02 m from the wall (see also fig. 7.3). Variations of the product throughput from 40 l/h to 90 l/h had no significant effect on the shape of the temperature profile. Thermocouple 2, positioned at the same height but in the centre of the column, registered similar profiles and therefore it can be concluded that the profile of the wash front does not depend on the radial position in the column. Only at low throughput (40 l/h) and low visual wash front height (0.025-0.07 m) irregular temperature fluctuations were registered by the thermocouples at 0.105 m. This indicates instabilities in the packing of the lowest part of the bed probably caused by the presence of the rotating knife and facilitated by the very low compressive stresses in the bottom part of the bed under these operating conditions (chapter 6). The instabilities had no effect on the shape of the visual wash front nor did they affect the product purity.

*Remark: Notice that the figures 7.4 and 7.5 contain raw data. The temperature profiles plotted were registered by thermocouples at fixed positions upon variation of the visual wash front height \( H_{wsh,v} \). \( H_{wsh,v} \) indicates the height/level of the visual wash front above the knife. The real temperature profile at the wash front as a function of the distance from the filters \( z \) is the mirror image of these plots relative to \( z=0.105 \) m (fig. 7.4) and \( z=0.205 \) m (fig. 7.5).
Figure 7.4: temperature profiles at the wash front for various product flows (registered by T1, 0.105 m above the knife)

Figure 7.5 shows temperature profiles for different product throughputs, registered by the thermocouples 3 and 4 positioned 0.20 m above the knife. In accordance with the above results, variation of the production capacity from 40 l/h to 60 l/h proved to have no effect on the profiles registered 0.02 m from the wall by thermocouple 3 (T3). It was not possible to achieve a product throughput of 90 l/h with a high wash front level, since the maximum pressure limit for the glass column (2.5 bar) would be exceeded. The profiles registered by thermocouples 1 and 3 are very similar.

Most striking in figure 7.5 is the temperature profile measured with thermocouple 4 (T4), positioned in the centre of the column. It never registered the melting point temperature of pure p-xylene even when the visual wash front was kept 0.23 m above the knife. Apparently, the wash front cannot completely pass T4. The flow pattern of the mother liquor presumably interferes with the shape of the wash front.
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in the vicinity of the filters. This presumption is supported by the fact that at 0.25 m above the knife the visual wash front was clearly wave shaped and by computer simulations of the flow pattern (presented in chapter 8). As might have been expected, variations in the amount of mother liquor flowing through the top section of the crystal bed and the number of filter tubes (six or three) had no significant effect on the profiles registered by the four thermocouples. It is concluded that the temperature profile at the wash front is independent of the axial and radial position in the column, provided the distance of the wash front to the filters is sufficient (∆ 0.10 m).

Figure 7.5: temperature profiles at the wash front for various product flows (registered by T3 and T4, 0.205 m above the knife)
7.5.2 composition of the product

The purity of the product upon crystallization at ± 6 °C from the original (toluene lean) feed stock was 99.93 ± 0.06 wt%. The product composition was not significantly affected by variation of the product throughput from 40 l/h to 100 l/h nor by changes in the bed height from 0.025 m to 0.22 m. The inclusion factor was approximately 0.01 for the eutectic impurities o-xylene and ethylbenzene. Toluene was incorporated in the crystals with $K_{eq} = 0.03$ upon crystallization from the enriched feed stock at ± 4.5 °C, which could be anticipated by extrapolation of data presented by De Goede [18]. In an experiment with the toluene rich feed stock a sample from the feed slurry was centrifuged and the crystals were analyzed. The (unwashed) feed crystals contained 350 ppm o-xylene, 200 ppm ethylbenzene and 1320 ppm toluene. The product of the wash column during this experiment contained ± 20 ppm o-xylene and virtually no ethylbenzene (≤ 10 ppm) but still 1150 ppm toluene. Apparently, the eutectic impurities (ethylbenzene and o-xylene) merely adhered to the unwashed feed crystals whereas toluene was also incorporated. The incorporated toluene is not removed from the crystals during their transport through the wash column.
7.6 SIMULATION RESULTS AND DISCUSSION

The physical properties of the C8-aromatic system, as used in the simulations, are listed in table 7.2.

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>liquid phase (L)</th>
<th>solid phase (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>specific heat ( (C_p) )</td>
<td>1.48 kJ/kgK</td>
<td>1.67 kJ/kgK</td>
</tr>
<tr>
<td>heat of fusion ( (\Delta H_m) )</td>
<td>161.1 kJ/kg</td>
<td>161.1 kJ/kg</td>
</tr>
<tr>
<td>specific weight ( (\rho) )</td>
<td>867 kg/m³</td>
<td>1006 kg/m³</td>
</tr>
<tr>
<td>thermal conductivity ( (\lambda) )</td>
<td>0.13 W/mK</td>
<td>0.29 W/m°C</td>
</tr>
</tbody>
</table>

Table 7.2: physical properties of the C8-aromatic system

The presented simulation results were all calculated with the same values for \( q \), \( K_{eq} \), \( X_{L,0} \), and \( \varepsilon_0 \). The slope of the liquidus curve \( q \) was obtained from the binary phase diagrams of the individual impurities (m-xylene, o-xylene, ethylbenzene and toluene) with p-xylene published by De Goede [18] and amounts approximately 40.7 K for each impurity. For the sake of simplicity \( K_{eq} \) in eq. (7.5) was assumed to be zero, which does not introduce a large error since the product of \( K_{eq} (0.03) \) and the toluene fraction in the original feed stock (0.003 kg/kg) is virtually negligible. The total initial impurity fraction in the mother liquor was determined by analysis of the filtrate during crystallization from the original feed stock: \( X_{L,0}=0.176 \). The porosity of the bed at the filters \( \varepsilon_0 \) was assumed to be equal to 0.40.
7.6.1 determination of Bo' and $D_{ax}$

The axial dispersion coefficient can be calculated from eq. (7.12) but first the value for Bo' must be obtained via a fit-procedure. This procedure involves variation of Bo' for one set of operating conditions until the simulated temperature profile matches the experimental profile as is illustrated in figure 7.6. The best fit was obtained with $Bo' = 0.5$. The plot for $D_{ax} = 0$ ($Bo' = \infty$) represents the result obtained with Players model [13].

![Graph showing temperature profile comparison]

Figure 7.6: determination of Bo' ($\varepsilon$*Bo) by fitting a measured temperature profile (conditions: $\Phi_{s,o} = 1.0$ kg/m²s, $X_{s,o}=10^{3}$ kg/kg, $R =3.4*10^{4}$)

$D_{ax}$ is mainly determined by the product throughput ($\Phi_{p} \propto V_{bed}$) and amounts $3.3*10^{-7}$ m²/s at $\Phi_{p}=40$ l/h, $4.9*10^{-7}$ m²/s at $\Phi_{p}=60$l/h and $7.4*10^{-7}$ m²/s at $\Phi_{p}=90$ l/h. The obtained values for $D_{ax}$ are significantly smaller then the values reported by most other authors (table 7.3) and indicate a dense packing of the crystal bed in
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the bottom section of the hydraulic wash column. Still, the temperature profile in the liquid phase is governed by axial dispersion and not by thermal diffusivity \( \alpha_T = 9 \times 10^{-8} \text{ m}^2/\text{s} \), which validates assumption 3. At very low throughput \( \Phi_p < 9.3 \text{ l/h or 0.15 kg/m}^2/\text{s} \) thermal diffusivity becomes dominant and consequently the model will break down. This limitation of the model is of little importance because operation at extremely low product throughput is economically unfavourable and in practice often unstable.

<table>
<thead>
<tr>
<th>Source</th>
<th>( D_{ax} [\text{m}^2/\text{s}] )</th>
<th>Column type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albertins and Powers [8]</td>
<td>1.6-3.5\times10^{-4}</td>
<td>Schildknecht, oscillating spiral conveyor</td>
</tr>
<tr>
<td>Gates and Powers [9]</td>
<td>1.3-1.7\times10^{-4}</td>
<td>Schildknecht, oscillating spiral conveyor</td>
</tr>
<tr>
<td>Ritter [21]</td>
<td>2.5-17\times10^{-6}</td>
<td>ice wash column</td>
</tr>
<tr>
<td>Moyers and Olson [14]</td>
<td>2.0-3.0\times10^{-5}</td>
<td>mechanical wash column (piston)</td>
</tr>
<tr>
<td>Matsuoka and Kiyomura [12]</td>
<td>2.7-6.4\times10^{-5}</td>
<td>gravity wash column</td>
</tr>
<tr>
<td>Present Study</td>
<td>3.6-8.1\times10^{-7}</td>
<td>hydraulic wash column</td>
</tr>
</tbody>
</table>

Table 7.3: comparison axial dispersion coefficients after Moyers and Olson [14]

In accordance with the experimental results the simulated temperature profiles, however, are independent of the product throughput. It follows that upon an increase of the product throughput, the larger convective heat transport is compensated by the increased axial dispersion.
7.6.2 other model variables

Besides temperature profiles, the model can be used to calculate the gradients in the porosity ($\varepsilon$), the liquid impurity fraction ($X_L$) and the liquid flux ($\Phi_L$), as well as the temperature difference between the solid and the liquid phase ($\Delta T_{L-S}$) as is illustrated in figure 7.7. The maximum $\Delta T_{L-S}$ amounts only 0.05 °C at the wash front, which is assumed to coincide with the inflection points in the concentration and temperature profiles. The calculated wash front height ($H_{\text{wash,c}}$) is defined as the distance from the position $z_1$, which marks the inflection point in the concentration profile and coincides with the maximum in the $\Delta T_{L-S}$ curve, to the position $z_2$ (at the knife), where $X_L$ equals $X_p$ (calculated with eq. 7.15).

![Graph showing porosity, liquid flux, and concentration profiles](image)

Figure 7.7: calculated profiles of various parameters at the wash front
(conditions: $\Phi_{s,o}=1.46 \text{ kg/m}^2\text{s}$, $X_{s,o}=10^{-3} \text{ kg/kg}$, $R=3.4\times10^{-4}$)
7.6.3 effect of wash front height

In figure 7.8, the calculated $X_p$ is plotted versus $H_{wsh,c}$ for different $X_{s,0}$ and this graph may be used to predict the wash front height required to achieve a certain desired product purity and vice versa. In example: if the feed crystals are 99.99 wt% pure ($X_{s,0} = 1*10^{-4}$) a wash front height of 7 mm is sufficient to produce 99.9 wt% pure product whereas a wash front height of 2.5 cm yields practically the optimal product purity ($X_p = 9.4*10^{-5}$ with $R_{max} = 3.4 * 10^{-5}$).

![Graph showing the effect of wash front height on product purity](image)

Figure 7.8: effect of the wash front height on the product (im)purity
($o-X = o$-xylene, $EB = ethylbenzene$, $TOL = tolene$)

Since the temperature profile at the wash front both in the experiments and in the simulations proved not to vary by product throughput, the curves plotted in figure 7.8 are also independent of the product throughput. Experimental data on the fractions of $o$-xylene, ethylbenzene and toluene in
product samples for different visual wash front heights are also plotted as a function of $H_{wsh,v}$ in figure 7.8. The product flow was kept at 50-60 l/h during these experiments. The toluene fraction at $H_{wsh,v} = 0.025$ m fell below the detection limit (GC-II method). Both experimental and simulation data show a virtually constant product composition for $H_{wsh} \geq 0.025$ m. Reliable data in the region $H_{wsh} < 0.025$ m would be most welcome but it is almost impossible to keep the wash front steady for half an hour at only 0.01 m above the knife over the whole cross-section of the column.

The good agreement between experimental and simulation results, which both indicate that the temperature profile at the wash front and the product composition do not depend on the product throughput nor on the wash front height (provided $H_{wsh} \geq 2.5$ cm), support the assumption (no. 6) that sweating and recrystallization of the crystals do not play a significant role in the purification process in hydraulic wash columns.

7.6.4  effect of crystal size

The effect of the size of the feed crystals can be studied from the figures 7.9 and 7.10. To obtain these figures the length based and surface based mean diameters, input to eqs. (7.16) and (7.18), were assumed to be equal. Figure 7.9 shows how the temperature profile at the wash front becomes steeper with decreasing crystal diameter ($d_p$). The axial dispersion coefficient ($D_{ax}$) is proportional to $d_p$ and the heat transfer product $h*\Delta T_p$ (eq. 7.10) is inversely proportional to $d_p^2$. 
Figure 7.9: effect of the crystal size on the temperature profiles at the wash front

Figure 7.10 demonstrates the dependence of $\Delta T_{LS}$, $H_{wsh}$, and $D_{ax}$ on $d_p$. The fact that $H_{wsh}$ and $\Delta T_{LS}$ depend linearly on $d_p$, indicates that for the C8-aromatic system heat transfer in the solid phase is not the rate determining step and therefore the purification process is mainly governed by axial dispersion. The simulations suggest that in order to minimize $H_{wsh}$, $d_p$ should be reduced but this is not recommendable because the permeability of a packed bed of crystals depends a.o. on $d_p$. The permeability particularly of the bottom section of the bed in the hydraulic wash columns determines to a large extent the magnitude of the hydraulic pressure which must be exerted to transport the bed through the column (chapter 6).
Figure 7.10: effect of the crystal size on the wash front height, the maximum temperature difference between liquid and solid phase and the axial dispersion coefficient

7.7 CONCLUSIONS

(1) The product purity and the temperature profiles at the wash front are independent of the product throughput and the wash front height in the ranges studied. Consequently, the maximum product throughput of hydraulic wash columns depends only on the transport force balance and is not limited by purification requirements.

(2) The developed model is well suited to describe the purification process in hydraulic wash columns since experimental data and model predictions are in good agreement.
(3) The purification process in hydraulic wash columns is governed by axial dispersion. Heat transfer in the solid phase is not the rate determining step. Purification occurs predominantly through displacement washing and crystallization of (pure) wash liquid on the crystals.

(4) The axial dispersion in the moving crystal bed can be described with $Bo' = 0.5$. It has been demonstrated mathematically that the axial dispersion coefficient is approximately constant throughout the bottom section of a wash column with a densely packed moving bed.

**Notation**

- $a_p$ surface area of a single particle [$m^2$]
- $A_p$ surface area of crystals per bed volume [$m^2/m^3$]
- $Bo$ Bodenstein number, definition in eq. (7.11) [-]
- $Bo'$ ($\varepsilon Bo$) [-]
- $C_p$ specific heat capacity [kJ/kg.K]
- $d_{p,a}$ surface based mean crystal size [m]
- $d_{p,l}$ length based mean crystal size [m]
- $D_{ax}$ axial dispersion coefficient [$m^2/s$]
- $K_{eq}$ equilibrium distribution coefficient [-]
- $h$ heat transfer coefficient in solid phase [kW/m$^2$ K]
- $H$ enthalpy [kJ/kg]
- $\Delta H$ heat of crystallization [kJ/kg]
- $q$ slope of the liquidus in a phase diagram [K]
- $R$ ratio of liquid and solid flux at $z=0$ [-]
- $R_{max}$ ratio $R$ at which the optimum product purity is reached [-]
- $T$ temperature [$^\circ C$, K]
- $V$ actual velocity [m/s]
- $X$ impurity fraction [kg/kg]
- $z$ axial position, ($z = 0$ m at the filters) [m]
Greek
\( \alpha_T \) thermal diffusion coefficient \((\lambda/\rho^*C_p)\) \([\text{m}^2/\text{s}]\)
\( \varepsilon \) porosity of the crystal bed \([\text{kg/kg}]\)
\( \Phi \) flux \([\text{kg/m}^2\text{s}]\)
\( \lambda \) thermal conductivity \([\text{kJ}/\text{m.K}]\)
\( \rho \) specific density \([\text{kg/m}^3]\)

Subscripts
0 at the filters \((z = 0 \text{ m})\)
bed (moving) crystal bed
c calculated, simulation result
L liquid phase
m melting point
P product
r relative to bed movement
S solid phase
v visual, experimental observation

References


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Appendix: heat transfer in a solid particle

According to Carslaw and Jaeger [22], the average temperature of a spherical particle $T_s$ during a condition of unsteady conduction of heat is given by:

$$\frac{T_S - T_o}{T_i - T_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \cdot Fo)$$  \hspace{1cm} (a.1)

here $T_i$ and $T_o$ denote the surface and the initial temperature and $Fo$ is defined as:

$$Fo = \frac{\alpha \cdot \theta}{r_p^2}$$  \hspace{1cm} (a.2)

where $\alpha$, is the thermal diffusivity of the sphere, $\theta$ is the time and $r_p$ is the radius of the sphere. It can be shown that for $Fo \approx 0.08$, eq. (a.2) is approximated by the first term in the series with an error less than 1%. In this case eq. (a.2) reduces to:

$$T_S - T_o = (T_i - T_o) \cdot (1 - \frac{6}{\pi^2} \cdot \exp(-\pi^2 \cdot Fo))$$  \hspace{1cm} (a.3)

The heat content of the sphere at any time is defined as:

$$\frac{4}{3} \pi r_p^3 \rho_s C_{ps} (T_s - T_r)$$  \hspace{1cm} (a.4)

where $T_r$ is a reference temperature.
The rate of heat transfer to the sphere can be written as:

\[
\frac{d}{d\theta} \left( \frac{4}{3} \pi * r_p^3 * \rho_s * C_{p,s} * T_S \right) =
\]

\[
= \frac{4}{3} \pi * r_p^3 * \rho_s * C_{p,s} * (T_I - T_S) * \frac{6}{\pi^2 * r_p^2} * \exp(-\pi^2 * F\theta)
\]  

(a.5)

\[
= \frac{4}{3} r_p^3 * \rho_s * C_{p,s} * \frac{\pi^2}{r_p^2} * (T_I - T_S)
\]  

(a.6)

\[
= \frac{\pi^2 * \lambda}{3 * r_p} * 4 * \pi * r_p^2 * (T_I - T_S)
\]  

(a.7)

In analogy with convective heat transfer in a liquid phase, the first term on the right hand side of eq. (a.7) is called the (modified) heat transfer coefficient in a sphere \( h \). The right hand side of eq. (a.7) can be simplified and rewritten in terms of \( T_s \) and \( T_L \):

\[
h * a_p * (T_I - T_S) = h * a_p * (T_L - T_S)
\]  

(a.8)

where \( a_p \) is the surface area of the solid particle, \( h \) is the heat transfer coefficient in the solid phase

\[
h = \frac{\pi^2 * \lambda}{3 * r_p}
\]  

(a.9)

and \( \lambda \) is the thermal conductivity.
chapter 8

A GENERAL CONTROL STRATEGY FOR
HYDRAULIC PACKED BED WASH COLUMNS

Abstract

Hydraulic packed bed wash columns are continuous solid/liquid separators, which combine a virtually complete crystal/mother liquor separation with a highly efficient washing action at high throughput. A control strategy for these columns has been developed. Optimal set-points for the bed and the wash front height were determined. The shape of the wash front, dependent on its level and the geometry of the filters in the wash column, has been monitored and the results were correlated to flow simulations. Irreversible consolidation of the moving crystal bed unexpectedly occurred in the start-up phase of the experiments and this phenomenon is discussed here. Finally, design considerations on hydraulic wash columns are briefly outlined.

P.J. Jansens, O.S.L. Bruinsma, G.M. van Rosmalen and R. de Goede
8.1 INTRODUCTION

Wash columns can be applied as the final purification step in fractional suspension crystallization processes aimed at *ultra-purification* of organic compounds and in freeze-concentration processes. Wash columns combine an efficient solid/liquid separation with a countercurrent washing action. Additional purification of the crystal phase through sweating and recrystallization may also occur. Three types of wash columns can be distinguished after the different mechanisms applied to transport the crystals: mechanical, gravitational and hydraulic (chapter 1). In hydraulic wash columns a liquid pressure drop is the driving force for bed transport and this mechanism is utilized in several industrial designs a.o. Phillips Petroleum [1], Brennan-Koppers [2] and TNO-Thijssen [3]. Basically these industrial designs only differ in the position of the filtrate removal filters.

*principle of operation*

The principle of a hydraulic wash column is illustrated by figure 8.1 (TNO-Thijssen type). A slurry is fed under hydraulic pressure at the top of the column (1). After a short zone of rapid thickening (2), the crystals are caught in a dense downward moving bed (3,4). The residual mother liquor flows through the crystal bed and leaves the column via filters (6) which are positioned in filter tubes (5). In other hydraulic wash column designs the filters are positioned in the wall of the column which is unfavourable from a scale-up point of view. The drag of the mother liquor on the crystal bed effectuates the bed transport. A so-called steering pump (8) is used to recycle filtrate (residual mother liquor) into the feed line. In this way the hydraulic bed transport force can be influenced without alteration of the feed condition. At the bottom of the column a rotating knife (9) scrapes off the descending crystal bed. The product crystals are removed from the reslurry chamber underneath the knife by a liquid flow and are subsequently molten in the melter (10). Part of the melt is withdrawn as product and the rest is refluxed to the
reslurry chamber as wash liquid. Due to a small overpressure in the reslurry chamber, which is controlled with the product valve (11), the wash liquid ascends in the column thus providing a washing action countercurrent to the direction of bed movement. The wash liquid does not leave the column via the filters but recrystallizes beforehand on the colder crystal bed thus producing a sharp wash front (7) beneath the filters. The released heat of crystallization heats the crystals to near their melting point. The wash front marks steep gradients in temperature, liquid composition and bed porosity.

![Diagram of hydraulic wash column](image)

**Figure 8.1: Principle of a hydraulic wash column (TNO-Thijssen type)**

1 = column wall, 2 = settling zone, 3 = bed level,
4 = moving crystal bed, 5 = filter tube, 6 = porous filter,
7 = wash front level, 8 = steering pump, 9 = rotating knife
10 = melter, 11 = product valve
**column characteristics**

It is important to keep the wash front at a constant level between the knife and the filters. If the wash front is too low the product will become polluted with impure mother liquor. If it is too high the wash liquid (molten product) will be lost via the filters or the filters will be blocked due to the crystallization of wash liquid. In order to guarantee the desired product purity and to optimize the design of the bottom section (below the filters), a minimum wash front height needs to be determined for various operating conditions and given feed conditions and a control strategy must be devised to keep the wash front at its set-point.

In this respect, knowledge on the shape of the wash front in relation to the particular feed, the geometry of the filters, the operating conditions and the height of the front in the column is also of crucial importance.

Another essential parameter is the bed height because the driving force for bed transport depends on the liquid pressure drop over the top section of the bed (above the filters). The demand to design a compact wash column and the need for sufficient driving force may be contradictory. It is therefore necessary to determine the minimum admissible bed height and to devise a control strategy to keep this level constant.

**objective**

The present study was primarily focused on the development of a control strategy for the bed and the wash front height, which is generally applicable to hydraulic wash columns. For this purpose experimental data, obtained with a C8-aromatic mixture and a caprolactam/water mixture in two pilot scale wash columns, are combined with results on the compressive stress distribution (chapter 6), the purification mechanism (chapter 7) and the streamlines in hydraulic wash columns. Design considerations e.g. on the position of the filters and the dimensions of the bottom and top sections surfaced in the course of this study and are outlined in this chapter as well.
8.2 EXPERIMENTAL PROCEDURE

Two series of experiments were performed (i) to select the operating parameters best suited to control the bed and the wash front height, (ii) to investigate the effect of the product throughput and the wash front height on the product purity and (iii) to determine the shape of the wash front at different heights in the column and under various operating conditions.

The unit, used for the first series of experiments, comprises a scraped cooling crystallizer and a pilot scale wash column (TNO-Thijssen type). The height of the wash column is 1 m and the columns internal diameter is 0.156 m. The column contains six filter tubes with an outer diameter of 0.02 m. In some experiments three filter tubes were removed to study the effect of the filter geometry on the shape of the wash front. The column wall is made of glass. A filter tube consists of a stainless steel tube, a porous filter and massive teflon bottom end. The porous filters are positioned 0.265-0.295 m above the knife. Four thermocouples were installed at different axial and radial positions in the bottom section of the column (fig. 8.2). It proved necessary to incorporate the thermocouples in smooth teflon bars which cover the whole length of the column to avoid disturbance of the wash front.

The standard feedstock, used in the first series of experiments, was a C8-aromatic system, containing p-xylene (89.2 wt%), m-xylene (7.0 wt%), o-xylene (2.0 wt%), ethylbenzene (1.5 wt%) and toluene (0.3 wt%), from which p-xylene was crystallized by cooling at about 6 °C. The melting point of pure p-xylene equals 13.3 °C. In some experiments the feed stock was enriched with 5 wt% toluene. A minor quantity of red dye was added to the mother liquor in order to visualize the wash front. The average mass based crystal size in the feed slurry was 500 μm. Product samples were analyzed using gas chromatography (GC).
control strategy for hydraulic wash column

The operating conditions (first series) were varied as follows:

- **Feed flow:** 400-600 [l/h]
- **Product flow:** 35-100 [l/h]
- **Steering flow (filtrate recycle):** 0-600 [l/h]
- **Bed height ($H_{bed}$):** 0.35-0.75 [m]
- **Wash front height ($H_{wash}$):** 0.025-0.25 [m]
- **Revolution rate of the knife (N):** 8-75 [rpm]

The second series of experiments was performed with a caprolactam/water system in a wash column with a diameter of 0.06 m. The column contained only one filter tube. The feedstock was a binary mixture and contained approximately 2.5 wt% water. Product samples were analyzed on their water content by Karl Fischer titration. The unit is equipped with pressure indicators.

---

**Figure 8.2:** Position of the thermocouples (T1-T4) in the pilot wash column
8.3 RESULTS

Unless described otherwise, the data reported in this section were obtained from
the first series of experiments with the C8-aromatic mixture in the 0.156 m wash
column. The reported phenomena and trends were also found in the experiments
with the caprolactam/water mixture in the 0.06 m wash column but the stability of
this operation was unsatisfactory. Details on the results obtained with the
caprolactam/water mixture are given in appendix I.

8.3.1 identification of control parameters

Three devices may be used for control purposes: the steering pump, the knife and
the product valve (see fig. 8.1). The feed pump is not usable in this respect
because normally in industrial practice a constant throughput must be guaranteed.

The steering pump can be used to vary the flow rate of the mother liquor, which
flows through the top section of the bed, and consequently to alter the driving force
for bed transport. The driving force (F) can be calculated from eq. (8.1), assuming
that the difference in specific density of the solid and the liquid phase is negligible.
The derivation of eq. (8.1) was presented in chapter 6.

\[
\frac{F}{A_c} = \left( -\Delta P_{ls} \cdot D \right) \left( 1 - \exp \left( \frac{-4 \cdot K_I \cdot H_{ls}}{D} \right) \right)
\]

(8.1)

where the liquid pressure drop over the top section of the bed (\(\Delta P_{ls}\)) is given by the
Darcy law:

\[
\frac{\Delta P_{ls}}{H_{ls}} = -\frac{\varepsilon \cdot \eta \cdot V_L}{B_{ls}}
\]

(8.2)

In steady state the driving force is balanced by the upward drag force, exerted by
the wash liquid on the moving bed, and the supporting force of the knife. The effect
of the steering flow on the bed height can be anticipated from eqs. (8.1) and (8.2).
An increase of the steering flow leads to a larger pressure drop, an increase of the driving force and consequently to an increase of the bed transport rate. Since the supply rate of crystals is not affected by the steering flow, the bed height will begin to lower. The lowering of the bed level reduces the pressure drop over the top section of the bed and the driving force decreases until the force balance is restored and a new steady state is reached. Experiments confirmed the described effect of the steering flow on the bed height and showed that the steering flow has no lasting effect on the wash front height.

The cutting capacity of the knife at a certain revolution rate limits the product throughput of the wash column. The knife in the pilot plant wash column basically consists of a flat disc with three cutting edges. Its cutting capacity can be calculated from eq. (8.3):

$$\Phi_{cut} = 3 * h * (1 - e_{bw}) * \pi * N * L^2$$  \hspace{1cm} (8.3)

The porosity below the wash front may be estimated from eq. (8.4):

$$e_{bw} = e_{b} - (1 - e_{b}) * \left( \frac{C_p \cdot S \cdot (T_m - T_f)}{\Delta H_m} \right)$$  \hspace{1cm} (8.4)

Figure 8.3 demonstrates that the bed height, but not the wash front height, can be altered by means of the revolution rate of the knife. The quickness of the response of the bed height on abrupt changes of the revolution rate N depends on the difference between the supply rate of the crystals and the cutting capacity of the knife.
The **opening of the product valve** governs the pressure in the reslurry chamber. A pressure increase in the reslurry chamber causes an increase of the flow rate of the wash liquid and consequently the level of the wash front is raised. Figure 8.4 demonstrates how an increase of the pressure in the reslurry chamber, after 40 minutes, has a significant effect on the wash front height and a smaller effect on the bed height. Analogous to the earlier discussion on the effect of the steering flow, the increase of the pressure drop over the bottom section results in a larger drag force of the wash liquid and slows down the bed transport. Since the supply rate of crystals is not affected by the position of the product valve, the bed height will start to rise and consequently the feed pressure will increase until the force balance is restored.

Provided the supply rate of crystals is kept constant, control of the level of the wash front through partial opening and closing of the product valve does not have a long term effect on the product throughput of the wash column. The flow through
a valve is a function of the pressure drop over the valve and its flow resistance factor $K_w$:

$$\Delta P \propto K_w \frac{1}{2} \rho \left( \frac{Q}{A_r} \right)^2$$  \hfill (8.5)

Variations in the flow resistance of the product valve due to partial opening or closing are compensated in hydraulic wash columns by changes in the pressure in the reslurry chamber. During the experiments the wash front height could be adjusted with the product outlet valve to any desired level independent of the product throughput.

![Graph showing the effect of pressure on bed height and wash front level](image)

**Figure 8.4:** Effect of the pressure in the reslurry chamber on the bed height and on the wash front level

An increase of the bed height by a reduction of the revolution rate of the knife results in a strong increase in the compressive stress exerted on the crystal bed and the knife (chapter 6). It is better to control the bed height with the steering flow
which, as is argued above, does not have a (permanent) effect on the stress level. The product valve is the most suited parameter to control the wash front height. Figure 8.5 demonstrates how the bed height could be changed, by means of the steering pump, while the wash front height is kept constant using the product valve.

![Figure 8.5: Independent control of bed and wash front height](image)

### 8.3.2 purity of the product

The product purity was 99.93 ± 0.06 wt% during crystallization from the standard feedstock and proved to be independent of the product throughput (40-100 l/h) and the wash front level, which has been varied from 0.025 m to 0.25 m above the knife. Toluene was incorporated in the crystals with a distribution coefficient of 0.03 during crystallization from the enriched feedstock at 4.5 °C, which is in good agreement with the results of Van Koningsveld et al. [4] and De Goede [5]. The incorporated toluene is not removed from the crystals in the wash column. The residence time of the crystals in the bottom section amounts only a few
minutes and this is not sufficient to allow significant further purification of the crystal phase through sweating, recrystallization of the crystals or solid phase diffusion. Figure 8.6 displays experimental data and simulation results, which demonstrate the effect of the wash front level on the impurity content of the product (chapter 7). The simulation results were obtained with a purification model which is based on the assumption that displacement of adhering impure mother liquor by wash liquid and recrystallization of wash liquid determine the separation efficiency of a hydraulic wash column. Both experimental and simulation results indicate that a wash front height of 0.025 m is sufficient to achieve the optimum product purity. At lower wash front heights the impurity level of the product will distinctly exceed that of the feed crystals due to axial dispersion.

![Graph showing the effect of wash front level on impurity content.](image)

**Figure 8.6:** Effect of the wash front level on the product (im)purity
(o-X = o-xylene; EB = ethylbenzene; TOL = toluene)
8.3.3 **Shape of the wash front**

To determine the shape of the wash front, it was slowly and repeatedly lowered and raised in such a way that two thermocouples at the same height but at different radial positions were passed (fig. 8.2). The thermocouples positioned 0.105 m above the knife detected similar temperature profiles at the same time upon passing of the wash front. Furthermore, the wash front observed through the glass column wall was a horizontal line. Measurements and visual observation indicate that the wash front is flat at 0.105 m above the knife.

At 0.205 m above the knife the wash front proved not to be flat. The temperature measurements indicated a deep pit at the centre of the column. Also, a wave pattern could be observed through the glass wall, which was more pronounced with the three tubes than with the six filter tubes installed. Such a wave shaped wash front can be explained by the flow pattern of the mother liquor in the region of the filters.

Figure 8.7A shows the streamlines and the expected wash front shapes, at two heights in the bottom section, for a hydraulic wash column with separate filter tubes (TNO-Thijssen type). Near the filters, the wash front is likely to be (wave) shaped after the stream lines and the pressure contours (not shown here) of the mother liquor. The shape of the wash front near the filters depends on the position of the filters and on the available filter surface area, the permeability of the top section of the packed bed, the velocity of the mother liquor and on the viscosity of the mother liquor. Figure 8.7B demonstrates a more pronounced wave pattern in the wash front, when the filters are positioned in the wall (Brennan-Koppers type) and the surface area of the filters is reduced. In figures 8.7A and 8.7B the diameter of the wash columns and the flow of mother liquor were kept the same. The flow patterns (2-dimensional) were calculated with commercial computational fluid dynamics software [6].

To assure a flat wash front, it must be kept at a sufficient distance from the filter region. With the C8-aromatic mixture in the 0.156 m wash column, containing 6
control strategy for hydraulic wash column

filter tubes evenly distributed over the cross-section of the column, the wash front must be kept at least 0.10 m below the filters.

Figure 8.7: Effect of the flow pattern of the mother liquor and the wash front level on the wash front shape in hydraulic wash columns with separate filter tubes (A) and with filters in the wall (B)
8.3.4 consolidation of the crystal bed

A quick and irreversible consolidation of the crystal bed in the wash column occurred during or shortly after the start-up phase, when the steering flow and the wash front height were both significantly increased at the same time. This phenomenon is relevant for a control strategy because the stability of the wash front improved upon consolidation. In the unconsolidated state the presence of the teflon bars with thermocouples more easily caused large perturbations of the wash front.

Since the permeability (B) of a crystal bed is directly related to the packing of the crystals this parameter is used to quantify the consolidation phenomenon.

The permeability of the top section of the bed (B_{tu}) can be calculated from eq. (8.2) when the porosity of the top section is assumed to be 0.40. When using eq. (8.2), to calculate the bed permeability below the wash front (B_{bw}), the porosity must be taken from eq. (8.4) and the wash liquid flow can be estimated from a simplified heat balance:

\[
\frac{\Phi_{wash}}{\Phi_P} = \frac{C_{\mu s}(T_m - T)}{\Delta H_m}
\]  
(8.6)

Figure 8.8 depicts the consolidation phenomenon as an abrupt change in permeability, particularly of the top section. In the first 45 minutes, the permeability of the top section of the bed amounted to approximately 5.5*10^{-11} m². At that time consolidation was effectuated by simultaneously increasing the steering flow and raising the wash front height. These control actions caused in fact a sudden increase of the compressive stress on the crystal bed which triggered its consolidation. After consolidation the permeability amounted to 1.4*10^{-11}m² and it remained constant at this low value even when the steering flow and the wash front height were reduced to their original level.
control strategy for hydraulic wash column

Figure 8.8: Consolidation of the crystal bed

The permeability below the wash front is about $2.0 \times 10^{-12} \text{m}^2$ after consolidation. This low value of $B_{bw}$ is caused by the recrystallization of wash liquid on the cold crystals. The ratio of $B_{ts}$ to $B_{bw}$ equals 7, which can not be explained from a porosity decrease alone. The Kozeny-Carman relation, given by eq. (8.7), predicts a permeability ratio of 1.56 when $\varepsilon_{ts} = 0.40$ and $\varepsilon_{bw} = 0.36$.

$$B \propto \frac{e^3}{(1-e)^2} \quad (8.7)$$

Apparently, the wash liquid recrystallizes preferentially in the more narrow openings between the crystals which results in the very low permeability below the wash front.
8.4 CONTROL STRATEGY

Devising a control strategy for hydraulic wash columns involves the making of a well considered choice of the set-points of the bed and wash front heights and the design of an operation scheme to keep both heights at their set-point. The arguments on the choice of the set-points and the developed control strategy are general but the actual values of the set-points given below are specific to processing of the C8-aromatic system in a TNO-Thijssen type hydraulic wash column (separate filter tubes).

8.4.1 set-point wash front height

Earlier work showed that the wash front must be kept as low as possible in order to minimize the compressive stress on the bed (eq. 8.2) and the mechanical stress on the knife (chapter 6). Flow simulations should be used to determine the level in the bottom section where the wash front is flat. For the C8-aromatic mixture in the 0.156 m wash column, the wash front proved to be flat at 0.10 m distance from the filters. From the product purity analysis presented above, it followed that the front must be kept at least 0.025 m above the knife. At very low wash fronts (0.025-0.07 m) and at low product throughput (40 l/h) some temperature fluctuations were registered by the thermocouples positioned 0.105 m above the knife. This indicates instabilities in the bed caused by the presence of the rotating knife and facilitated by the very low compressive stresses under these conditions in the lower part of the crystal bed (chapter 6). The instabilities do not affect the flatness of the front nor do they affect the product purity but to assure an unambiguous detection of the wash front height with thermocouples or other sensors it is advised to set the wash front height at 0.10 m above the knife.
8.4.2 set-point bed height

The bed height must be kept as low as possible to minimize the wall friction (eq. 8.2) and the equipment dimensions. A reduction of the bed height can be compensated by an increase of the steering flow to maintain sufficient driving force.

There is however a minimum bed height as came forth during the experiments with the caprolactam-water system in the 0.06 m wash column. When during these experiments the bed height became too low, channelling occurred from the top of the bed to the filters and the transport of the bed immediately stopped. To avoid such problems of channel formation the bed height should be kept at sufficient distance from the filters. The value of this distance critically depends on the position of the filters in the hydraulic wash column while an even distribution of the feed crystals over the cross-section is essential. In the experiments with the 0.06 m wash column, which contained only one filter tube and featured maldistribution of the feed crystals, the minimum bed height above the filters was 0.20 m. In the experiments with the 0.156 m wash column, which contained 6 filter tubes and featured a nearly homogeneous distribution of the feed crystals, a minimum bed height of 0.10 m above the filters sufficed.

8.4.3 control scheme

The proposed control scheme is presented in figure 8.9. The wash front height must be controlled via the product valve because it is the only parameter suited for this purpose. The bed height should preferably be controlled with the steering flow because control via the revolution rate of the knife results in significantly larger compressive and mechanical stresses (chapter 6). However, when the bed height becomes too low and the steering flow is zero, a reduction of the revolution rate of the knife seems the only remaining option. To avoid the necessity of bed height control with the knife preconcentration of the feed slurry can be considered.
Figure 8.9: Control scheme for hydraulic packed bed wash columns
8.4.4 automation

The temperature gradient over the wash front can be utilized to measure the level of the wash front in the column. In several experiments, the output signal of a thermocouple, positioned 0.105 m above the knife, was sent to a Proportional Integral controlling device which ruled the position of the product valve. The set-point was chosen at 11 °C. If the thermocouple registered a lower temperature the PI controller gradually shut the product valve and the opposite occurred when the temperature was too high. Using this simple strategy the 0.156 m wash column run successfully for 30 hours on end without any interference. The control strategy proved to be robust to stepwise changes in the steering flow, the feed flow, the feed temperature and the revolution rate of the knife.

![Graph showing Hbed, Hwsh, and product flow over time.]

**Figure 8.10: Robust PI-control of bed and wash front height**

Figure 8.10 demonstrates how the system reacts to an increase in the production capacity (after 20 minutes) and a 5 minutes blockage of the product outlet (after...
117 minutes). The bed height was not controlled during this experiment. Until now this level was controlled with the steering flow based on visual detection (fig. 8.5). A sensor for automatic control is currently being developed.

8.5 DESIGN CONSIDERATIONS

In a hydraulic wash column five different sections can be discerned, which all require a minimum height. These sections are discussed here from the bottom to the top of the wash column.

Section 1 comprises the washed part of the bed from the knife to the wash front. The minimum height of this section can be calculated with a purification model and depends on physical properties of the mother liquor and the wash liquid, morphology and size of the crystals and on the operating conditions. Purification models for packed bed wash columns, based on different assumptions, were presented by Player [7], by Moyers and Olson [8], and in chapter 7 of this thesis. For the C8-aromatic system, a distance of only 0.025 m is sufficient to achieve the optimal product purity as demonstrated above. To avoid irregularities in the packing of this part of the bed, a safe wash front height of 0.10 m is recommended.

Section 2 between the wash front and the filters should be large enough to assure a flat wash front. The height of this section can be determined through computational fluid dynamics and depends on the surface area and the position of the filters in the column, the velocity and the viscosity of the mother liquor and on the permeability of the crystal bed. In the experiments with the C8-aromatic system in the 0.156 m wash column equipped with 6 filter tubes, a height of 0.10 m sufficed for this section.

Section 1 and 2 together make up the bottom section indicated in figure 8.2.
Section 3 involves the filters. In general, it is better to use separate filter tubes, which can be evenly distributed over the whole cross-section of the column, rather than to place the filters only in the wall of the column. Usage of separate filter tubes is also favourable from a scale-up point of view because the distance which has to be overcome by the mother liquor to travel to the filters in radial distance decreases. The radial pressure drop does not contribute to the driving force for bed transport but on the contrary contributes to larger wall friction. Optimization of the height, the number and the position of the filter tubes and determination of the minimum distance between the filters and the wash front can be done using computational fluid dynamics (i.e. Fluent [6]). A sufficient filter height is usually 0.03–0.05 m.

Section 4 is the top section of the bed, which provides the driving force for bed transport. Too low bed heights may lead to cracks in the top section, as occurred during the experiments with the caprolactam/water system. A minimum height of 0.10 m is recommended here.

Section 5 is the settling zone above the bed. In this section the falling feed crystals are homogeneously distributed over the whole cross-section of the column. Also this zone acts as a buffer volume to prevent plugging of the feed inlet in case the bed height rises. Roughly the height of this section should be 0.10–0.15 m.

The mechanical stresses exerted on the knife and the friction forces exerted on the column wall can be predicted from a compressive stress analysis. Stress models were presented by Schneiders and Arkenbout [9] and in chapter 6 of this thesis.
8.6 CONCLUSIONS

A control strategy, generally applicable to hydraulic wash columns, has been developed. The control strategy is based on the control of the wash front height using the product valve and on the control of the bed height via the steering pump or the knife. The bed height and the wash front height can be controlled independently by the combined actions with the product valve and the steering pump. Based on the developed control strategy the column operation could be automated using a simple PI controller and a temperature sensor. The automated operation was stable with respect to significant stepwise changes in the feed conditions and proved robust when the product removal was blocked.

Notation

\begin{tabular}{lll}
\text{A}_c & cross-sectional surface area wash column & [m^2] \\
\text{A}_V & cross-sectional surface area open valve & [m^2] \\
\text{B} & permeability of the packed bed & [m^2] \\
\text{C}_{p,s} & specific heat of the solid phase & [kJ/kg.K] \\
\text{d} & downstream tube diameter & [m] \\
\text{D} & hydraulic diameter of the wash column & [m] \\
\text{D}_{ax} & axial dispersion coefficient & [m^2/s] \\
\text{F} & driving force for bed transport & [N] \\
\text{h} & height of a cutting edge on the knife & [m] \\
\text{ΔH}_m & heat of crystallization & [kJ/kg] \\
\text{H} & height or level in the column & [m] \\
\text{K}_f & wall friction factor & [\cdot] \\
\text{K}_W & flow resistance factor & [\cdot] \\
\text{L} & length of the cutting edges on the knife & [m] \\
\text{N} & revolution rate of the knife & [s^{-1}] \\
\text{ΔP} & liquid pressure drop & [Pa] \\
\text{T}_f & feed temperature & [K] \\
\text{T}_m & melting point temperature & [K] \\
\text{V}_{L} & actual liquid velocity relative to the bed movement & [m/s] \\
\text{<V}_{P}> & average downstream liquid velocity & [m/s] \\
\end{tabular}
Greek letters

ε  porosity or void fraction of the packed bed  [wt%]  
Φ_{cut} cutting capacity of the knife  [m³/s]  
Φ_{p} product flow, production capacity  [m³/s]  
η viscosity of the liquid phase  [Pa.s]  
ρ specific density  [kg/m³]

Subscripts

bw below the wash front
bed crystal bed (from knife to top)
ts top section of the crystal bed
wsh wash front level

References

Appendix: caprolactam/water separation in a hydraulic wash column

The separation of caprolactam crystals from a mother liquor, which is mixture of caprolactam and water, is more difficult than the purification of p-xylene crystals in wash columns, because of the high viscosity of the mother liquor. Pure liquid caprolactam has a viscosity of 12.5 mPa.s whereas a binary mixture containing 7 wt% water has an even higher viscosity of 17 mPa.s due to the formation of hydrogen bonds. The viscosity of p-xylene equals 0.7 mPa.s. A high viscosity inevitably leads to higher pressures and compressive stresses as can be seen from eqs. (8.1) and (8.2).

It proved possible to operate the 0.06 m wash column with the caprolactam/water mixture but some difficulties were encountered. The maximum production capacity amounted to 6 l/h but under this condition no clear wash front developed indicating an incomplete separation and purification. By gradually closing the product valve a wash front started to appear. The appearance of the wash front resulted however, in an increased pressure at the top of the column and soon the safety-limit for the glass column wall (350 kPa) was reached. In this situation there was no alternative but to reduce the feed flow. Finally the column could be operated with a clear wash front 0.10 m above the knife but only at very low product throughput (0.1-0.5 l/h). The low throughput resulted in a shockwise transport of the bed and caused a scala of practical difficulties (i.e. blockage of the inlet tubes due to settling of crystals).

Unfortunately, it was not possible to achieve a steady state operation with a stable wash front and for this reason the product purity did not exceed 99.7 wt%.
control strategy for hydraulic wash column

Nevertheless, it could be demonstrated that the control parameters (steering pump, knife and product valve) had exactly the same effect on the bed and wash front height as described for the C8-aromatic mixture in the 0.156 m wash column. Technically, it seems to be possible to purify caprolactam crystals in hydraulic packed bed wash columns but only at a high pressure level.
SUMMARY

Fractional crystallization (FC) is a separation technique, which can be applied for large scale ultrapurification of organic compounds in an economically favourable and environmentally safe way. Chapter 1 of this thesis presents an extensive overview, which covers basic concepts as well as industrial applications, of the field of FC. In this thesis a new FC process is proposed, consisting of a GMF Cooling Disc Crystallizer (CDC) followed by a TNO-Thijssen wash column.

Chapter 3 describes a pilot plant of this FC process, which is designed and constructed at the Laboratory for Process Equipment of the Delft University of Technology. A mixture of caprolactam and water (0-8 wt%) was used in experimental programs with the pilot plant and a bench scale batch crystallizer at the T.U. Delft. The same feed stock was also used in single crystal growth experiments performed at the University of Nijmegen. A C8-aromatic mixture, consisting mainly of p-xylene, was used in a separate experimental program, which was focused on the TNO-Thijssen wash column and has been performed with a pilot unit from TNO-IMET at Apeldoorn.

Chapter 4 discusses the effect of crystallization conditions on the morphology and permeability (filterability) of caprolactam crystals. Single crystal growth experiments revealed that elongated (needle like) crystals were formed under two conditions: (i)
high water content (8 wt%) and fast growth rates (10⁻⁶ m/s) and (ii) pure melt and 
low growth rates (10⁻⁶ m/s). Batch experiments with a pure melt yielded needle like 
crystals but no elongated crystals were found upon growth with a water rich feed 
stock. The experiments with the pilot CDC did not yield significantly elongated 
crystals. Variations in the permeability of the crystalline product from the CDC 
cannot be explained by changes in morphology but must be contributed to changes 
in the crystal size distribution.

**Chapter 5** presents the results from the optimization of the operating conditions of 
the CDC with respect to the permeability of the crystalline product. Furthermore, an 
integral model description of a Cascade of Crystallizers with Backmixing (CCB) is 
developed. Optimum product permeability was achieved at high crystal content 
(35 wt% in the last comp. of the CDC), high coolant flow (500 l/h), low water 
content (1-3 wt%) and long residence time (nearly 2 hours). Agreement between 
the experimental data and CCB simulations is quite satisfactory.

**Chapter 6** presents an analytical model which can be used to predict compressive 
stresses exerted on the crystals and equipment during the operation of a hydraulic 
packed bed wash column. Experimental support for the model was obtained with 
the C8-aromatic system using the pilot unit from TNO-IMET. It was found that an 
increase of the product throughput, an increase of the wash front height and a 
reduction of the revolution rate of the knife result in higher compressive stresses, 
whereas the recirculation of filtrate to the feed inlet (the steering flow) does not 
affect the stress level.

**Chapter 7** deals with the purification process in hydraulic wash columns. The effect 
of operating conditions on the axial temperature profile and the product purity was 
experimentally determined with the C8-aromatic system using the pilot unit from 
TNO-IMET. Product purity and temperature profile proved to be independent on the
product throughput and the wash front height within the experimental ranges. A model was developed which can be used to calculate axial profiles in temperature, concentration and bed porosity dependent on the operating conditions. Model predictions are in good agreement with the experimental data. The purification process in the TNO-Thijssen wash column is governed by displacement washing, recrystallization of wash liquid and axial dispersion.

Chapter 8 presents a general control strategy for hydraulic wash columns. The strategy is based on control of the bed height with the steering pump and control of the wash front level using the product valve. Selection criteria for the settings of the bed height and the wash front level are formulated using the compressive stress model (chpt. 6), the purification model (chpt. 7) and computation of the flow pattern of the mother liquor in different types of hydraulic wash columns. The control strategy was applied to automate the operation of the pilot wash column of TNO-IMET.

In the appendix to chapter 8 the results on caprolactam/water separation in the TNO-Thijssen wash column, obtained with the T.U. Delft pilot plant are summarized. It proved possible to operate the column with a clear wash front but only at very low product throughput (40-200 kg/m²h) and relatively high feed pressure (350 kPa). The low product throughput resulted in a shockwise transport of the crystal bed and caused many practical difficulties. It was not possible to achieve a steady state operation and for this reason the product purity amounted only 99.7 wt%. Experiments with a new pilot wash column, which can be operated at higher pressures, are necessary to decide on the technical feasibility of caprolactam purification with the FC process proposed in this thesis.
SAMENVATTING

Fraktioneerende kristallisatie is een scheidingstechniek, waarmee grootschalige ultrazuivering van organische grondstoffen op een economische en milieu-vriendelijke manier kan worden uitgevoerd. Hoofdstuk 1 van dit proefschrift presenteert een uitgebreid overzicht, dat zowel basisprincipes als industriële toepassingen omvat, van het vakgebied der fraktioneerende kristallisatie (FK). In dit proefschrift wordt een nieuw FK proces voorgesteld, dat bestaat uit een schijven-kristallisator (CDC) van de GMF-Gouda gevolgd door een hydraulische TNO-Thijsse waskolom. Hoofdstuk 3 beschrijft een semi-industriële proefinstallatie (hierna "pilot plant" genoemd) van dit proces, die is ontworpen en gebouwd in het laboratorium Apparatenbouw voor de ProcesIndustrie van de Technische Universiteit Delft. Een mengsel van caprolactam en water (0-8 gew.%) werd gebruikt voor experimenten met de pilot plant en met een kleinschalige "batch" kristallisator. Hetzelfde mengsel werd gebruikt voor kristalgroei-experimenten, die werden uitgevoerd aan de Katholieke Universiteit Nijmegen. Een mengsel van C8-aromaten, dat hoofdzakelijk uit p-xyleen bestond, werd gebruikt in een apart experimenteel programma, waarin de TNO-Thijsse waskolom centraal stond en dat werd uitgevoerd met een pilot plant van TNO-IMET in Apeldoorn.
Hoofdstuk 4 behandelt het effect van de kristallisatiecondities op de morfologie en de permeabiliteit (filtrerbaarheid) van caprolactam kristallen. De kristalgroei-experimenten toonden aan dat langwerpige (naaldvormige) kristallen werden gevormd bij twee condities: (i) hoog watergehalte (8 gew.%) en hoge groeisnelheid ($10^6$ m/s) en (ii) zuivere smelt en lage groeisnelheid ($10^6$ m/s). De batch experimenten met een zuivere smelt leverden naaldvormige kristallen op maar bij experimenten met een waterrijke voeding werden geen langwerpige kristallen gevormd. De experimenten met de pilot CDC leverden geen langwerpige kristallen op. Verschillen in de permeabiliteit van het kristalline produkt van de CDC kunnen niet worden verklaard door morfologische veranderingen maar worden veroorzaakt door verschillen in de kristalgrootteverdeling.

Hoofdstuk 5 presenteert de resultaten van de optimalisatie van de operatiecondities van de CDC met betrekking tot de permeabiliteit van het kristalline produkt. Er wordt een integrale modelmatige beschrijving van het kristallisatieproces in een cascade van kristallisatoren met terugmenging (CCB model) voorgesteld. De optimale produktpermeabiliteit werd bereikt bij een hoog kristalgehalte (35 gew.% in het laatste compartiment van de CDC), een hoog koeldebiet (500 l/h), een laag watergehalte (1-3 gew.%) en een lange verblijftijd (bijna 2 uur). De overeenkomst tussen de meetgegevens en de CCB-simulaties is bevredigend.

Hoofdstuk 6 beschrijft een analytisch model dat kan worden gebruikt om de vaste-stofdruk, die tijdens de operatie van een hydraulische waskolom op kristallen en apparatuur wordt uitgeoefend, te voorspellen. Het model wordt ondersteund door een serie experimenten, die werd uitgevoerd met het C8-aromatische mengsel in de pilot plant van TNO-IMET. Er werd gevonden dat een verhoging van de produktdoorzet, een verhoging van het wasfront en een verlaging van het mestoerental resulteren in een verhoging van de vaste-stofdruk in de kolom.
Recirculatie van het filtraat naar de voedingstoevoer (het stuurdebiet) blijkt geen effect op de (maximale) vaste-stofdruk te hebben.

**Hoofdstuk 7** behandelt het zuiveringsproces in hydraulische waskolommen. Het effect van de operatiecondities op het axiale temperatuurprofiel en op de produktzuiverheid werd onderzocht aan de hand van experimenten met het C8-aromatische mengsel in de TNO-IMET pilot plant. De produktzuiverheid en het axiale temperatuurprofiel bleken onafhankelijk te zijn van de produktdoorzet en de wasfronthoogte. Een model wordt gepresenteerd waarmee temperatuur-, concentratie- en porositeitsgradienten kunnen worden berekend in afhankelijkheid van de operatiecondities. De modelvoorspellingen zijn in goede overeenkomst met de meetgegevens. Het zuiveringsproces in een TNO-Thijssen waskoloom wordt bepaald door wassen, rekristallisatie van wasvloeistof en axiale dispersie.

**Hoofdstuk 8** presenteert een algemene regelstrategie voor hydraulische waskolommen. De strategie is gebaseerd op regeling van de bedhoogte met de stuurpomp en regeling van het wasfron niveaumet de produkt klep. Selectie criteria voor de instelwaarden van de bedhoogte en het wasfront niveau worden geformuleerd met behulp van het vaste-stofdrukmodel (hoofdstuk 6), het zuiveringsmodel (hoofdstuk 7) en simulaties van het stromingspatroon van de moederloop in verschillende typen soorten hydraulische waskolommen. De regelstrategie werd gebruikt om de operatie van de pilot waskoloem van TNO-IMET te automatiseren.
Samenvatting

In de bijlage van hoofdstuk 8 worden de resultaten met betrekking tot caprolactam/water scheiding in een TNO-Thijssen waskolom kort samengevat. De experimenten zijn uitgevoerd met de pilot plant van de T.U. Delft. Het bleek mogelijk om de waskolom te bedrijven met een duidelijk wasfront maar alleen met een lage produktdoorzet (40-200 kg/m²h) en bij een relatief hoge voedingsdruk (350 kPa). De lage produktdoorzet had een schoksgewijs bedtransport tot gevolg en veroorzaakte veel praktische problemen. Het was echter niet mogelijk om een stabiele stationaire operatie te bereiken waardoor de produktzuiverheid niet meer dan 99,7 gew.% bedroeg. Experimenten met een nieuw te bouwen pilot waskolom, die kan worden bedreven met hogere voedingsdrukken, moeten definitief uitwijzen of caprolactam zuivering met het voorgestelde FK proces technische haalbaar is.
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LIST OF PUBLICATIONS


publ ications


CURRICULUM VITAE

Peter Jansens
geboren op 9 september 1966 te Roosendaal
gehuwd met Rian Meesters

1978-1984  **Atheneum B**, Gertrudislyceum te Roosendaal

1984-1989  **Scheikundige Technologie**, Technische Universiteit Delft
  *Afstudeerproject*: continue precipitatie van jarosiet,
                    onder leiding van Prof. dr. ir. G.M. van Rosmalen

1989-1994  **Promotie**, Technische Universiteit Delft,
           faculteit der werktuigbouwkunde en maritieme techniek,
           laboratorium apparatenbouw voor de procesindustrie
           *Onderwerp*: fraktioneerende suspensie kristallisatie
           *Promotoren*: Prof. dr. ir. G.M. van Rosmalen
                          Prof. dr. ir. J. de Graauw
                          Dr. ing. O.S.L. Bruinsma

Mei 1994  **Associate Research Engineer** bij Shell Research BV
           (Koninklijke/Shell Laboratorium Amsterdam)

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