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Using complex layer melt crystallization models for the optimization of hybrid distillation/melt crystallization processes

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ABSTRACT

Layer melt crystallization is a highly selective method for the separation of narrow boiling mixtures which are difficult to separate with conventional separation techniques like distillation due to low driving forces. Contrawise, layer melt crystallization has the drawback of limited capacity due to the direct connection between crystal product and required cooled surface. Here, the combination of the high throughput distillation and highly selective layer melt crystallization into an integrated hybrid process can lead to enormous benefits. Since the separation efficiency of the crystallization is not predictable, it has to be described with empirical correlation. Here, studies from literature use strongly simplified correlations by, e.g. assuming complete separation. This bears the serious risk of overestimating the efficiency of the hybrid process. Further, the effective post purification step sweating was not implemented into hybrid processes in studies from literature. This study fills this gap in literature. A distillation/melt crystallization hybrid process is optimized by realistically describing crystallization separation efficiency and by implementing sweating. The required crystallization models are presented and experimentally validated. The optimization of the hybrid process is done with different modelling depths and the results underline impressively the importance of the adequate description of the crystallization separation efficiency.

1. Introduction

Layer melt crystallization is a proven and highly selective method for the separation of azeotropic or narrow boiling mixtures whereby one component is primarily crystallizing on a cooled surface [1–4]. It has gained high importance in the last decades and is applied for various industrial processes like the separation of xylene mixtures or the purification of naphthalene [5–8].

In particular, layer melt crystallization can technically be realized as a dynamic and a static process. In the dynamic case, the crystals grow from a well-mixed melt caused by, e.g. stirring or pumping [9] whereby a circulation of the melt in static case is, due to the absence of mixing devices, only induced by natural convection [9–11]. The high degree of mixing in the dynamic case leads to a high mass transport at the crystal surface and a good transportation of the impurities into the bulk of the melt [12]. This results, compared to the static case, to higher separation efficiencies at similar or even faster crystal growth rates [12–14].

A proven and applied dynamic layer melt crystallization technique is the falling film crystallization [4,10]. Here, the crystals grow from a thin liquid film which flows down a cooled cylindrical surface. Due to its simple setup, falling film crystallization is a mechanically robust and reliable unit separation which ensures a facile solid–liquid separation [2,7,8,15]. Further, gained data from laboratory experiments generally meet the needs for the development of multi-ton industrial applications [4,13], which mainly has two reasons. Firstly, the hydrodynamics of the liquid film can be characterized via dimensionless numbers and secondly, the scale-up is realized by simply numbering up the cooled surface [3,4].

A drawback of the falling film technology is the direct correlation between the amount of crystal product and the cooled surface area. Consequently, falling film crystallization has a limited capacity compared to high throughput separation techniques like distillation. In turn, the separation of narrow boiling mixtures by distillation is difficult due to low driving forces which leads to a high level of required stages and therefore high investment and operating costs [16]. By using synergetic effects of the high capacity of distillation and the high selectivity of melt crystallization, the

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Notation

Roman symbols

A	freezing rate, surface area [m^2]
a	constant of parabolic temperature profile in crystal layer [K/m^2]
b	constant of parabolic temperature profile in crystal layer [K/m]
c	constant of parabolic temperature profile in crystal layer [K]
c_p	heat capacity [kJ/kg/K]
D	diffusion coefficient [m^2/s]
D_{AB}^{∞}	diffusion coefficient of A in B in highly diluted mixtures [m^2/s]
e	constant in parabolic approach of Wellinghoff
f	constant in parabolic approach of Wellinghoff
H	height of falling film crystallizer [m]
$\dot{H}_{fus}^{SL}$	heat of fusion per time [kJ/s]
K	exponential part of the dimensionless number from Wellinghoff
k	thermal diffusivity [m^2/s]
k_{diff}	differential distribution coefficient
k_{int}	integral distribution coefficient
$k_{int,aSW}$	integral distribution coefficient after sweating
$k_{int,bSW}$	integral distribution coefficient before sweating
m	mass [kg]
$\dot{m}$	mass flow of falling film [kg/s]
Nu	Nusselt number
P	parachor [cm^3 mN/mol/m]
Pr	Prandtl number
$\dot{Q}^{cr}$	heat flow through crystal layer [W]
R	ideal gas constant [kJ/kg/K]
R	thermal resistance [K/W]
r	radius [m]
r_{cf}	inner radius of falling film crystallizer [m]
$r_{cf,w}$	outer radius of falling film crystallizer [m]
r_{cf+s}	radius of falling film crystallizer plus crystal layer [m]
$r_{dj,w}$	inner radius of double jacket [m]
Re	Reynolds number
s	crystal layer thickness [m]
Sc	Schmidt number
Sh	Sherwood number
T_{0i}^{LV}	boiling temperature of component i [K]
T_{eq}	equilibrium temperature [K]
$T^m(y)$	temperature of falling film as function of falling height [m]
T^{SL}	melting temperature [K]
T_{SW}	sweating temperature [K]
t_{SW}	sweating time [min]
u	circumference of falling film crystallizer tube [m]
v	crystal growth rate [m/s]
w	mass fraction
Y	yield in sweating process
Δh_{fus}^{SL}	specific heat of fusion [kJ/kg]
Δk_{int}	purification by sweating

Greek symbols

Π_{SW}	sweating number
α	heat transport coefficient [W/m^2/K]
β	mass transport coefficient [m/s]
δ	thickness of falling film [m]
η	dynamic viscosity [Pa s]
λ	thermal conductivity [W/m/K]
ν	kinematic viscosity [m^2/s]
ρ	density [kg/m^3]
σ	surface tension [kg/s^2]
φ	dimensionless number defined by Wellinghof
Γ	falling film volume flow per circumference of the crystallizer tube [L/s/m]

Subscript

0	initial
aSW	after sweating
bSW	before sweating
cf	cooling agent in falling film crystallizer
cf, w	outer surface of falling film crystallizer
cf + s	falling film crystallizer plus crystal layer thickness
cr	crystal
cryst	crystallizing compound
diff	differential
eq	equilibrium
fus	fusion
i	impurity
n	n-aldehyde
int	integral
LV	liquid–vapour
m	bulk of falling film
pX	p-xylene
sf	surface
SL	solid–liquid
SW	sweating
t	time
α	heat transport
a, cf	thermal resistance due to heat transport in falling film crystallizer
λ	heat conduction
γ, cf	thermal resistance due to heat conduction of falling film crystallizer

combination into an integrated hybrid process can lead to enormous benefits [16,17]. Such hybrid separations are industrially applied for the separation of isomers like xylenes [5], dichlorobenzenes [18] carbon acids [19,20] and diphenylmethane diisocyanates [21]. Micovic et al. [16] presented a four-step approach for the optimization of hybrid processes containing melt crystallization and distillation demonstrated with a narrow boiling isomeric long-chain aldehyde mixture [16]. The essence of the study was the identification of a priori unknown parameters which significantly influence process performance parameters like energy consumption or total costs. In particular, they found that the separation efficiency of the melt crystallization significantly affects the energy demand and costs of the hybrid process and, therefore, a reliable description of it is necessary. The separation efficiency of melt crystallization depends on the amount of embedded impurities in the crystalline layer and is basically a function of process conditions like crystal growth rate, melt concentration and mass transport [3]. Since it is not possible to predict the separation efficiency of crystallization [3,22], it is necessary to use empirical correlations. Therefore, to cover large operating windows, the identification of correlation parameters requires an extensive knowledge of the crystallization step. To avoid this effort, it is often assumed that a pure crystal product can be obtained [23,24]. However, such ideal separation steps are technically infeasible and the energy demands of real processes are numerous times higher [16]. Micovic et al. [16] characterized the separation efficiency of the crystallization step more realistic by using the differential