Intensification of falling film melt crystallization process through micro and milli-structured surfaces

Marie Le Page Mostefa [a,*], Hervé Muhr [a], Anthony Biget [b], Edouard Palasari [a], Michel Fauconet [c]

[a] Laboratory of Reactions and Process Engineering (LRGP) – CNRS Lorraine University, 1 rue Grandville BP 20451, 54001 Nancy Cedex, France
[b] PROGEPI, 1 rue Grandville, 54000 Nancy, France
[c] ARKEMA Centre R&D de l'Est CRDE, BP 61005, 57501 Saint-Avold Cedex, France

A B S T R A C T

This paper shows how falling film melt crystallization process can be intensified by using micro/milli-structured surfaces. This work takes part in the development of purification techniques of bio-acrylic acid. The current acrylic acid synthesis is based on propylene, a petroleum derivative. Thus, a new production route of a bio-acrylic acid is developed, based on glycerol, a green by-product of oleochemistry and biofuel industry. However, the impurity profile of this bio-AA differs from that of propylene-based: crude bio-AA contains much more propionic acid (PA). Classical purification techniques do not allow the separation of these two chemicals whose structures are similar.

[1] showed that falling film melt crystallization halves propionic acid contents in purified AA with yields reaching 60% and purification time less than five hours. Increasing the exchange surface between the cold surface and the melt to purify can improve heat transfer, decrease purification time and intensify melt crystallization process. Thus, micro/milli-structured crystallization surfaces have been designed and tested. Results show that these innovative surfaces can increase productivity by 84%. Heat transfer has been modeled during the crystallization process, and it clearly appears that thermal gradient is divided by ten with milli-structured surface compared to smooth surface.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Bio-based acrylic acid

With a global market reaching 4.2 million tons per year, acrylic acid (AA) is a major chemical intermediate. In fact, acrylic acid and acrylate esters are used in several fields such as superabsorbent, water treatment, paint formulation, building industry. The global demand of AA is increasing each year by 4%. Currently, AA synthesis is based on propylene, which is produced by the steam cracking of oil fractions and therefore, AA is totally dependent on the oil market. To diversify the resources for AA production, a route based on renewable raw materials is considered, from glycerol, a green by-product of oleochemistry and biofuels. Indeed, "bio-AA" synthesis route is based on a first dehydration of glycerol to produce acrolein, which is then oxidized. However, the

impurity profile of this bio-AA is different from that of propylene-based AA. In particular, propionic acid (PA) is present in higher concentration. Classical purification techniques do not separate efficiently these two acids to reach the desired purity of glacial AA (>99.5%).

1.2. Melt crystallization and solid liquid phase diagram

Melt crystallization allows the separation of compounds from a melt by cooling and solidification of a component according to the liquid–solid equilibrium of the initial mixture to purify. In the case of AA + PA binary system, the phase diagram [1] exhibits a peritectic behavior at 50.0% (mol) of AA. This point delimits a wide area where AA crystallizes in a pure form as shown in Fig. 1. The composition of the liquid phase at a temperature T of a system at liquid–solid equilibrium is given by the liquidus curve.

A liquid mixture AA + PA at $x_{AA(i)}$ composition, represented by the point M_i, is cooled. When the point M exceeds the liquidus curve and is in the metastable zone, supercooling prevents the

* Corresponding author.
  E-mail address: marie.le-page-mostefa@univ-lorraine.fr (M. Le Page Mostefa).

Nomenclature

C_P	Heat capacity ($J\,kg^{-1}\,K^{-1}$)
CR	Cooling rate of crystallization surface ($K\,h^{-1}$)
e	Thickness of the crystalline layer (mm)
eff	Process separation efficiency (-)
F	Force per volume unit (-)
g	Gravitational acceleration ($m\,s^{-2}$)
h	Height of crystallization tube (m)
k	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)
m	Mass (kg)
m_0	Mass of the initial mixture to purify (kg)
m_{sol}	Solid mass produced after the crystallization step (kg)
m_{sw}	Mass of residual liquid from sweating step (kg)
p	Pressure (Pa)
P	Global productivity ($kg\,m^{-3}\,h^{-1}$)
P_C	Crystallization step productivity ($kg\,h^{-1}\,m^{-3}$)
P_{sw}	Sweating step productivity ($kg\,h^{-1}\,m^{-3}$)
R_C	Production rate of crystals by tube height ($kg\,m^{-1}\,h^{-1}$)
R_{sw}	Production rate of liquid from sweating by tube height ($kg\,h^{-1}\,m^{-1}$)
T	Temperature (K)
T_l	Liquidus temperature (K)
u	Velocity field ($m\,s^{-1}$)
V	Volume (m^3)
$x_{AA(i)}$	Acrylic acid molar fraction in the phase i (-)

Greek symbols

α	Coefficient of thermal expansion (K^{-1})
ΔT	Thermal gradient in the crystalline layer (°C)
Δt_C	Time of crystallization step (h)
Δt_{sw}	Time of sweating step (h)
η	Yield (%)
μ	Dynamic viscosity (Pa s)
ρ	Density ($kg\,m^{-3}$)
ω_{PA}^i	Propionic acid mass fraction in the phase i (-)

Subscripts

0	From initial mixture to purify
∞	External
AA	Acrylic acid
C	Crystallization step
cryst	Crystalline phase
l	Liquidus
liq	Liquid phase
PA	Propionic acid
sol	Solid phase
sw	Sweating step

Fig. 1. Liquid–solid phase diagram of the binary system AA + PA (Temperature T/K – Molar proportion x_{AA}/-) [1].

- feeding the crystallizer with the liquid mixture (AA + PA) to purify,
- crystallization by gradual cooling of the melt,
- draining off the impure liquid phase, enriched in PA,
- slow heating of the crystallization surface to partially melt the crystal layer. This step, called "sweating", improves the

crystal formation. AA crystals should appear according to thermodynamics. In fact, solid phase is formed after an infinitely long time or following a system disturbance (stirring, impurities, seeds . . .). When the point M is at the limit of the metastable zone, AA crystallizes spontaneously. Then, the solid phase formed contains theoretically 100% AA, on a thermodynamical point of view, whereas the liquid phase is enriched in PA.

1.3. Solid layer melt crystallization

In the static melt crystallization, heat and mass transfers depend on natural convection, unlike the dynamic crystallization, where heat and mass transfers are influenced by forced convection.

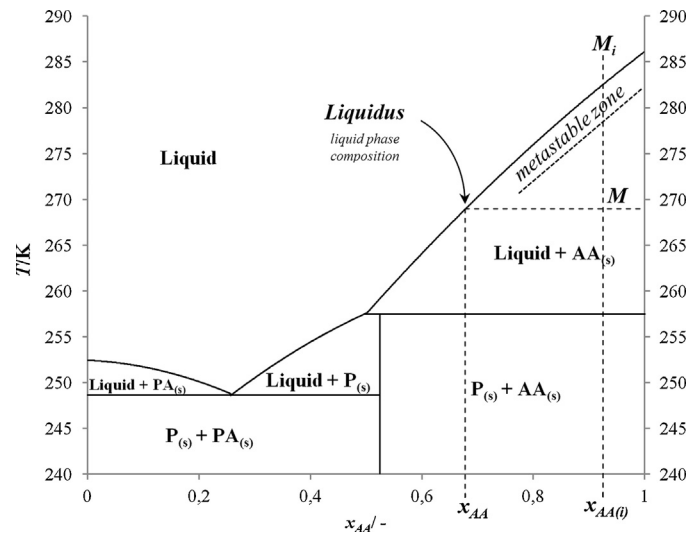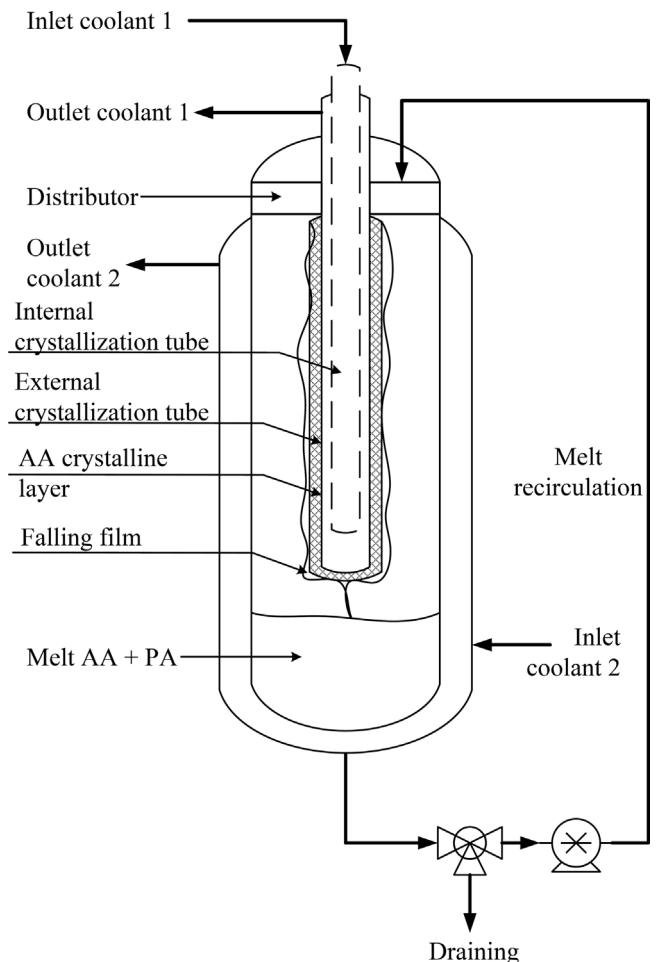A solid layer melt crystallization cycle is composed of six steps:

Fig. 2. Falling film melt crystallization device designed.