



A purification route of bio-acrylic acid by melt crystallization respectful of environmental constraints



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ABSTRACT

Bio-acrylic acid (AA) is produced from glycerol, a by-product of biodiesel production and oleochemistry. However, conventional purification techniques cannot purify this biobased AA owing to its impurity profile and the significant content of propionic acid (PA). The liquid–solid phase diagram of the binary AA + PA shows that acrylic acid crystallizes as a pure form from melts containing between 50 and 100% (mol/mol) of AA. Thus, a new falling film melt crystallization device has been developed and tested in which:

- supercooling is limited by the use of a crystallization surface made of 316L stainless steel,
- melt is thermostated,
- visual observation of the crystal layer is possible, and
- morphology of the crystal layer limits the retention of impure liquid.

Purification tests in this falling film device show that AA is separated from the PA in reduced crystallization cycle times and high crystallization yields.

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1. Introduction

Every year, more than 4.2 million tons of acrylic acid (AA) is produced around the world. The annual demand growth of this major intermediate chemical is estimated between 4 and 5%. Indeed, the acrylic acid and derivatives are used in polymer and copolymer forms in many industrial fields such as water treatment, superabsorbent, building industry... AA is currently synthesized from propylene, which is obtained by the steam cracking of oil fractions. Thus, to diversify the feedstock for AA production, a novel production route from renewable material is envisioned, based on glycerol, a green by-product of oleochemistry and biodiesel production. Nevertheless, the impurity profile of the crude bio-based AA is different, and specifically, propionic acid (PA) is produced significantly. Classical purification techniques of AA cannot efficiently separate these two acids to reach the desired purity of glacial AA (>99.50%). The liquid–solid phase diagram AA + PA [1] exhibits a eutectic behavior at 25.65% (mol) of AA and a peritectic point at 50.00% (mol) as shown in Fig. 1. Between 100.00% (mol) and 50.00% (mol) of AA, acrylic acid crystallizes in a pure form, allowing melt crystallization to be a promising separation technique. These fundamental thermodynamic data are favorable to the development of melt

crystallization process and good theoretical yields can be expected for the production of high purity AA. Moreover, melt crystallization process is a particularly advantageous separation technique owing to:

- low energy consumption,
- low maintenance cost,
- process free from additional solvent,
- high environmental safety: since operations are done at lower temperatures,
- production of high purity products, and
- purification of heat sensitive products without degradation and formation of undesirable by-products.

In the AA purification case, melt crystallization limits the formation of the 2-acryloxypropionic acid. Indeed, this compound is generated by a Michael addition reaction of two AA molecules, favored at high temperatures, such as in distillation conditions.

This process can be considered as “green” [2] and it takes place into process intensification. Indeed, melt crystallization allows a product purification consuming less energy and involving less compounds. Besides, melt crystallization is sometimes the only technique able to separate products such as isomeric compounds. Thus, this separation technique is particularly adapted to chemical industries which need to design innovative process, to be competitive and to respect new environmental constraints.

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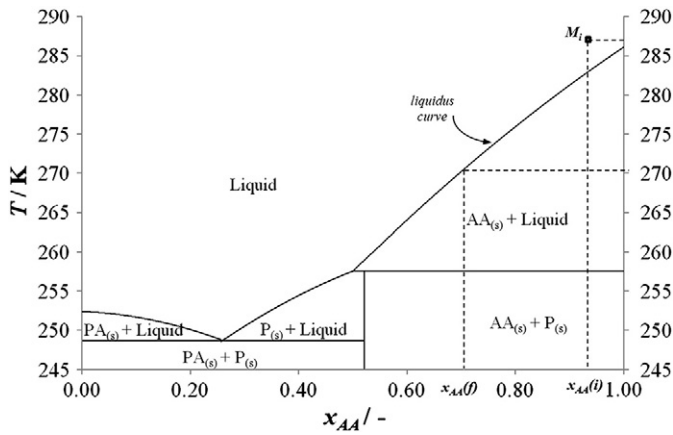


Fig. 1. Liquid–solid phase diagram of the binary system AA + PA [1], T/K the temperature, x_{AA} – the AA molar fraction.

Melt crystallization consists in isolating a compound from a melt by cooling and crystallizing the desired product according to the thermodynamic equilibrium of the initial system. Le Page Mostefa et al. [1] determined the phase diagram of the binary system AA + PA. This solid–liquid equilibrium exhibits a peritectic point at 50.00% (mol/mol) defining a wide area where the AA crystallizes in a pure form, as shown in Fig. 1. A binary mixture AA + PA, containing a mass fraction $x_{AA}(i)$ and represented by point M_i , is cooled. The solid phase formed is pure AA 100% (mol/mol), whereas the liquid phase is enriched in PA. The composition of the liquid phase at a temperature T is given by the liquidus curve.

In static layer crystallization, heat and mass transfers depend on natural convection, whereas in dynamic layer crystallization, the liquid phase is pumped and this crystallization mode improves heat and mass transfers which are influenced by forced convection [3].

A layer melt crystallization cycle is composed of seven steps:

- formation of the first thin crystalline layer, to prevent supercooling,
- feeding the liquid mixture (AA + PA) to purify into the crystallizer,
- slow cooling of the crystallization tube for the AA crystalline layer growth,
- draining off the impure liquid phase (enriched in PA),
- partial melting of the crystal layer by gradual warming of the crystallization tube. This step, called “sweating”, improves the efficiency of the purification, first by migration of impurities included outside of the crystal layer, and secondly through a washing effect of the outer crystalline layer which was in contact with the residual liquid phase,
- draining off the sweating liquid phase,
- complete melting of the crystal layer and recovering the purified liquid (AA).

2. Material and method

A device has been developed to study the AA purification by falling film crystallization. In this experimental set-up, the liquid phase is pumped and injected into a distributor located at the top of the device, which allows spreading the melt all around the crystallization tube. This distributor has been designed in order to ensure a total wetting of the crystallization tube: a 30 cm long cooled tube, composed of two coaxial cylinders made of 316L stainless steel in which a coolant fluid circulates.

This conception ensures a uniform temperature along the crystallization tube. In addition, the use of a stainless steel surface improves heat transfer and reduces supercooling, responsible for a too rapid

crystal growth and a decrease of the purification efficiency. The impure liquid phase which does not crystallize is collected in the lower part of the device.

The double jacketed glass tank (2 L) contains the crystallization tube and the melt. This glass tank allows both to control the temperature of the melt by the circulation of a coolant, and to visually observe the development and morphology of the crystal layer.

It has been shown that the morphology of acrylic acid crystals is strongly influenced by the presence of impurities [4], such as water and propionic acid, which lead to the formation of macroscopic cavities in acrylic acid crystals. These inclusions retain the impure liquid phase and reduce the separation efficiency. In this new device, the high recirculation flow rate of the melt aims to allow better macroscopic organization of the crystalline layer, to prevent the formation of these cavities and thus to reduce the impure liquid retention on the surface of AA crystals.

In this falling film device, AA crystallizes on the external part of the tube, unlike most of falling film crystallizers (Fig. 2). With this configuration, plugging risk is avoided, since acrylic acid crystallizes outside the tube, so a large proportion of the initial melt can crystallize and high yield is possible.

3. Experimental results

3.1. Operating conditions

Experiments were conducted on 300 mL synthetic binary mixtures AA + PA containing between 2000 and 7000 ppm (mass) of PA, at a constant recirculation flow rate of 100 mL/min. To avoid supercooling,

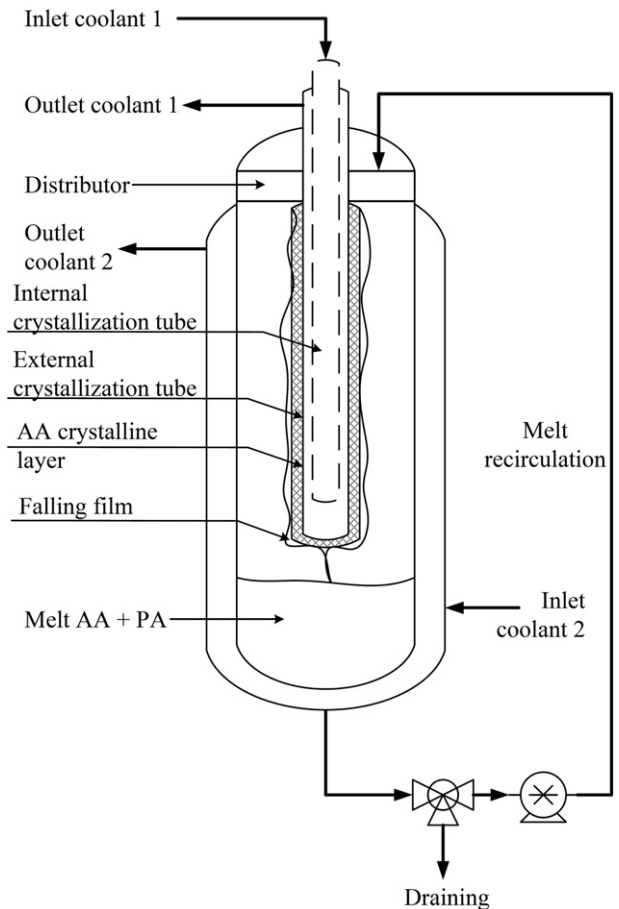


Fig. 2. Schematic view of the falling film crystallizer.

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