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Membranes and crystallization processes: State of the art and prospects

Elodie Chabanon*, Denis Mangin, Catherine Charcosset

Univ Lyon, Université Claude Bernard Lyon 1, CNRS UMR 5007, LAGEP, F-69622, Lyon, France

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ABSTRACT

Crystallization is one of the major unit operations of chemical process industries and plays a key role for particulate solids production in the pharmaceutical, chemical, electronic, minerals sectors. Most of the current crystallization processes are performed under batch or continuous mode based on a stirred tank process; the need for breakthrough technologies has been highlighted by numerous authors and reports. Membranes are one of the potentially attracting strategies in order to achieve this target. Nevertheless, a relatively limited number of publications have been reported on membranes and crystallization processes, compared to other unit operations. This study intends to provide a state-of-the-art review of the different approaches combining membranes and crystallization processes. Hybrid and integrated systems are discussed and the different role and function potentially provided by dedicated membrane materials are analyzed. Based on the results and analyses gained through the different approaches that have been tested, unexplored issues and open questions have been listed. The research efforts which are required in order to make membranes processes for crystallization/precipitation an industrial reality are finally discussed.

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1. Introduction

Crystallization is one of the oldest chemical operations to produce, purify or separate the solid products but it is only since the 70's that it has been considered as a unit operation [1]. Nowadays, crystallization and precipitation (solids produced from a chemical reaction) are major processes used in the chemicals, pharmaceuticals, food and electronics industries due the high level of product purity required and the need for low energy requirement [2]. Regardless the crystallizer technology, the crystallization process or the operating conditions, crystallization occurs by a

* Corresponding author.
E-mail address: elodie.chabanon@univ-lyon1.fr (E. Chabanon).

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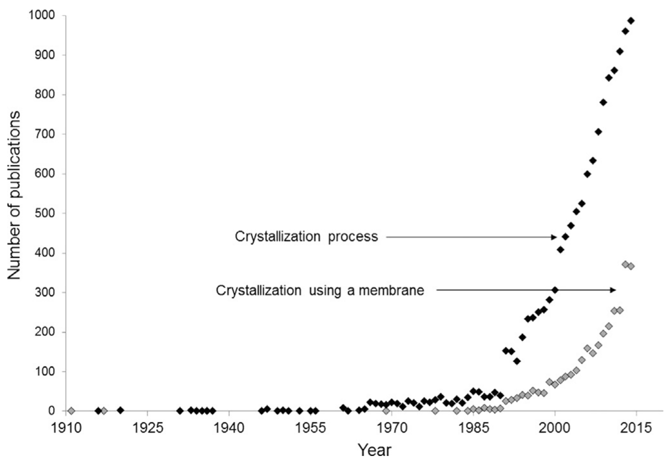

Fig. 1. Evolution of the number of publications per year in scientific journals which include the keywords "Crystallization" (black diamond) and "membrane crystallization or membrane distillation" (gray diamond). ISI Web of Science, April 2015.

change of the temperature and/or the composition (solvent evaporation, antisolvent added, seeding, etc.) of a saturated solution. Hence, heat and/or mass transfer processes are key issues for the crystallization/precipitation processes.

Membrane processes have recently been proposed in order to improve performance of crystallization operations and are considered as one of the most promising strategies [3–5]. The number of publications dedicated to crystallization/precipitation [6,7] processes using a membrane have effectively increased these last years (cf. Fig. 1). Generally speaking, membrane processes make use of a porous or a dense material acting as a physical semi-permeable barrier between two phases. In terms of mass transfer, the use of a membrane logically adds a supplementary resistance [5] which has to be taken into account in the process analysis. Similarly, from the heat transfer point of view, the thermal conductivity of membrane materials is usually low [8]. These two disadvantages are however potentially counterbalanced by the unique possibilities offered by membranes such as selective mass transfer, improved fluid distribution and extremely high interfacial area (a) leading to intensified heat and mass transfer fluxes [5,8]. These characteristics can be of interest for enhanced process productivities and/or product quality purposes.

In crystallization/precipitation processes, the solid products are indeed characterized by their purity level, polymorphic form, crystal shape and crystal size distribution (CSD) which has usually to be as narrow as possible [9]. These features define the product quality and are governed by the supersaturation which is the process driving force. Hence, for crystallization/precipitation processes, the control of the supersaturation appears as being of primary importance and membranes are one promising way to fulfill that aim [9–11].

This study intends to provide a state-of-art review of the different approaches combining membranes and crystallization processes which have been reported so far. Hybrid and integrated systems are discussed and the different roles and functions potentially provided by dedicated membrane materials are analyzed. Based on the results and analyses gained through the different approaches that have been tested, unexplored issues and open questions have been listed. The research efforts which are required in order to make membranes processes for crystallization/precipitation an industrial reality are finally discussed.

2. Crystallization/precipitation processes: framework

Crystallization/precipitation processes have long been used in the pharmaceutical, food, chemicals and materials sectors as a means to isolate, to purify and to control the solid products materials regarding the crystal shape, the polymorphic form and the CSD. Industrial applications of large scale continuous processes are available for commodity chemicals (ammonium nitrate, urea, ammonium sulfate, phosphoric acid, sodium chloride, adipic acid, xylenes, etc.) and for specialty chemicals (e.g. pharmaceutical, food, fine chemicals). For materials, batch processes are more often employed.

Several reports and reviews have addressed the challenges of crystallization processes for these different industrial applications and, schematically, two types of developments are often cited as of high priority:

i) *Product quality* issues (quality by design), aims the polymorphic form, the CSD and the crystal shape factor to be mastered [4,12–15].
ii) *Process issues* include batch to continuous breakthrough approaches, scale up challenges, intensification and green engineering developments [14,16].

In both cases, new crystallizer concepts are expected to replace the reference technology, namely the stirred tank. For instance, the transition from batch to continuous and the ease of scale up has been attempted by a strategy in which the number of smaller unit operations is increased. This is the case of microstructured reactors [4]. Unfortunately, channel blocking issues limit, for the moment, the industrial application [4].

From a more fundamental point of view, the complex interaction of the physical chemistry (nucleation, crystal growth rates) and chemical engineering (hydrodynamics, transport processes, scale up), which controls the polymorphic form, crystal stability and CSD, is a key topic. More specifically, studies, coupling hydrodynamics thanks to Computational Fluid Dynamics (CFD) and population balances [17], would be of major interest in order to offer an improved understanding of the crystallization process and the technology. However, both targets still remain very challenging from the computing and the mechanisms quantitative description point of view.

The specific feature of crystallization as a separation process is that it involves a phase change from liquid to solid (e.g. ions or molecules). Fig. 2 shows a classical temperature/concentration diagram where the supersaturation, i.e. the driving force of the liquid/solid phase change, is represented. In terms of process, different possibilities, listed in Table 1 are offered in order to generate supersaturation. Basically, two major means, corresponding to the two axes of Fig. 2, can be applied:

i) a change in concentration (in red, i.e. solute concentration by solvent removal or dilution through adding an antisolvent)
ii) and/or a change in temperature (in green).

Interestingly, it will be shown and discussed hereafter that each of the supersaturation generation method shown in Table 1 can be performed thanks to different membrane processes.

3. Membrane and crystallization/precipitation processes: a short historical overview

Like many scientific discoveries, the use of a membrane material to crystallize is due to an unexpected observation. Hence, the first