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ScienceDirect
Chemical Engineering and Processing 46 (2007) 25–36
Chemical Engineering and Processing
www.elsevier.com/locate/cep

Separation of *para*-xylene from xylene mixture via crystallization

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Received 21 December 2005; received in revised form 9 April 2006; accepted 10 April 2006
Available online 23 May 2006

Abstract

Crystallization kinetics of *para*-xylene from xylene isomers mixture using a lab-scale cooling batch crystallizer were determined. The cooling batch crystallizer type is simple, flexible and requires less process development. Dynamic mass and population balances were used to model the batch crystallizer. The model equations were solved using the numerical method of lines; a new proposed solution method. The kinetic parameters of nucleation and growth rates were estimated by measuring the concentration and the total mass of *para*-xylene suspended crystals during the process time. A nonlinear optimization technique was then applied to estimate the parameters. The effect of the cooling strategy on the estimated parameters was studied. It was found that model predictions using the optimum estimated parameters were in good agreement with the experimental results under various cooling strategies. The optimal kinetic parameters were then used to find the optimum cooling strategy to maximize the yield of *para*-xylene crystals which have an average size greater than 0.5 mm. A new objective function was formulated and also, a nonlinear optimization technique was applied to find the optimum cooling strategy to achieve this product characterization. The optimization technique converged successfully and the proposed objective function was found to be effective to optimize the *para*-xylene crystallization process.

Keywords: Batch crystallization; para-Xylene; Parameters estimation; Optimum cooling; Method of lines; Population balance

1. Introduction

Xylene, which is a colorless liquid with a sweet odor, occurs mainly in petroleum and coal tar. However, xylene is primarily a man-made chemical. Xylene is mainly produced from petroleum and to a smaller extent from coal [1]. There are three isomers of xylene having the same chemical formula $C_6H_4(CH_3)_2$, but with different structural configurations. These isomers are: *meta*-xylene, *ortho*-xylene and *para*-xylene. In production of xylene, a mixture of the three isomers is usually formed and other chemicals may also be present in smaller amounts such as benzene and ethylbenzene. The term "mixed xylene" is used to refer to the mixture of xylene isomers that usually contains 6–15% ethylbenzene.

Xylene is used in many applications in the modern industry. Solvents and thinners for varnishes and paints often contain xylene. Xylene is used in airplanes fuel and gasoline. It is also used in rubber, cleaning agents and in leather industries. However, among the three isomers, *para*-xylene is in high demand for conversion to terephthalic acid (TPA) and then to dimethyl terephthalate (DMT).

Dimethyl terephthalate (DMT) is then reacted with ethylene glycol to form polyethelene terephthalate (PET).

Polyethelene terephthalate (PET) is the raw material for most polyesters used in production of fibers, packaging materials and containers. Worldwide production of *para*-xylene in year 2001 was near 21.4 million metric tons (approximately 679 kg/s).

In production of *para*-xylene, *ortho*-and *meta*-xylenes and other substances are either separated from or converted to *para*-xylene. These substances boil so closely together that separating them by fractional distillation is not practical. Therefore, other methods are used to separate *para*-xylene from the mixture. One of *para*-xylene separation methods is the UOP Parex Process [2]. This process depends on adsorption of *para*-xylene molecules by a *shape-selective* zeolite adsorbent, which is selective only to the *para* structure. However, the high cost of the *para*-selective

Abbreviations: CSD, crystal size distribution; DMT, di-methyl terephthalate; GC, gas chromatography; MOL, method of lines; ODE, ordinary differential equation; PBE, population balance equation; PET, poly-ethelene terephthalate; TPA, tere-phthalic acid; TSS, total suspended solid

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doi:10.1016/j.cep.2006.04.002

Table 1
Thermodynamic properties of xylene isomers and ethylbenzene

Component	Melting point, T_m (°C)	Boiling point, T_b (°C)
para-Xylene	13.3	138.5
ortho-Xylene	−25.2	144.0
meta-Xylene	−47.9	139.3
Ethylbenzene	−95.0	136.2

catalyst makes this method limited to small scale productions. One of the recently used methods for *para*-xylene separation is the fractional crystallization process. This process depends on the variation of melting points of the chemicals in the mixed xylene. Therefore, by lowering the temperature of this mixture, *para*-xylene, which has the highest melting point, will crystallize firstly (as solid crystals) and then can be separated. Table 1 shows some of the thermodynamic properties of the "mixed xylene" components, including the boiling and the melting points [3].

The first step in cooling crystallization technique is to reach supersaturation. Supersaturation, which is the driving force for crystallization, occurs as a result of the reduction in solute solubility when the temperature is reduced. After that, formation of nuclei occurs and finally the subsequent growth of these nuclei to form large crystals. Thus, continuous cooling is necessary and the conventional way for cooling is by using jacketed crystallizers or similar forms of heat exchange devices.

In any crystallization process, the crystal size distribution (CSD) is a key issue since most quality requirements and end-use properties of the crystals are strongly dependent on the CSD [4]. One of the separation methods mainly used to separate the solid crystals from the solution after crystallization is filtration. If the obtained crystals have relatively small sizes, the filtration process is expected to be difficult because small crystals will cause filter clogging. Thus, it is of great importance to control the crystallizer conditions to obtain the desired CSD. The CSD depends mainly on the degree of supersaturation, as well as on crystals nucleation and growth rates. All these three processes (i.e. supersaturation, nucleation and growth of crystals) may occur simultaneously in the crystallizer [5]. Controlling the CSD is usually achieved by cooling the solution following a pre-determined cooling strategy, or a *cooling profile*. In general, the temperature of the solution should be reduced slowly in the early stages of the process, and more rapidly in the final stages to get relatively large crystals [6]. To determine the suitable cooling profile, the behavior of the crystals under cooling should be known and this is provided from the study of *crystallization kinetics*, i.e. nucleation and growth rates. Quantitatively, each system has its own crystallization kinetics which should be investigated experimentally.

In order to get a complete description of the CSD, it is necessary to apply the conservation laws of mass, energy and *crystals population* in addition to nucleation and growth rates kinetics [4,7]. For crystals population, the concept of population balance has been a major contribution to crystallizers analysis and design. The CSD is affected by generation and destruction of crystals by breakage and agglomeration processes as well as by nucleation and growth processes [4]. Thus, all crystals present in the crystallizer must be accounted for, and this is accomplished by the Population Balance Equation (PBE).

The aim of this study is to present a methodological framework for optimization of *para*-xylene crystallization process using a developed rigorous model and model parameters estimation. The kinetic model parameters were estimated by reconciling experimental data of *para*-xylene concentration and total mass of *para*-xylene suspended crystals with model predictions using a nonlinear optimization technique. For this purpose, the numerical method of lines (MOL) was used to solve the model's mathematical equations. The effect of cooling strategy on the estimated parameters was studied. To find the optimum cooling profile, a new objective function was proposed and also, a nonlinear optimization technique was applied. The new proposed objective function maximizes the yield of crystals which have a certain required average size or greater. This objective function requires the calculation of mass crystals along the size range.

In this study, the homogenous well-mixed cooling batch crystallizer was used for *para*-xylene crystallization in order to investigate its advantages. In addition, batch crystallizer is suitable equipment for the study of nucleation and growth rates.

1.1. para-Xylene crystallization

de Goede [1] studied the crystallization of *para*-xylene with scraped surface heat exchangers. He studied the structure and growth phenomena of *para*-xylene crystals as well as the heat transfer properties of the scraped surface crystallizer under both crystallizing and non-crystallizing conditions on pilot-plant scale. He concluded that decreasing the wall temperature below −30 °C did not result in further cooling of the bulk, because the effect of the increasing temperature difference is countered by a decrease in heat transfer coefficient due to an increasing thickness of the crystals layer.

Patience et al. [8] determined crystallization kinetics of *para*-xylene from xylenes mixture containing about 25% *para*-xylene produced in Amoco plants using a batch pilot-scale scraped surface crystallizer. They found that the xylene mixture was always saturated during all runs of crystallization and thus developed a reduced two-parameter model to describe these crystallizers. They assumed that nucleation of crystals occurs at the walls of the crystallizer and growth of the crystals occurs in the bulk.

de Goede and de Jong [9] studied heat transfer properties of a scraped surface heat exchanger for *para*-xylene separation in the turbulent flow regime. They found that the heat transfer coefficient depends more strongly on the rotational frequency of the scrapers than the theoretical model predicts. This was because of the generation of vortices due to the scraper action. They corrected the crystallizer model to take into consideration the occurrence of these vortices and get satisfactory agreement between the heat transfer coefficients predicted by the corrected model and those determined experimentally. However, the disadvantages of the scraped crystallizers arise from the fact that the scraping blades cause crystals damage and thus producing slurries which are difficult to filter. Also these devices are often costly and require considerable maintenance.