

# The inhibition of acrylic acid and acrylate ester polymerisation in a heterogeneously catalysed pilot-scale reactive distillation column

A. Niesbach<sup>a</sup>, J. Daniels<sup>a</sup>, B. Schröter<sup>a</sup>, P. Lutze<sup>a,\*</sup>, A. Górak<sup>a,b</sup>

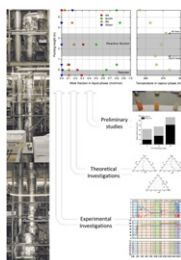
<sup>a</sup> TU Dortmund University, Laboratory of Fluid Separations, Dortmund 44227, Germany

<sup>b</sup> Lodz Technical University, Department of Environmental and Process Engineering, Lodz, Poland

## HIGHLIGHTS

- ▶ Influence of atmosphere, temperature and inhibitor concentration on IP is shown.
- ▶ Investigation of influence of LLE and startup and shutdown period.
- ▶ Concept for polymerisation inhibition in RD columns is introduced.
- ▶ Successful implementation of concept validated by conducting an RD experiment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 6 July 2012

Received in revised form

16 August 2012

Accepted 4 October 2012

Available online 29 November 2012

### Keywords:

Polymerisation

Distillation

Butyl acrylate

Phenothiazine

Hydroquinone monomethyl ether

Catalytic distillation

## ABSTRACT

Due to a complex thermodynamic behavior and a high risk of polymerisation, the current production process for *n*-butyl acrylate is challenging and cost-intensive. The process intensification for the esterification reaction between acrylic acid and *n*-butanol to synthesise *n*-butyl acrylate in a reactive distillation column has not been studied much experimentally and is addressed in this paper. A main challenge that currently hinders the implementation of this promising process is the risk of polymerisation of acrylic acid and *n*-butyl acrylate. This article presents an experimental investigation of the inhibition period of acrylic acid and *n*-butyl acrylate polymerisation, which is dependent on the amount of inhibitor added, the temperature and the gas phase composition. Hydroquinone monomethyl ether and phenothiazine are the most common inhibitors and are hence used within this study. The liquid–liquid separation is also studied together with the experimental investigation of the inhibition period. Furthermore, the dilution of the inhibitor in a pilot-scale reactive distillation column is investigated together with the development of startup and shutdown procedures. The results of the experimental and theoretical investigations are used to develop a concept to avoid any polymerisation occurring in a pilot-scale reactive distillation column. This concept was used to successfully conduct a pilot-scale reactive distillation experiment.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Acrylic acid (AA) and its derivatives receive increasing attention because they are basic building blocks for the chemical industry

(Susan L. Bell, 2003). Approximately half the acrylic acid is used for the production of acrylates, where approximately 60% of this half accounts for the production of butyl acrylate (BA) (Nexant Inc., 2006). The overall world production rate of acrylic acid increased from 3.4 million tons per year in 2003 (Susan L. Bell, 2003) to 4.7 million tons per year in 2006 (Glauser et al., 2007). The growth in the global demand of acrylic acid for the period 2010–2015 is estimated to be 4.8% per year (I.H.S. Inc., 2011).

\* Corresponding author. Tel.: +49 231 7552670.

E-mail address: philip.lutze@bci.tu-dortmund.de (A. Niesbach).

*n*-Butyl acrylate is widely applied in the industry and used for example as a precursor for adhesives, varnishes and finishes of papers and textiles (Zeng et al., 2006). It is produced, together with water, by an equilibrium-limited esterification reaction of *n*-butanol (BuOH) with acrylic acid. The current process used for the production of *n*-butyl acrylate is challenging and cost-intensive because it possesses a complex thermodynamic behaviour and a high risk of polymerisation. The production of *n*-butyl acrylate is currently conducted in a homogeneously catalysed multistage process using two reactors with a total residence time of approximately three hours. Three distillation columns are used for the recovery of the reactants and the purification of the product (Susan L. Bell, 2003).

Reactive distillation (RD) integrates chemical reactions and distillation into one unit and is one of the best known examples of process intensification. The use of RD to exploit synergistic effects between reaction and separation aids the overcoming of reaction or separation limitations such as those of reaction equilibria or azeotropes. RD has been used in a multitude of industrial applications, which have been discussed in the reviews of Hiwale et al. (2004), Sundmacher and Kienle (2003), Górak and Stankiewicz, (2011).

However, little attention has been focused on developing an RD column for the production of *n*-butyl acrylate. An RD potentially may enhance the performance for this reaction system by shifting the equilibrium of the reaction. Besides, the heat of reaction can be used for the separation. Additionally, a reactive distillation column may decrease the amount of equipment required for the process, therefore reducing the investment and operating costs as well. However, for implementation of this concept, reaction and distillation operating windows need to match. This window may be limited for selecting temperatures and pressures due to potential polymerisation risk and catalyst deactivation.

Schwarzer and Hoffmann (2002) investigated the reaction equilibrium and the kinetics of the esterification reaction experimentally. They used their kinetic data to simulate a process producing *n*-butyl acrylate with a catalytic tube reactor and a reactive distillation column using an equilibrium-stage model. Zeng et al. (2006) studied the theoretical design and control of a single reactive distillation column for the production of *n*-butyl acrylate. They provided a control strategy for the industrial reactive distillation column to produce high purity *n*-butyl acrylate based on the kinetics provided by Schwarzer and Hoffmann (2002). Keller et al. (2010) presented a theoretical study using a nonequilibrium-stage model. They implemented the kinetic data of Schwarzer and Hoffmann (2002) in their model and simulated a pilot-scale reactive distillation column to prove the technical feasibility of *n*-butyl acrylate synthesis in a heterogeneously catalysed RD column theoretically.

Nevertheless, all of these publications have only studied the production of *n*-butyl acrylate in an RD column on a theoretical basis. This might be a result of the high risk of polymerisation of acrylic acid and *n*-butyl acrylate (Ohara et al., 2000). Due to the theoretical basis, neither the paper of Zeng et al. (2006) nor the papers of Schwarzer and Hoffmann (2002) and Keller et al. (2010) considered the polymerisation risk of the used components. Zeng et al. (2006) and Keller et al. (2010) mentioned the necessity of using a polymerisation inhibitor for experimental investigations, but they did not provide any further details.

One of the main challenges that may circumvent the implementation of this promising process is the aforementioned polymerisation tendencies exhibited by acrylic acid and *n*-butyl acrylate. Stabilisers are added to reaction mixtures to prevent the polymerisation of the reactants during the production of *n*-butyl acrylate in industrial processes (Ohara et al., 2000).

Phenothiazine (PTZ) and hydroquinone monomethyl ether (MeHQ) are typically used as radical interceptors for inhibiting polymerisation. Other polymerisation inhibitors that were more effective for inhibiting the polymerisation of acrylic acid in distillation systems were proposed by Mosnáček et al. (2012) but have not been fully established thus far. A detailed study on the polymerisation behaviour of acrylic acid and *n*-butyl acrylate is necessary for an experimental investigation of the *n*-butyl acrylate synthesis in a pilot plant reactive distillation column to proceed. This study may lead to the use of reactive distillation technology at an industrial production level.

Therefore, a study was conducted to investigate the inhibition period of acrylic acid and *n*-butyl acrylate that were stabilised with phenothiazine and hydroquinone monomethyl ether, where the inhibition period is defined as the time taken for a significant extent of polymerisation to occur. This study was conducted by varying the initial inhibitor concentrations, the temperature and the composition of the atmosphere. The results were used to develop a procedure for inhibiting polymerisation in a pilot-scale reactive distillation column. The synthesis of *n*-butyl acrylate can be considered as an example for any system that has issues with polymerisation. A safe way for adding the inhibitors into the pilot-scale columns was identified and will be described within this paper. Finally, pilot-scale reactive distillation experiments were conducted to demonstrate the successful operation of the column and the proper concept of polymerisation inhibition.

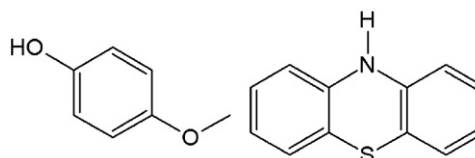
## 2. Inhibition mechanisms

Both the acrylic acid and the *n*-butyl acrylate have to be polymerised before use; however, polymerisation has to be avoided during the esterification and separation of acrylic acid and *n*-butyl acrylate because the polymerisation reactions (detailed as a scheme in the supplementary material) that are investigated in this system are highly exothermic, as shown in Table 1. Therefore, an uncontrolled polymerisation occurring at high temperatures in processes that are not properly prepared would lead to an uncontrollable self-accelerating reaction. (Brand, 2011)

The polymerisation of acrylic acid and *n*-butyl acrylate is initiated by radicals present in the mixture. Radical polymerisation is a three-step process and is described in the supplementary material. Polymerisation is prevented by the addition of inhibitors, which can be categorised into inhibitors that are used for shipment and storage and inhibitors that are used for inhibiting during chemical processes. The conventional chemicals that are used to stabilise acrylic acid and other acrylates are hydroquinone

**Table 1**  
The polymerisation enthalpies of acrylic acid (Becker, 2003) and *n*-butyl acrylate (Lovell and El-Aasser, 1997).

Monomer	$\Delta H_{pol.}(\text{kJ mol}^{-1})$
Acrylic acid	-76
<i>n</i> -butyl acrylate	-77



**Fig. 1.** Chemical structure of the polymerisation inhibitors MeHQ (left) and PTZ (right).

Download English Version:

<https://daneshyari.com/en/article/155468>

Download Persian Version:

<https://daneshyari.com/article/155468>

[Daneshyari.com](https://daneshyari.com)