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Separation of acetic acid-methanol-methyl acetate-water reactive mixture



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HIGHLIGHTS

- The coupling of reaction and pervaporation.
- The reactive mixture with methyl acetate synthesis reaction.
- Pervaporation of mixtures which are close to chemical equilibrium.
- Removing of methyl acetate from reaction zone in pervaporation.
- Developed PPO/MFFC membranes are effective to shift equilibrium.

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ABSTRACT

The aim of this research is to study the separation of a mixture with a methyl acetate synthesis reaction by pervaporation. The feed solutions that have compositions close to a chemical equilibrium are the main object of this work. The pervaporation of these solutions leads to the shifting of the composition from its chemical equilibrium. As a result, ester synthesis reaction coupled with pervaporation allows for more effective conversion of reagents. The hybrid process "reaction+pervaporation" was studied using membranes with a base of poly-(2,6-dimethyl-1,4-phenylene oxide) (PPO): a homogeneous PPO membrane and a composite membrane consisted of a PPO thin selective layer ($\sim 5 \mu$ m) on the surface of a fluoroplastic composite hydrophobic membrane (MFFC). The transport properties of homogeneous and newly developed composite membranes based on the PPO were studied through the pervaporation of quaternary system acetic acid–methanol and water–methyl acetate. The sorption experiments were carried out to explain the pervaporation data. The possibility of using transformed composition variables for the analysis of pervaporation of mixtures in chemical equilibrium is demonstrated.

It was shown that homogeneous and composite membranes are effective in shifting the esterification reaction equilibrium in pervaporation by the removal of methyl acetate or other esters from the reaction mixture. Composite membranes exhibited higher transport parameters (permeability and selectivity) than homogeneous membranes.

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1. Introduction

The study of separation processes in systems with chemical reactions could be important in the development of a theory of coupled reaction–mass-transfer processes. In modern chemical engineering, mass-transfer processes coupled with chemical reactions are used in the design of resource- and energy-saving technologies and should be considered a significant element of green chemistry. Coupled processes have numerous industrial

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applications. One of the well-known examples is reactive distillation (Sundmacher and Kienle, 2003; Shah et al., 2012): Reactive distillation, which favorably shifts equilibrium through the removal of one of the products, is becoming more common in plant-scale production. It is, however, an energy-demanding operation and is not recommended when dealing with temperaturesensitive chemicals or biocatalysts (Lim et al., 2002). Reactive distillation can be combined with membrane separation (Aiouache and Goto, 2003; Liu et al., 2005a, 2005b; Steinigeweg and Gmehling, 2004). For example, the processes in reactive distillation-pervaporation hybrid columns for tert-amyl alcohol etherification with ethanol has been considered (Aiouache and Goto, 2003). Membrane separation can also be coupled with synthesis reaction. The combination of

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a chemical reactor with a separate membrane pervaporation unit may lead to an effective coupled reaction–mass-transfer process. The processes in a pervaporation membrane reactor has been studied in various experimental works and theoretical research (Huang et al., 2004; Sanz and Gmehling, 2006; Domingues et al., 1999; Korkmaz et al., 2011; Rewagad and Kiss, 2012; Suttichai et al., 2003; Liu and Chen, 2001; Xuehui and Lefu, 2001; Assabumrungrat et al., 2003; Feng and Huang, 1996; Dos Reis Gonçalves et al., 2005; Liu et al., 2005a, 2005b; Delgado et al., 2009; David et al., 1991a, 1991b; Kita et al., 1988, 1987). Most of these studies concern the esterification reaction

Alcohol (R_1) + Acid (R_2) = Water (P_1) + Ester (P_2) .

Esterification of carboxylic acids with alcohols is a typical example of an equilibrium-limited reaction. The conversion of reagents in such reactions depends on the thermodynamic constant of chemical equilibrium. Correspondingly, shifting the equilibrium leads to a higher conversion. Using excess alcohol as a cheap reagent is a practical method to achieve a high ester yield. On the other hand, the use of a large amount of reactant increases operation costs because it is necessary to separate the excess alcohol.

The other way is to combine reaction and separation processes for the extraction of a main product or side-product. The esterification reaction could be driven by the extraction of products through reactive distillation. Another attractive method is the use of a pervaporation membrane reactor. The pervaporation is a ratecontrolled process and its efficiency in separation is not limited by related volatility as it would be in reactive distillation. In addition, the pervaporation separation could be carried out at a reaction temperature that is important for the technological design of the process. Finally, energy consumption in pervaporation is usually low (Mulder, 1996; Baker, 2004). Preliminary results on the use of a pervaporation membrane reactor as well as the description of a hybrid process of ester production have been presented in recent papers (David et al., 1991a, 1991b; Kita et al., 1988, 1987; Keurentjes et al., 1994; Kwon et al., 1995).

The typical scheme of the hybrid process "reaction+pervaporation" (Feng and Huang, 1996) is shown in Fig. 1. Reagents (acid and alcohol) and a catalyst that is either homogeneous or heterogeneous are merged in a reactor (1). During the reaction, a quaternary equilibrium mixture is obtained. This mixture is transmitted to a membrane cell (2), where one of the reaction products is removed by pervaporation (3). The residual reaction mixture that does not pass though the membrane goes back to the reactor. In this way, excess acid and alcohol appears in the reactor and increases the conversion.

The development of the new membranes which are effective for the application in the hybrid process "reaction+pervaporation" is also an important element of chemical engineering design.



Fig. 1. Scheme of hybrid process of ester production: (1) reactor, (2) membrane, and (3) permeate (Sanz and Gmehling, 2006).

Primarily, hydrophilic membranes based on polyvinyl alcohol and polyesterimide have been used for reactive pervaporation (Zhu et al., 1996; Nemec and Robert van, 2005), and this membrane type facilitated water removal from the reaction zone. In our previous work, organophilic membranes based on poly-(2,6dimethyl-1,4-phenylene oxide) (PPO) were studied through the pervaporation of a quaternary mixture containing components of ethyl acetate synthesis in equamolar content (Polotskaya et al., 2007, 2005). It established selective properties of PPO membrane with respect to ethyl acetate. Removal of the ester from the reaction medium by the membrane pervaporation can shift the esterification equilibrium and, at the same time, point to potentially important industrial solvents.

In this presented paper, we consider the various aspects of reactive pervaporation in the system with methyl acetate reaction. The important element of the current study is the composition of the feed reactive solution. Most of the work on non-reactive and reactive pervaporation is focused on a binary feed mixture. On the other hand, it is evident that shifting the chemical equilibrium through reactive pervaporation should be studied for solutions close to chemical equilibrium compositions. Correspondingly, we consider the feed mixture compositions nearing an equilibrium state of methyl acetate synthesis. In this paper, we present some of our results of a systematic study of pervaporation of a reactive mixture for the case of compositions that are close to chemical equilibrium. The shifting from chemical equilibrium leads to a greater conversion of reagent, which is necessary for the development of resource-saving chemical technologies.

The objects of this study were two membrane types based on PPO: a homogeneous PPO membrane and a composite membrane consisted of a thin PPO selective layer ($\sim 5 \,\mu$ m) on the surface of hydrophobic fluorocarbon polymer porous support (MFFC). The dense film homogeneous membrane makes it possible to research transport properties of chosen selective polymer PPO. The composite membrane with a thin layer of selective polymer can ensure high-level permeability for the industrial application of a developed membrane process.

2. Material and methods

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a molecular weight of 172 000 and intrinsic viscosity of 1.58 dl/g (Brno, Czech Republic) was used for the work. Methyl acetate, methanol, and acetic acid were purchased from Vecton (Russia).

The microfiltration fluoroplastic composite hydrophobic membrane MFFC (Vladipor, Russia) is composed of a porous fluoroplast F42L layer on a polypropylene support. The pore size is 0.05 mcm, with a total porosity of 80%.

2.2. Membrane preparation

2.2.1. Homogeneous membranes

The homogeneous PPO membranes with a thickness of $60 \,\mu m$ were prepared by casting a 2 wt% PPO solution in chloroform on a cellophane surface and drying to remove the solvent. After that, the PPO film was separated from the cellophane and dried to a constant weight in a temperature set at 333 K.

2.2.2. Composite membranes

The formation of a thin selective PPO layer in the composite membrane was created by casting 2 wt% PPO solution in chloroform on a surface of MFFC support and drying in vacuum at 313 K. To provide the formation of the selective layer at a thickness of Download English Version:

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