Journal of Polytechnic, 2017; 20 (2) : 437-440

Enhancement of Conversion using Ceramic Membrane in Esterification of Acrylic Acid with Butanol

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(Received : 13.04.2016 ; Accepted : 16.05.2016)

ABSTRACT

The esterification reaction between butanol and acrylic acid was performed in a batch reactor coupled with ceramic membrane. The tubular ceramic membrane was used to selectively remove water which coursed during the reaction. Due to water removal, equilibrium shifted to the product side and conversion of acrylic acid increased. The effects of some process parameters such as temperature, catalyst loading, molar ratio of reactants on conversion of acrylic acid and flux of water were investigated. Especially, the increases in temperature facilities increase in conversion of acrylic acid markedly.

Keywords: Esterification, Acrylic Acid, Ceramic Membrane, Pervaporation, Butyl Acrylate.

ÖZ

Bütanol ve akrilik arasındaki esterleşme reaksiyonu seramik membran modülü ile birleştirilmiş kesikli reaktörde gerçekleştirilmiştir. Kullanılan seramik membran reaksiyon sırasında oluşan suyu seçimli olarak reaksiyon karışımından uzaklaştırmıştır. Suyun uzaklaştırılması sebebiyle, denge ürünler yönüne kaymakta ve akrilik asit dönüşümü artmaktadır. Deneylerde katalizör olarak iyon değişim reçinesi kullanılmıştır. Sıcaklık, katalizör miktarı ve reaktantların mol oranlarının akrilik asit dönüşümü ve suyun uzaklaşma akısı üzerine etkileri incelenmiştir.

1. INTRODUCTION

Esterification of alcohols and carboxylic acids is one of the most significant reactions in organic synthesis [1]. The reaction is limited by the thermodynamic equilibrium. In order to overcome the equilibrium, an excess of one reactant or removing water can be used to shift the equilibrium [2]. While the use of excess alcohol may increase the operation costs on the downstream reagent recovery and result in unwanted ether formation [3]. The integration of reaction and separation processes such as distillation, adsorption or pervaporation becomes very attractive. Integration may lead to substantial savings in capital as well as operating costs, which can come as a result of higher conversion and selectivity, smaller equipment size, energy integration etc. [4]. Among these hybrid processes reactive distillation is only useful when the products and reactants are not close boiling points [5].

Pervaporation, a membrane process, is one of the most promising approaches to perform this task because it allows a very selective water removal from the reaction medium combined with lower energy requirements [6]. In pervaporation processes, the transport of the components from the feed liquid mixture to the vapor phase involves the following steps; i) mass transfer from the feed bulk to the feed membrane interface, ii) partition of penetrants between the feed and the membrane, iii) selective diffusion through the membrane, iv) desorption into the vapor phase on the permeate side [7]. Generally, polymeric membranes are used to separate gas and liquid specifications. Polymers, like polyvinyl alcohol (PVA), polyimide and Nafion have a high permselectivity to a number of chemical compounds [8].

Several studies show that the equilibrium shifting could be occurred when a polymeric membrane is used [9-12]. However, organic polymer membranes typically work in a temperature range from ambient to 130°C, operation at higher temperatures is difficult with the current polymeric membranes [13]. Inorganic membranes or ceramic mebranes are resistant to relatively harsh chemical environment. Also, esterification reactions are usually catalyzed by homogeneous catalyst, which are strong acids such as sulfuric acid. These have been found to attack the ceramic membranes which as a result quickly lose their performance [4]. Generally heterogeneous catalysts such as ion exchange resins are used as catalysts to prevent the degradation of ceramic membrane. Other than prevention of membrane, there are several advantages of solid catalysts; easy separation from the reaction mixture, high selectivity, reusability etc.

Generally, acrylic acid esters are clear colorless liquid with a characteristic fruity odor. Acrylates were produced from catalytic esterification of acrylic acid with an alcohol catalyzed by acidic catalysts;

C_2H_3-COOH + C_4H_9-OH ↔ C_4H_9-COO-C_2H_3 + H_2O

Acrylic acid + Butanol ↔ Butyl acrylate + Water

In the previous study, the kinetic study of catalytic esterification of acrylic acid with n-butanol was investigated [14]. The kinetic expression was obtained in the presence of Amberlyst 131 according to Langmuir-Hinshelwood-Haugen-Watson mechanism which correlates the experimental data with minimum error. In another study, n-butyl acrylate was synthesized by pervaporation assisted esterification process and

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Digital Object Identifier (DOI) : 10.2339/2017.20.2 437-440

polymeric membrane, Pervap 2201, was used to remove water from the reaction mixture. Conversion of acrylic acid increased from 70% to 92% at a temperature of 358 K due to the water removal [15]. However, polymeric membrane cannot be used at high temperatures and also it may be damaged due to the acidity of the reaction mixture.

In this study, the synthesis of n-butyl acrylate was investigated by using ceramic-tubular membrane. The effects of temperature, catalyst loading, molar ratio of n-butanol to acrylic acid and feed flow rate to membrane module on the conversion of acrylic acid and the fluxes of components were studied.

2. MATERIALS AND METHODS

Catalyst; the esterification reaction was carried out using ion exchange resin, Amberlyst 131. The main properties of Amberlyst 131 were given in our previous study [15]. Used ion exchange resin as catalyst is a macroreticular polymer type; its matrix type and functional group are styrene divinyl benzene and sulfonic acid, respectively.

Ceramic Membrane; water selective membrane with hydrophilic characteristics, was provided from Pervatech BV. It consists of an γ alumina tubular membrane which has a length of 25 cm and inside diameter of 7 mm. The membrane can withstand up to 150°C and 10 bars.

Reactants; Acrylic acid (Merck, purity>99%) and n-butanol (Merck, purity>99%) were used as reactants and phenothiazine was used as inhibitor to prevent possible polymerization reactions.

Procedure; the pervaporation aided esterification process was studied in a batch reactor and membrane module given in Figure 1. Experiments were performed in the liquid phase in a 2 L reactor. The stirrer speed was maintained at 1000 rpm. Alcohol, Amberlyst 131 and phenothiazine were charged to the reactor and heated up to the reaction temperature. The preheated acrylic acid was added to the reactor and temperature was kept constant at desired temperature. After half an hour, the reaction mixture was pumped using a peristaltic pump (Masterflex) to the membrane module. The pressure in the membrane module was maintained at 4 mbar by Vacuubrand RZ 2.5 vacuum pump. The permeate was collected using cold traps and the reaction mixture was recycled to the reactor.

The samples taken from reactor were analyzed by Gas Chromatograph (Agilent 7890). The conditions of the GC analysis were given in our previous study [14]. The temperature program of gas chromatographic analysis was given as follows: waiting 3 min at 60°C; heating from 60 to 180°C at a rate of 5°C/min; waiting for 3 min at 180°C. The water content in the reaction mixture was measured using a Karl Fisher titrator (Mettler Toledo v20).

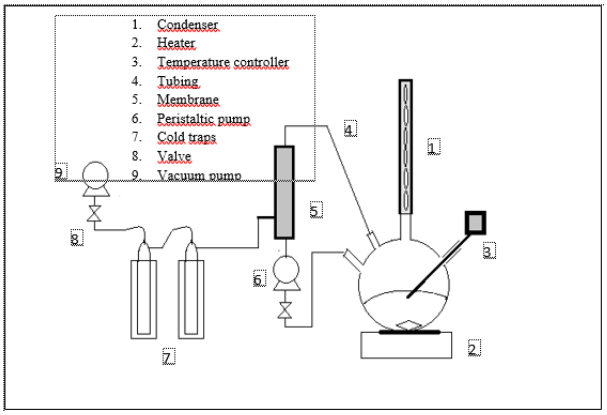

Figure 1. The experimental setup for esterification-pervaporation module

3. RESULTS AND DISCUSSION

The preliminary experiments were performed without membrane module at a molar ratio of n-butanol to acrylic acid of 4 and a catalyst loading of 10 g/L. The results were given in our previous study [15]. These results are useful to understand the effect of pervaporation on conversion of acrylic acid.

Figure 2 shows the effect of temperature on the conversion of acrylic acid for esterification-pervaporation hybrid process which utilizes by ceramic membrane. Conversion of acrylic acid increased from 36% to 48.6%, from 53% to 63.5%, and from 70% to 85.1% at temperatures of 338, 348 and 358 K, respectively.

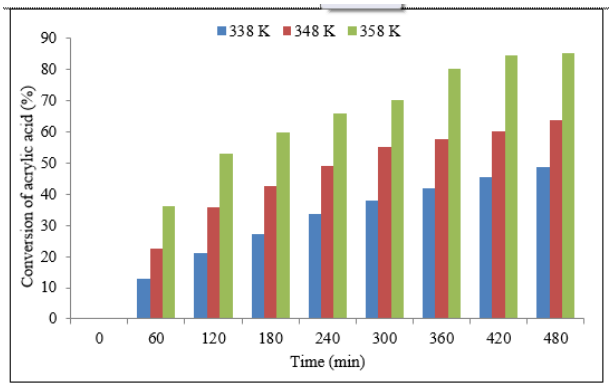

Figure 2. Effect of temperature on conversion of acrylic acid for pervaporation assisted esterification process using ceramic membrane

Pervaporation increases the conversion of acrylic acid as a result of water removal. The collected permeate was analyzed and found to be as pure water. The fluxes of water at different temperatures were given in Figure 3. As temperature was increased, the flux of water increased because of decreasing driving force. As might be expected, the conversion of acrylic acid increased as the flux of water that permeates through the membrane increased. Upon temperature increase the diffusion of water is becoming faster [13].

In our previous work, the esterification of acrylic acid with n-butanol was studied by polymeric membrane, Pervap 2201 [15]. The higher conversions were achieved but the surface area of polymeric membrane is four times larger than that of ceramic membrane. The ceramic membrane also shows a good stability under the same reaction conditions. The flux through the ceramic membrane remained as pure water as the reaction proceed; no traces of acrylic acid, n-butanol, n-butyl acrylate were detected at the permeate side.

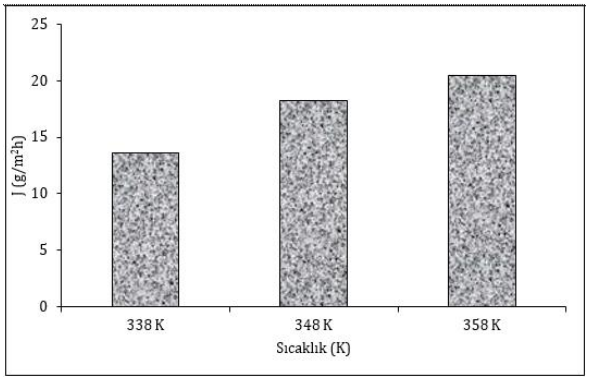

Figure 3. Effect of temperature on flux of water for pervaporation assisted esterification process using ceramic membrane

As an operation parameter, the amount of catalyst plays an important role for all catalytic processes. In the production of butyl acrylate by pervaporation-esterification hybrid process, the effect of catalyst loading was studied at the catalyst loadings of 10, 15 and 20 g/L. The conversion of acrylic acid values of 87.8%, 85.6% and 85.0% at catalyst loadings of 20,15 and 10 g/L.

Figure 4 indicates the effect of catalyst loading on flux of water passing through the ceramic membrane. It can be concluded that, the yield of butyl acrylate improved with the increase of catalyst loading as expected, because of the increasing catalyst active sites and decreasing of reaction activation energy which can speed up the reaction rate. According to Figure 4, catalyst loading increases rate of flux passing as increasing water formation which resulted in higher water concentration in reaction mixture and rendered faster removal rate of water by pervaporation.

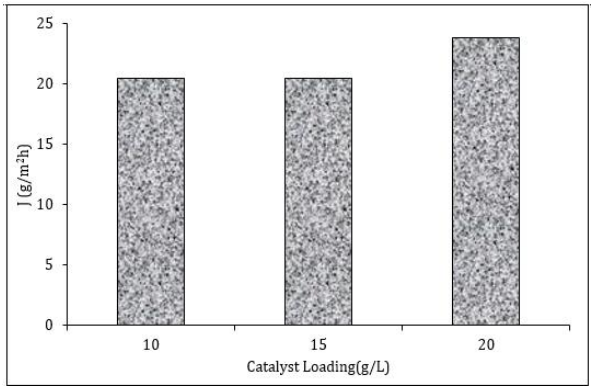

Figure 4. Effect of catalyst loading on the flux of water for pervaporation assisted esterification process using ceramic membrane

Initial molar ratio of butanol to acrylic acid was investigated at temperature of 358 K and catalyst loading of 10 g/L by using ceramic membrane unit. Molar ratios of butanol to acrylic acid were selected as 4, 6 and 8 to decrease pH of mixture and prevent the membrane unit from acidic effect of acrylic acid. As it seen from Figure 5, the yield of butyl acrylate did not remarkably increase with the initial molar ratio of butanol to acrylic acid.

This result may be explained by the flux of water for each molar ratio of butanol to acrylic acid (Figure 6).

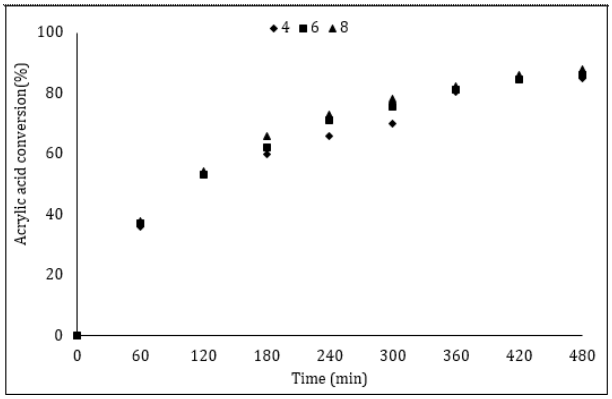

Figure 5. Effect of molar ratio of butanol to acrylic acid on conversion of acrylic acid for pervaporation assisted esterification process using ceramic membrane

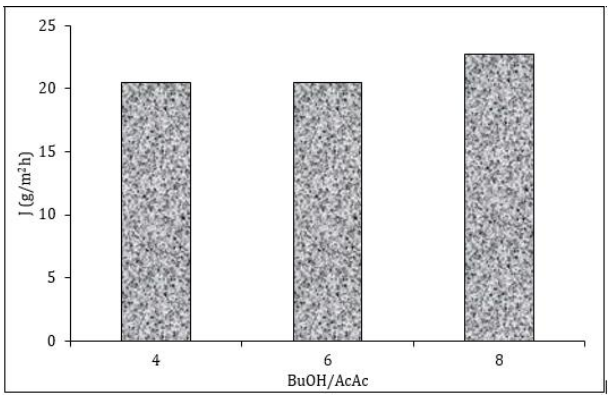

Figure 6. Effect of molar ratio of butanol to acrylic acid on flux of water for pervaporation assisted esterification process

The comparison of conversion of acrylic acid obtained from conventional batch reactor without membrane [14], polymeric membrane, Pervap 2201 [15] and ceramic membrane (PVM 035, Pervatech) is shown in Figure 7. As seen in Figure 7, pervaporation process increases conversion of acrylic acid for both polymeric and ceramic membrane. When polymeric and ceramic membranes are compared, polymeric membrane is more efficient according to acrylic acid conversion rate. But the selectivity of ceramic membrane was found to be higher than that of polymeric membrane. In the case of ceramic membrane, permeate contains pure water.

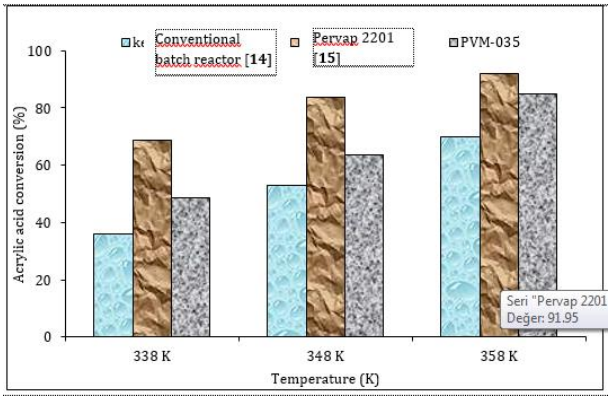

Figure 7. Comparison of the conversion values of acrylic acid obtained from different processes

An important aspect of pervaporation process is the pervaporation membrane with high permeate flux, in the case of pervaporation assisted chemical reaction, the most important point is the selectivity. The selective removal of one of the products, in this work water, is performed successfully. High conversion of acrylic acid and the absence of other components prove the success of the operation. Other than selectivity, other crucial point is the stability of membrane. As stated before, ceramic inorganic membranes withstood harsh chemical environments especially acidic nature of reaction mixture better than polymeric membranes and also give longer life.

4. CONCLUSION

Pervaporation-coupled esterification of acrylic acid with butanol was performed in a batch reactor coupled with membrane using ion exchange resin as catalyst. The tubular ceramic membrane was used to remove water selectively. As a result of water removal, conversion of acrylic acid increased markedly. The conversion of acrylic acid was increased from 69.9% to 85.09% in the presence of ceramic membrane at 358 K. As a result, pervaporation was used to overcome the reversible chemical equilibrium limitation by removal of water as soon as produced successfully.

ACKNOWLEDGEMENT

The authors acknowledge the financial supports from TUBITAK (The Scientific and Technological Research Council of Turkey) under project no. 110 M 462, from EBILTEM (Research and Application Center of Science and Technology) under project no. 2012 BIL 022.

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