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PAGES: 1-12

JOTCSB
Journal of the Turkish Chemical Society
Section: B
Chemical Engineering
Turkish Chemical Society

(This article was initially submitted to the UKMK 2016 (National Chemical Engineering Congress) and finally evaluated by the JOTCSB editorial staff).

Production of Bioadditive Ethyl Levulinate in the Catalytic Membrane Reactor

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Abstract: Fuel bioadditive ethyl levulinate is the biofuel of the future. Reactants of ethyl levulinate are produced from biomass. Therefore, esterification of ethanol and levulinic acid is an environmentally friendly green process for the production of ethyl levulinate. In this study, synthesis of ethyl levulinate was carried out in the batch reactor and in the catalytic membrane reactor by using sulfated zirconia loaded catalytic membrane. Catalytic membrane reactor (CMR) has higher conversion values than the conventional batch reactor. Optimum operation conditions were specified as T=70°C, M=1:1, and C_{cat}=8 g/L. The levulinic acid conversion reached 36 % and 89% in the batch reactor (BR) and in the CMR, respectively.

Keywords: Bioadditive; Ethyl levulinate; Catalytic Membrane Reactor.

Submitted: September 15, 2016**. Revised:** October 05, 2016**. Accepted:** November 02, 2016**.**

Cite this: Ünlü D, Hilmioğlu N. Production of Bioadditive Ethyl Levulinate in the Catalytic Membrane Reactor. JOTCSB. 2017;1(1):1–12.

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INTRODUCTION

Global warming caused by greenhouse gases is known as one of the serious environmental problems in our age. As a result of the usage of fossil-derived fuels and also the reduction of the vegetation cover, the amount of carbon dioxide in the atmosphere has been increasing. Except for CO_2, during combustion of other gases occur, such as chlorofluorocarbons, hydrocarbons, methane, nitrous oxide (NO_x) and sulfur oxides (SO_x). This situation increases the effect of greenhouse gases. Greenhouse gases cause the global warming and climate change. Utilization of biofuels reduces the effect of greenhouse gas and acid rains. As an option of renewable fuel, while biodiesel and bioethanol have been used in the recent time, Fischer-Tropsch diesel-derived biomass and additives derived cellulosic biomass will be important in the medium term. Ethyl levulinate is an important bioadditive material. The use of ethyl levulinate as biofuel provides higher motor efficiency, long operation life, less carbon monoxide (CO) and NO_x emissions. Diesel engines have a high exhaust and NO_x emissions. Therefore, they have a negative effect to environment. The addition of oxygenates to fossil fuels is one of the most important methods to eliminate these problems. Levulinates are known as oxygenate additive. Ethyl levulinate has properties such as high flash temperature (low ignition temperature) and 33% oxygen content, clean combustion with high efficiency [1-4].

Levulinic acid and ethanol are used as the reactants for the ethyl levulinate production. Each reactant is biomass-based. While levulinic acid is obtained by the acidic hydrolysis of cellulose, ethanol can be produced from biological and waste sources such as sugars, starch, cereal grains, and agricultural and wood residues. The use of biomass based reactants for ethyl levulinate production makes the process the environmentally friendly green production process [5].

Reaction products of ethanol and levulinic acid are ethyl levulinate and water. For the usage of ethyl levulinate as fuel additive, ethyl levulinate must be obtained as pure. Distillation, which is one of the conventional separation methods, is used for the purification in literature researches. Distillation is quite a costly process to obtain a pure product. In this situation, new separation processes are investigated by researchers. Membrane reactor is one of the developing membrane separation process and it is used for obtaining pure products economically [6].

Production of ethyl levulinate occurs in the presence of homogeneous or heterogeneous catalysts.

For overcoming the equilibrium limit, excess amount of limiting reactant is used or by-products are removed by conventional methods such as reactive distillation and reactive stripping. The utilization of excess reactant increases the operating costs and results in the formation of undesired by-products. Reactive distillation is not suitable for azeotropic liquids. The use of membrane reactor is more attractive at this point, because the processing cost reduces by the minor amount of reactants and high conversions are obtained too [7].

The system, which uses a catalytic membrane, is called as the catalytic membrane reactor (CMR). CMR integrates the reaction and separation into one single unit. Catalytic membranes are used in this process. Reaction is carried out on the catalytic layer of the membrane and reaction products are obtained. As a result of the reaction, the formed product is selectively removed through the membrane. The continuous removal of selective product from the reaction mixture shifts the reaction equilibrium to the product side. Therefore, it facilitates the enhancement of reaction conversion [8-9].

In this study, catalytic membranes, which had catalytic and separation properties, were prepared. The purpose of the combination of the catalyst and membrane is to make the reaction in one step. Hydrophilic biodegradable polymer hydroxyethyl cellulose was used in this study [10]. Sulfated zirconium oxide (SO_4^{2-}/ZrO_2) is used as a catalyst. SO_4^{2-}/ZrO_2 was chosen for the esterification reactions due to their acidic properties. High conversion values were obtained while SO_4^{2-}/ZrO_2 was used in similar esterification reactions. SO_4^{2-}/ZrO_2 has a problem as leaching. This situation caused the catalytic activity loss. Therefore, catalyst was embedded into the polymeric membranes as an alternative. In this case, recovery of the catalytic membrane and reuse were easy and practical. Also, leaching problems were prevented when the SO_4^{2-}/ZrO_2 catalytic membranes were utilized. The effects of reaction parameters such as temperature, catalyst concentration, and the molar feed ratio on conversion were examined.

MATERIALS AND METHODS

Chemicals

Hydroxyethyl cellulose polymer and ethanol, levulinic acid, isopropanol, sodium hydroxide, and phosphoric acid were obtained from Sigma Aldrich and Merck.

Experimental procedure

Preparation of catalytic composite membrane: The catalytic composite membrane was prepared by the solution casting method. The composite membrane consisted of catalytic layer and separation layer. The aqueous HEC polymeric membrane solution was first prepared for the separation layer. The polymeric membrane solution was mixed for 24 hours at room temperature. Then, the solution was poured on PMMA surface. After one day, diluted polymeric membrane solution was prepared by the addition of 2, 5 and 8 g/L of catalyst SO_4^{2-}/ZrO_2. The prepared catalytic polymer solution was poured onto the separation HEC layer. After drying, membrane was immersed in isopropanol-water and phosphoric acid solution for crosslinking. Finally, the membrane was washed with pure water and dried in the oven [11-12]. The pristine and catalytic composite membrane were characterized by Scanning Electron Microscopy.

Esterification reaction

The esterification reaction of ethanol with levulinic acid was carried out by using catalytic membrane as catalyst under the various conditions. The experiments of batch reactor were performed in a 100 mL round-bottom flask fitted with a reflux condenser, magnetic stirrer and thermometer. The prepared catalytic membrane was cut into small pieces and added in the batch reactor. Scheme of the batch reactor was shown in Figure 1.

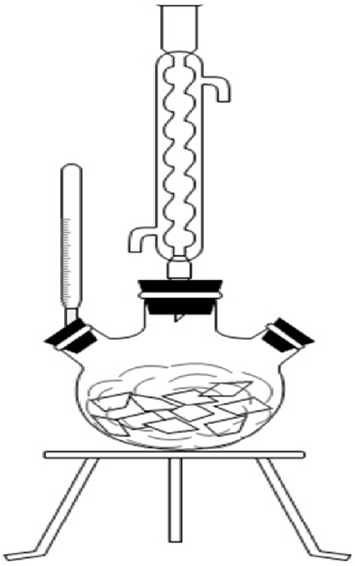

Figure 1. Batch reactor.

Levulinic acid conversion values are calculated by the titration with NaOH. Conversion values were calculated by using the following Equation (1).

$$x = \frac{N_{Ao} - N_A}{N_{Ao}} \quad \text{(Eq. 1)}$$

In this equation, N_{Ao} is the number of moles of levulinic acid at t = 0, N_A is the number of moles of levulinic acid at any of the time of the reaction [13].

The esterification reaction of levulinic acid and ethanol was conducted in the catalytic membrane reactor by using SO_4^{2-}/ZrO_2 loaded catalytic composite membrane. Reactants were fed into the membrane cell. The reaction occured in the catalytic layer of the membrane. Reactants are converted to products by the reaction. According to affinity of the membrane, one of the products was removed through the membrane. Figure 2 shows the CMR process.

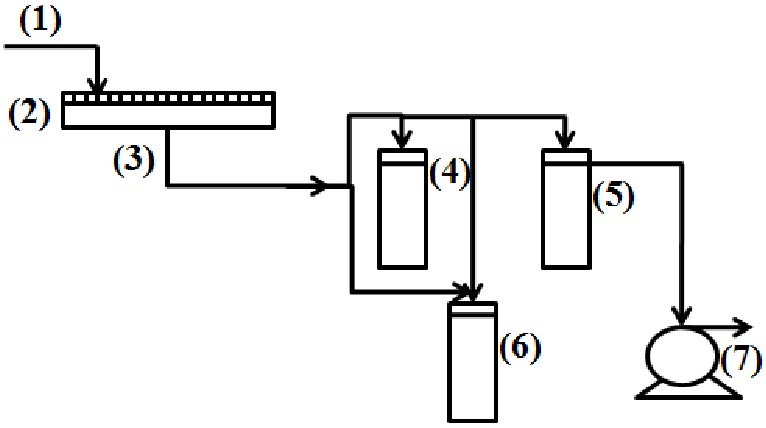

Figure 2. CMR process (1) Feed (2) Catalytic membrane (3) Permeate (4), (5), (6) Cold trap (7) Vacuum pump.

Levulinic acid conversion values were determined by titration and GC analysis. Obtained conversion values were compared with batch reactors and efficiency of CMR for increment of conversion was exhibited.

RESULTS AND DISCUSSION

Membrane Characterization by SEM

The surface and cross-section images of the catalytic composite membrane were viewed by SEM. Figure 3 shows pristine membrane surface (a), catalytic membrane surface (b), pristine membrane cross-section (c) and catalytic membrane cross-section (d), respectively.

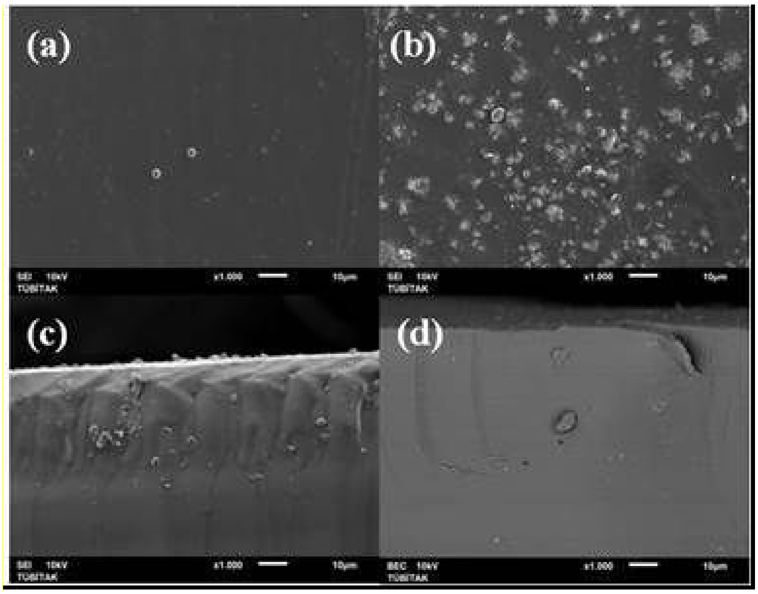

Figure 3. SEM images of the pristine and catalytic membrane: (a) pristine membrane surface and (b) catalytic membrane surface (c) pristine membrane cross-section (d) catalytic membrane cross-section.

As shown in Figure 3(a) the pristine HEC membrane has a homogeneous surface. In Figure 3(b) catalysts of SO_4^{2-}/ZrO_2 are dispersed on the catalytic layer of the composite membrane. Fig. 3(c) shows the cross-section of pristine membrane. It has only a single layer. Cross section image of catalytic composite membrane is shown in Figure 3(d). It was observed in Figure 3(d), catalytic composite membrane has two layers: catalytic layer and separation layer. Also, the compatibility of the separation layer and catalytic layer can be seen in Figure 3(d).

Effect of the temperature on levulinic acid conversions in the batch reactor and in the CMR

Experiments of CMR and BR were realized by using 8 g/L of SO_4^{2-}/ZrO_2 loaded catalytic membrane with equimolar condition (M=1) at temperature of 50 °C, 60 °C, and 70 °C. The effect of the temperature on levulinic acid conversion was shown in Figure 4.

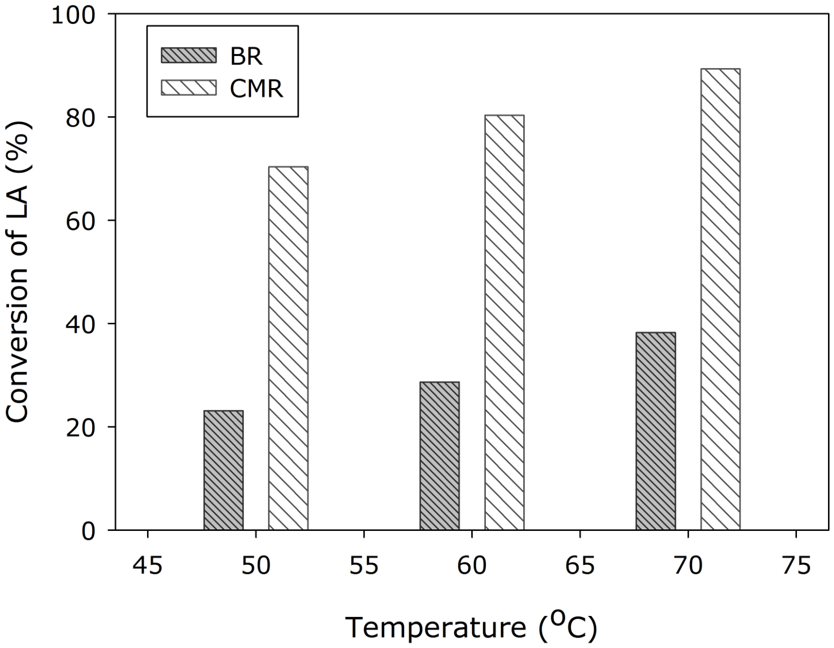

Figure 4. Effect of the temperature on conversion (8 g/L catalyst loaded membrane, M=1).

Conversion was increased by temperature in both BR and CMR. However, conversion of CMR was higher than conversion of BR. In CMR, water, which occurred from the result of the reaction, was removed from the reaction medium. Therefore, reaction equilibrium shifted toward the products. Thermal mobility of the polymer chains increased with increasing temperature. This situation created free volume in the membrane matrix. Transport of selected components increased through the membrane. Thus, by removing the water had improved the conversion [14-16].

After 7 hours, the highest conversion was obtained as 38% at 70 °C in the batch reactor. Under the same reaction conditions, the highest conversion was obtained as 89% in the CMR [17].

Effect of the catalyst concentration on levulinic acid conversions in the batch reactor and in the CMR

Different ratios of SO_4^{2-}/ZrO_2 loaded catalytic membranes were prepared and experiments were performed by using equimolar reactant (M=1) at 70 °C. Figure 5 shows the change of levulinic acid conversion values in the different catalyst loading amounts.

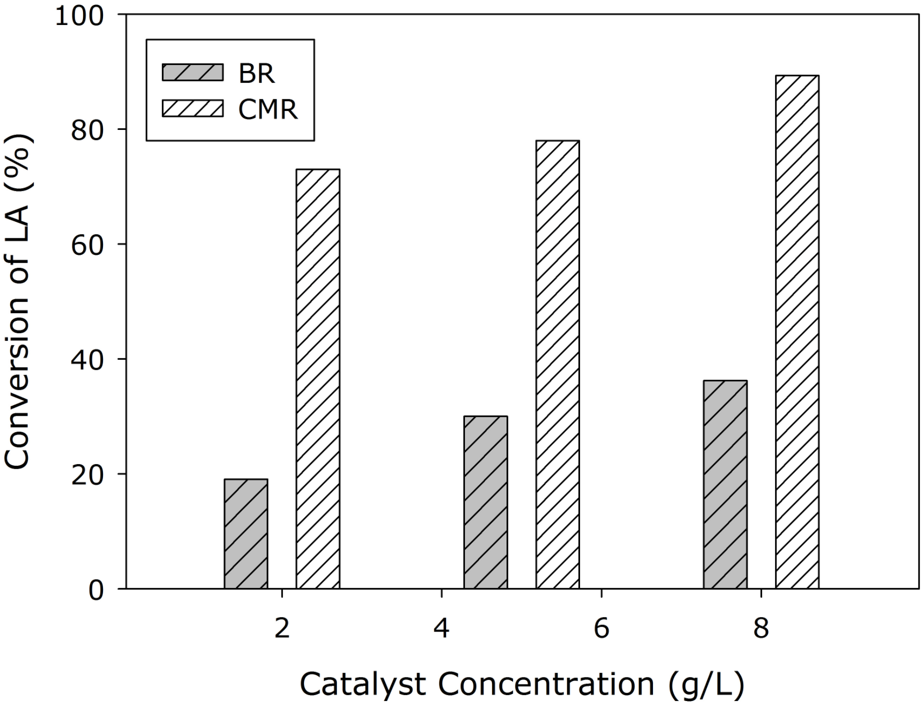

Figure 5. Effect of the catalyst concentration on conversion (70°C, M=1).

Levulinic acid conversion increased with increasing catalyst concentration. Higher conversion was obtained in the CMR in the first hours of reaction. The increase in catalyst concentration of the membrane provided the intense catalyst distribution on the membrane surface and the reactants could be reached easily active site of the catalyst [18-20]. Conversions obtained in the CMR was higher than in the BR. While the 36% of conversion was obtained by 8 g/L SO_4^{2-}/ZrO_2 catalyst loaded membrane for 7 hours in the batch reactor, 89% of conversion was obtained under the same reaction conditions in the CMR [17].

Effect of the molar feed ratio of alcohol to acid on levulinic acid conversions in the batch reactor and in the CMR

BR and CMR experiments were carried out by using 8 g/L SO_4^{2-}/ZrO_2 catalyst loaded HEC catalytic membrane at 70°C, different alcohol/acid molar feed ratios. Figure 6 shows the change of conversion of levulinic acid with molar feed ratio.

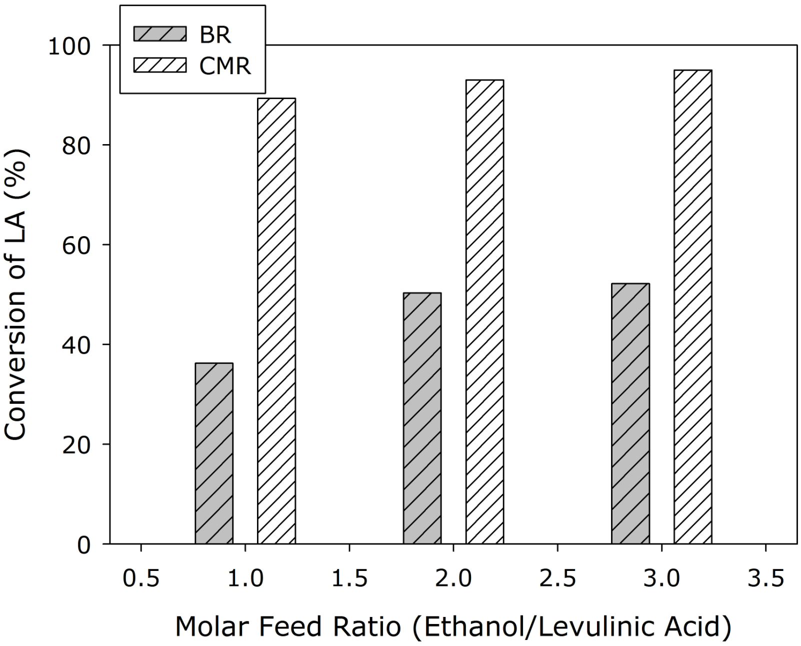

Figure 6. Effect of molar feed ratio on conversion (8 g/L catalyst loaded membrane, T=70 °C).

Conversions obtained in the CMR were higher than in the BR, because the water was removed through the membrane continuously and equilibrium was shifted towards the products. While the conversion was obtained as 52% at M=3 for 7 h in the batch reactor, conversion was obtained as 95% in the CMR under the same reaction conditions [17].

Levulinic acid conversion was increased by the molar feed ratio. One of the ways for increasing the conversion is usage of excess reactant. According to Le Châtelier's principle, the utilization of excess reactant changes the reaction equilibrium towards the product. Therefore, conversion increases. Besides, the usage of excess reactant increases the possibility of contact of all reactants, levulinic acid conversion increases [3 , 21]. However, the aim of the CMR was increasing the conversion by the removal of one of products, therefore (M=1) was chosen as an appropriate value.

CONCLUSIONS

In this study, the esterification reaction was performed by the catalytic membrane in both BR and CMR. Compared to BR, higher conversion was obtained in CMR. Because reaction equilibrium was changed towards the product by removal of byproduct water and so conversion was increased. Results of experimental studies show that the CMR is a suitable method for the synthesis of ethyl levulinate.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from The Scientific and Technological Research Council of Turkey, TÜBİTAK (Project No. 114M147) and Kocaeli University Scientific Research Projects Unit (Project No. 2014/076).

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Türkçe Öz ve Anahtar Kelimeler

Katalitik Membran Reaktörde Biyokatkı Maddesi olan Etil Levulinatın Üretimi

Derya Unlu, Nilufer Hilmioglu

Öz: Yakıt katkı maddesi olan etil levulinat geleceğin biyoyakıtıdır. Etil levulinatı oluşturacak reaktifler biyokütleden üretilmektedir. Bu sebeple, etanol ve levulinik asidin esterleştirilmesi, etil levulinatın üretimi için çevreyle dost ve yeşil bir süreç olarak karşımıza çıkmaktadır. Bu çalışmada, etil levulinatın sentezi kesikli ve katalitik membran reaktörde yapılmıştır ve katalitik membran olarak sülfatlı zirkonya yüklenmiş membran kullanılmıştır. Katalitik membran reaktör (CMR) geleneksel kesikli reaktörden daha yüksek dönüşüm değerleri vermiştir. En uygun operasyon koşulları T=70°C, M=1:1, and C_{cat}=8 g/L olarak tespit edilmiştir. Levulinik asit dönüşümü kesikli reaktörde (BR) %36 ve CMR'de %89 olarak elde edilmiştir.

Anahtar kelimeler: Biyokatkı maddesi; etil levulinat; katalitik membran reaktörü.

Gönderme: 15 Eylül 2016**. Düzeltme**: 05 Ekim 2016**. Kabul:** 02 Kasım 2016**.**