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Reactive separation system for effective upgrade of levulinic acid into ethyl levulinate

Derya Unlu, Oguzhan Ilgen, Nilufer Durmaz Hilmioglu*

Kocaeli University, Chemical Engineering Department, 41380 Kocaeli, Turkey

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ABSTRACT

In this study, the reactive separation system has been designed and operated for fuel bioadditive ethyl levulinate synthesis from ethanol and levulinic acid by using a catalytic composite membrane. The catalytic composite membrane was prepared by coating hydroxyethyl cellulose membrane with a thin layer of sulfated zirconia. The membranes were characterized and the stability of the catalytic composite membrane was confirmed by consecutive experiments. Batch reactor experiments were carried out by using powder sulfated zirconia catalyst. While the levulinic acid conversion was 34.92% in 7 h by using the powder sulfated zirconia catalyst in the batch reactor, the conversion reached to a level of 95% in 7 h by using sulfated zirconia coated hydroxyethyl cellulose catalytic membrane under the same conditions (reaction temperature 70 °C, catalyst concentration 8 g/L and initial molar ratio 3:1) in the pervaporation catalytic membrane reactor (PVCMR). Results showed that the conversion in the PVCMR was much higher than those in the batch reactors. The effects of temperature, catalyst concentration and initial molar ratio of ethanol to levulinic acid on the conversion value of levulinic acid were investigated for both batch reactor and the pervaporation catalytic membrane reactor.

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1. Introduction

Usage of biomass and biomass based materials has received the especial attentions in the last years. Biomass is used as alternative feedstock for the synthesis of various chemicals and fuels (Qin et al., 2016). Levulinic acid is one of the most important green and biomass derived chemicals. Levulinic acid is obtained by the acid hydrolysis of lignocellulosic residues (Caretto and Perosa, 2013; Demolis et al., 2014). It is also considered as one of the top-twelve building blocks (Oliveira and Teixeira da Silva, 2014). Levulinic acid contains two functional groups, a ketone and a carboxylic acid (Fernandes et al., 2012). This structure makes levulinic acid a versatile building block for the synthesis of several organic chemicals such as levulinate esters, γ -valerolactone, acrylic acid, 1,4-pentanediol, α -angelica lactone, 2-methyl THF etc. (Dharme and Bokade, 2011). A schematic representation of the production of levulinic acid, levulinic acid molecule and its products is shown in Fig. 1. Levulinate esters are important chemical compounds that are

used as fuel additives, solvents and plasticizers. Especially, ethyl levulinate attracts considerable attention in recent years. Ethyl levulinate can be used as a bioadditive in diesel fuel up to 5 wt.%. Usage of ethyl levulinate as fuel additive for diesel causes an improvement in fuel properties such as a clean burning, decrease in sulfur constituents, development in viscosity. Also, ethyl levulinate is a good alternative to diminish the consumption of fossil fuels (Kuwahara et al., 2014; Pileidis et al., 2014; Joshi et al., 2011; Windom et al., 2011).

Ethyl levulinate is usually synthesized by using homogeneous catalysts such as H_2SO_4 . H_2SO_4 is widely used for esterification reactions associated with high yield within a short reaction time. However, this catalyst is unrecyclable, corrosive and toxic (Huang et al., 2016). Therefore, H_2SO_4 is embedded in zirconium oxide for the overcome the disadvantages of liquid H_2SO_4 catalyst. This form of the catalyst is classified as a heterogeneous super acid catalyst and called as sulfated zirconia (SO_4^{2-}/ZrO_2). Acidity of sulfated zirconia is higher than concentrated H_2SO_4 , because the SO_4^{2-}/ZrO_2 catalyst has Bronsted and

* Corresponding author at: Department of Chemical Engineering, Engineering Faculty, Kocaeli University, 41380 Kocaeli, Turkey.
Fax: +90 262 359 12 62.

E-mail addresses: derya.unlu@kocaeli.edu.tr (D. Unlu), oilgen@kocaeli.edu.tr (O. Ilgen), niluferh@kocaeli.edu.tr, niluferhilmioğlu3@gmail.com (N. Durmaz Hilmioglu).
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Nomenclature

α	Selectivity
n_0	Initial mole number (mol)
n_t	Mole number at time t (mol)
A	Effective membrane area (cm^2)
C_{cat}	Catalyst concentration (g/L)
CMR	Catalytic membrane reactor
HEC	Hydroxyethyl cellulose
J	Flux ($\text{kg}/\text{m}^2 \text{ h}$)
m	Permeate weight (g)
M	Initial molar ratio
PVCMR	Pervaporation catalytic membrane reactor
$\text{SO}_4^{2-}/\text{ZrO}_2$	Sulfated zirconia
t	Time (h)
W_s	Weights of swollen membranes
W_d	Weights of dried membranes
x	Conversion of levulinic acid
X_a, X_b	Weight fraction of a and b components in the feed
Y_a, Y_b	Weight fraction of a and b components in the permeate

Lewis acidic sites. Sulfated zirconia displays high catalytic activity and good stability in the esterification reaction (Sang et al., 2014; Kansedo and Lee, 2012). However, a main disadvantage of the use of sulfated zirconia powder catalyst in the reactions is hydrolysis and leaching of the active sulfate groups. Leaching of sulfate groups reduces the catalytic activity of the catalyst (Omota et al., 2003). Catalytic membrane is an important technology to overcome these problems at this point.

Heterogeneous catalysts such as sulfated zirconia are added into polymeric membrane solution and catalytic membrane is prepared from the solution by solution casting technique. The polymeric environment around the catalyst avoids the leaching problems. The basic features of a catalytic membrane are high catalytic activity and selectivity, high thermal and mechanic stability under the reaction conditions. The production cost of the catalytic membrane, which is nontoxic, is lower than that of the conventional catalyst. Also, the use of catalytic membrane facilitates the recycling and reuse of the catalyst (Ceia et al., 2014; Diosos et al., 2006; MacLeod et al., 2010; Drioli and Fontananova, 2010). For ethyl levulinate synthesis, catalytic membrane is firstly used as the catalyst in the batch reactor in our previous study. Sulfated zirconia coated catalytic hydroxyethyl cellulose membrane pieces had been used as the catalyst in the batch reactor (Unlu et al., 2016).

The catalytic membranes are preferred to pure membranes. When a catalyst is immobilized within a membrane or coated on the surface of a membrane, the membrane characteristics (hydrophobic or hydrophilic) and the membrane structure (dense or porous) can be changed and the

catalytic activity and sorption and diffusion properties of the components can be affected from this situation. Hence, choice of the polymer material used for catalytic membrane preparation is important. Polymeric material should be mechanical, chemical and thermal stable. Interaction of catalyst and polymer is also important for good dispersion and miscibility. Another advantage of the catalytic membrane is insolubility in the reaction mixture (Drioli and Fontananova, 2010; Drioli et al., 2008).

Systems which used catalytic membrane are called as the catalytic membrane reactor (CMR). In a membrane reactor, reaction and separation occur simultaneously (Vospornik et al., 2004). If separation is realized by pervaporation membrane process, the system is called as pervaporation catalytic membrane reactor (PVCMR) (Ceia et al., 2014; Zhang et al., 2014a).

Pervaporation is a membrane aided separation technique for liquid–liquid mixture. Pervaporation is based on permselective evaporation. Driving force is created by using a vacuum pump on the permeate side. According to affinity, one of the components in the mixture sorbs into the membrane, diffuses across the membrane, and desorbs into vapor at the permeate side (Bruggen, 2010).

The pervaporation unit is combined with the reactor and the hybrid system PVCMR has important applications on esterification reactions. Esterification reactions have an acid and an alcohol as reactants, and ester and water as product and byproduct, respectively. Higher conversion is obtained by removal water according to Le Chatelier–Braun principle in the reversible esterification reactions. Byproduct water is continuously removed from the reaction medium by the membrane. Thus the reaction equilibrium shifts towards to product side and conversion is enhanced (Bruggen, 2010).

The use of PVCMR can be an ideal alternative process especially for esterification process, because it would overcome the drawbacks of the conventional separation process which has high energy consumption, huge environmental problems (Sorribas et al., 2015). In PVCMR, separation is independent of volatilities of the reactants and products; it depends on the solubility and transport rate of each component (Iglesia et al., 2016; Fontananova and Drioli, 2014). It can be also operated at mild reaction conditions. Thereby, PVCMR has some important advantages such as operation at low temperature, separation of azeotropic mixtures and giving higher conversion for the thermodynamically limited esterification by selective separation of products. It is more compact process with less capital cost, operated easily, The PVCMR is also energy efficient, environment friendly process (Zhu et al., 2016; Sert and Atalay, 2014).

Esterification reaction of levulinic acid and ethanol using sulfated zirconia loaded hydroxyethyl cellulose catalytic membrane in PVCMR was not investigated until now. The PVCMR studies from the literature have been reported as following.

Chandane et al. (2016) described the esterification of propionic acid with isobutyl alcohol in a pervaporation assisted hybrid process. A polyvinyl alcohol–polyethersulphone (PVA–PES) hydrophilic membrane was used to produce isobutyl propionate. Conversion of 89.82% was obtained at 90 °C, initial molar ratio of 2:1, the catalyst loading of 3 wt.% for the reaction time of 8 h in PVCMR (Chandane et al., 2016). Zhang et al. (2014b) presented PVA/PES membrane immobilized with lipase for the synthesis of lauryl stearate in a pervaporation membrane reactor. A conversion of 83% was observed in PVCMR (Zhang et al., 2014b). Zhang et al. (2014a) studied the esterification of acetic acid and *n*-butanol, catalyzed by an ion-exchange resin consisting of highly cross-linked styrene–divinyl benzene copolymer beads, using a PVA/PES composite membrane. The acetic acid conversion reaches 91.4% in 20 h at 85 °C by using the catalytic membrane (Zhang et al., 2014a). A similar approach was presented by Figueiredo et al. (2008) who described the preparation of Amberlyst 35 coated PVA membranes for the esterification reaction of ethanol and acetic acid. An increment of 60% in conversion value by PVCMR was stated (Figueiredo et al., 2008). Peters et al. (2005) carried out pervaporation-assisted esterification using zeolite coated ceramic membrane. The activity of the catalytic membrane was investigated in the esterification reaction between acetic acid and butanol. Conversion value of acetic acid was calculated to be 85% in a pervaporation catalytic membrane reactor (Peters

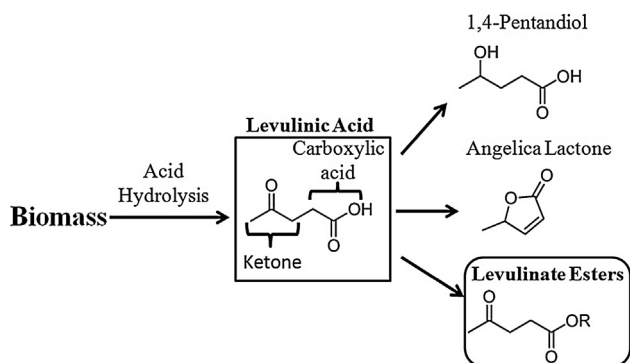


Fig. 1 – Schematic representation of the production of levulinic acid, levulinic acid molecule and its products.

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