



Biofuels production by esterification of oleic acid with ethanol using a membrane assisted reactor in vapour permeation configuration



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ABSTRACT

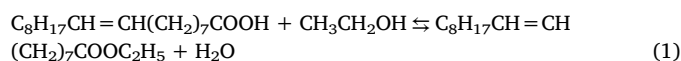
Biodiesel production by performing the oleic acid esterification reaction in a new reactor system, realized by coupling the batch reactor with a tubular permeoselective membrane, has been investigated. Such reactor configuration was adopted to remove the water produced as by-product during the reaction thus increasing the oleic acid conversion and the alkyl ester production. The activity of acid catalysts and zeolites was evaluated in presence of methanol and ethanol. The membrane resulted much more selective towards water separation when ethanol was used, allowing to force thermodynamic equilibrium at higher conversion values. Very interesting results in terms of oleic acid conversion were achieved with both methanol and ethanol (96% and 98% respectively) in presence of a commercial Amberlyst-15 catalyst, at 80 °C, at a low membrane surface to gas volume ratio (0.20 cm⁻¹) and low acid/alcohol molar ratio (2/1 and 1/1 respectively). Over zeolite samples, conversion values higher than 60% were obtained at 100 °C after 5 h in the esterification reaction performed in vapor permeation configuration.

1. Introduction

Biodiesel is a fatty acids alkyl esters (FAAEs) mixture, derived from renewable lipid feedstocks (vegetable oils, animal fats or waste cooking oils), which could be considered a suitable substitute for petroleum derivate fuels due to its environmental benefits [1]. Cetane number, energy content, viscosity and phase changes of biodiesel are similar to those of fossil diesel [2–4]. FAAEs are generally produced by transesterification reaction between the triglycerides contained into oils or fats and an alcohol; anyhow, the moisture and the free fatty acids (FFAs) present into the feedstock could react with the homogenous alkali catalyst used in the industrial process, producing soaps and gels. This reduces the FAAEs yield and deeply influences the performance and the economics of biodiesel production [5]. So, to use low-cost feedstocks (waste frying oils or fats and oils with high FFAs amount), a pretreatment esterification step is mandatory to reduce the free acidity level below 1% wt/wt. Therefore, the esterification reaction can be exploited both as a pre-treatment step of a conventional transesterification process [6,7] or as biodiesel direct production [8,9]. Methanol (MeOH), ethanol (EtOH) and butanol (ButOH) are the most employed alcohols [10]. Anyhow, the biological nature of EtOH and its extra-carbon atom,

which slightly increases the heat content and the esters cetane number, make ethyl esters (EEs) more interesting than methyl esters (MEs). Moreover, EtOH is nontoxic and has better solvent properties than MeOH for oil solubility and EEs have cloud and pour points lower than the MEs [10].

The esterification of oleic acid (OlAc) can represent well the biodiesel production, since it is present in most of oil crops [11]. With EtOH, ethyl oleate (OleOEt) is produced and water is the by product, according to the following equation:



The industrial esterification processes carried out with strong Brønsted acid catalysts [12–14] are not environmentally benign, since they require special treatments as neutralization involving costly catalyst separation steps from the homogeneous reaction mixtures. Heterogeneous catalysts could be easier separated, they show high activity and stability and could be reused offering milder operating conditions. Ion exchange resins [15,16], zeolites [17–19], heteropolyacids [20] and modified zirconia [21,22] are the most used solid acid catalysts for OlAc esterification. Besides, niobic acid [23], polymers with acid

Abbreviations: A_i, initial acidity; A_f, final acidity; FAAEs, fatty acids alkyl esters; FFAs, free fatty acids; EEs, ethyl esters; MEs, methyl esters; MVol, micropore volume; OlAc, oleic acid; OleOEt, ethyl oleate; PV, pervaporation; PVol, pore volume; SA, surface area; S_m, surface of the membrane; TPD, temperature programmed desorption; VP, vapor permeation; V_g, volume of gas phase

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groups [24]; ammonium salt of TPA [25], carbon material [26] were used too. Anyhow, considering the reaction equilibrium, the water produced and that contained into waste oils could hinder the esterification, accelerating the inverse reaction. Amberlyst-15 (A-15), for example, resulted to be a suitable catalyst for OIAC esterification with MeOH [27], but the conversion rate increased only replacing MeOH and catalyst with fresh one or by removing water from the reaction mixture. For this reason, it is of great interest, from a practical point of view, to study separation processes able to eliminate the water during the reaction [28].

On this account, Son et al. [29] obtained high MEs yield by performing the OIAC esterification in a three-phase fixed bed reactor (80 °C–120 °C) coupled with a continuous water evaporation system. Nijhuis et al. [30] exploited a reactive stripping operation in a monolithic reactor; Lucena et al. [5] employed a reactor coupled to an adsorption column filled with zeolite 3A in the OIAC esterification with MeOH using H₂SO₄ as catalyst and shifted the biodiesel yield from 88.2% to 99.7% at 100 °C.

Recently, the integration of chemical reaction with the membrane separation has received great attention: the use of a reactor equipped with a permselective membrane significantly improves the process efficiency favoring not only the chemical equilibrium shift but also a longer catalyst lifetime [31–33]. Specifically, pervaporation (PV) and vapor permeation (VP) technologies could be considered as clean technologies which, because of low temperatures and pressures involved, could efficiently replace conventional energy-intensive separation processes [34–37]. They are based on the use of a semi-permeable active or passive membrane which allows the separation of one or more species of a mixture by their passage from one site to the other one on the basis of a sorption-diffusion mechanism. Considering that in PV, the feed is a liquid, a liquid-vapour phase change is required involving an enthalpy of vaporization, as a function of the concentration gradient between the phases on the opposite site of the interfacial barrier. Instead, in VP the feed is a vapour mixture. In such a case, no phase change or no significant temperature differences across the membrane are required, the driving force being the partial pressure of the component in the feed. A noteworthy advantage of VP configuration is that the membrane is not in contact with the liquid reaction mixture rather, thus a longer membrane lifetime is assured [38].

So far, PV process has been exploited in some liquid-phase equilibrium reactions for biofuels production, while very low papers deal with the use of VP technique. Kita et al. [39] published one of the first papers regarding gas separation in the carboxylic acids esterification with alcohols, demonstrating that, by selecting suitable permeation conditions, total conversion could be achieved. The water vapor was removed using a polyimide hollow fiber membrane module placed on the top of a stirred batch vessel; *p*-toluenesulfonic acid was the catalyst [39,40]. Yamamoto et al. [41] and Okamoto et al. [42] exploited the very high permeation flux, water affinity and selectivity of NaA zeolite membrane in VP configuration to improve the esterification reaction performance.

In this paper, the efficiency of a coupled reactor-membrane set-up was demonstrated by performing the heterogeneous esterification of OIAC in presence of a commercial permselective membrane in VP configuration. In this case, two separate units, a batch reactor and an external separation module, were employed. This set-up allows to make clean-up or regeneration steps easier and to optimize independently both the catalytic behavior and the separation step. Solid acid catalysts, as A-15 resin and some zeolites, have been used in the esterification either with MeOH or EtOH. The obtained results have been compared with typical runs performed without the use of membrane.

2. Materials and methods

2.1. Reagents

OIAC purchased from Sigma Aldrich presented 99% oleic acid and 1% mixture of palmitoleic acid, palmitic acid and myristic acid, with an acid value of 139.9 mg of NaOH/g. Methanol (> 99%) or anhydrous ethanol (> 99%) were supplied from Fluka.

2.2. Catalysts

Amberlyst-15 wet ion exchange was purchased from the Dow Chemical Company, whereas the zeolite catalysts were supplied by Alpha Aesar. A-15 resin was used without any pretreatment. Zeolites have been calcined for 6 h at 500 °C. Two solid acid supported catalysts have been prepared by dry impregnation of two microspherical silica (ES70Y and MS3030 by PQ Corporation) in an ethanolic solution with Hyflon[®] Ion S4X perfluorosulphic ionomer (20 wt%) with an equivalent weight of 730 (Solvay Solexis) [43].

2.3. Catalyst testing

OIAC esterification reaction was carried out in two stainless steel reactors of different volumes (90 and 300 cc), with a constant stirring rate of 1100 min⁻¹. Experiments were performed under autogenous pressure by maintaining the temperature in the range 65–100 °C. The amount of catalyst, in respect to the OIAC ($R_{cat/OIAC}$) was varied from 1 to 15 wt.% and the alcohol/OIAC molar ratio ($R_{Alcohol/OIAC}$) was in the range 1–1 to 20–1. The reactants and the catalysts were loaded into the reactor in the fixed ratio, nitrogen flux was employed for reactor cleaning and then the reactor was heated to the desired temperature. At the end of the reaction, the reactor was cooled down with an ice bath to condense gaseous products. The catalyst was recovered by filtration.

The batch reactor and the water separation module were two distinct units and the schematic configuration of the reaction system was shown in Fig. 1. The gas phase (mainly containing the alcohol and the water) was recirculated through the water permselective membrane (HybSi), provided by Pervatech BV [35,36]. The membrane (250*10*7 mm) had an effective area of 0.005 m², the substrate material was a γ -alumina phase whereas the top layer was a hybrid silica coated on inside of the support tube. It could operate at a maximum temperature of 150 °C and a pressure of 10 bar, in the pH range of 2–8.5, showing a permeability to pure H₂O of 19.66 l/m² bar at 150 °C. To avoid the gas phase condensation, during the reaction, the recirculation loop was maintained at 115 °C. The recirculation of gas phase was maintained constant (2.8 L/min) by using a gas-pump equipped with a variable potentiometer. At the permeate side of the membrane, the permeate was purged with a stream of carrier gas (N₂, 2 L/min) and the permeate was finally obtained in the liquid state after condensation to be subsequently analyzed.

2.4. Biodiesel analysis

Conversion of OIAC was calculated based on the AOCs (American Oil Chemist's Society) official methods for acid value (Cd 3d-63) and FFA amount (Ca 5a-40). Samples were analyzed by a standard acid-base titration procedure for the evaluation of the free residual acidity. The analysis repeatability has been improved by removing methanol or ethanol in excess and water formed in a vacuum condenser, prior to submit the samples to titration. A weighed amount of the sample was dissolved in an ethanol/ethyl ether mixture 1/1 wt/wt and then was titrated with a NaOH 0.5 M solution and phenolphthalein as indicator. The volume of alkaline solution consumed was recorded and the acidity of the sample was determined by means of the Eq. (2), referred to the oil phase (oleic acid + ester) with an error less than 1–2% on the free acidity

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