Chemical Engineering and Processing 108 (2016) 220–225

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Membrane contactor reactor for transesterification of triglycerides heterogeneously catalyzed

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ARTICLE INFO

Article history:
Received 4 July 2016
Accepted 1 August 2016
Available online 7 August 2016

Keywords:
Transesterification
Biodiesel
Glycerol
Ion-exchange resins
Membrane contactor

ABSTRACT

A membrane reactor was developed for coupling heterogeneously catalyzed transesterification and glycerol extraction using a membrane contactor. The membrane contactor has two compartments of 0.4L separated by a nylon or PTFE microporous membrane. Ion-exchange resins were used as a catalyst under mild conditions with or without glycerol extraction. Water and ethanol were used as the extraction phase. The mass transfer coefficients of the reaction medium components were estimated using a synthetic reaction medium and different extraction phases. The reaction was followed by triglyceride conversion measuring free glycerol and combined glycerol. Triglyceride conversion increased by 18% when using an anionic resin (Amberlyst® A26) and ethanol as the extracting phase. A simplified mass transfer model was developed and applied to simulate the coupled system. The simulated results indicated that a ratio of membrane area to the reactor volume of 2.2 cm^{-1} results in a 97.3% reduction of the glycerol content in the reaction medium. These results demonstrate the potential of coupling transesterification and a membrane contactor by shifting the reaction equilibrium and reducing the purification steps of the process.

1. Introduction

Triglycerides are converted to glycerol and a mixture of fatty acid alkyl esters (FAAEs) via transesterification reactions. Currently, the main use of this type of reaction is to produce biodiesel, employing conventional reactors, with methanol and refined vegetable oil as reagents and a strong soluble base as a homogenous catalyst [1,2]. However, these reaction products can also be applied as raw materials for further synthesis or directly used as high value-added chemicals [1–4].

There are several drawbacks in the conventional transesterification process: a) phase separation limiting the mass transfer, b) conversion limited by equilibrium, and c) intensive downstream purification steps [1,2]. Conventional product purification processes, such as water washing, may generate a large amount of emulsified toxic wastewater, ranging from 3 to 10 L/L of biodiesel produced [2,5]. In heterogeneous catalysis, the solid catalyst can be easily recovered and reused, avoiding saponification reactions, which reduces both the wastewater volume and the operational costs [6,7]. Ion-exchange resins based on styrene-divinylbenzene are commonly used as catalysts due to their larger specific area and chemical stability [8,9]. However, in general, a solid catalyst requires a higher temperature or pressure or excess reactant due to the slower reaction rate relative to soluble catalysts [6,7,10,11]. Therefore, an intense research effort has been made to develop a more active catalyst or heterogeneously catalyzed process [6–12].

Novel reactors have also been investigated to overcome the limitations of the conventional transesterification process [12,13]. The use of membrane separation processes integrated with reactors is one of most promising approaches of process intensification. Dubé et al. [13] developed a two-phase membrane reactor for the transesterification of canola oil and methanol. In this reactor, a microfiltration membrane retains the oil droplets, whereas the membrane allows permeation of FAMEs, glycerol and methanol. Other authors applied a similar approach and reported the effect of membrane pore size, catalyst, methanol recycle and permeate flux [14,15]. This membrane reactor allows the production of a high-quality biodiesel with a low content of unreacted feed oil, but further purification steps were still required to separate glycerol, methanol or the catalyst from the biodiesel. Furthermore, membrane separation technologies have been studied to improve crude biodiesel purification [5,16]. So far, the

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http://dx.doi.org/10.1016/j.cep.2016.08.001
0255-2701/

most studied approach is the glycerol removal from biodiesel using ultra and microfiltration membranes to provide high purity and quality finished products [17].

A membrane contactor is another alternative that can be coupled to the transesterification reaction to avoid the shortcomings associated with liquid–liquid extraction. The membrane allows for contact of the reaction medium with the extraction phase without emulsion formation or typical phase separation problems [18], and the contact area between two phases is easily controlled and scaled-up. However, in the literature, membrane contactors are only investigated for biodiesel purification [5,19,20] and not directly coupled to a transesterification reactor.

The objective of this study was to investigate the performance of heterogeneously catalyzed transesterification coupled with a membrane contactor. This new conception of a membrane reactor has the potential to enhance triglyceride conversion under mild conditions and to reduce the number of purification steps via direct extraction of glycerol without phase dispersion. Ion-exchange resins were used as the catalyst, and glycerol extraction was investigated by using a synthetic reaction medium or directly from the transesterification reactor.

2. Experimental

2.1. Materials and chemicals

Anhydrous ethanol (99.8%, Vetec®), glycerol (99.5 PA, Vetec®) and refined soybean oil (Liza®) were purchased and used without further purification. Microporous flat sheet nylon (Whatman® Nytran™ N) and polytetrafluoroethene (PTFE, Milipore Fluoropore®) membranes were used in the experiments. The nylon membrane is hydrophilic, whereas the PTFE membrane has a high hydrophobic character. Both membranes have 0.22 μm of nominal pore size and about of 150 μm of thickness.

Cationic (Amberlyst® A15) and anionic resins (Amberlyst® A26 and Amberlite® IRA 410) were purchased from Sigma-Aldrich. The main catalyst properties of the ionic resins selected are presented in Table 1. Before use in the transesterification reaction, the cationic resin was previously treated for 1.0 h with hydrochloric acid (1.0 M), whereas the anionic resins were treated for 1.0 h with sodium hydroxide (1.0 M). After this treatment, the resins were washed with distilled water until a neutral pH was reached. Before the resins were used in the reaction, water was replaced by anhydrous ethanol and the resins were dried under vacuum for 12 h [21,22].

2.2. Reaction tests

Triglyceride transesterification catalyzed by acidic or basic ion-exchange resins was conducted with and without simultaneous glycerol removal. In both cases, the resins were previously immersed in ethanol for 12 h. Afterwards, ethanol and the catalyst were stirred and heated to the reaction temperature. In this condition, soybean oil was added to start the reaction.

The reaction temperature ranged from 298 to 343 K, while the catalyst loading varied from 1.0 to 10.0% wt. and the soybean oil/ethanol molar ratio varied from 1:6 to 1:9. Fig. 1 illustrates the membrane reactor employed in this work. The reactor consisted of two comportments of 400.0 cm^3 each, separated by a microporous flat sheet membrane with an average pore size of 0.22 μm and a permeation area of 113 cm^2. Two PTFE o-rings were used to fix the membrane in the holder. The transesterification reaction was carried out in one of the compartment of the reactor, whereas the other compartment was used with the extracting phase.

2.3. Permeation tests

To determine the transport coefficient of the membrane contactor, a synthetic reaction medium was prepared with soybean oil, ethanol and the transesterification products of glycerol and monoethyl ester. The monoethyl ester that was used to prepare the synthetic reaction medium was previously produced by the conventional alkaline-catalyzed transesterification method [25,26]. The transport coefficients were determined directly in the reactor shown in Fig. 1. For these tests, one compartment was filled with the synthetic reaction medium, and the extracting phase (distilled water or anhydrous ethanol) was added to the other compartment. Both compartments were subjected to mechanical stirring. The component concentrations were monitored in both phases.

2.4. Analytical procedures

The triglyceride conversion, Eq. (1),was evaluated according to the iodometric-periodic acid method in AOCS Ca 14–56 by determining the free (FG), combined (CG) and total glycerol (TG) concentrations [27–29]. The total glycerol is determined after

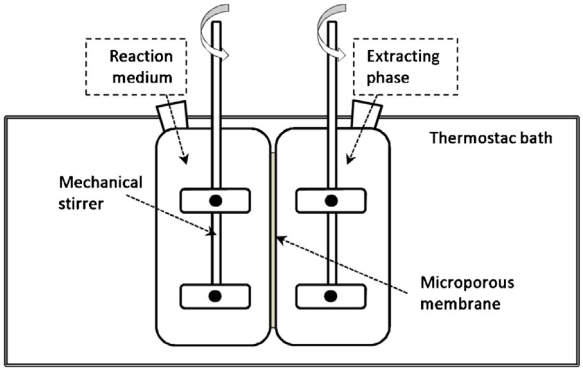

Fig. 1. Membrane transesterification reactor.

Table 1
Properties of the ion exchange resins used in transesterification reaction [8,23,24].

PROPERTIES	*IRA 410*	*A15*	*A26*
Matrix structure	Styrene divinylbenzene copolymer	highly cross-linked Styrene-divinylbenzene	highly cross-linked Styrene-divinylbenzene
Functional group	Quaternary ammonium	Sulfonic acid group	Quaternary ammonium
Concentration of active sites (meq/mL by wetted bed volume)	≥1.25	≥1.7	≥0.8
Moisture holding capacity (%)	45–51	52–57	45–65
Particle size (mm)	0.60–0.75	0.60–0.85	0.56–0.70
Average pore diameter (Å)	n.a.[a]	250	400
Surface area (m^2/g)	n.a.[a]	45	30

[a] n.a. not avaliable.