# Base catalyzed ethanolysis of soybean oil in microreactors: Experiments and kinetic modeling

Stefan Schwarz [a], Ekaterina S. Borovinskaya [a,b], Wladimir Reschetilowski [a,*]

[a] Dresden University of Technology, Institute for Industrial Chemistry, Zellscher Weg 19, D-01069 Dresden, Germany
[b] Saint-Petersburg State Institute of Technology (Technical University), System Analysis Department, Moskovsky Avenue 26, 190013 St. Petersburg, Russia

HIGHLIGHTS

- Continuous ethanolysis of soybean oil was carried out in seven microreactors.
- Micromixing efficiency was analyzed by modified *Villermaux–Dushman*-method.
- Better performance of microreactors was observed compared to batch process.
- Kinetic modeling under consideration of mass transfer limitations was performed.
- Heavy influence of reactor geometry on kinetics was observed.

GRAPHICAL ABSTRACT
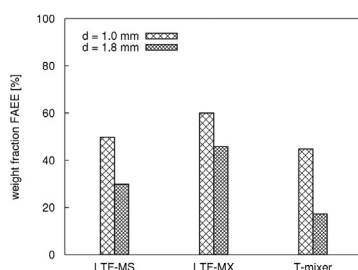
ABSTRACT

The base catalyzed alcoholysis of vegetable oil is a common industrial process for the production of biodiesel. The performance of the methanolysis reaction could be improved by applying continuous processes and using microreactors because of the strong mass transfer limitation of this reaction. This limitation is often neglected for the base catalyzed ethanolysis reaction. The KOH catalyzed ethanolysis of soybean oil was carried out in continuous and in batch. The experimental results and kinetic modeling of the data show strong mass transfer limitations of the reaction. The limitation is reduced by increasing the efficiency of micromixing which leads to performances exceeding the batch process under otherwise identically reaction conditions.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The ongoing industrial development worldwide leads to a high inquiry of diesel fuels, especially in the rural and transport sector.

Due the increasing shortage of mineral oil there is a growing demand on alternative resources. The heavy usage of fossil fuels will lead to an increasing environmental impact. Regarding these economic and ecologic problems the industrial production of biofuels derived from renewable sources is an important field of research (Meher et al., 2006; Stamenković et al., 2011).

Biodiesel is a mixture of esters of low aliphatic alcohols and high fatty acids obtained by alcoholysis of biological feedstocks with a high amount of triacylglycerols. In industrial scale biodiesel

---

* Corresponding author. Tel.: +49 351 4633 7056; fax: +49 351 4633 2658.
  E-mail addresses: wladimir.reschetilowski@chemie.tu-dresden.de, melik_v@mail.ru (W. Reschetilowski).

is commonly produced by homogenous base catalyzed methanolysis or ethanolysis of vegetable oils applying NaOH or KOH as catalyst (Stamenković et al., 2011). The most common feedstocks are highly refined rapeseed, sunflower, soybean or palm oils (Santacesaria et al., 2012b). To achieve high yields under industrial conditions the raw materials must not contain free fatty acids and water above 0.5 wt% (Moser, 2009). Otherwise the reaction is strongly hindered because of soap formation and catalyst deactivation. The reaction occurs in three reversible consecutive steps shown in Eqs. (1)-(3). Triacylglycerol (T) reacts with the alcohol (ROH) to diacylglycerol (D) and one equivalent of fatty acid ester (E). In two additional steps monoacylglycerol (M) and finally glycerol (G) is formed, each under formation of additional E (Richard et al., 2013).

$$T + ROH \rightleftarrows D + E \tag{1}$$

$$D + ROH \rightleftarrows M + E \tag{2}$$

$$M + ROH \rightleftarrows G + E \tag{3}$$

Methanol is the most common used alcohol in biodiesel production because of its favorable physico-chemical properties (Stamenković et al., 2011). Methanol is usually produced from petrochemical materials. Ethanol on the other hand is produced in a high amount from biomass and is therefore from high interest for the production of completely bio-based biodiesel (Moser, 2009). The rate determing step for each reaction is the nucleophilic attack of an alkoxide on a carbonyl carbon of the acylglycerol leading to a tetraedric intermediate (Kulkarni et al., 2007). The rate of the homogeneous base catalyzed alcoholysis depends on the reactivity of the alkoxide. Since the reactivity of methoxide is higher than the reactivity of ethoxide the reaction rate of the methanolysis is higher. In general there are three stages of the transesterification reaction (Marjanović et al., 2010). The initial phase is highly influenced by mass transfer limitations because the reactants are not completely miscible and two phases are formed. In the following stage the reaction is controlled by the chemical kinetics and continues hereby much faster. In the final step the chemical equilibrium is setting up slowly. While at the methanolysis reaction all stages have been thoroughly investigated, mass transfer limitations of the ethanolysis reaction often can be neglected because of the much higher solubility of vegetable oil in ethanol. The solubility of soybean oil in methanol is 5.7 g l^{-1} at 30 °C (Boocock et al., 1996) while ethanol can solve 58 g l^{-1} at the same temperature (Gandhi et al., 2003). Most commercial processes use a large excess of alcohol and a high catalyst loading in order to reach high yields of biodiesel. Under industrial conditions mass transfer limitations do not influence the ethanolysis reaction (Richard et al., 2013). Common reaction conditions for ethanolysis and methanolysis are a molar alcohol–oil-ratio of 6:1, 0.5 wt% of alkali catalyst (with respect to triacylgylcerol) and a temperature close to the boiling point of the alcohol. The reaction is usually carried out in a batch reactor with above 600 rpm for 1 h to give total conversion to fatty acid esters (Moser, 2009).

However it is desirable to use as less alcohol and catalyst as possible in order to reduce the costs of production and product separation. Various studies upon the continuous methanolysis reaction in microreactors showed high yields in short reaction times and under mild conditions (Qiu et al., 2010; Sun et al., 2008; Wen et al., 2009). Sun et al. (2008) carried out the KOH catalyzed methanolysis of rapeseed oil in tube reactors. Reducing the inner diameter of the tube from 2.0 mm to 0.25 mm lead to an increase of the yield of esters from 80% to 98.8% at a reaction time of 6 min at 60 °C and a MeOH–oil-ratio of 6:1. According to the authors the interfacial area increased due the decrease of the tube diameter which led to an improved mass transfer. By utilizing a split-and-

recombination micromixer combined with a tube reactor Guan et al. (2008) observed yields of 99% at the KOH catalyzed methanolysis of sunflower oil after a reaction time of less than 2 min at 60 °C. The MeOH–oil-ratio was quite high (22.9:1). Application of an unstructured t-shaped mixer under identical conditions lead only to yields of 50%. The increased mixing at the beginning of the reaction formed higher interfacial areas and caused an acceleration of the reaction. The ethanolysis reactions have not been thoroughly studied yet. Investigations considering mass transfer limitations of ethanolysis reactions were published by Richard et al. (2013) recently. The KOH catalyzed ethanolysis of sunflower oil was carried out in a capillary reactor combined with a t-shaped mixer at 65 °C and various EtOH–oil-ratios. Using a EtOH–oil-ratio of 6:1 a yield of 82% after 12 min was observed (Richard et al., 2013).

In this work the KOH catalyzed ethanolysis of soybean oil is carried out in seven different continuous reactor systems and in batch reactor. Commercially refined soybean oil is used because of its low amount of water and free fatty acids (Bertoldi et al., 2009). By varying the total flow rate, reaction time and reactor geometry independently the effects on the yields of fatty acid ethyl esters (FAEE) were analyzed. The effectivity of micromixing in the micromixers was investigated by a modified *Villermaux–Dushman*-method. The kinetic data obtained was modeled by modification of a kinetic model proposed by Richard et al. (2013). It was shown that the base catalyzed ethanolysis of soybean oil is controlled by mass transfer limitations. The application of continuous reactors with a high effectivity of micromixing leads to an acceleration of the reaction. The continuous process outperforms the batch process under otherwise identically conditions.

2. Experimental

2.1. Reactor composition

The continuous ethanolysis of soybean oil was carried out in microreactors which were assembled by combining three mixers each with three different tube reactors. The experimental setup is shown in Fig. 1. The reactants were provided into the mixer C1 by two syringe pumps P1 and P2. The outlet of the mixer was connected by a PTFE-tube with an inner diameter of 1.8 mm to the tube reactor C2. The outgoing stream was captured in a container B1. The microreactor was tempered by a water bath B2, W1.

The specifications of the three continuous mixers used in this work are shown in Table 1. The T-mixer made from stainless steel
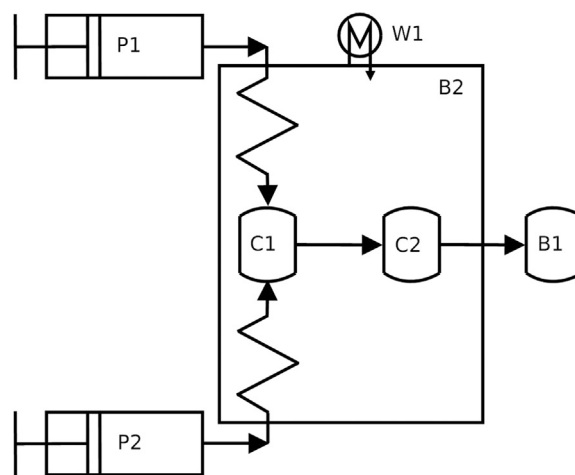

Fig. 1. Experimental setup for the continuous ethanolysis reaction.