A kinetic study of quicklime-catalyzed sunflower oil methanolysis

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ABSTRACT

The quicklime-catalyzed sunflower oil methanolysis was studied at mild reaction conditions. Quicklime (calcined at 550 °C for 4 h) in amounts of 1.0, 2.5, 5.0 and 10.0% (based on the oil weight) and different molar ratios of methanol-to-oil (6:1, 12:1 and 18:1) were employed to investigate their influence on the methyl esters content and the kinetics of the methanolysis reaction. The optimal methanol-to-oil molar ratio and quicklime amount for achieving the highest fatty acid methyl esters content were established to be 12:1 and 5% (based on the oil weight), respectively. The sigmoidal kinetics of quicklime-catalyzed methanolysis reaction was described by a model which included the changing mechanism of the reaction and the triacylglycerols mass transfer limitation. The kinetic parameters were determined and correlated with the process variables. A good agreement between the kinetic model and the experimental data for all applied reaction conditions was observed.

1. Introduction

Biodiesel industry has grown worldwide because of high energy demand, economy, environmental benefits and sustainability. During the past years the researchers have made considerable effort to design technical and economically feasible process for biodiesel production. Biodiesel, a mixture of fatty acids alkyl esters, usually methyl esters (FAME), is derived from renewable vegetable oils, waste oils, animal fats, and algae oils. The reaction of a triacylglycerols (TAG) with an alcohol, well known as alcoholysis or transesterification, is the most often used process for biodiesel production.

Besides known advantages, the major drawback of biodiesel is its high production cost, which is approximately 1.5 times higher than that of diesel fuel (Math et al., 2010). The feedstock cost contributes 70–95% of the total price of biodiesel production (Krawczyk, 1996). However, the use of low-cost waste oils could significantly reduce biodiesel cost. In addition, replacement of conventional homogeneous catalysts by heterogeneous ones could reduce the biodiesel production cost for almost 50% (Glišić et al., 2009). Furthermore, heterogeneous catalysts are easier to handle and separate from the reaction mixture, less corrosive and environmentally friendly (Dossin et al., 2006). Their major drawbacks are low reaction rate due to the existence of the three-phase reaction system, high initial methanol-to-oil molar ratios, high reaction temperatures, and in some cases the complex catalyst preparations.

The recent investigations have been focused toward on the development of new, inexpensive solid catalysts, such as calcium oxide (CaO) (Boey et al., 2011a), obtained from natural materials, which are efficient under mild reaction conditions and therefore have a positive economic effect. CaO is a promising heterogeneous catalyst because of high basicity, low solubility, no toxicity, high availability, relatively low price and easy handling. A very important characteristic of CaO as a catalyst for methanolysis reactions is the potential to be reused without any significant loss in the biodiesel yield

c_A	concentration of TAG (mol/dm^3)
c_{A0}	initial concentration of TAG (mol/dm^3)
c_{B0}	initial concentration of methanol (mol/dm^3)
c_{cat}	concentration of catalyst (mol/dm^3)
c_R	concentration of FAME (mol/dm^3)
c_{R0}	model parameter, i.e. the hypothetic initial FAME concentration corresponding to the initial available active catalyst surface (mol/dm^3)
D	pore diameter (nm)
k	reaction rate constant (dm^6/(mol^2 min))
k_m	apparent reaction rate constant (min^{-1})
K	model parameter defining the TAG affinity for the catalyst active sites (mol/dm^3)
K'	TAG affinity for the catalyst active sites (dm^3/mol)
p/p_0	relative pressure, 1
S_{BET}	specific surface area (BET) (m^2/g)
S_{Hg}	intra pore specific surface area (m^2/g)
t	time (min)
V_{inter}	inter-particle volume (mm^3/g)
V_{intra}	intra-pore volume (mm^3/g)
V_{mes}	volume of mesopores (mm^3/g)
V_{mic}	volume of micropore (mm^3/g)
$V_{tot\text{-}Hg}$	total mercury intrusion volume (mm^3/g)
$V_{tot\text{-}N_2}$	total pore volume at maximal adsorption pressure (mm^3/g)
x_A	degree of TAG conversion, 1

Greek symbols

ρ_{bulk}	bulk density (g/cm^3)
ρ_{Hg}	apparent density (g/cm^3)

(Granados et al., 2007; Kouzu et al., 2009a; Singh et al., 2011). In addition, it can be used for methanolysis of low-value and inexpensive oily feedstocks, such as waste-frying and semi-refined oils without prior water removal or neutralization of the free fatty acids (Dias et al., 2013; Puna et al., 2013). However, CaO can leach into the reaction mixture influencing the quality of biodiesel product, reducing the number of repeated use as a catalyst in batch operation and shortening the operation time of continuous process (Granados et al., 2007, 2009; Kouzu et al., 2009b). These problems could be overcome by removing the leached calcium species from the biodiesel product using appropriate purification methods (Alba-Rubio et al., 2012; Kouzu et al., 2009b).

CaO can be obtained from cheap sources such as calcium carbonate, calcium acetate and calcium nitrate (Cho et al., 2009). Recently, CaO derived from waste and natural resources, because of low or no cost, have become often interest to researches. At the same time, the use of waste resources is a good solution for protecting the environment. Table 1 presents a review of waste and natural materials used as resources for obtaining the CaO catalyst, usually by calcination at high temperatures, as well as the reaction conditions of methanolysis reaction catalyzed by the obtained catalysts.

Knowing the kinetics of a heterogeneously catalyzed reaction is important for the reactor design, analysis, simulation, control of the process, as well as for the development of industrial scale process. Different kinetics models have been reported based on the investigation of heterogeneously

catalyzed methanolysis kinetic. For instance, some of the proposed models include the pseudo-first order kinetic model with respect to TAG for the overall reaction in the presence of pure CaO (Veljković et al., 2009), CaO obtained by calcination of snail shells (Birla et al., 2012), CaO·ZnO (Lukić et al., 2013a,b), Ca(OH)$_2$ (Stamenković et al., 2010) and nano-MgO (Wang and Yang, 2007) as catalysts. Veljković et al. (2009) and Lukić et al. (2013a,b) included the mass transfer limitation in the kinetic model of the methanolysis of sunflower and used cooking oil catalyzed by CaO and CaO·MgO, respectively. The kinetics of crude soybean oil catalyzed by magnesium methoxide was determined by: (1) the mass transfer limitation at the beginning of the reaction; (2) an irreversible pseudo-second order reaction in the middle stage; and (3) a reversible pseudo-second order reaction model near the equilibrium (Huang et al., 2009). The modified first-order reaction kinetics was used to describe K/γ-Al$_2$O$_3$ catalyzed soybean oil methanolysis in a rotating packed bed reactor (Chen et al., 2011). The first order kinetic model with respect to methanol fitted the methanolysis of soybean oil catalyzed by CaO, MgO, PbO and MnO$_2$ (Singh and Fernando, 2007). More complex models consisting of three (Bokade and Yadav, 2009) and four (Qing et al., 2011) consecutive and reversible second-order reactions were used for describing the kinetics of different vegetable oils methanolysis over heteropolyacids supported on K-10 clay and carbon-based solid acid catalysts, respectively. A kinetic model developed on the basis of the Eley-Rideal mechanism with methanol adsorption (Dossin et al., 2006) and the surface reaction of TAG with adsorbed methanol (Xiao et al., 2010) as the rate determining step were applied for describing the methanolysis of triolein and palm oil, respectively. Kapil et al. (2011) analyzed and compared Langmuir–Hinshelwood–Hougen–Watson (LHHW), Eley-Rideal and Hattori kinetic mechanism in biodiesel synthesis catalyzed with different hydrotalcites. The best fit of the experimental data was obtained using the LHHW kinetics with methanol adsorption as the rate limiting step. The three step kinetic equation derived from LHHW model was successfully used for modeling the soybean oil methanolysis reaction catalyzed by Ca(C$_3$H$_7$O$_3$)$_2$/CaCO$_3$ (Hsieh et al., 2010). The canola oil methanolysis catalyzed by KOH/MgO was considered as an irreversible reaction, and the kinetics was described using power law model. The reaction orders of TAG and methanol were experimentally found to be 1.08 and 0.46, respectively (Ilgen and Akin, 2012). Commonly, the kinetic models of the complex reactions are experimentally derived (Wilkinson, 1980).

Existing kinetic models of heterogeneously-catalyzed methanolysis have specific advantages and disadvantages. The simple models are easy to use but they include two or three reaction periods, hence they describe the time variation of the reaction mixture composition with two or three correlations. The complex models are applicable for modeling the reaction rate during the whole course of methanolysis, but they require complicated computations. However, the kinetic model that takes advantages and disables drawbacks of for ahead mentioned models would be beneficial for engineering purposes.

This work reports the possibility of application of quicklime as a cheap source of CaO for catalysis of the sunflower oil methanolysis in a batch stirred reactor. Until now, only Kouzu et al. (2009a) have reported the use of quicklime as a catalyst for the methanolysis of rapeseed oil in a fixed-bed reactor located in the circulating stream of a batch reaction