



Synthesis of magnetic mesoporous nanocrystalline KOH/ZSM-5-Fe₃O₄ for biodiesel production: Process optimization and kinetics study



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ABSTRACT

This study attempts to synthesize magnetic mesoporous nanocrystalline KOH/ZSM-5-Fe₃O₄ and employ them for biodiesel production through transesterification of canola oil. In this respect, ZSM-5 zeolite has been selected as an appropriate support since it possesses a high specific surface area and noticeable porosity that can enhance physical contact between oil molecules and the catalyst. After synthesis of the catalyst, different characterization techniques including XRD, FESEM, BET, XRF and VSM were used to unravel physical and chemical features of the zeolite based materials. Then, the prepared catalysts were applied to transesterification of canola oil to produce biodiesel. Furthermore, impacts of reaction time, catalyst amount and alcohol to oil molar ratio parameters on the process were investigated by Box-Behnken method. Optimization of the process gave maximum biodiesel yield of 93.65% at 65 °C reaction temperature, 3.26 h reaction time, 12.3 molar ratio of alcohol to oil and 9.03% catalyst loading. Moreover, magnetic property of the catalytic facilitated its separation from the reaction mixture. So that, the catalyst was removed after completion of the process by an external magnetic field and reused for five successive cycles. Acceptable yield (above 80%) was achieved for the first three cycles. In addition, the kinetics of the transesterification reaction was explored, which declared that the process obeys the behavior of pseudo-first order reactions with activation energy of 122.7 kJ mol⁻¹ and frequency factor of 2.15 × 10¹⁷ min⁻¹.

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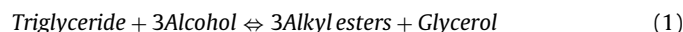
1. Introduction

CO₂ emission to atmosphere as a result of fossil fuel combustion is associated with climate change and has been declared to affect human society adversely and threaten equilibrium of ecosystem. That is why emission of carbon dioxide has turned out to be a global concern. Furthermore, global energy security is concerned to be influenced by different crises and export associated political instabilities that fluctuate supplying fossil fuel (Asif and Muneer 2007). Consequently, it is important to promote capacity of renewable energy to reduce emission of greenhouse gases by attenuating global dependence on fossil fuels.

Using renewable fuels can guarantee cleanliness of the environment and eliminate negative impacts of any energy crisis on economy, which is threatened by restricted resources of fossil fuel (Lin et al., 2011). One of the renewable fuels and the most commonly employed liquid biofuel for transportation purposes is biodiesel. As biodiesel can be used as an alternative to petrodiesel,

it is known as the most attractive liquid biofuel, in the transport sector (Demirbas and Balat 2006). Moreover, biodiesel is a fuel that can be easily produced and is credited environmentally. Some other advantages of biodiesel include biodegradability, reduction of pollutant emission to atmosphere, water and soil, non-toxicity, being a clean fuel due to lack of carcinogenic substances, low level of Sulphur content compared with petrodiesel, being safer than petrodiesel due to its high temperature of flash point and containing ca. 10% built-in oxygen that helps it to be burnt completely. Also, cetane number of biodiesel is high, which enhances quality of ignition even when it is combined with petrodiesel (Kalligeros et al., 2003; Khan et al., 2009; Smith et al., 2009; Yatish et al., 2016).

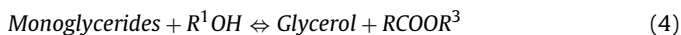
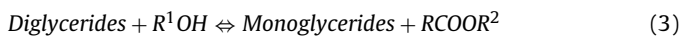
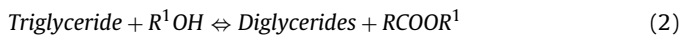
Since vegetable oils are highly viscous, they can deposit carbon and block nozzles. Therefore, they cannot be directly used as fuels and they require to be modified chemically by different methods, e.g. cracking, microemulsion, transesterification or blending with oil derivatives (Lang et al., 2001). The conventional way of producing biodiesel is application of transesterification by using alcohol and oil. The products of this approach are biodiesel and glycerol (Demirbas 2005):



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Transesterification is a reversible reaction. As an outcome, it is hard to reach 100% conversion (Tariq et al., 2012). Transesterification process includes three subsequent steps. At each step, a reversible reaction takes place and gives one ester. In the first step, triglycerides (TG) convert into diglycerides (DG). In the second step, the produced diglycerides convert into monoglycerides (MG). In the last step, the resulted monoglycerides are consumed to produce glycerol Eqs. (2)–(4).



In this process, stoichiometric ratio of triglyceride to alcohol equals to three, theoretically. However, a slightly higher ratio should be adopted in practice to obtain a maximum ester yield (Sharma et al., 2008). These reactions can benefit from various primary alcohols, e.g. methanol, ethanol, propanol and butanol, specifically methanol, as primary alcohols have low prices and are widely available (Xie and Yang 2007; Atapour et al., 2014). In this process, quality of the products relies on type and amount of the selected catalyst, type of the utilized oil feedstock, ratio of alcohol to oil, contents of free fatty acid (FFA) and water in the oil and the operating conditions, for example speed of agitation and temperature (Clark et al., 2013; Hamze et al., 2015).

The most commonly applied transesterification catalysts for biodiesel production are enzymes, acids or bases (homogeneous or heterogeneous). Any of these kinds of catalysts are accompanied with some advantages and disadvantages, with respect to their properties. For example, applying base catalysts can provide higher rates of reactions compared with acid catalysts, in biodiesel production (Kouzu and Hidaka 2012). Previous studies have demonstrated that heterogeneous catalysts, particularly base catalysts, are efficient and effective and can give high yield of biodiesel using oils with high contents of free fatty acids as they can absorb water molecules of the oil (Semwal et al., 2011). Furthermore, heterogeneous catalysts do not involve soap formation, which results in loss of glyceride molecules, and can be recovered from the reaction medium and reused, conveniently (Vyas et al., 2010). However, there are some serious mass transfer limitations associated with heterogeneous catalysts, which causes three phases form together with oil and alcohol. Also, heterogeneous catalysts need high operational temperatures and more time to provide high conversion and reach optimum biodiesel yield. Also, some disadvantages of enzymes are recognized that prevent their industrial application including their high prices, inactivity, pollution of biodiesel and long reaction times (Zhao et al., 2013).

Zeolites have been the choice of industries as heterogeneous catalysts since they are inexpensive and eco-friendly and they present high size selectivity, porosity, thermal stability and surface area. However, the negative aspect of zeolite application for transesterification catalysis is that pore sizes of zeolites are narrow, which limits diffusion and adsorption of triglyceride onto their active sites. Therefore, if mesoporous zeolites be developed, then a great opportunity will be provided to overcome diffusion limitation and improve transesterification of vegetable oils (Nandiwale et al., 2013; Alaba et al., 2016). Zeolites do not possess any catalytic activity. However, when zeolites are loaded with KNO_3 , NaOH, KF, KOH, KI or K_2CO_3 and are activated at high temperatures, high catalytic activities can be expected from the supported solid catalyst (Wu et al., 2013). In addition, it has been clarified that the support, i.e. the zeolite, impacts activity of the heterogeneous catalyst. KOH supported on various types of zeolites, e.g. NaX, NaY, ZSM-5 and mordenite, have exhibited excellent catalytic performance in biodiesel production (Saba et al., 2016).

Another issue related to zeolites is their separation from the reaction products and reusing them, especially in case of zeolite nanoparticles. Though nanocrystals of zeolites are highly active, their separation is very difficult to be affordable. This problem can be resolved through using magnetic catalysts. Compared with filtration and centrifugation separation techniques, conducting magnetic separation can prevent catalyst loss and enhance its reusability. To facilitate catalyst separation, various types of ferrites have been employed as catalyst support or magnetic catalyst (Ali et al., 2017).

Many forms of iron oxides exist in nature while their most common forms are magnetite (Fe_3O_4), hematite ($\gamma-Fe_2O_3$) and maghemite ($\alpha-Fe_2O_3$). Among these forms, magnetite presents the strongest magnetism, as compared to any transition metal oxide (Teja and Koh 2009). Various methods of thermal decomposition, microemulsion, hydrothermal and coprecipitation have been employed to synthesize magnetic nanoparticles (MNPs) while coprecipitation has been preferred to other approaches. Coprecipitation is a simple synthesis method, needs low reaction temperature and completes in a short time. Moreover, coprecipitation solvent is water, which does not cause any environmental problem. The influential parameters on shape, size and composition of the MNPs obtained from coprecipitation are the salt (chloride, nitrate or sulfate), reaction temperature, speed of stirring, the type of alkaline solution, pH and nitrogen gas injection. Higher speeds of stirring decreases sizes of the MNPs. Nitrogen gas injection protects the MNPs against oxidation and gives smaller particles (Kim et al., 2001).

To unravel simultaneous impacts of different parameters on the yield of fatty acid methyl esters (FAME) and interactions between the parameters, experiment design combined with analysis by response surface methodology (RSM) can be used (Hamze et al., 2015). In this way, the number of experiments can be reduced and all coefficients attributed to quadratic terms of the proposed regression model and factors' interactions can be predicted. With this purpose, compared with other designs such as factorial or central composite designs, Box-Behnken design is advantageous for three-level–three-factor designs as it demands for fewer number of experiments (Charoenchaitrakool and Thienmethangkoon, 2011).

In this study, ZSM-5 zeolite nanoparticles were synthesized through a microwave assisted hydrothermal method. After that, the parent ZSM-5 was modified by Fe_3O_4 and KOH. Then, physiochemical properties of the synthesized catalysts were determined by XRD, BET, FESEM and VSM techniques. In the next step, transesterification performance of the magnetic mesoporous nanocrystalline, i.e. KOH/ZSM-5- Fe_3O_4 , was evaluated. Several parameters that could affect quantity of the generated biodiesel were optimized by Box-Behnken design. These parameters included ratio of methanol/oil, amount of the catalyst and reaction time. Catalyst reusability was considered and leaching of the active species from KOH/ZSM-5- Fe_3O_4 was investigated by XRF analysis. Further, a kinetics study was carried out to calculate rate constant (k) and activation energy (E_a) of the reaction.

2. Materials and methods

2.1. Materials

In this study, sodium aluminate ($NaAlO_2$, Al_2O_3 wt%=55), colloidal silica (Ludox, 40 wt% aqueous solution), tetrapropylammonium hydroxide (TPAOH, 40 wt%), sodium hydroxide pellets (NaOH, 99.6 wt%), potassium hydroxide pellets (KOH, >99.7 wt%), $FeSO_4 \cdot 7H_2O$ (99%), methanol (>99 wt%) and $FeCl_3 \cdot 6H_2O$ (97%) were used, which were purchased from Merck Company in Germany.

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