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Kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia

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ABSTRACT

The esterification of myristic acid with methanol in presence of triglycerides using sulfated zirconia prepared by solvent-free method as the heterogeneous catalyst was studied. The effects of reaction temperature (393–443 K), catalyst loading (1–3 %wt) and molar ratio of oil to methanol (1:4–1:20) on the conversion of myristic acid were investigated. The experimental data was interpreted with a second order pseudo-homogeneous kinetic model. The kinetic parameters were obtained. A good agreement between the experimental data and the model was observed. Sulfated zirconia prepared by solvent-free method exhibited high catalytic activity for this reaction. Low activation energy of 22.51 kJ mol^{-1} was obtained in the range of temperature of 393–443 K.

1. Introduction

Biodiesel represents a promising alternative fuel for use in diesel engines due to its many advantages: it is renewable fuel, it creates low emissions of CO, SO_x, NO_x, it is biodegradable and non-toxic [1,2]. Biodiesel can be produced through transesterification process. Normally, refined vegetable oils such as rapeseed, soybean, sunflower and palm oils are used as biodiesel feedstock [3]. Even though these oils yield a high quality biodiesel, they are very expensive. This causes a higher cost of biodiesel as compared to the traditional petroleum diesel [4]. Moreover, an availability of these feedstocks is limited as they are used in the food industry [5]. The use of low quality oils like non-edible oil, waste grease, fats can result in a lower production cost of biodiesel [6]. However, these oils usually have high free fatty acids (FFA) concentrations for example used cooking oil and greases have free fatty acid levels greater than 6% [7].

The presence of large amounts of FFA strongly influences the performance of homogeneous base-catalyzed transesterification. These components cause the formation of soap through ponification which makes a serious problem of product separation [8]. Homogeneous acid catalysts have potential to simultaneously catalyze both esterification and transesterification processes of high FFA feedstock [9]. However, the use of these catalysts are non-practical for biodiesel production due to slow reaction rate, requirement of high temperature, high molar ratio of oil to alcohol, the separation of catalyst, serious environmental and corrosion related problems [10]. Recently, a two-step process is proposed to prepare biodiesel from high FFA oils. The first step is esterification of FFA with methanol which is catalyzed by homogeneous acid catalysts (generally sulfuric acid). When FFA content in oil is reduced to lower than 0.5–1 %wt, transesterification of triglyceride with methanol, the second step, is then carried out by homogeneous base catalysts (normally sodium or potassium hydroxide). This process increases the production cost of biodiesel since it requires extra separation steps to remove the catalyst in both stages [8,10,11].

Heterogeneous acid catalysts are developed to solve the problems associated with homogeneous catalysts. The main advantages of these catalysts are easy separation, reusability, low corrosion, and more environmentally friendly [12]. The heterogeneous base catalysts show high catalytic activity, however, most of them are very sensitive to trace amount of FFA and/or water in raw material [13]. Therefore, the use of heterogeneous acid catalysts is potentially attractive because of they can catalyze the transesterification of vegetable oils or animal fats with high content of FFA and water, such as deep-flying oils from restaurants and food processing

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without the formation of undesired products. These catalysts can also promote simultaneously transesterification of triglycerides and esterification of FFA that causes cheaper product cost [7]. Usage of heterogeneous acid catalysts in both transesterification and esterification reactions have been reported in several literatures. Heteropolyacids are typical strong Bronsted acids and have great potential to catalyze biodiesel synthesis. However, a major drawback of these catalysts is their relatively low thermal stability, low surface area and solubility in polar media [14]. Even though the supported heteropolyacid catalysts were developed to improve qualities, they still have problem associated with the continuous leaching of heteropolyacid from support into the reaction medium [15]. Cs-salt heteropolyacids exhibits high catalytic activity and high stability to leaching [15,16]. However, because of their insolubility, makes it is more difficult to prepare by conventional aqueous impregnation method [17]. Suflonic ion-exchange resins like Amberlyst 15 and Nafion NR50 showed higher catalytic activity in esterification than transesterification reaction [11]. These resins are expensive and have low thermal stability [18–20].

Sulfated zirconia (SO_4^{2-}/ZrO_2) is classified as a heterogeneous superacid catalyst. It has recently received considerable attention as a promising catalyst for industrial processes due to its strong acid properties [21]. This catalyst presents both active Bronsted and Lewis acidic sites [22]. It is also higher acid strength than heteropolyacid, suflonic ion-exchange resins and other heterogeneous acid catalysts [23]. Sulfated zirconia was found to be a potential catalyst in the esterification of dodecanoic acid with 2-ethylhexanol, 1-propanol and methanol at 130–180 °C, compared to the various heterogeneous catalysts such as zeolites ion-exchange resins and mixed metal oxides [18]. This catalyst has been successfully used as heterogeneous catalyst for esterification of palmitic acid in sunflower oil with methanol at 60 °C [24] and esterification of high FFA in refined soybean oil with methanol at 35–60 °C [25]. Six solid catalysts (ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2) were carried out for transesterification of crude palm kernel oil and crude coconut oil with methanol at 200 °C and sulfated zirconia gave highest catalytic activity [26]. In addition, sulfated zirconia exhibited good catalytic activity and good stability in several simultaneous transesterification of triglycerides and esterification of FFA [27–29]. However, a major concern of the use of this catalyst in the reactions is the leaching of sulfate groups by hydrolysis. It causes the deactivation of catalyst [18,27–29]. Previously, simultaneous transesterification of rapeseed oil and esterification of myristic acid with methanol using sulfated zirconia prepared by solvent-free method as a catalyst was studied [29]. The esterification of myristic acid seems to be a promising reaction for biodiesel production. However, no researcher has reported the kinetic of this reaction.

There are several reports on the kinetic of FFA esterification in presence of triglyceride using different heterogeneous acid catalysts. Various models were proposed for this system either to explain the phenomenon of reaction or determine the corresponding kinetic parameters. Eley-Ridal (ER) model as represented the adsorption phenomenon, was a superior model for esterification of high FFA (approximately 50%) in the presence of soybean oil [30]. Langmuir–Hinshewood–Hougen–Watson (LHHW) model as characterized by increasing number of parameters was reasonable model to describe esterification of FFA in waste cooking oil [31]. A pseudo-homogeneous second order reversible (PH) model was realizable and applied for several esterification reactions of FFA in the presence of triglyceride [3,30,32,33].

In this work, the kinetic model of myristic acid esterification with methanol in presence of triglycerides using sulfated zirconia as catalyst was investigated. The effect of operating parameters namely reaction temperature, catalyst loading and molar ratio of oil to methanol over this kinetic were also studied. The corresponding kinetic parameters were obtained.

2. Materials and methods

2.1. Materials

Refined rapeseed oil was purchased from Henry Colbeck Ltd, England. The water content and free fatty acid content of this oil were determined which are 0.01 %wt and 0.3 %wt respectively. Myristic acid (purity $\geq$ 98%) and silver nitrate (purity $\geq$ 99.5%) were supplied from Fluka. Zirconium (IV) oxide chloride octahydrate (purity $\geq$ 99.5%), ammonium sulfate (purity $\geq$ 99%) and Karl – Fischer reagent were obtained from Riedel de Haen. Sulfuric acid (purity $\geq$ 97.5%) and heptane for HPLC analysis were purchased from Sigma–Aldrich. Methanol (HPLC grade), 2- propanol (purity 99.99%), 35% ammonia solution (laboratory reagent grade) were obtained from Fisher Scientific. Barium chloride dehydrate was supplied from Acros Organics. Methyl heptadecanoate (purity $\geq$ 99.5%) for GC analysis from Fluka was used as an internal standard. Supelco standard 37 Component FAME mix from Sigma–Aldrich was used to identify fatty acid methyl ester peaks.

2.2. Catalyst preparation of sulfated zirconia

Sulfated zirconia was prepared following the solvent-free method by Sun et al. [22]. $ZrOCl_2.8H_2O$ and $(NH_4)_2SO_4$ in a molar ratio of 1:6 were ground in an agate mortar for 20 min at room temperature (25 °C). After standing for 18 h at room temperature in air, the sample was calcined at 600 °C for 5 h.

2.3. Equipment

A 100 ml mini bench top reactor, model 4560 (Parr Instrument Company, Illinois, USA) was used for esterification of myristic acid with methanol in presence of triglycerides. The reactor vessel made of Type 316 stainless steel. The reactor was equipped with a magnetic stirrer drive, a four-blade impeller and thermocouple. The head assembly of reactor was also equipped with a gas inlet valve for charging N_2 gas into the reactor and a gas release valve for releasing pressure. A HPLC pump K-120 was provided for injection of material into the reactor vessel with flow rate 10 ml/min. The pressure in the reactor was used to force out the liquid samples through a dip tube which was fitted with a fine filter through the sampling tube. The process conditions including the heating mantle, reaction temperature, pressure, feed rate, and impeller speed were controlled by WinISO software from H.E.L (H.E.L Inc., Lawrenceville, NJ).

2.4. Reaction procedure

Initially, 30 g of rapeseed oil with 10% by weight (3.611 g) of myristic acid and catalyst were charged into the reactor. After the reactor was closed, nitrogen was used in order to purge the air left in the reactor. When the reactant and catalyst were heated to the desired reaction temperature with stirring rate at 600 rpm, nitrogen was introduced into the system to ensure that at the desired reaction temperature, the reactants are the liquid phase. The reaction was started when methanol was added into the reactor. Liquid samples were withdrawn through a sampling line at different time during a run.