Effect of reaction conditions in the catalytic esterification of palm fatty acid distillate to produce fatty acid methyl ester

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Abstract. Biodiesel or fatty acid methyl ester (FAME) obtained via esterification process is an alternative for industrial and transportation fuel. In this study, chromium-titanium mixed oxides catalyst synthesized via sol-gel method was used to catalyse the esterification of palm fatty acid distillate (PFAD) to produce FAME. Esterification was conducted in a batch reactor. The effects of reaction temperature, methanol to PFAD molar ratio, reaction time and reusability of catalyst were studied. Reaction conditions yielding the best performance of 89% FAME content were reaction temperature of 160°C, methanol to PFAD molar ratio of 3:1 and reaction time of 3 h. The catalyst can be reused for 3 times with 20% performance reduction between the first run and the third run. The results revealed that the mixed oxides of Cr-Ti is a potential heterogeneous catalyst for use in the esterification of high acid value feedstock of PFAD.

1. Introduction

Biodiesel or fatty acid methyl ester (FAME) is an alternative energy source to resolve the issues of diminishing petroleum reserves and environmental concerns [1]. Despite its many advantages, the economic aspect of biodiesel production is unfavorable mainly due to the high cost of feed stock, which accounts for about 75% of the production cost. The oils originated from plant can be used as feedstocks for FAME synthesis [2]. The utilization of less expensive feedstocks such as by-products of plant oils industries and waste oils are several measures towards lowering the cost of production [3]. PFAD is a by-product from the physical refining of palm oil where it is removed by steam distillation as fatty acids residue. It is composed mainly of free fatty acids (FFA > 85%), partial glycerides (<15%) and other substances. The fatty acids compositions are mostly palmitic acid, oleic acid and linoleic acid. The current applications of PFAD are as fuel in industrial boilers, as animal feed ingredient and as raw material for oleochemical industries [4].

The used of homogeneous catalyst in the production of FAME have several disadvantages such as its solubility in reaction mixture, which makes separation difficult and corrosive to equipment. The heterogeneous catalyzed process has more benefits than the homogeneous process such as catalyst reusability, simplified separation method and environmental friendly. The use of base catalyst is unsuitable for FAME synthesis from high FFA feed stocks such as PFAD because the FFA reacts with base to form soap that lower the product yield, thus acid catalyst is more favorable [5]. Sulfated
zirconia was used in the transesterification of cottonseed oil that obtained 90% FAME content. The reaction was conducted at high temperature of 230°C for 8 h at 12:1 methanol to oil molar ratio [6]. The mixed oxides ZnO-La₂O₃ was used in the transesterification of waste cooking oil. However, the high operating temperature above 200°C leads to undesirable hydrolysis of FAME that lowers the product yields [7]. The metal oxides Cs/Al/Fe₃O₄ were used for the transesterification of used sunflower oil. The solid-catalytic reaction obtained high conversion above 88% at low operating temperature of 58 °C but considerable high methanol to oil molar ratio of 14:1 was used [8]. While most of these catalysts reported high activity, several disadvantages are energy intensive reaction conditions such as high temperature (>200 °C) and high methanol to oil ratio.

The purpose of this study is to evaluate the effect of reaction conditions in the esterification of PFAD to produce FAME. In this regard, the solid catalyst of chromium and titanium mixed oxides of 2:1 metal ratio by mass was prepared using sol gel method and used in the reaction. The best reaction conditions (reaction temperature, reaction time, alcohol to oil ratio) were examined. The reusability of catalyst for several reaction cycles was also studied to determine its stability as heterogeneous catalyst.

2. Materials and methods

2.1. Materials and chemicals

PFAD (93% FFA content) was purchased from IOI Oleochemical Industries Berhad in Penang, Malaysia. Chromium nitrate (Cr(NO₃)₃•9H₂O), titanium (IV) butoxide and methanol was purchased from Merck (Malaysia). Methyl heptadecanoate (purity 99.5%) used as internal standard for gas chromatography analysis was purchased from Sigma-Aldrich (Malaysia), whereas n-hexane (purity 96%) used as solvent for GC analysis was purchased from Merck (Malaysia). Ethanol (purity 99%) and HNO₃ (purity 65%) used for the catalyst preparation were purchased from Merck (Malaysia).

2.2. Catalyast preparation

The heterogeneous catalysts with chemical formula of CrₓTiₓO₃ with different Cr:Ti ratio by mass (x = 2; z = 1) were prepared via sol-gel method. The typical catalyst preparation process for chromium and titanium mixed oxides was as follows: 5.8 g of Cr(NO₃)₃•9H₂O was dissolved in 10 mL of distilled water. A 250 mL beaker containing 40 mL of ethanol is continuously stirred while the solution containing Cr(NO₃)₃•9H₂O is slowly added. Next, 10.7 mL of titanium butoxide and 1 mL of nitric acid are added into the same beaker and the solution is left to stir at 400 rpm for 4 h on a hot plate at 40 °C. The sample was then left for 24 h aging process, until gel was formed before it was dried in an oven for 12 h at 100 °C, followed by calcinations in a muffle furnace at a desired temperature of 500 °C (heating rate of 10°C/min) for 2 h. The calcination process allows for the treatment at high temperature to remove the substances through decomposition such as nitrate and other impurities that were presence in the precursors. The metal elements then form a strong bond with oxygen to generate metal oxides.

2.3. Esterification of PFAD and analysis of FAME

The esterification of PFAD with methanol was carried out in a 100 mL stainless steel batch reactor equipped with an impeller and a thermocouple. In a typical process, the semi-solid PFAD was liquefied by heating in an oven at 80 °C. The reactants mixture consist of 2.1 methanol to oil molar ratio equivalent to 10.6 mL methanol and 39.5 mL PFAD were charged into the reactor. Catalyst loading of 0.53g (1.5 wt.% of oil) was used and the reactor and its contents were continuously stirred. The reactions were carried out at temperatures ranging from 130 °C to 170 °C that is set by a heater with a programmable PID temperature controller. The stirrer speed was set at maximum of 500 rpm in order to sufficiently keep the system uniform in temperature and suspension and to ensure the reaction is free from mass transfer limitations. At the end of the reaction (ranging from 2 h to 6 h), the heater and stirrer were turned off and the reactor was immediately cooled to room temperature by quenching in cold water bath. The catalyst was separated from the product mixture by centrifugation at 3000 rpm for 15 min. The products were collected and left to settled for 12 h to separate into two phases that are

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FAME (top layer) and water (bottom layer). The FAME was analyzed by gas chromatography. The FAME obtained was calculated using the EN14103 application note (the recommended standard for obtaining total FAME content in biodiesel) [9].

3. Results and discussion

3.1. Effect of reaction conditions on esterification of PFAD

The influence of reaction temperature on the esterification of PFAD is shown in figure 1. The FAME content increases with temperature increment up to 89.5% at 160°C. Beyond this temperature, the FAME content shows no significant increase. In heterogeneous catalysis, the mobility of reactants would be slowed down by diffusion resistance between the different phases. In order for a chemical reaction to occur, the reactant particles must collide with enough energy to break the appropriate bonds in the reactants. Thus, the increase in temperature provides the reactant molecules with sufficient energy to overcome the activation energy barrier to form the desired product. However, further increase in temperature may cause unwanted side reactions such as decomposition of FFA and methanol that reduces the amount of available reactants [10]. In other work, the transesterification of jatropha oil in the presence of Bi$_2$O$_3$-La$_2$O$_3$ catalyst showed reaction conversion increases as temperature increases from 100 °C to 160 °C to achieve greater than 90 % FAME [11].

![Figure 1. Effect of reaction temperature (reaction conditions: 2:1 methanol:PFAD molar ratio; 1.5 wt.% catalyst dosage; 3 h)](image1)

![Figure 2. Effect of methanol to PFAD molar ratio (reaction conditions: 160 °C; 1.5 wt.% catalyst dosage; 3 h)](image2)
The methanol to feed stock molar ratio is one of the important factors that affect the reaction. Figure 2 shows the influence of methanol to PFAD molar ratio from 1:1 to 2:1 is significant to increase the FAME content from 61.4% to above 86.8% but reduced beyond 3:1 molar ratio. Theoretically, the esterification requires a minimum of 1:1 molar ratio of methanol and FFA to produce one mole each of FAME and water as shown in Equation 1. The excess methanol promotes the reversible reaction forwards to produce more FAME. The excess methanol extracts the products thus helps to renew the catalyst surface from adsorbed species, thereby increase the active sites [10]. However, surplus of methanol may results in flooding of the active sites that prevented the adsorption of FFA on the catalyst surface causing low activity [12].

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\text{RCOOH} + \text{CH}_3\text{OH} \leftrightarrow \text{H}_2\text{O} + \text{RCOCH}_3
\]

(FFA) (Methanol) (Water) (FAME) (1)

Figure 3 shows the FAME content increases at reaction time of 2 h to 3 h. However, the FAME content decreases further after 4 h. Long reaction time would allow sufficient contact time between the reactants and catalyst surface whereby the reactant molecules interact that resulted in bond breaking and forming to yield the product(s). The best reaction time was achieved at 3 h, whereby beyond that conversion decreases because the increasing amount of water in the reaction mixture leads to hydrolysis of FAME to FFA [13].

![Figure 3](image)

**Figure 3.** Effect of reaction time (reaction conditions: 160 °C; 3:1 methanol:PFAD molar ratio; 1.5 wt.% catalyst dosage)

### 3.2. Catalyst reusability

The reusability of heterogeneous catalyst is an important advantage compared to homogeneous catalyst. Figure 4 shows the FAME content is 87%, 77% and 69% for the first, second and third run, respectively. The reduction in catalytic performances during the reusability tests would likely due to active sites blockage by adsorbed products or unreacted reactants. The leaching of catalyst active components into the solution could also be reason for catalyst deactivation [14]. Several reported heterogeneous catalysts such as FeTiO [10], CrWO\textsubscript{2} [15] and CrWTiO\textsubscript{2} [16] have shown reduction of 17-20% catalyst performance from the first run to the third run in the esterification of PFAD.
Figure 4. Catalyst reusability of Cr-Ti mixed oxides

4. Conclusion
This study on FAME production using Cr-Ti mixed oxide catalyst revealed good potential as heterogeneous catalyst for use in the esterification of high FFA feedstock of PFAD. The reaction conditions significantly influence the production of FAME. A maximum FAME content of 89% was obtained at methanol:PFAD molar ratio of 3:1, reaction temperature of 160 °C and reaction time of 3 h. The stability study showed the catalyst can be reused up to the third run. The catalyst benefits such as good activity at moderate reaction conditions, reusable and simple method of catalyst preparation.

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