



Optimization of free fatty acid reduction in waste frying oil via sulfamic acid-catalyzed esterification

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ABSTRACT

This study presents the esterification process using sulfamic acid as a catalyst for pretreatment of high free fatty acid (FFA) waste frying oil (WFO), which contained FFA 3.34% w/w. The acid catalyzed esterification with methanol was carried out to investigate the optimum condition for the reduction of FFA content in WFO. Also studied were the effects of reaction variables which included methanol amounts of 20-50% v/v, catalyst amounts of 0-9% w/v of oil, reaction temperatures of 31-60 °C, and reaction times of 0.5-4 hrs. The FFA content from each reaction condition was determined by AOAC Official Method 940.28 (AOAC 2012). The optimum condition was achieved at a methanol amount of 50% v/v, a catalyst amount of 7% w/v of oil, a reaction temperature of 60 °C, and a reaction time of 2 hrs. At the optimum condition, there was 0.93% w/w of FFA in oil product.

INTRODUCTION

In recent years, biodiesel has been one of the important alternative fuels and has emerged as a substitute for conventional petroleum diesel. Biodiesel is monoalkyl esters of long chain fatty acids and most of biodiesel can be commercially produced from vegetable oils and animal oils/fats via a one-step alkali-catalyzed transesterification. The alcohols used in the process are low molecular weight alcohols such as methanol and ethanol. The oils or fats used as raw material in the process should have free fatty acid (FFA) content of less than 1% w/w (good quality oils or fats) [1,2], otherwise FFA reacts with alkaline used as catalyst in transesterification to form soap. Soap increases the viscosity of the reactants during the reaction and results in a lower yield of biodiesel. Furthermore,

soap inhibits the separation of biodiesel from glycerin and wash water [3]. The price of good quality oils and fats are high, thus the less expensive raw materials such as waste cooking oil, high FFA vegetable oil and animal fat were used. In addition, the use of waste cooking oil provides environmental, economic and health advantages and waste cooking oil can be available in large amounts. However, in general, waste cooking oil contains the FFA content of more than 1% w/w which is due to the hydrolysis of triglyceride at high temperatures during the cooking process [4]. Therefore, the two-step process, acid-catalyzed esterification followed by alkali-catalyzed transesterification is used to produce biodiesel. In the acid-catalyzed esterification step, FFA react with methanol to form methyl ester which results in the reduction of FFA content to less than 1% w/w. In the second step, oil is transesterified with methanol by using alkaline catalyst to convert the triglyceride to methyl ester.

In esterification reaction, sulfuric acid is often used as catalyst. However, the reaction has several drawbacks such as excess of water requires to wash the oil product, acid wastewater requires treatment, corrosiveness and recovery of methanol is difficult [4]. These drawbacks can be relieved by using the heterogeneous acid catalyst. Several researchers have reported that Smopex-101, ferric sulphate, amberlyst 15, amberlyst 16, and amberlyst 35 are the effective heterogeneous catalysts for the acid-catalyzed esterification step [4]. Recently, Montes D'Oca, M.G. and et al. demonstrated that sulfamic acid could be utilized as an effective catalyst for the conversion of fatty acid to fatty acid methyl ester [5]. Furthermore, Martins de Oliveira, P. and et al. indicated that sulfamic acid is an effective and eco-friendly catalyst for the pretreatment of oil with a high level of FFA in biodiesel production [6].



Sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) is a dry, odorless, non-corrosive, nonvolatile and non-hygroscopic crystalline solid with excellent physical stability. It is slightly soluble in methanol and dissolves moderately in water [5,7]. Besides, sulfamic acid is low in cost and commercially available. Nowadays, sulfamic acid has been extensively used for acid-catalyzed reaction and have been reported as a promising solid-acid catalyst for acid-catalyzed reactions, such as synthesis of isoamyl acetate [8], 1,5-benzodiazepines [9], β -Amino carbonyl compounds [10]. In regards to these findings, sulfamic acid was selected for use as a catalyst for esterification of FFA in WFO with methanol. The objectives of this study were: (a) To investigate the optimum reaction conditions for the reduction of FFA in WFO by using sulfamic acid as catalyst, and (b) To study the effects of the variables on the acid-catalyzed esterification of WFO with methanol.

MATERIALS AND METHODS

All chemicals used in this study, such as absolute ethanol, sodium hydroxide, potassium hydrogen phthalate, sulfamic acid and phenolphthalein were analytical grade. Sulfamic acid, sodium hydroxide, potassium hydrogen phthalate and phenolphthalein were purchased from Ajax Finechem Pty Ltd. Absolute ethanol was purchased from Merck. WFO was obtained from a deep-fried dough stick shop in Kaeng Khoi district, Saraburi province.

Preparation of WFO

The WFO was viscous with slight turbidity and deep red in color. In the preparation step, WFO was heated to 60 °C and filtered with Whatman Filter Paper No.93 to remove food residue and other impurities. The WFO was then checked to determine the FFA content by AOAC Official Method 940.28 (AOAC 2012). In addition, some physical properties such as viscosity, density and water content were tested by standard test method and the results are shown in Table 1.

Apparatuses

The apparatuses used for esterification consisted of a 250 mL three-necked flat-bottom flask and hotplate with a magnetic stirrer. One neck of the flask was used as the inlet for catalyst feeding and the two others were equipped with a reflux

condenser and a thermometer. The condenser was used to reduce the loss of methanol vapor from the reaction mixture.

Experimental conditions

In this study, the esterification was performed with the aim of investigating the optimum condition for the reduction of FFA content in WFO to less than 1% w/w and to study the effects of dominant variables on the esterification reaction. These dominant variables include methanol amounts (20, 30, 40 and 50% v/v), catalyst amounts (0, 3, 5, 7, and 9% w/v of oil), reaction temperatures (room temperature, 40, 50 and 60 °C) and reaction times (0.5, 1, 1.5, 2, 3, 4 h). The esterification reaction of WFO was carried out at the atmospheric pressure.

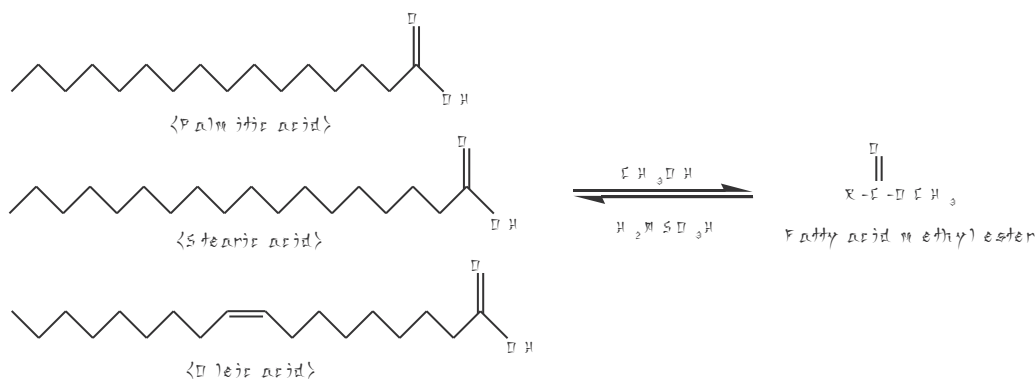
Experiment

In this study, the experiments were performed at a small scale. The WFO, methanol and sulfamic acid were used in amounts established for experiment. The WFO was initially added to the reaction flask and heated to the established reaction temperature. Methanol and sulfamic acid were then added to the WFO respectively. The reaction mixture was stirred at constant stirring speed for the established reaction time. At the end of the established reaction time, the reaction mixture was transferred to separatory funnel and allowed to settle overnight. The three layers formed with the top layer consisting of unreacted methanol and water formed during the esterification. The middle layer consisted of oil product with lower FFA content while the spent catalyst formed in the bottom layer. The oil product was separated and subjected to heating at 110 °C to remove residual methanol and water. After that, the oil product was then filtered with Whatman Filter Paper No.93 to remove residual catalyst and impurities. The clear oil product was obtained and the FFA content in oil was determined by AOAC Official Method 940.28 (AOAC 2012).

RESULTS AND DISCUSSION

Characterization of the WFO

The WFO used in this study was palm oil. It is the refined palm olein from pericarp. After filtration, the oil was clear, viscous and light brown in color. Its important properties are shown in Table 1.



Scheme 1. Esterification reaction of FFAs

Table 1. Properties of WFO

Property	Method	WFO
FFA content (as oleic acid), % w/w	AOAC (2012), 940.28	3.34
Kinematic viscosity at 40 °C, mm ² /s	ASTM D 445	51.46
Density at 15°C, Kg/m ³	ASTM D 4052	0.9224
Water content, % w/w	ASTM E 1064	0.168

It can be seen that the viscosity of WFO is more than conventional diesel fuel. The viscosity of diesel was specified as 1.8-4.1 mm²/s at 40 °C by ASTM D 445 in Thai diesel specification. Thus, WFO is not suitable for direct use in a diesel engine as fuel due to the high viscosity of oil causes serious problems in fuel pumping and poor fuel atomization through a fuel injector. The initial FFA content of WFO was 3.34% w/w which is higher than the limited value (1% w/w) of oil used for biodiesel production via alkali-catalyzed transesterification. Thus, the reduction of FFA content to less than 1% w/w is necessary and it can be achieved via acid-catalyzed esterification. WFO contained minute traces of water so it was not a hindrance for the esterification reaction. In this study, the researchers focused on the optimization of the esterification of WFO with methanol by using sulfuric acid as catalyst and the effects of predominant variables on the reaction. In general, palm olein contains both saturated fatty acids and unsaturated fatty acids. The saturated fatty acid comprises 36.3% palmitic acid (C16:0), 3.7% stearic acid (C18:0), 0.8% myristic acid (C14:0) and trace

of lauric acid (C12:0) and arachidic acid (C20:0). The unsaturated fatty acids comprises of 47.7% oleic acid (C18:1), 10.4% linoleic acid (C18:2) and trace of palmitoleic acid (C16:1) and linolenic acid (C18:3) [11]. Therefore, during esterification reaction, the FFA reacted with methanol to form methyl ester such as methyl palmitate, methyl stearate and methyl oleate as shown in Scheme 1.

Effect of methanol amount

The acid-catalyzed esterification is a typical reaction in which the products and reactants are in equilibrium. The equilibrium may be influenced by employing an excess of methanol. Hence, one important variable affecting the reduction of FFA content of the WFO is the amount of methanol. To investigate this effect, the esterification took place with different methanol amounts (20, 30, 40 and 50% v/v), sulfuric acid 5% w/v of oil, reaction temperature of 60°C and a reaction time of 2 hrs. FFA conversion versus methanol amount are shown in Figure 1.

It was found that FFA conversion increased rapidly when the methanol amount increased. This can be explained by Le Chatelier's principle. When methanol amount increased, the equilibrium shifted to the right which resulted in the forming of more fatty acid methyl ester. These results were in accordance with the results obtained by Montes D'Oca, M. G. and et al. [5]. In addition, the viscosity of the reaction mixture decreased when increasing the methanol amount. This led to the better mixing



between reactants and catalyst which resulted in the higher conversion of FFA to methyl ester [4]. At 50% v/v, the highest FFA conversion was obtained and the FFA content was reduced to 1.23% w/w. From these results, the 50% v/v was selected as the optimum methanol amount. In a commercial application, the excess of methanol in the top layer after esterification can be recovered by fractional distillation and recycled in the process.

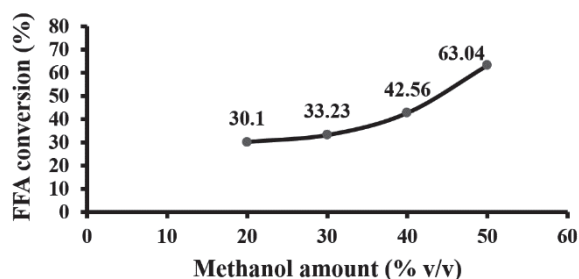


Figure 1. Variation of the FFA conversion with methanol amount.

Effect of catalyst amount

The esterification reaction is both slow and reversible. Thus, the acid catalyst is necessary to accelerate the reaction and the catalyst amount is one of the important variables directly influencing the reaction. In this study, sulfamic acid was used as catalyst and the effect of catalyst amounts (0, 3, 5, 7, 9% w/v of oil) was investigated at the methanol amount of 50% v/v, the reaction temperature of 60°C and reaction time of 2 hrs. The results obtained are displayed in Figure 2.

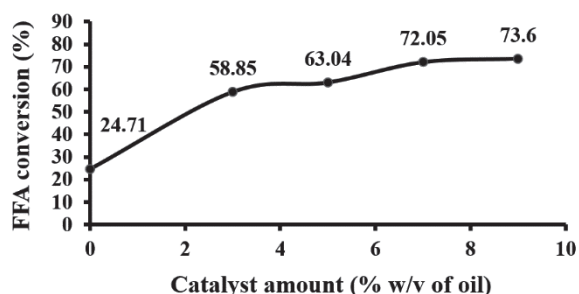


Figure 2. Variation of the FFA conversion with catalyst amount.

It can be seen clearly from Figure 2 that in the absence of sulfamic acid, 24.71% of FFA conversion was observed and this resulted from auto-catalysis [4].

The use of sulfamic acid produced a significant increase in the conversion of FFA in WFO. The same result was observed by Montes D'Oca, M. G. and et al. in which only 21% yield of methyl oleate was obtained when oleic acid was esterified with methanol in the absence of sulfamic acid as catalyst but the methyl oleate yield reached 71% when 5% sulfamic acid was used [5]. Increasing catalyst amount led to a positive effect on esterification and resulted in the continuous fatty acid methyl ester increasing. These results were in accordance with the results obtained by Montes D'Oca, M.G. and et al. [5]. Furthermore, the same results were also reported by Martins de Oliveira, P. and et al. who studied the use of sulfamic acid / methanol system to reduce FFA content in soybean oil containing a high FFA level of 20% and the results showed that an increase in catalyst concentration from 2 to 8% increased FFA conversion from 37.90 to 63.52% [6]. From an economical point of view, 7% w/v of oil is selected as the optimum catalyst amount because it was the lowest catalyst amount which provided the FFA content less than 1% w/w (0.93% w/w) and the FFA conversion was 72.05%.

Sulfamic acid is slightly soluble in methanol and dissolves moderately in water so it is the semi-heterogeneous catalyst. Therefore, at the end of the reaction, a small quantity of sulfamic acid was found to have dissolved in the methanol-water layer. However, most of the sulfamic acid separated to the bottom layer. Sulfamic acid could be reused, however, the catalytic activity rapidly decreased in the second cycle [5]. The sulfamic acid in the methanol-water layer should be recovered and recycled at the industrial scale. Hence, the recovering process is of interest for future work for the researchers.

Effect of reaction temperature

Another important variable that affects the FFA conversion in the acid-catalyzed esterification is the reaction temperature. To study the effect of reaction temperatures (31, 40, 50 and 60 °C), methanol amount, catalyst amount and reaction time were fixed as 50% v/v, 7% w/v of oil and 2 hrs, respectively. The results were shown in Figure 3.

Figure 3 shows that acid-catalyzed esterification could occur at different temperatures and it played a significant role in the acid-catalyzed esterification. As can be seen that the FFA conversion increased

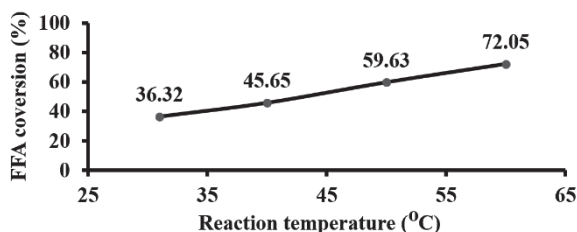


Figure 3. Variation of the FFA conversion with reaction temperature.

by increasing the reaction temperature. This was in accordance with the results obtained by Montes D'Oca, M.G. and et al. [5]. Methanol is not greatly soluble in WFO, hence, the agitation is very important in order to create a pseudo-homogeneous reaction mixture [4]. Esterification could occur at room temperature (31°C) but the reaction was not complete. When the reaction temperature increased, the viscosity of WFO decreased. This resulted in better mixing between the two reactants and catalyst which led to the more completion of the reaction [4]. At 60°C, the highest FFA conversion was obtained and the FFA content was reduced to less than 1% w/w (0.93% w/w). Thus, 60°C was selected as an optimum reaction temperature. A reaction temperature that exceed 60°C should be avoided to protect the loss of methanol by evaporation (boiling point of methanol 64.5°C).

Effect of reaction time

In this study, the effect of reaction times (0.5, 1, 1.5, 2, 3 and 4 h) was investigated at methanol amount of 50% v/v, catalyst amount of 7% w/v of oil and reaction temperature of 60 °C and the results are shown in Figure 4.

It is observed from Figure 4 that the three-phase division was performed. This can be ascribed to the production of water during the esterification reaction. The rate of esterification was high in the first one hour due to the minimal water formation. When the reaction proceeded, the water content in the reaction mixture consecutively increased. This resulted in the conversion of fatty acid methyl ester back to the FFA via hydrolysis. This negative effect occurred following the Le Chatelier's principle and can be obviously observed after 1 h in this study. From 1 to 3 hrs (2nd phase), the esterification

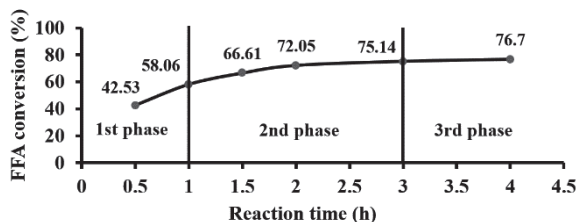


Figure 4. Variation of the FFA conversion with reaction time.

rate gradually decreased due to the negative effect above. After 3 hrs, the esterification rate and the hydrolysis rate were equal, the reaction reached its equilibrium which resulted in insignificant FFA conversion. These results were in accordance with the results obtained by Gan, S. [4]. The FFA content was reduced to less than 1% w/w (0.93% w/w) since 2 hrs. From the economic point of view, 2 hrs was selected as the optimum reaction time.

Properties of oil product

The properties of oil product produced at the optimum condition was tested and the results are shown in Table 2.

Table 2. Properties of oil product

Property	Method	Oil product
FFA content (as oleic acid), % w/w	AOAC (2012), 940.28	0.93
Kinematic viscosity at 40°C, mm ² /s	ASTM D 445	47.73
Density at 15°C, Kg/m ³	ASTM D 4052	0.9210
Water content, % w/w	ASTM E 1064	0.1350

The results shows that the use of sulfamic acid as catalyst in esterification reaction reduced the viscosity of the WFO from the initial value of 51.46 to 47.73 mm²/s. This indicates that sulfamic acid catalyzed both esterification of FFA and transesterification of triglyceride at the same time. However, the acid-catalyzed transesterification of triglyceride is slower than alkali-catalyzed transesterification about 4,000 times [12]. In transesterification, high molecular weight triglyceride was converted to lower molecular weight fatty acid methyl ester. This resulted in the viscosity reduction of oil product.



The oil product had an FFA content less than 1% w/w and contained minute traces of water. Thus, this oil was suitable to use as a raw material for the alkali-catalyzed transesterification to produce biodiesel

CONCLUSIONS

This study demonstrates that the FFA content in WFO can successfully be reduced to less than 1% w/w by acid-catalyzed esterification with methanol in the presence of sulfamic acid as catalyst. The optimal esterification reaction of FFA in WFO was achieved at methanol amount of 50% v/v, catalyst amount of 7% w/v of oil, 60 °C and 2 hrs. At the optimum condition, the FFA content was reduced from the initial value of 3.34 to 0.93% w/w (72.05% FFA conversion). All of the variables such as methanol amount, catalyst amount, reaction temperature and reaction time had the positive effect on the sulfamic acid-catalyzed esterification. This process is so attractive in biodiesel production and has high potential as a practical pretreatment step for vegetable oil or animal fat containing high level of FFA (1 < FFA content ≤ 3.34% w/w).

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