# Selective Removal of Saturated Fatty Acid Methyl Ester from Biodiesel Fuel by Hot Water Treatment

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## *Abstract*

The present study investigated the selective removal of saturated fatty acid methyl ester (FAME) from biodiesel fuel by water washing. Complete transesterification of palm oil was achieved at 60 °C for 1 hour in the presence of a KOH catalyst. Water washing treatment of the synthesized crude biodiesel was carried out at 30-70 °C to remove saturated FAME selectively. When the ratio of saturated FAME to unsaturated FAME in the palm oil based biodiesel became the minimum value at the washing temperature of 50 °C, the minimum temperature of the cloud point was 6 °C.

Keywords: Transesterification, saturated fatty acid methyl ester, washing treatment, cloud point

## 1. Introduction

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fat. The transesterification of oils or fat with methanol in presence of a catalyst yields the corresponding mono methyl esters (FAME). The advantages of biodiesel include renewability, biodegradability, higher flash point, and clean exhaust emission. However, one of the problems with biodiesel is its poor cold flow properties. When biodiesel is cooled below a certain point, some of the molecules aggregate and form crystal. The cloud point is the temperature at which a cloud of wax crystals first appears in a fuel sample. The fraction of saturated FAME in a biodiesel fuel actually affects on the cloud point of biodiesel. In order to improve the cold flow properties, biodiesel is blended with petro diesel [1,2]. Winterization [3-5] is the process of removing saturated FAME by cooling the fuel to cause crystallization and then separating the high melting components by filtration. This method however lacks efficient because of the low yield of the separation process.

The typical process to convert oil into biodiesel has three steps. The first step is pre-treatment to put the oil in a form in which it can be reacted properly in the reactor. The second is the transesterification reaction step, and the third is the purification step in which the final desired product is obtained. The most popular method to purify biodiesel is washing with water. Washing the biodiesel is necessary to remove residual glycerol and catalyst. If hot water is used, a small amount of FAME may be dissolved into water phase. Berrios et al. [5] tested water washing with deionized water and found that increased washing temperatures improved soap removal but glycerin removal was not significantly improved by temperatures elevated above ambient. However, there is no report of depressing the cloud point of biodiesel by water washing.

In this study, transesterifications of palm oil and the mixture of corn oil and beef tallow were carried out in a methanol solution containing 2 wt% KOH at 60 °C for 1 h. The resulting crude biodiesel fuels were washed with water at 30-70 °C for the selective removal of saturated FAME.

## 2. Experimental

For the present study, corn oil, beef tallow, methyl palmitate (>95%), dehydrated methanol, and potassium hydroxide, were obtained from Wako Pure Chemical, Japan. Standard palm oil for cooking purposes was also obtained. Methyl oleate (>90%), and methyl stearate (99%) were obtained from Sigma-Aldrich. Methyl linoleate was obtained from MP Biomedicals Inc. The acid value in the palm oil was determined by volumetry analytical method to be 0.37 mg-KOH/g-oil. The density of the palm oil at 298 K was 0.857 g/cm$^3$ and the saponification value was 200 mg-KOH/g-oil. The average molecular weight evaluated from the saponification value and the acid value was 841.

A dissolution test of pure FAME was performed in a test tube capped with a septum rubber. A mixture (1 mL) of equal volume of methyl oleate, methyl linoleate, methyl palmitate and methyl stearate was added into 3 mL of water. The segregated sample was gently shaken in a constant-temperature bath at 30-70 °C for 1 hour to achieve equilibrium. 0.1 mL of water was withdrawn from the test tube with a syringe after sedimentation separation and then injected into 2 mL of hexane for the analysis of FAME concentration with

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GC-FID (Packed column: Unisole 3000, Carrier gas: He, Column temperature: 240 ºC).

Transesterification of oil was carried out in a methanol solution containing 2 wt% KOH at 60 ºC for 1 hour. The volume ratio of methanol to oil was kept at 1:1. After completion of the reaction, the glycerol phase was recovered from the mixture by gravitational phase separation. The resulting crude biodiesel was put into equal parts of water. The segregated sample was gently shaken in a constant-temperature bath at 30-70 ºC for 10 min to remove not only impurities such as glycerol, methanol, soap and KOH but also saturated FAME selectively. These washing procedures were repeated three times.

FAME concentration in the sample was determined with a FID-GC. The cloud point of the purified biodiesel was determined by visual observation. This was done by placing a mirror close to a sample tube in a constant-temperature bath and observing a change in clarity as the sample was cooled.

## 3. Results and discussion

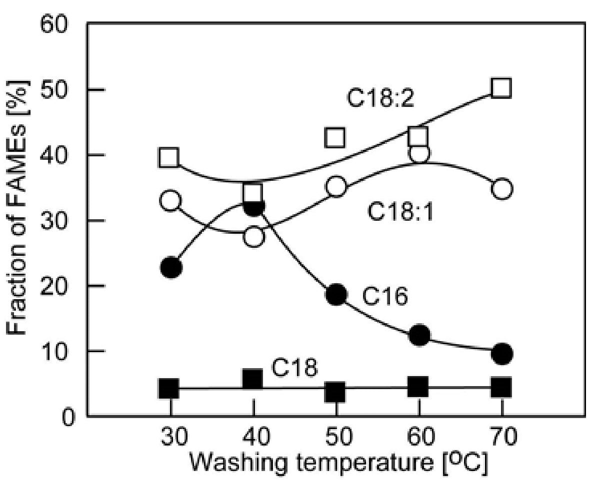


**Figure 1:** Effect of washing temperature on FAME fraction dissolving in water from the mixture of methyl oleate (C18:1), methyl linoleate (C18:2), methyl palmitate (C16) and methyl stearate (C18).

Fig. 1 shows the fraction of FAME dissolving in water at 30-70 ºC, when a mixture of equal volumes of methyl oleate (C18:1), methyl linoleate (C18:2), methyl palmitate (C16) and methyl stearate (C18) was used. The total peak area of FAME on GC increased with an increase in water washing temperature. Solubility of FAME into water becomes low when increasing the carbon number of the corresponding FAME due to their hydrophobicity. The solubility of the methyl stearate was evaluated to be one fourth times smaller than that of methyl palmitate. Furthermore, the solubility of methyl linolate (C18:2) was slightly higher than that of methyl oleate (C18:1) due to the nucleophilicity of C-C double bond. As shown in Fig. 1, the fraction of methyl palmitate indicated the maximum value at 40 ºC and then decreased with an increase in water washing temperature. Although a clear explanation for the existence of the maximum solubility is required, selective removal of methyl palmitate may be effective for improving the cold flow properties of biodiesel fuel.

Transesterifications of palm oil and the mixture of corn oil and beef tallow were performed at 60 ºC for 1 hour. The volume ratio of beef tallow to corn oil was 4. There was no triglyceride in the synthesized biodiesel fuel, indicating a complete reaction. Water washing treatment was carried out at 30-70 ºC to remove the residual KOH, unreacted methanol and potassium salt of fatty acids as a byproduct from the synthesized biodiesel fuel.

**Table 1:** Composition of FAME in palm-based biodiesel

| Fatty acid | Fraction [%] in biodiesel without water washing | Fraction [%] in biodiesel washed at 50 ºC |
|---|---|---|
| Myristic acid (C14) | 6.6 | 1.2 |
| Palmitic acid (C16) | 43.8 | 38.1 |
| Stearic acid (C18) | 3.0 | 4.1 |
| Oleic acid (C18:1) | 36.1 | 43.1 |
| Linoleic acid (C18:2) | 10.1 | 13.0 |
| Linolenic acid (C18:3) | 0.4 | 0.5 |

Table 1 indicates the percentage content of FAME for each acid in the palm-based biodiesels obtained without water washing and washing at 50 ºC. Fig. 2 shows the effect of washing temperature on the FAME composition in the purified biodiesel fuel derived from palm oil. The fraction of methyl palmitate decreased with an increase in washing temperature, reaching a minimum between 50 and 60 ºC and then increasing. For the dissolution of unsaturated FAME, the reversed tendency was obtained. The molar ratio of saturated FAME to unsaturated FAME was calculated from the concentration of the main FAME (C14, C16, C18, C18:1, C18:2 and C18:3). As shown in Fig. 3, the ratio achieved a minimum value for the biodiesel obtained from palm oil by water washing at 50-60 ºC. Meanwhile, no significant change in the ratio was observed for the biodiesel fuel obtained from the mixture of corn oil and beef tallow due to the low fraction of C16 compared with that in palm oil.

For the biodiesel fuel obtained from palm oil, the optimum temperature for the selective removal of methyl palmitate shifted to a high temperature compared with that of a mixture of pure FAME as shown in Fig. 1. The residual components in the crude biodiesel such as KOH, soap, glycerol and methanol might be affected to the dissolution properties of FAME. The cloud point is highly related to the fatty acid composition of biodiesel [7,8]. The high percentages of saturated fatty acids of long chains are responsible for high cloud points.

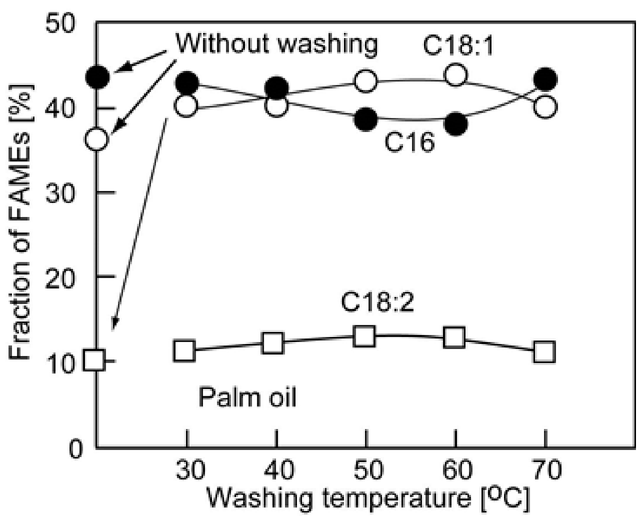


**Figure 2:** Effect of washing temperature on FAME composition in purified biodiesel derived from palm oil. Methyl oleate (C18:1; ○), methyl linoleate (C18:2; □), methyl palmitate (C16; ●).

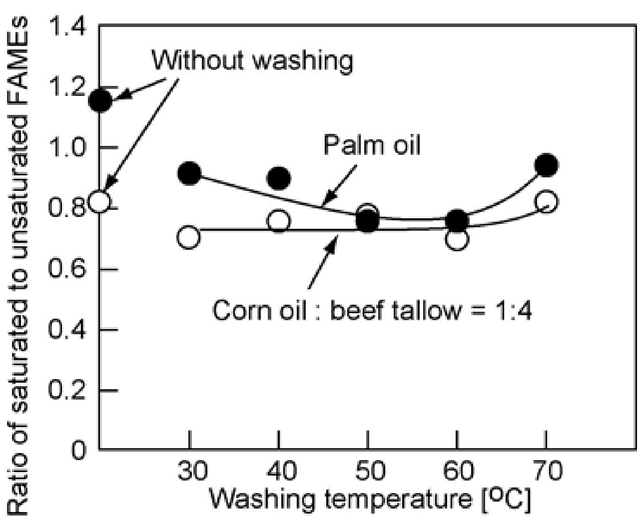


**Figure 3:** Effect of washing temperature on ratio of saturated to unsaturated FAMEs in palm oil and mixture of corn oil and beef tallow.

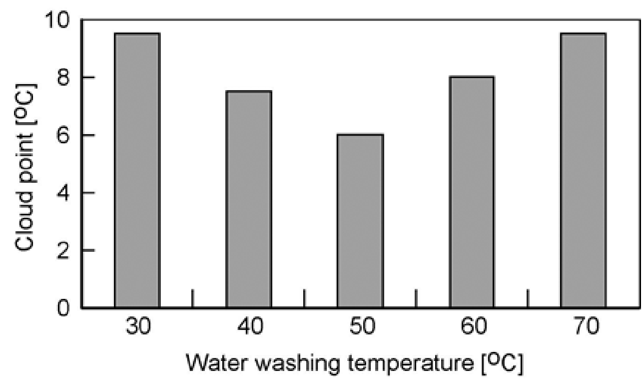


**Figure 4:** Effect of washing temperature on cloud point of purified biodiesel derived from palm oil

Fig. 4 indicates the cloud point of palm oil-based biodiesel obtained with different water washing temperatures. The cloud point of palm oil-based biodiesel at the washing temperature of 30 °C was as high as 9.5 °C. The cloud point decreased from 9.5 °C to 6.0 °C when the washing temperature was raised to 50 °C. The cloud point increased from 6.0 °C to 9.5 °C when the washing temperature was changed from 50 °C to 70 °C. Imahara et al. [7] investigated the quantitative relationship between the composition of biodiesel and cloud point by using the thermodynamic phase heterogeneous equilibrium approach. The thermodynamic model used to predict the cloud point in a two component system was described as follows.

$$(x_i/y_i) = \exp\{[(T - T_{m'i})/RT](\Delta H_{m'i}/T_{m'i})\} \quad (1)$$

where $x_i$ is the molar fraction of component i in liquid phase, $y_i$ the molar fraction of component i in solid phase, T the cloud point, $T_{m'i}$ the cloud point of pure component, $\Delta H_{m'i}$, the molar melting enthalpy of component i. Methyl palmitate is the main component of palm oil. The cloud point was calculated by equation (1) from the values of $\Delta H_{m'i}$, (55350 J.mol$^{-1}$) and $T_{m'i}$ (288 K) for methyl palmitate. The value of yi was unity because the solid phase at the cloud point is composed of methyl palmitate. The calculated cloud point at $x_i = 0.38$, which corresponds to the palm-based biodiesel washed at 50 °C as indicated in Table 1, was 4 °C.

## 4. Conclusions

Water washing of synthesized biodiesel is an important operation to remove KOH, unreacted methanol, and the soap byproduct. In this research, the selective removal of saturated FAME from biodiesel obtained from palm oil was realized by water washing treatment at 50-60 °C. As a result, the optimum cloud point of the palm oil-based biodiesel was achieved by water washing at 50 °C which resulted in a cloud point temperature of 6.0 °C.

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