# Potential Of Supercritical Methyl Acetate Technology In Biodiesel Production

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## ABSTRACT

Conventional biodiesel production methods utilize alcohol as acyl acceptor and produces glycerol as side product. Hence, with escalating production of biodiesel throughout the world, this leads to oversupply of glycerol and subsequently causes devaluation in the market. In this study, methyl acetate was utilized as acyl acceptor to produce fatty acid methyl esters (FAME) in a non-catalytic supercritical methyl acetate (SCMA) process, which produced triacetin as side product, a valuable fuel additive instead of glycerol. Consequently, the properties of biodiesel produced (FAME and triacetin) were superior compared to conventional biodiesel method (FAME only). In the research, the effects of reaction temperature, reaction time and molar ratio of methyl acetate to oil on the yield of biodiesel were thoroughly investigated. Apart from that, the influence of impurities commonly found in waste oils such as free fatty acids and water were studied as well. Results show that biodiesel yields in SCMA process did not suffer from adverse effect from the presence of impurities. Hence, this proves that SCMA has a high tolerance for impurities, allowing the employment of waste oils which is more economical than refined oils.

**Keywords**: Biodiesel; Methyl Acetate; Supercritical.

## 1.0 INTRODUCTION

Biodiesel is a mixture of fatty acid methyl esters (FAME) which is commonly derived from renewable oils/fats and has comparable physico-chemical properties compared to petroleum-derived diesel [1]. Hence, biodiesel has a huge potential to replace exhaustible fossil fuel and ensuring the sustainability of human development and energy sources. However, high processing costs and expensive feedstock of refined oils have limited its commercialization efforts and application in the industries [2]. In addition, glycerol is produced as side product and the abundance of glycerol in the market has lead to oversupply and depreciation in value. Furthermore, biodiesel shows a relatively poor performance at low temperature compared to diesel in terms of viscosity and pour point which restricted its application in cold climate countries. Consequently, biodiesel additives are usually employed to improve the properties of biodiesel and subsequently fulfilled established international standards.

Currently, there are many research works focusing on producing biodiesel additives in the literatures [3, 4]. One of them is to revalorize glycerol into triacetylglycerol or commonly known as triacetin which is a valuable anti-knocking additive in biodiesel. This effort not only generates side income to biodiesel refinery but could solve the overwhelming supply of glycerol in the market. However, the total production costs to produce FAME and triacetin separately will be enormous and subsequently leads to uneconomical cost of biodiesel compared to diesel. Hence, it would be very interesting if both these compounds can be produced concurrently in a single-step reaction which not only could reduce the production costs substantially but overcome the problem of poor biodiesel properties. This reaction route can be achieved via transesterification reaction between triglycerides and methyl acetate which produces FAME and triacetin as side product, instead of glycerol as shown in Figure 1. Hence, the downstream processes can be substantially simplified and the mixture of FAME and triacetin can be employed as biodiesel, rather than FAME only.

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\begin{array}{c}
CH_2-OCOR^1 \\
| \\
CH-OCOR^2 \\
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CH_2-OCOR^3
\end{array}
+ 3\, CH_3COOCH_3 \leftrightarrow
\begin{array}{c}
R_1COOCH_3 \\
\\
R_2COOCH_3 \\
\\
R_3COOCH_3
\end{array}
+
\begin{array}{c}
CH_2-OCOCH_3 \\
| \\
CH-OCOCH_3 \\
| \\
CH_2-OCOCH_3
\end{array}
$$

Triglycerides    Methyl Acetate    FAME    Triacetin

Figure 1: Reaction stoichiometry for transesterification reaction between triglycerides and methyl acetate to produce fatty acid methyl esters (FAME) and triacetin

Presently, there are limited research works that have been carried out concerning transesterification between triglycerides and methyl acetate. Xu et al. (2003) carried out enzymatic reaction to produce FAME and triacetin simultaneously but the reaction suffers from long reaction time [5]. Subsequently, Isayama and Saka (2008) conducted similar process but without the presence of catalyst with the employment of supercritical methyl acetate (SCMA) technology [6]. In their works, the molar ratio of methyl acetate to oil was fixed at 42 and it was found that SCMA process can produce FAME and triacetin in a shorter reaction time and the product mixture complies with international standards. However, there is still no reported article on the effect of molar ratio or impurities normally found in oils/fats such as water and free fatty acids (FFA) which might adversely affect the performance of SCMA reaction. Hence, in this study, a comprehensive investigation on SCMA reaction will be carried out which includes effect of temperature, reaction time, molar ratio, water and FFA content. These effects have huge influence on biodiesel yield and need to be examined thoroughly.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

Purified palm oil was purchased from Yee Lee Edible Oils Sdn. Bhd., Malaysia. Methyl acetate (99%) was used as the solvent ($T_c$ = 234$^o$C, $P_c$ = 4.69 MPa). Methyl heptadecanoate was used as internal standard while standard references for FAME analysis which include methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were also obtained from Fluka Chemie.

### 2.2 SCMA transesterification

SCMA transesterification reaction was carried out by using a batch-type tube reactor (12 ml) made of Stainless Steel Super Duplex® which can sustain high temperature and pressure needed in supercritical treatment as reported by Tan et al. (2009) [7]. Initially, methyl acetate and oil were charged into the tube reactor without any prior mixing and subsequently immersed in a furnace heated at pre-determined temperature. A thermocouple and a pressure gauge were utilized to monitor the reaction temperature and pressure, respectively. After a fixed reaction period, the reaction tube will be transferred into the water bath to quench the reaction immediately. Finally, the product mixtures will be subjected to evaporation process by using rotary evaporator at 60$^o$C for 20 minutes to recover excessive methyl acetate and subsequently pure biodiesel sample can be obtained.

### 2.3 Product analysis

The analysis of FAME content in sample was carried out by using gas chromatography (PerkinElmer, Clarus 500) with Nukol™ capillary column (15 m × 0.53 mm, 0.5 µm film thickness) and Flame Ionization Detector (FID) as the detector. Helium was used as carrier gas with the initial oven temperature at 110$^o$C held for 0.5 minute and subsequently increased to 220$^o$C (hold 8 minutes) at 10 $^o$C/min. Temperatures of the injector and detector were set at 220$^o$C and 250$^o$C respectively. In each run, 1 µL of sample was injected into the column. Methyl heptadecanoate was used as internal standard. The yield of FAME was calculated by the following Equation (1).

$$\text{Yield of FAME, \%} = \frac{\text{Total weight of methyl esters}}{\text{Total weight of oil in the sample}} \times 100\ \% \quad \text{......................(1)}$$

The mass ratio of FAME to triacetin was found to be approximately 4:1 in weight percent basis. Hence, the total theoretical weight of biodiesel (FAME and triacetin) is 125%, instead of 100% (FAME only).

## 3.0 RESULTS

### 3.1 Effect of temperature

Reaction temperature plays a crucial role in SCMA process as it can influence the phase behaviour of supercritical methyl acetate. In this study, the temperature range investigated was from 340- 420°C while the reaction time and molar ratio of methyl acetate to oil were fixed at 60 minutes and 30 mol/mol, respectively. Figure 2 shows the changes in biodiesel yield in correspond with reaction temperature for SCMA reaction. From the figure, it can be seen that the yield augmented proportionally with the increment of temperature until the optimum temperature was achieved at 400°C. This observation can be explained by the enhancement of reactivity between methyl acetate and triglycerides due to elevation of reaction temperature which leads to higher yield of FAME and triacetin. However, beyond the optimum temperature, the yield remained constant although the reaction temperature was increased to 420°C. The high temperature employed could have adverse effect on the FAME which has relatively low thermal stability at extreme conditions. Hence, elevation of temperature beyond optimum value has insignificant effect on the yield of biodiesel.

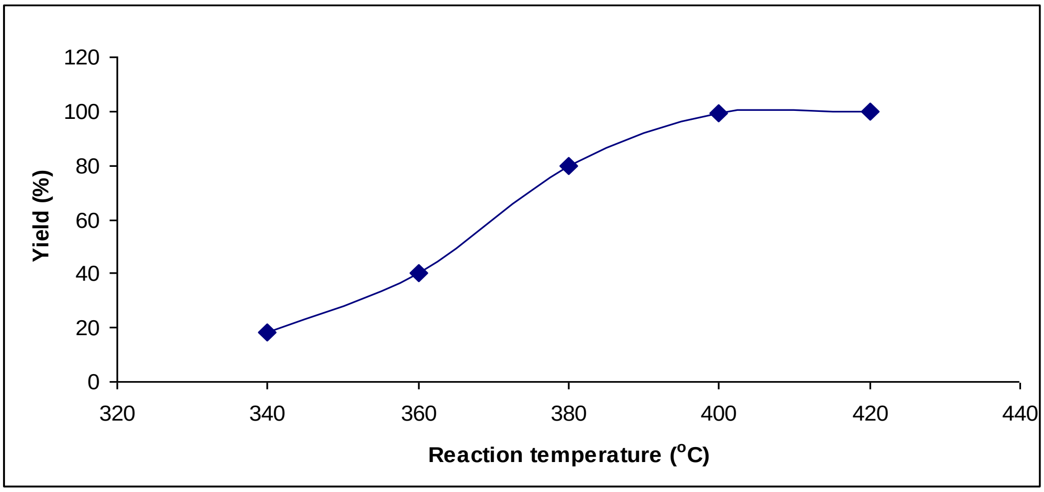


Figure 2: Effect of reaction temperature on the yield of biodiesel for SCMA reaction with molar ratio of 30 and 60 minutes reaction time.

3.2 Effect of molar ratio

In SCMA reaction, high molar ratio of methyl acetate to oil was employed to push the reaction to produce more FAME and triacetin. Therefore, a wide range of molar ratio from 20- 60 was investigated in this study to determine the effect of molar ratio on the yield of biodiesel as shown in Figure 3. In these experiments, the temperature was kept at 400°C and the reaction time was fixed at 60 minutes. It can be seen that the yield increases with the augmentation of molar ratio until the optimum ratio of 30 (mol/mol) and further addition of methyl acetate leads to lower yield of biodiesel. Although increasing the concentration of methyl acetate can induce higher yield in transesterification reaction, the constraints of reversible reaction causes the effect to be minimal after the optimum molar ratio is achieved. In addition, higher molar ratio also leads to diluted products of FAME and triacetin which could severely make the separation process difficult. Hence, the yield suffers a minor reduction when extreme molar ratio is employed in SCMA reaction.

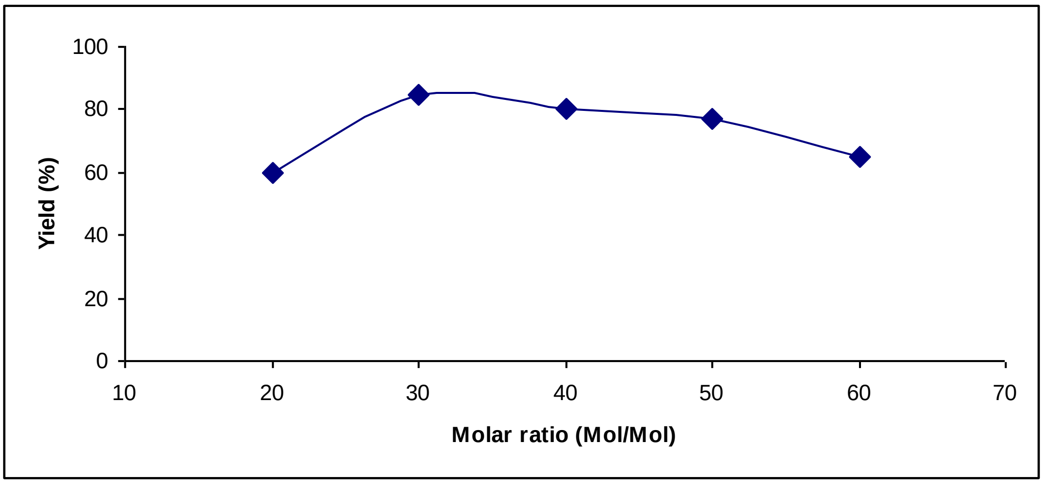


Figure 3: Effect of molar ratio on the yield of biodiesel for SCMA reaction with reaction temperature of 400$^{o}$C and 60 minutes reaction time.

3.3 Effect of reaction time

Figure 4 shows the effect of reaction time on the yield of biodiesel in SCMA reaction. Although SCMA is a non-catalytic process, it requires a shorter amount of reaction time compared to catalytic reactions. In this study, the reaction time was varied from 15- 75 minutes while maintaining the temperature and molar ratio at 400$^{o}$C and 30 mol/mol, respectively. From the figure, it is obvious that increment in reaction time induces higher biodiesel yield until the optimum reaction time of 60 minutes was reached. The prolong duration of time allows the reaction to achieve completion and higher biodiesel yield. However, beyond the optimum reaction time, the high temperature employed in SCMA might causes decomposition of FAME and subsequently lower the yield as shown in the figure. Hence, the optimum reaction time for SCMA process is 60 minutes.

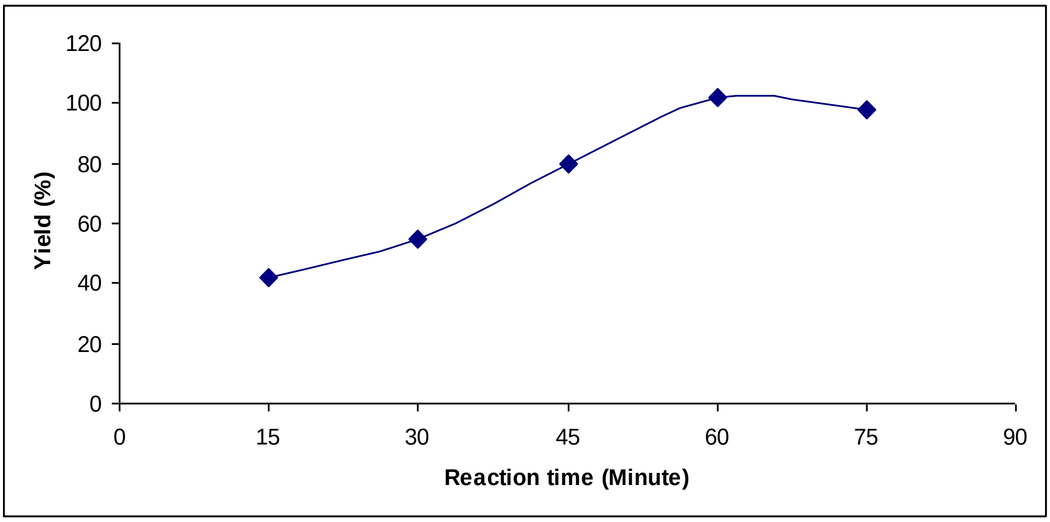


Figure 4: Effect of reaction time on the yield of biodiesel for SCMA reaction with reaction temperature of 400$^{o}$C and 30 molar ratio.

3.4 Effect of water and FFA content

Impurities such as FFA and water are commonly found in oils/fats which lead to side reactions and complicated downstream processes in transesterification reaction. Hence, refined oils with minimal impurities are employed in the industries but its high price leads to uneconomical total production costs. Hence, it is vital to investigate the effects of these impurities and subsequently validate the feasibility of employing cost-effective waste oils/fats in SCMA reaction. From Figure 5, it can be seen that these impurities do no cause any adverse effect on the yields of biodiesel although the oils/fats containing 20% of impurities. For FFA, increasing the content of FFA in the reaction mixture leads to higher yield of approximately 120% as the FFA can be esterified to FAME and acetic acid. On the other hand, the presence of high concentration of water in the reaction mixture also does not cause unwanted side reaction and subsequently lower yield which are common phenomenon in catalytic reaction. Instead, the yield increases steadily with the increment of water in the reaction mixture. With the presence of water, there are two simultaneous reactions occurring in SCMA which are hydrolysis of triglycerides to produce FFA and triacetin and subsequently esterification of FFA to FAME and acetic acid. Hence, the yield is not affected by the presence of water in oils/fats, allowing the utilization of inexpensive feedstock of unwanted waste oils/fats.

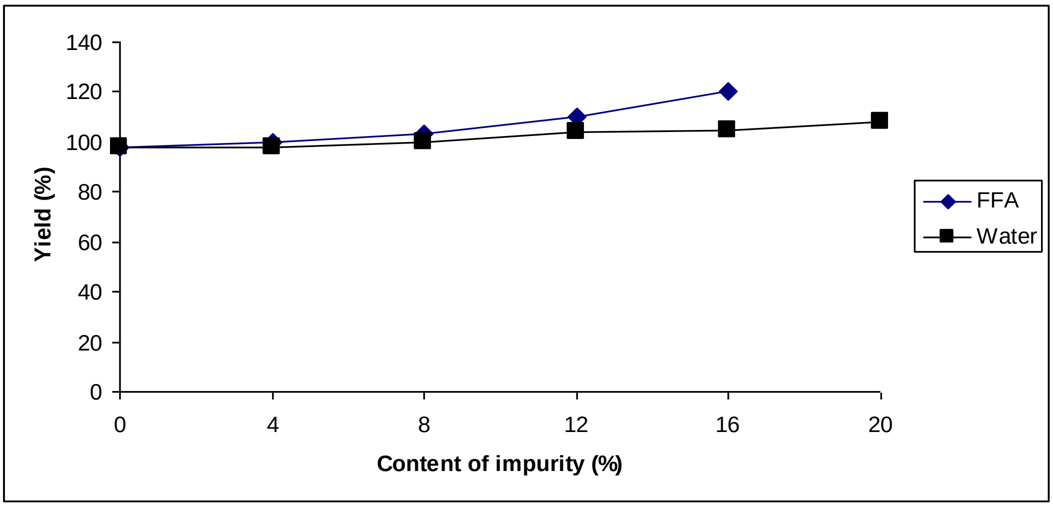


Figure 5: Effects of impurities on the yield of biodiesel for SCMA reaction with reaction temperature of 400$^{o}$C, 60 minutes of reaction time and 30 molar ratio.

## 4.0 CONCLUSION

This study has shown the potential of SCMA reaction in producing FAME and value-added triacetin in a single-step process. Triacetin is an important biodiesel additive which can improve the properties of this renewable energy particularly in cold conditions. Hence, it is very promising and economical to produce FAME and triacetin simultaneously rather than via two independent reactions which might have elevated the total production costs. Apart from that, in SCMA reaction, a high yield of 102% (FAME and triacetin) can be achieved by employing conditions of 400°C reaction temperature, molar ratio of 30 and 60 minutes reaction time. In addition, it has been proven that SCMA process has a high tolerance in impurities such as FFA and water which are normally found in waste oils/fats. Hence, it is feasible to utilize inexpensive waste as the source of triglycerides rather than high-quality refined oils.

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