Optimization of Biodiesel Production by Supercritical Methyl Acetate*

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Abstract

This work has been done to find out the optimum condition of supercritical methyl acetate method in biodiesel production. The reaction temperature, pressure, time and molar ratio in methyl acetate to oil were the key parameters that must all be considered to produce an optimum condition. Evaluation of thermal decomposition on products, *cis-trans* isomerization and tocopherol content were required to further optimize the reaction condition. It was, therefore, concluded that for the supercritical methyl acetate method, reaction condition of 350°C/20MPa/45min/42 molar ratio gave the highest yields of FAME (96.7wt%) and triacetin (8.8wt%). Yet, at such a reaction condition, the optimum reaction condition was compromised due particularly to the unavoidable thermal decomposition of products, and tocopherols as natural anti-oxidants.

Keywords: biodiesel, optimization, supercritical methyl acetate, triacetin

1. Introduction

Due to the increasing worldwide concerns of excess glycerol production on the marketplace from biodiesel (Bonet *et al.*, 2009), a new method in biodiesel production that prevents glycerol production must be developed. A non-catalytic supercritical methyl acetate reaction can be utilized to avoid the production of glycerol during biodiesel production (Saka, 2005). Instead of forming glycerol, the supercritical method produces triacetin as its by-product. Stoichiometrically, 3 moles of fatty acid methyl esters (FAME) and 1 mole of triacetin are produced from every 1 mole of triglycerides.

Furthermore, Saka and Isayama (2009) have reported that triacetin, a by-product from interesterification of triglycerides, is miscible with FAME even at room temperature and atmospheric pressure. This mixture hardly has any negative effect on the resultant biodiesel, in fact, it improves some of biodiesel properties, such as viscosity, oxidation stability and cold-flow properties. Therefore, the mixture of FAME and triacetin can be considered as biodiesel resulting in a maximum theoretical yield of 125wt% from the interesterification reaction of triglycerides (Saka and Isayama, 2009). In addition, Goembira *et al.* (2012) further reported that supercritical methyl acetate acquires the highest yield among various supercritical carboxylate esters in biodiesel production.

Due to the potential of the supercritical method, it has been studied by other research groups (Campanelli *et al.*, 2010; Niza *et al.*, 2011; Tan *et al.*, 2010, 2011). Some of them (Tan *et al.*, 2010, 2011; Niza *et al.*, 2011) claimed that the reaction conditions used in their studies were optimized. However, the obtainable yields were far below the maximum theoretical yield of 125wt%.

This study has been undertaken to show key parameters that must be considered before attaining optimum reaction conditions. Additionally, this work was done along the line of our previous Letter to the Editor (Saka *et al.*, 2011).

2. Experimental

2.1. Materials

Rapeseed oil was used in this experiment as the source of triglycerides, consisting of 99.8wt% triglyceride content. High purity chemicals such as methyl acetate, various FAME and triacetin were utilized, whereas for standard compounds, analytical grade of individual FAME, triacetin and tocopherols were used. All chemicals were purchased from Nacalai Tesque Inc., Kyoto, Japan.

2.2. Methods

Supercritical methyl acetate treatment was carried out by using a flow-type reaction system to study the effect of molar ratio in methyl acetate to oil, reaction pressure, reaction temperature and reaction time on product yields. The flow-type reaction system was the same as the one reported previously (Saka and Isayama, 2009). On the other hand, a batch-type reaction system was utilized for experiments on thermal decomposition of products, *cis-trans* isomerization of FAME and tocopherol degradation. The batch-type reaction vessel was equipped with an additional gas charging inlet for purging the vessel with nitrogen. Furthermore, additional initial pressure can be added by charging nitrogen, thereby a designated reaction pressure being obtainable.

Quantifications of FAME, triacetin and tocopherols were carried out by using high performance liquid chromatography (HPLC), with methanol as the mobile phase. Refractive index detector (RID) was used for FAME and triacetin, while fluorescent detector was applied for tocopherols. The HPLC setting for the RID was the same as the one used by Goembira *et al.*(2012), whereas for the fluorescent detector was similar to the work by Xin *et al.* (2008). Moreover, evaluation of *cis-trans* isomerization of FAME was made by using fourier transform infra red (FT-IR). All sets of experiments were done in triplicate with less than 1% variation in the results, indicating that they can be replicated in a high precision state.

3. Results and discussion

3.1 Effect of molar ratio of methyl acetate to oil on product yield

As explained earlier, 3 moles of methyl acetate is stoichiometrically needed to convert 1 mole of triglycerides into 3 moles of FAME and 1 mole of triacetin. Nevertheless, in order to proceed the reaction towards the product side, an excessive amount of methyl acetate must be applied.

Fig. 1 shows the effect of molar ratio in methyl acetate to rapeseed oil on the yields of FAME and triacetin. It can be seen from Fig. 1 that the higher molar ratio resulted in the higher FAME and triacetin yields. This is due to the availability of excess reactants for reactions to proceed and the prevention of backward reaction. The formation of FAME could firstly be observed when the molar ratio was set at 6:1, nonetheless, molar ratio of 42:1 was required in order to obtain FAME yield higher than 96.5wt%, as the minimum ester content in European biodiesel standard (EN-14214). On the other hand, triacetin was formed at molar ratio of 21:1, which was higher than molar ratio for the initial formation of FAME.

A molar ratio increase from 42:1 to 54:1, however, did not significantly increase the yield. FAME yield was only increased from 96.7 to 97.2wt%, while for triacetin, it increased from 8.8 to 9.0wt%. Insignificant yield increase at the higher molar ratio than 42:1 was presumably due to an additional role of the solvent to minimize the occurrence of thermal decomposition. The excessive amount of solvent inhibits thermal decomposition of product by a cage-effect mechanism (Ehara *et al.*, 2002). Similar result was reported by Campanelli *et al.*

(2010), although different biodiesel feedstock was used in their experiment.

Conversely, different trend line was reported by Tan *et al.* (2011), where the higher molar ratio than 30:1 resulted in the lower yield. They explain the phenomenon was due to difficulties in separating the products from the unreacted methyl acetate, which is unacceptable because there should be no problem in removing methyl acetate from the mixture of FAME and triacetin since their boiling points (at 1atm) are so much different, i.e. 57, 374 and 260°C, respectively.

3.2 Effect of reaction pressure on product yield

Fig. 2 shows the effect of reaction pressure on biodiesel yield in supercritical methyl acetate treatment. Reaction pressure higher than critical pressure of methyl acetate (P_c=4.69MPa) was required to ascertain that the supercritical state has been attained.

However, Fig. 2 shows that at reaction pressure of 5MPa, no FAME and triacetin formations were observed. Gil *et al.* (2008) stated that there is a possibility of changes in the critical pressure of a binary mixture. It is presumed that the critical pressure of the binary mixture of oil and solvent was higher than 5MPa. The use of 5MPa in reaction pressure, therefore, resulted in the absence of FAME and triacetin due presumably to the unreached supercritical state of the binary mixture.

It is obvious from Fig. 2 that the higher reaction pressure resulted in the higher yields of FAME and triacetin, possibly due to the higher density of the reactant mixture that increased the occurrence of collisions among reactant molecules noted by Turro (2005). However, no increase in the yield of triacetin up to reaction pressure of 15MPa. This phenomenon could be due to the fact that the formation of triacetin must be initiated by inducing complete acyl replacement in the glycerol backbone with CH_3COO^- from methyl acetate. At reaction pressures of 20 and 30MPa, complete acyl replacement occurred.

Nevertheless, insignificant increases in yields of FAME from 96.7 to 98.1wt% and triacetin from 8.8 to 8.9wt% were noted when the reaction pressure was increased from 20 to 30MPa. This slight yield increase could be due to the role of the higher reaction pressure in minimizing thermal decomposition of products as well as the higher interesterification.

3.3 Effect of reaction temperature on product yield

In general, the higher reaction temperatures would result in the higher reaction rates, which eventually correspond to the higher biodiesel yields. This can evidently be seen in Fig. 3, where the higher reaction temperature under the same pressure of 20MPa contributed to the higher biodiesel yield.

However, Fig. 3 also shows that at 300°C there was no observable product formation. Meanwhile, starting from 320°C, biodiesel will be formed, although the yield was still below 50wt%. These lines of evidence show that in the non-catalytic reaction, reactivity of triglycerides towards supercritical methyl acetate was relatively low, particularly at reaction temperatures below 320°C.

The highest total yield of 105.5wt% (96.7wt% FAME; 8.8wt% triacetin) was acquired at reaction condition of 350°C/20MPa/45min. The yield of this study was relatively higher compared to the other research groups. Campanelli *et al.* (2010) obtained 104.0wt% under the same reaction temperature used in this study. However, Niza *et al.* (2011) and Tan *et al.* (2011) could only obtain 71.9 for *Jatropha* oil and 99wt% for palm oil, correspondingly, at a much severe reaction condition of 400°C, although palm oil can be expected to be higher yield due to the less amount of poly-unsaturated fatty acids.

3.4 Effect of reaction time on product yield

The effect of reaction time on FAME and triacetin yields can be evaluated from Figs. 1 through 3. As we can see from the figures, in most cases, the longer reaction time resulted in the higher FAME yields. This situation was due to the fact that the longer reaction time has increased the contact time of the solvent with triglycerides and the intermediate compounds.

In Fig. 3, we can also see that in some cases, particularly at the higher reaction temperatures that the biodiesel yield was increased to a certain extent, but it was decreased over a prolonged reaction time. The reaction time of only 15min was required to obtain total yield of 90.8wt% (76.4wt% FAME; 14.4wt% triacetin) when reaction condition of

380°C/20MPa was used, while under 350°C/20MPa, a comparable total yield of 91.94wt% (84.5wt% FAME; 7.5wt% triacetin) will only be achieved in 30min reaction time. Nevertheless, in the former case, longer reaction time up to 45min could only slightly increase the total yield up to 97.7wt% (86.7wt% FAME; 10.9wt% triacetin), whereas for the latter case, the total yield of 105.5wt% (96.7wt% FAME; 8.8wt% triacetin) was obtainable under the same reaction time.

The similarity of the two reaction conditions was the yield decrease at reaction time longer than 45min. At 60min reaction time, total yields were 80.6 (75.3wt% FAME; 5.3wt% triacetin) and 98.1wt% (90.7wt% FAME; 7.4wt% triacetin) under 380 and 350°C reaction temperatures, respectively. Although applying different feedstocks and reaction conditions in supercritical methyl acetate treatments, however, the yield reduction under the higher reaction temperatures was also observed by the other research groups (Campanelli *et al.*, 2010; Niza *et al.*, 2011; Tan *et al.*, 2011). It is most likely that this situation was due to the occurrence of thermal decomposition.

3.5 Thermal decomposition of individual fatty acid methyl esters (FAME) and triacetin

Fig. 4 shows the recovery of individual FAME and triacetin after exposure to various reaction temperatures under the same reaction pressure of 20MPa. We can clearly observe the occurrence of severe thermal decomposition in all products at 380°C, particularly when longer reaction time was applied. On the other hand, at reaction condition of 350°C, only methyl linolenate exhibited significant thermal decomposition. Furthermore, a reaction temperature of 300°C gave the least thermal decomposition, in good agreement with the results presented by Imahara *et al.* (2008) for conversion by supercritical methanol.

Oils from rapeseed (*Brassica napus*) and oil palm (*Elaeis guineensis)* were also utilized to compare the effect of thermal decompositions on biodiesel feedstocks that have different degrees of unsaturation. As can be seen from Table 1, rapeseed oil represented biodiesel feedstocks with a high degree of unsaturation, while on the other hand, palm oil was corresponding to feedstocks with a lower degree of unsaturation, i.e., it has a higher content of saturated fatty acids.

Fig. 5 shows that no FAME and triacetin yields were obtainable at reaction condition of 300°C/20MPa for both feedstocks. Furthermore, under 350°C/20MPa, at longer reaction times than 45min, reductions of FAME and triacetin were noticeable. As expected, the use of higher reaction temperature of 380°C/20MPa resulted in more thermal decomposition in both oils.

The use of oil from oil palm that has considerable amount of saturated fatty acid did not prevent thermal decomposition from taking place. This situation was most likely due to the presence of unsaturated fatty acid in the feedstock, which is also vulnerable to thermal decomposition, particularly at such a severe reaction condition. This result, however, is contradict the results reported by Niza *et al.* (2011) and Tan *et al.* (2010, 2011) that suggested even a higher reaction temperature of 399°C/59min and 400°C/32min, respectively, as their optimum reaction conditions for supercritical methyl acetate method for the biodiesel production from palm oil.

3.6 *Cis-trans* isomerization of FAME

Cis-trans isomerization of individual FAME can be used to indicate the cold-flow properties of biodiesel. Most natural fatty acids with double carbon bonds have *cis*-isomer structure that makes them have lower melting points. Imahara *et al.* (2008) reported that *cis-trans* isomerization happens during biodiesel production process by supercritical methanol, particularly when relatively high reaction temperatures are applied.

Using the same method as Imahara *et al.* (2008), identification of *cis*- and *trans*-types C=C was done by recognizing FT-IR spectra peaks at wavenumber of 690 and 970cm^{-1}, respectively. Methyl stearate (C18:0) that has no double carbon bond was used as a control to show that there was neither *cis*- nor *trans*-isomers formed at any reaction conditions. On the other hand, FT-IR spectra from methyl oleate (C18:1), methyl linoleate (C18:2) and methyl linolenate (C18:3) show the appearance of *trans*-isomer peak as a compensation of the disappearance of the *cis*-isomer peak.

For poly-unsaturated FAME, at the most severe reaction condition used in this experiment, i.e., 380°C, the appearance of *trans*-type C=C peak was very observable. From these lines of evidence, it is clear that the use of very high reaction temperatures is not preferable in preventing *cis*-*trans* isomerization of poly-unsaturated FAME.

3.7 Decomposition of tocopherols

Tocopherols as natural anti-oxidants are proven to be present in some biodiesel feedstocks and can provide anti-oxidant effect in biodiesel produced from those feedstocks (Fröhlich and Schober, 2007; Xin *et al.*, 2008). However, the presence of tocopherols can be affected by the production process of biodiesel, due particularly to their vulnerability towards decomposition at high temperatures. Table 2 shows the effect of various reaction temperatures in supercritical methyl acetate treatments on the presence of tocopherols in FAME from rapeseed and oil palm.

From the table, we can see that the initial tocopherol content in FAME from oil palm was 450ppm, higher than that from rapeseed FAME, i.e., 300ppm. Reaction temperatures below 300°C could prevent significant tocopherol reduction. The higher reaction temperatures resulted in more reduction of tocopherol contents in FAME. However, as mentioned earlier, due to the lower reactivity of triglycerides towards supercritical methyl acetate, the use of 350°C was unavoidable since at this temperature, the highest FAME and triacetin yields were obtainable.

At the higher reaction temperature of 380°C, tocopherol contents were considerably reduced to 70 and 30ppm in oil palm and rapeseed FAME, respectively, which were much less than their original concentrations. Higher reaction temperatures as proposed by other research groups (Tan *et al.*, 2011; Niza *et al.*, 2011) will, therefore, further diminish more tocopherol in biodiesel. Such lower anti-oxidant content makes biodiesel more susceptible to oxidation, particularly during its storage.

4. Concluding remarks

This study showed that reaction temperature, pressure, time and molar ratio of methyl acetate to oil were the key parameters in biodiesel production by the supercritical methyl acetate method. Furthermore, evaluations on thermal decomposition, *cis-trans* isomerization and tocopherol content were necessary for determining an optimum condition. The reaction condition with the highest FAME and triacetin yields was, therefore, 350°C/20MPa/45min/42 molar ratio. However, at such a reaction condition, we could not totally avoid the occurrence of thermal decomposition, thus, an optimum condition was not entirely attainable in this reaction system.

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Figure Captions

Fig. 1 Effect of molar ratio in methyl acetate to oil on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 350°C/20MPa

Fig. 2 Effect of reaction pressure on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 350°C and molar ratio of 42:1 in methyl acetate to oil

Fig. 3 Effect of reaction temperature on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 20MPa and molar ratio of 42:1 in methyl acetate to oil

Fig. 4 Recovery of various FAME and triacetin as exposed to supercritical methyl acetate at 20MPa under different reaction temperatures and times

Fig. 5 FAME and triacetin yields from oils of rapeseed (*Brassica napus*) and oil palm (*Elaeis guineensis*) as treated in supercritical methyl acetate under various reaction temperatures at 20MPa and 42 molar ratio

Table 1 Fatty acid composition of oils from rapeseed (*Brassica napus*) and oil palm (*Elaeis guineensis*)

Oil Source	Fatty Acid Composition (wt%)					
	C16:0	C18:0	C18:1	C18:2	C18:3	Others
Rapeseed	4.0	1.7	62.5	21.2	9.0	1.6
Oil Palm	40.0	4.3	43.5	10.8	0.2	1.2

Table 2 Effect of various reaction temperatures on the tocopherol content in FAME from oil palm and rapeseed as treated in supercritical methyl acetate at 20MPa for 30min

FAME	Tocopherol Content (ppm)					
	Unexposed	270°C	300°C	320°C	350°C	380°C
Rapeseed	300	296	289	270	87	30
Oil Palm	450	447	438	425	150	70

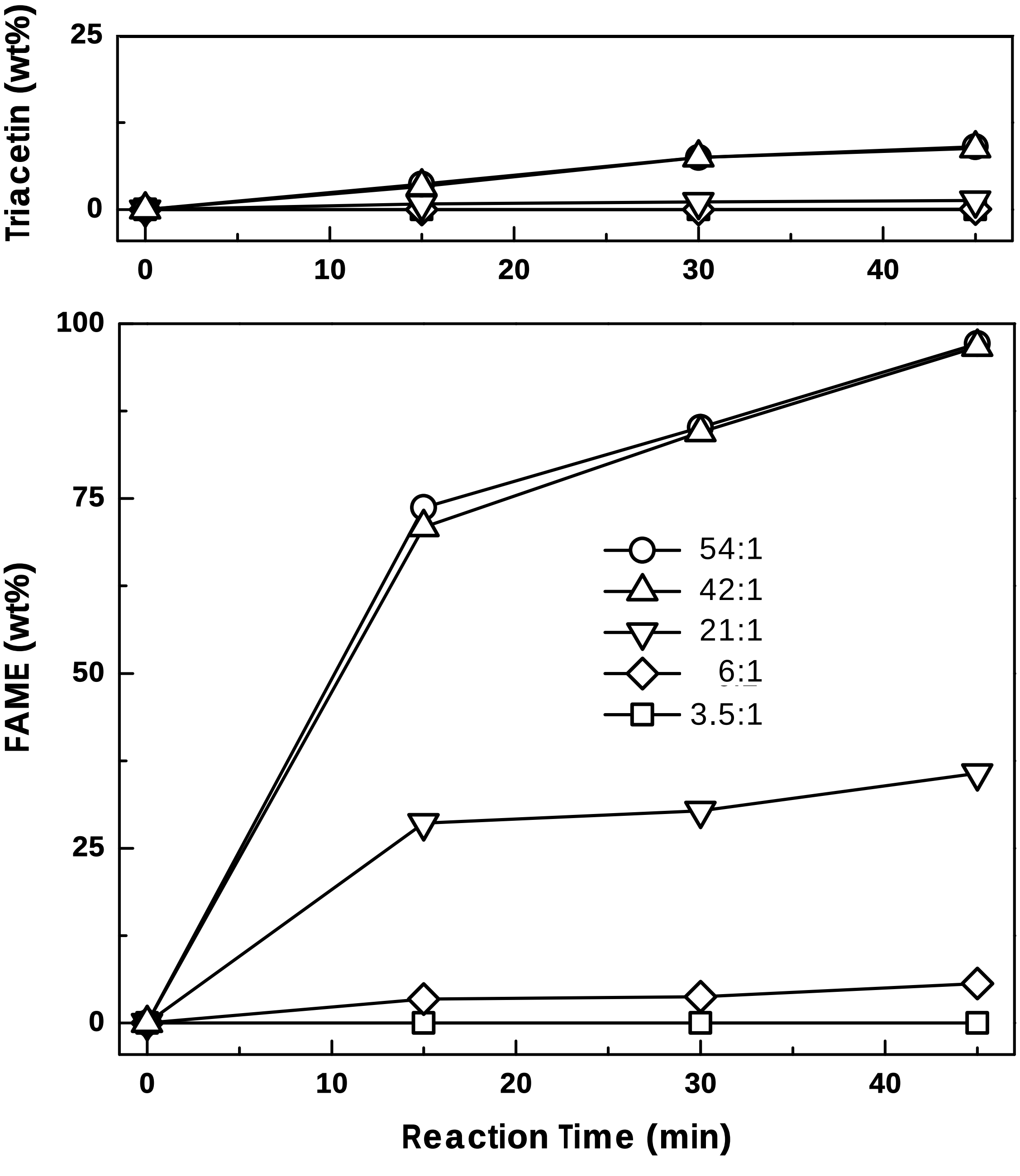


Fig. 1 Effect of molar ratio in methyl acetate to oil on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 350ºC/20MPa

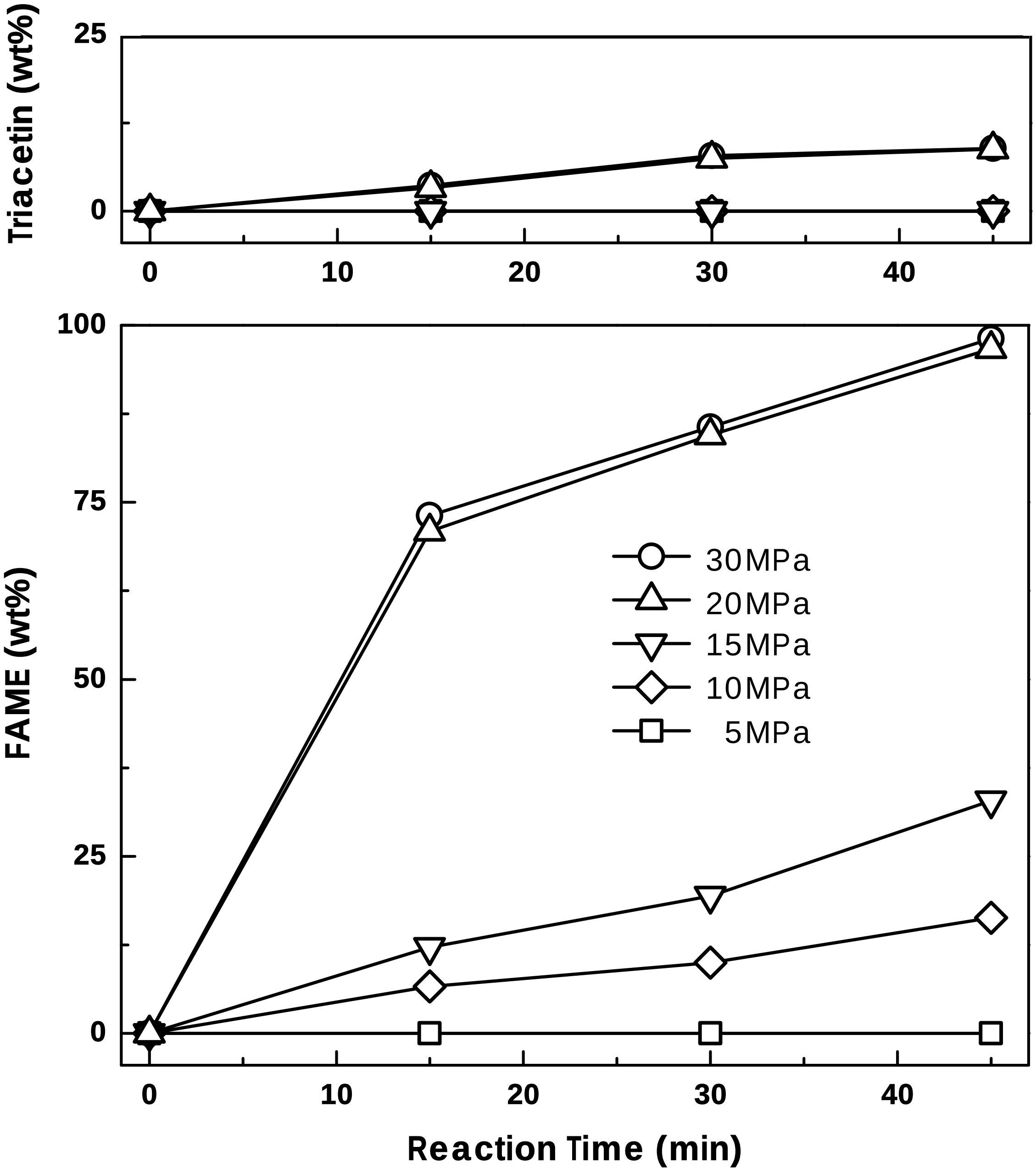


Fig. 2 Effect of reaction pressure on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 350ºC and molar ratio of 42:1 in methyl acetate to oil

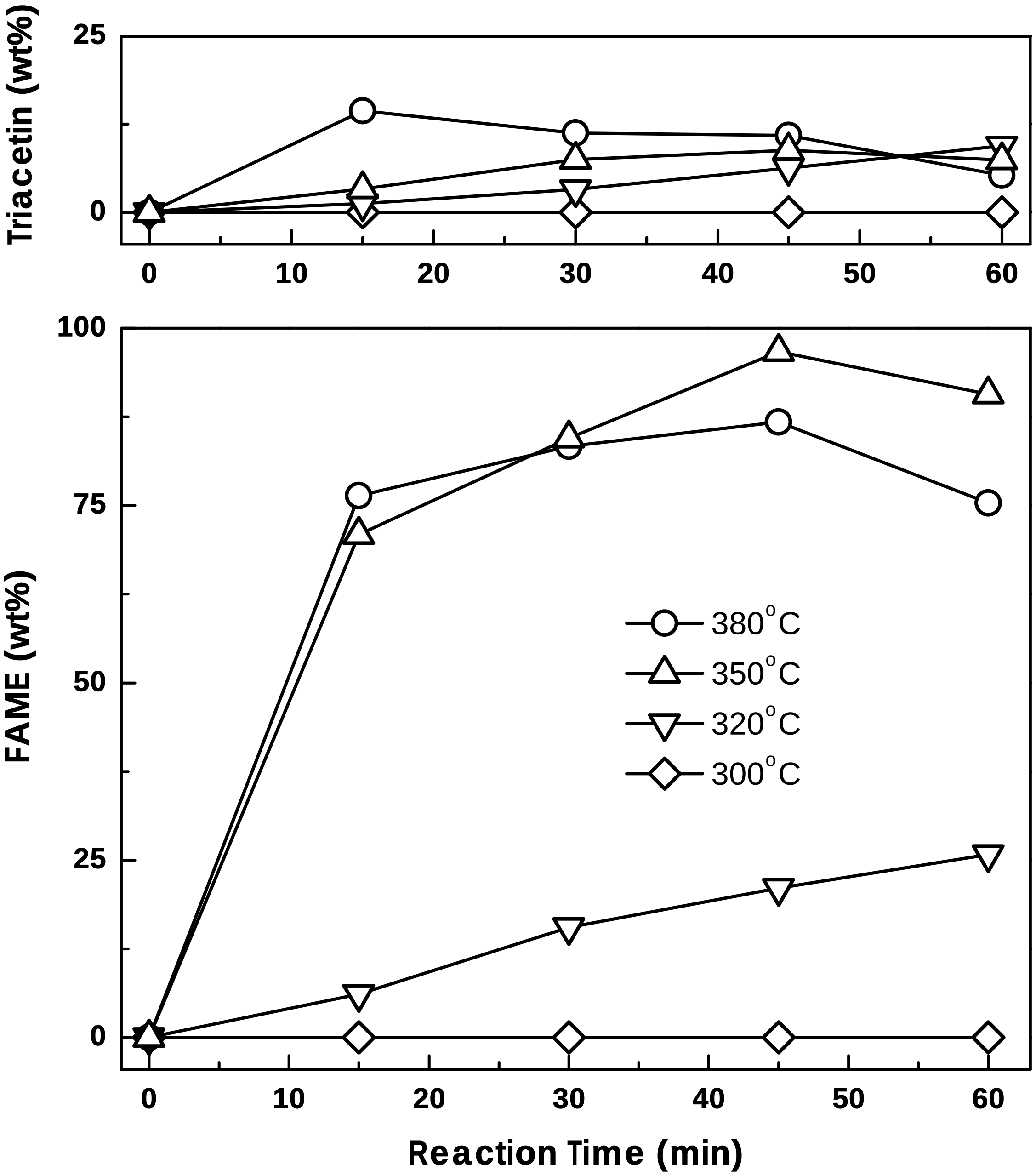


Fig. 3 Effect of reaction temperature on FAME and triacetin yields from rapeseed oil as treated in supercritical methyl acetate at 20MPa and molar ratio of 42:1 in methyl acetate to oil

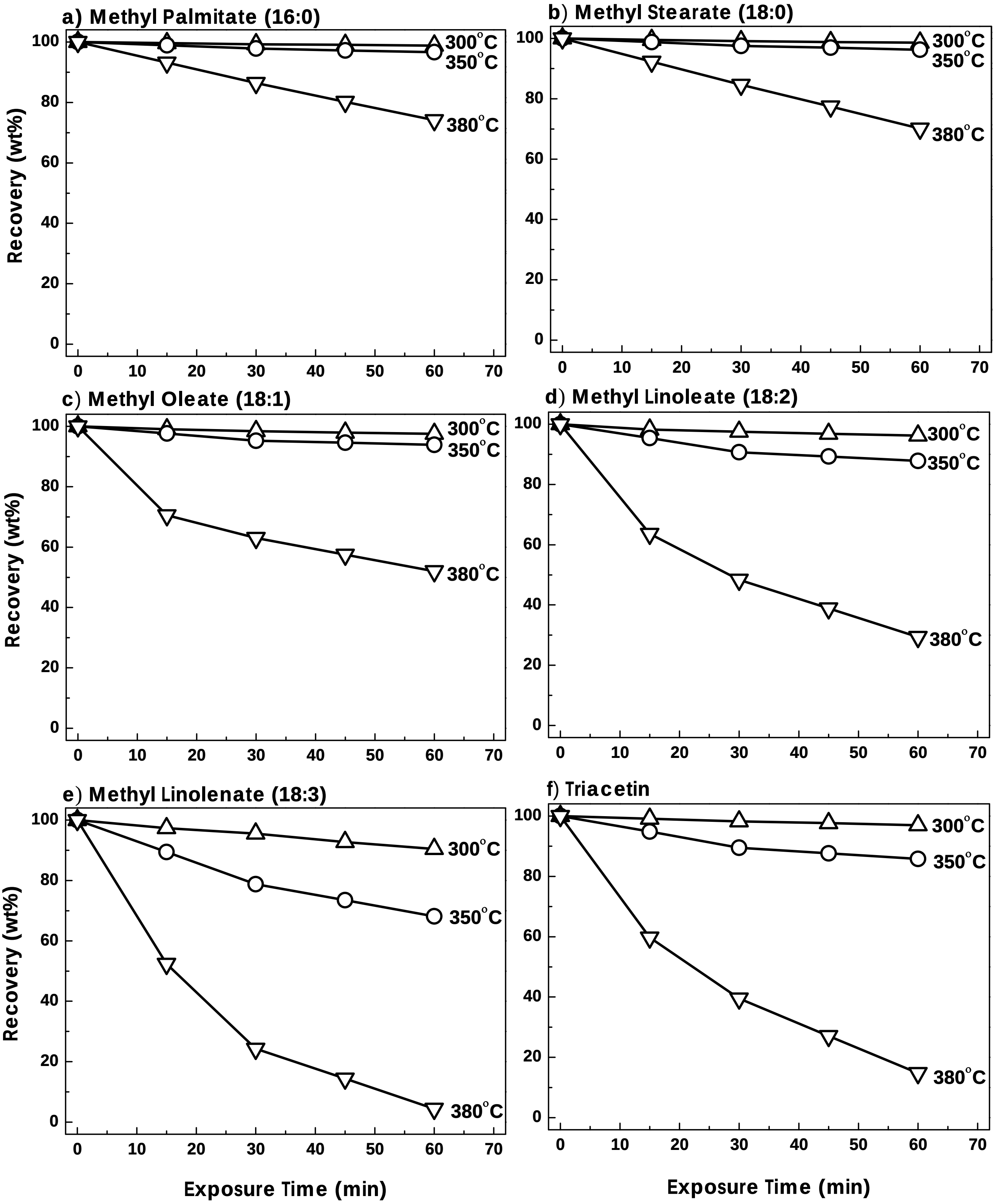
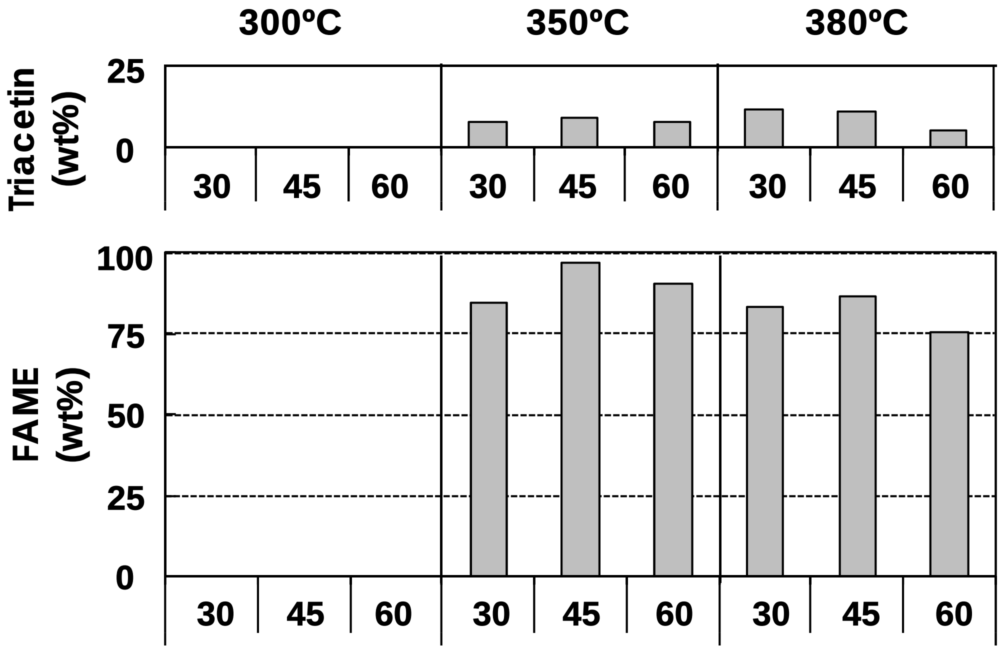


Fig. 4 Recovery of various FAME and triacetin as exposed to supercritical methyl acetate at 20MPa under different reaction temperatures and times

a) Rapeseed



b) Oil Palm

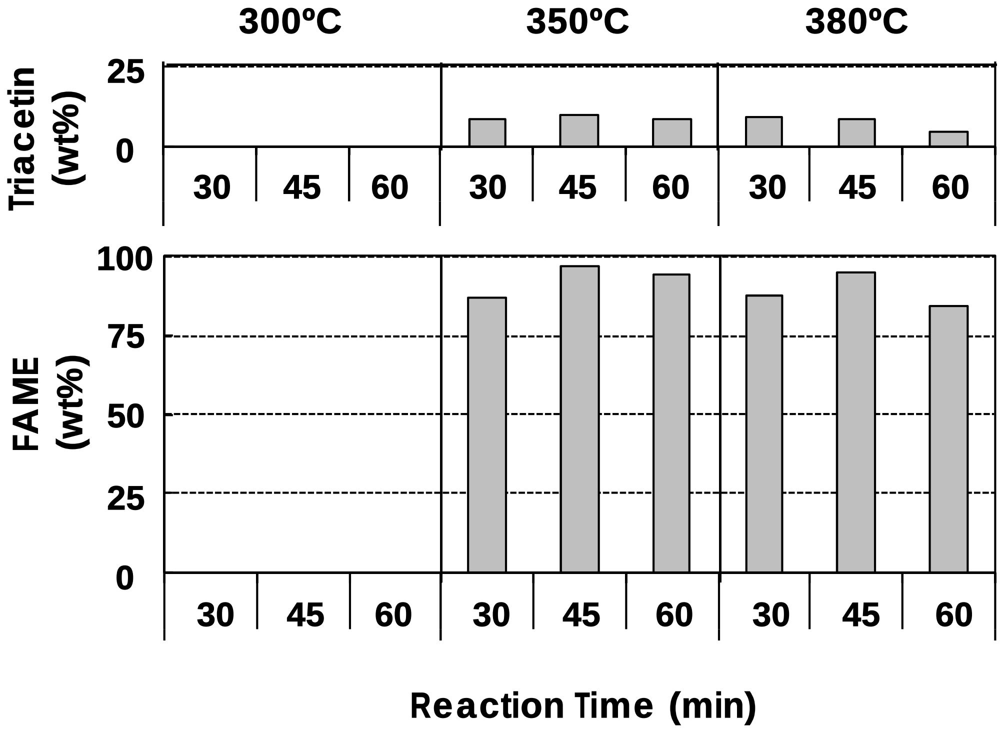


Fig. 5 FAME and triacetin yields from oils of rapeseed (*Brassica napus*) and oil palm (*Elaeis guineensis*) as treated in supercritical methyl acetate under various reaction temperatures at 20MPa and 42 molar ratio