



# New approach of catalyst-free biodiesel production from canola oil in supercritical tert-butyl methyl ether (MTBE)



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## HIGHLIGHTS

- Non-catalytic transesterification of canola oil in supercritical MTBE was proposed.
- MTBE could react with canola oil in supercritical MTBE to generate FAME and GTBE.
- No glycerol was obtained as a by-product under these reaction conditions.
- The FAME yield increased with temperature, but decreased above 400 °C due to thermal decomposition.
- A first-order kinetic model expressed the experimental yield well.

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## ABSTRACT

This paper reports a novel approach for biodiesel production from canola oil in supercritical tert-butyl methyl ether (MTBE) without the addition of a catalyst. Using this technique, canola oil was reacted with MTBE to generate fatty acid methyl esters (FAMEs) and glycerol tert-butyl ether. No glycerol was obtained as a by-product in this reaction. The effects of temperature, pressure, and reaction time on product yield were investigated in supercritical MTBE. A FAME yield of 0.94 was obtained in a short reaction time of 12 min at 400 °C, with a molar ratio of MTBE-to-oil of 40:1, and under a pressure of 10 MPa. The kinetics of the reaction was first order, and the activation energies and pre-exponential factors were calculated from the temperature dependence of the reaction rate constants.

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## 1. Introduction

Biodiesel is an environmentally benign fuel produced from oils such as canola oil via a transesterification reaction with alcohols such as methanol and ethanol. It has many advantages over conventional diesel fuel, such as good biodegradability and low toxicity [1–3], low particulate matter and CO exhaust emissions [4–7], high flash point (>130 °C) [8], low sulfur and aromatic content [5–9], and inherent lubricity that prolongs the life of diesel engines [10,11].

Currently, biodiesel is commonly produced using homogeneous catalysts such as potassium hydroxide and sodium hydroxide [12]. These catalysts are commonly used at an industrial scale owing to their relative abundance and low cost. However, these catalysts are very sensitive to the presence of free fatty acids (FFAs) and water,

which lead to lower biodiesel yield and unwanted side reactions [13,14].

Another problem with biodiesel production using homogeneous catalysts is the production of a by-product, glycerol, which needs to be separated and refined for further use. However, to obtain pure glycerol for commercial use, the catalyst must be neutralized by an acid or alkali, which forms a large quantity of salt and waste water [15]. The crude glycerol phase can also be purified by ion exchange on the strong acid resin Amberlite-252, and it has been suggested that the macroporous Amberlite can be useful for the removal of sodium ions from glycerol/water solutions with a high salt concentration [16]. Therefore, the purification of crude glycerol is not only complicated and costly, but the process also causes substantial environmental pollution issues.

To circumvent these problems, a reaction that does not produce glycerol as a by-product is required. In particular, alternatives to alcohols that react with oils to produce biodiesel, but which do not produce glycerol are required. Using this approach, Saka and

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Isayama [17] developed a new process using methyl acetate to produce fatty acid methyl esters (FAMES) (biodiesel) and triacin without producing glycerol. Furthermore, Ilham and Saka [18] studied dimethyl carbonate as a potential reactant for biodiesel production. The by-products of this process were glycerol carbonate and citramalic acid, which are considerably higher value products than glycerol. Moreover, Goembira et al. [19] recently investigated the biodiesel production using various carboxylate esters as reactants.

Among the various alkyl groups that can substitute the hydrogen atom in the hydroxyl group, the tert-butyl group is very interesting. In this case, the product is 1,2,3-tri-tert-butoxy-propane, or glycerol tert-butyl ether (GTBE) as shown in Fig. 1. This compound has been used as an octane enhancer as tert-butyl methyl ether (MTBE) has been banned. The reaction between canola oil and MTBE should enable a new process of biodiesel production that does not produce glycerol as a by-product but generates an octane enhancer as a by-product instead. As MTBE is plentifully available, it would be interesting to determine the applicability of this reaction to biodiesel production. However, this reaction has not been studied well, and so the purpose of this study is to elucidate the reaction characteristics of canola oil and MTBE.

## 2. Experimental

### 2.1. Experimental apparatus

The transesterification reaction was carried out in the supercritical MTBE using the flow reactor schematically illustrated in Fig. 2. The reactor was made of SS 316 steel tubing (i.d., 1 mm; o.d., 1.59 mm) with a length of 1.5 m. The feedstock and MTBE were fed into the reactor at the desired temperature and pressure. The obtained products were removed from the reactor after passing them through a filter and a back pressure regulator. In this study, the transesterification reaction was carried out in a temperature range of 200–500 °C and a pressure range of 6–15 MPa since the critical temperature and pressure of MTBE are 223.85 °C and 3.448 MPa, respectively [20]. The molar ratio of the oil to MTBE used in this study was fixed at 1:40 since some Refs. [21–24] reported that the optimum molar ratio of oil to reactant for biodiesel production under supercritical conditions is 1:40. The feedstock used in this study was canola oil.

### 2.2. Analytical methods

The liquid product was analyzed using gas chromatography (GC-390B; GL Sciences), which employed a column (MET-Biodiesel, w/int. 2 m guard, Sigma Aldrich, Supelco) and a flame ionization detector (FID). Argon was used as the carrier gas. The program began at a temperature of 50 °C, which was held constant for 1 min. Then, the temperature was ramped by 15 °C/min to 250 °C and was held constant for 10 min. Finally, after increasing the temperature to 380 °C at a rate of 15 °C/min, it was maintained constant for 5 min. The temperatures of the injector and detector

were both set at 380 °C. The standard and sample injection volumes were both 3 µL, and peak identification was achieved by comparing the retention times between the standard and sample compounds. Tricaprin (IUPAC name: 2,3-di(decanoxy)propan-2-yl decanoate) was used as an internal standard and the methyl ester content was calculated using a calibration curve on the basis of peak areas.

### 2.3. Reagents and materials

The feedstock of canola oil was obtained from Every mall, Higashi Hiroshima, Japan that was supplied by J-Oil Mills, Tokyo, Japan, and MTBE was purchased from Nacalai Tesque, Inc., Kyoto, Japan. Standard compounds of fatty acid methyl esters (methyl oleate, methyl linoleate, methyl linolenate, methyl palmitate, and methyl stearate) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triolein, diolein, and monoolein standards were purchased from Nacalai Tesque, Inc., Kyoto, Japan, Sigma-Aldrich, Co., Japan, and Tokyo Chemical Industry Co., Ltd., Japan, respectively. GTBE standard was purchased from Sigma-Aldrich, Co., Japan. To prepare GC standard solutions, all chemicals (tricaprin and n-hexane) used were of analytical grades.

## 3. Results and discussions

### 3.1. Comparisons of transesterification of oil in supercritical methanol, dimethyl carbonate, and MTBE

Saka and Kusdiana [25] reported that methanol can convert triglyceride (TG) in rapeseed oil into FAME by transesterification under supercritical conditions. It is well known that biodiesel production using methanol can proceed in three consecutive reversible reactions. Firstly, TGs are converted to diglycerides (DGs), followed by the conversion of DGs to monoglycerides (MGs). Then, the final step involves the conversion of MGs to glycerol. Each reaction step produces FAME. Consequently, three FAMES are produced in the transesterification process as shown in Fig. 3. Similarly, the reaction mechanism of biodiesel production in supercritical MTBE also comprises three consecutive reversible reactions. Firstly, the triglyceride reacts with MTBE to produce diglyceride mono tert-butyl ether (DGE), and then this intermediate moiety further reacts to generate monoglyceride di tert-butyl ether (MGE). Finally, MGE reacts with MTBE to yield FAME GTBE as by-products. This series of reaction is shown in Fig. 4.

Fig. 5 presents a comparison of the yield of FAME as produced under supercritical methanol (375 °C/15 MPa) [26], ethanol (350 °C/20 MPa) [22], methyl acetate (350 °C/20 MPa) [27], and MTBE (400 °C/10 MPa) in continuous mode reactor. The increase in FAME yield that occurred using the supercritical methanol route was higher than that for other supercritical conditions. MTBE can convert TG into FAME without the addition of catalyst. The FAME yield of the supercritical MTBE route is lower than those of the supercritical methanol route over the same reaction time despite

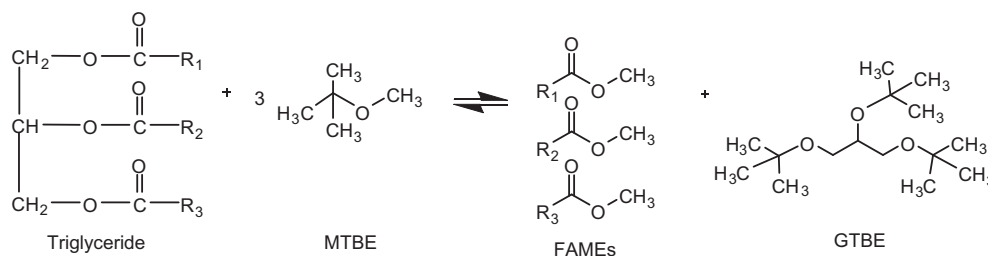


Fig. 1. Reaction between oil and MTBE.

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