Doctoral Thesis

BIODIESEL PRODUCTION USING SUPERCRITICAL TERT-BUTYL METHYL ETHER (MTBE) AND ALCOHOLS

(超臨界メチルターシャリーブチルエーテル(MTBE)とアルコールを用いたバイオディーゼル生産)

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ABSTRACT

Nowadays, researches on biodiesel have attracted a tremendous attention as a consequence of the world facing the challenges due to depletion of fossil fuel reserves, global warming issues, and environmental pollution problems. Various methods to synthesize biodiesel have been approached since biodiesel was firstly invented in 1893 by Rudolph Diesel. Among them, biodiesel production under supercritical condition is the most promising method since it enjoys a lot of advantages such as no catalyst requirement and short reaction time. In addition, this technology is promising because it can be applied for a wide variety of feedstock, no pre-treatment requirement, and easier separation and purification of products.

Since biodiesel production increases rapidly in recent years, the overproduction of the main by-product glycerol, obtaining approximately 10% is unavoidable, leading to the significant decrease of price in the market. To circumvent this problem, biodiesel production without generating glycerol as well as without producing waste water is needed. Thus, a new approach of catalyst-free biodiesel production under supercritical MTBE conditions was proposed in this study. Experimental investigations were carried out in a temperature range of 200–500 °C under a pressure of 10 MPa and a fixed oil-to-MTBE molar ratio of 1:40 over 3–15 min. MTBE could react with triglyceride under supercritical conditions, generating fatty acid methyl ester (FAME) and glycerol tert-butyl ether (GTBE). No glycerol was observed under these reaction conditions. The FAME yield increased with temperature from 200 to 400 °C, but it decreased above 400 °C due to thermal decomposition. The highest biodiesel yield (0.94) was obtained at 400 °C in the short reaction time of 12 min under a pressure of 10 MPa and an oil-to-MTBE molar ratio of 1:40.

Considering that supercritical conditions require elevated temperatures and high pressures, large amounts of heat must be added. To recover the heat efficiently, a novel spiral reactor was proposed in this study. This spiral reactor comprised a parallel-tube heat exchanger and high-temperature transesterification reactor. The parallel tube heat exchanger, where heat is recovered, is in turn composed of two tubes placed side-by-side in a spiral formation. Meanwhile, the high-temperature transesterification reactor, where the reaction mainly takes place, consists of insulated tubing. In this study, ethanol was

firstly selected as a simple reactant. Experiments were performed at reaction temperatures of 270–400 °C, a fixed pressure of 20 MPa, oil-to-ethanol molar ratio of 1:40, and reaction times of 3–30 min. The results revealed that the spiral reactor employed in this study was not only as effective as conventional reactor in terms of transesterification reactor but also superior in terms of heat recovery. The quantitative analysis of the heat recovery efficiency was 85.5%. Thus, it was concluded that spiral reactor is a good candidate of reactor for biodiesel production under supercritical conditions.

Owing to the successful recovery of heat for biodiesel production using spiral reactor and considering the good merits of biodiesel production conducted under supercritical MTBE conditions, the study of effectiveness of spiral reactor for biodiesel production in supercritical MTBE is interesting. Using a fixed oil-to-MTBE molar ratio of 1:40 and a pressure of 10 MPa, experiments were performed at 250–400 °C and over 6–30 min. It was observed that the spiral reactor performed well for biodiesel production in supercritical MTBE, affording a higher FAME yield compared to the conventional flow reactor for the same residence time. This was partly because of the portion of the reaction that takes place in the heat exchanger. In addition, the spiral reactor employed here was effective for biodiesel production using MTBE under supercritical conditions owing to the successful recovery of heat. The comparison of FAME production characteristics of the spiral reactor in supercritical MTBE was also elucidated with previous reports of biodiesel production using supercritical methanol, ethanol, methyl acetate, and dimethyl carbonate. Biodiesel yield in supercritical MTBE was observed the same with the supercritical methanol and dimethyl carbonate at a residence time of 15 min, obtaining 98.3 wt% of FAME. Interestingly, FAME yields for the supercritical method are higher than those for supercritical methyl acetate route at the same reaction time owing to the solubility effect. Note that the solubility of MTBE with oil is much better than that of methyl acetate with oil at room temperature and room pressure.

Since supercritical MTBE method was conducted at high pressure, the investigation of pressure effect on product composition as well as reaction kinetics is crucial. Transesterification reactions were carried out at various pressures (10–30 MPa), temperatures (300–400 °C), reaction time (3–30 min), and a fixed oil-to-MTBE molar ratio of 1:40 using the spiral reactor. The effect of pressure on final product composition as well as reaction rate was negligible for the conditions employed here. This negligible effect could be attributed to the almost constant density of MTBE.

Finally, reaction behavior of biodiesel production under supercritical methanol, ethanol, and MTBE conditions was compared in this study. A series of experiments were carried out at reaction temperatures of 270–400 °C, reaction times of 3–30 min, a pressure of 20 MPa, and oil-to-reactant molar ratio of 1:40. The results showed that biodiesel yield increased with reaction time and temperature for all cases. Under the same reaction conditions, supercritical methanol method gave the highest yields of biodiesel. At 270 °C, biodiesel yield in supercritical MTBE was higher than that in supercritical ethanol owing to the solubility effect, whereas above 270 °C, biodiesel yield in supercritical ethanol was higher than that in supercritical MTBE due to the bulkier structure of MTBE. At 350 °C and 20 MPa, a complete conversion to biodiesel was achieved after 10, 30, and 30 min for biodiesel production in supercritical methanol, ethanol, and MTBE, respectively.

THESIS STRUCTURE

This thesis comprises ten chapters that are briefly described below. The thesis structure showing relationship among chapters is presented in **Fig. 0.1.**

Chapter 1: Introduction This chapter provides the milestones of biodiesel production process. The fundamental research on biodiesel including the selection of feedstock as well as biodiesel production process is also briefly explained with the aim to give information in this particular field of study. In addition, biodiesel production under supercritical conditions was also discussed in this chapter for better understanding of this process.

Chapter 2: Literature review This chapter is mainly divided into three sections. Firstly, the existing biodiesel production technology such as homogeneous acid and alkali-catalyzed transesterification, heterogeneous acid and alkali-catalyzed transesterification, enzymatic-catalyzed transesterification, non-catalytic supercritical conditions, and microwave as well as ultrasound-assisted transesterification are thoroughly discussed. This information is crucial in order to know the advantages and disadvantages of each method. Biodiesel production under various supercritical reactants such as methanol, ethanol, methyl acetate, and dimethyl carbonate is further reviewed to find out the significance and novelty of biodiesel production under supercritical conditions. Finally, main factors affecting biodiesel production under supercritical conditions including temperature, reaction time, pressure, and oil-to-reactant molar ratio are then explained in more details. This information provides the fundamental concept needed to select parameters used in this study.

Chapter 3: Aim and Objectives This chapter firstly describes the research motivation behind this study and what strategy that should be carried out from that motivation. The aim and objectives of the present work are then indicated.

Chapter 4: Experimental Method Experimental setup and procedures used in this study are addressed in this chapter since this study is based on the experimental work. In addition, reagents and materials, apparatus, experimental procedure, analyses of products are described in detail to allow this work to be reproduced.

Chapter 5: New approach of biodiesel production in supercritical MTBE This chapter figures out the new approach for biodiesel production under supercritical conditions of MTBE. The effect of temperature on biodiesel yield conducted in temperature range of 200–500 °C under a pressure of 10 MPa and oil-to-MTBE molar ratio of 1:40 over 3–15 min was firstly investigated. In addition, reaction time effect on biodiesel yield conducted under supercritical MTBE conditions was further examined. Since this is a new approach to produce biodiesel production, a comparative study between this study and the previous reports was also conducted. Finally, reaction kinetics as well as reaction mechanism of biodiesel production under supercritical MTBE conditions were elucidated.

Chapter 6: Biodiesel production in supercritical ethanol using a novel spiral reactor This chapter highlights the new finding of spiral reactor for biodiesel production in supercritical ethanol. To examine the fundamental characteristics of spiral reactor, temperature profile is firstly presented. The effects of temperature and reaction time on biodiesel yield are also discovered in order to know the features of this spiral reactor in more details. To achieve this goal, transesterification of oil under supercritical ethanol conditions were carried out under a pressure of 20 MPa and a fixed oil-to-ethanol molar ratio by varying temperatures and reaction times of 270–400 °C and 3–30 min, respectively. Under these reaction conditions, reaction kinetics of canola oil conversion to biodiesel is also deduced. In the last section, the difference characteristics between conventional flow and spiral reactors in terms of energy efficiency and product yields are compared.

Chapter 7: Effectiveness of spiral reactor for biodiesel production in supercritical MTBE The effectiveness of the spiral reactor on supercritical MTBE biodiesel production by elucidating the effects of temperature and reaction time on FAME yields is described in this chapter. To examine the characteristics of spiral reactor for biodiesel production in supercritical MTBE, the effect of temperature on biodiesel yield is firstly presented. The effect of residence time on triglyceride consumption as well as FAME and GTBE yields is further described. A series of experiments were performed under a pressure of 10 MPa and a temperature range of 250–400 °C and over 6–30 min. Biodiesel yields obtained using spiral reactor is also compared with those using conventional flow reactor reported in Chapter 5. Heat recovery characteristics and thermal efficiency of heat exchanger are then reported. The comparisons of FAME production characteristics in supercritical MTBE using spiral reactor with the previous studies are finally explained.

Chapter 8: Effect of pressure on biodiesel production in supercritical MTBE The effect of pressure on biodiesel yield in supercritical MTBE was conducted by varying pressures from 10 MPa to 30 MPa at a fixed oil-to-MTBE molar ratio of 1:40 over 3–30 min. The effects of pressure on final product composition as well as reaction kinetics are presented in this chapter.

Chapter 9: A comparative study of biodiesel production in supercritical methanol, ethanol, and MTBE This chapter explores the comparison of reaction behavior for biodiesel production in supercritical methanol, ethanol, and MTBE. The comparison of their reaction behavior is elucidated from the effect of temperature, reaction time, and reaction kinetics. To examine the difference of reaction behavior among supercritical methanol, ethanol, and MBTE, transesterification reactions were performed under the same reaction conditions, i.e., temperature range of 270–400 °C, a pressure of 20 MPa, and reaction time of 3–30

Chapter 10: Conclusion and recommendations for future work This chapter finally closed this thesis by concluding remarks and recommendations for future work in this field of study.

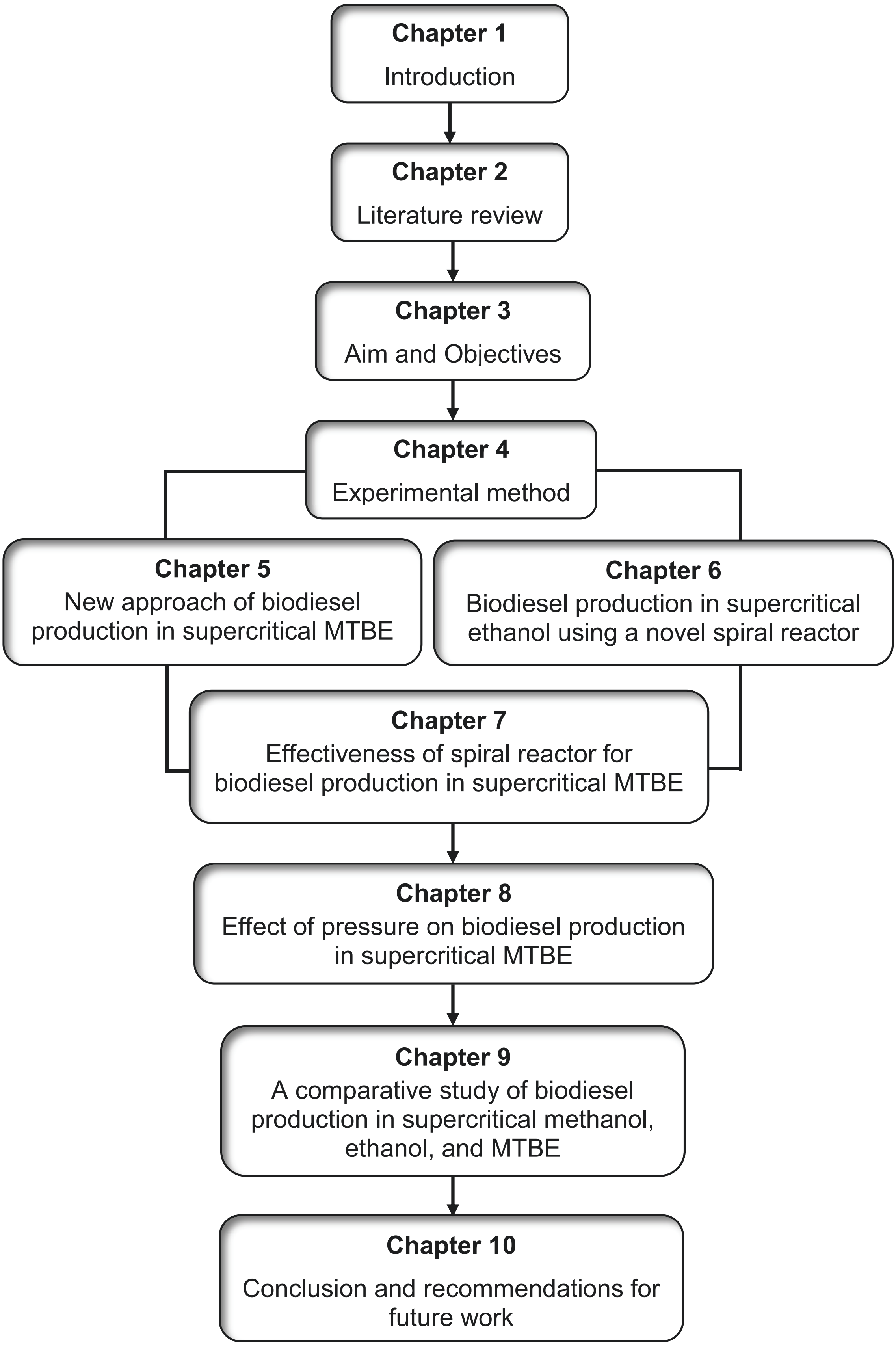

Fig. 0.1. Thesis structure showing relationship among chapters.

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GLOSSARY

A	Pre-exponential factor
[cal]	Calculated yield estimated by set of kinetic parameters χ [-]
$C_{p,BDF}$	Specific heat of biodiesel fuel (1.80 kJ/kg-°C)
$C_{p,ethanol}$	Specific heat of ethanol (2.46 kJ/kg-°C)
$C_{p,glycerol}$	Specific heat of glycerol (2.41 kJ/kg-°C)
$C_{p,oil}$	Specific heat of canola oil (1.913 kJ/kg-°C)
[DGE]	Diglyceride mono *tert*-butyl ether yield [-]
[exp]	Experimental yield [-]
Ea	Activation energy (kJ mol^{-1})
E_b	Energy output biodiesel (J)
E_i	Total primary energy inputs (J)
E_o	Total energy outputs (J)
[FAME]	Fatty acid methyl ester yield [-]
[GTBE]	*tert*-butyl glycerol ether yield [-]
k_{i}	reaction rate constants
m	Mass flow rate (g/min)
MPa	Megapascal
[MGE]	Monoglyceride di *tert*-butyl ether yield [-]
[MTBE]	*tert*-butyl methyl ether yield [-]
Pc	Critical pressure (MPa)
Q_{eff}	Heat recovery efficiency

$Q_{reaction}$	Energy required to achieve reaction temperature (J)
$Q_{recovery}$	Energy from the recovered heat (J)
R	Ideal gas constant (8.315 J/K.mol)
r^2	Coefficient of determination (dimensionless)
T	Temperature [K]
t	residence time [min]
Tc	Critical temperature (K)
$T_{\infty 2,o}$	Temperature of the cold flow at the exit of heat exchanger (K)
$T_{\infty 2,i}$	Temperature of the cold flow at the inlet of heat exchanger (K)
$T_{\infty 1,o}$	Temperature of the hot flow at the exit of heat exchanger (K)
$T_{\infty 1,i}$	Temperature of the hot flow at the inlet of heat exchanger (K)
[TG]	triglyceride yield [-]
v	volumetric flow rate (m^3/s)
V	Reactor volume (cm^3)
Wt	Energy from pump (J)
η_{th}	Thermal efficiency of heat exchanger

Greek Letters

ρ	Density (kg/m^3)
ρ_o	Density of oil at room temperature (0.9 kg/m^3)
ϑ	Viscosity of oil at 37.8 ºC (44.34 cSt)
ΔP	Pressure increase (Pa)

Abbreviation

ASTM	American Society for Testing and Materials
BDF	Biodiesel fuel
CPO	Crude palm oil
DDRBO	Dewaxed degummed rice bran oil
DG	Diglyceride
DGE	Diglyceride mono *tert*-butyl ether
DMC	Dimethyl carbonate
FA	Fatty acid
FAAE	Fatty acid alkyl ester
FAEE	Fatty acid ethyl ester
FAGC	Fatty acid glycerol carbonate
FAME	Fatty acid methyl ester
FAO	Food and Agriculture Organization
FFA	Free fatty acid
FFB	Fresh fruit bunches
GC	Gas chromatography
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
GTBE	Glycerol *tert*-butyl ether
ID	Inner diameter
IUPAC	International Union of Pure and Applied Chemistry
LHV	Lower heating value
LSE	Least squares of error
MG	Monoglyceride
MGE	Monoglyceride di *tert*-butyl ether

MPOC	Malaysian palm oil council
MTBE	*tert*-butyl methyl ether
OD	Outer diameter
RBDPO	Refined bleached deodorized palm oil
RSM	Response surface methodology
SBRC	Surfactant and Bioenergy Research Center
SCE	Supercritical ethanol
SCM	Supercritical methanol
SCMTBE	Supercritical *tert*-butyl methyl ether
SS316	Stainless steel 316
TCI	Tokyo Chemical Industry
TG	Triglyceride
THF	Tetrahydrofuran
USDA	United States Department of Agriculture
WVO	Waste vegetable oil

LIST OF PUBLICATIONS

(1) **Farobie**, **O**.; Yanagida, T.; Matsumura, Y. New approach of catalyst-free biodiesel production from canola oil in supercritical *tert*-butyl methyl ether (MTBE). *Fuel*, **2014**, 135, 172–181.

(2) **Farobie**, **O**.; Matsumura, Y. Effectiveness of spiral reactor for biodiesel production using supercritical tert-butyl methyl ether (MTBE). *J. Jpn. Pet. Inst.,* **2015** (accepted, publication date: March, 2015, Vol. 58 No. 2).

(3) **Farobie**, **O**.; Matsumura, Y. Biodiesel production in supercritical methanol using a novel spiral reactor. *Procedia Environ. Sci.* **2015** (accepted).

(4) **Farobie**, **O**.; Hasanah, N.; Matsumura, Y. Artificial neural network modeling to predict biodiesel production in supercritical methanol and ethanol conducted using spiral reactor. *Procedia Environ. Sci.* **2015** (accepted).

(5) **Farobie**, **O**.; Sasanami, K.; Matsumura, Y. A novel spiral reactor for biodiesel production in supercritical ethanol. *Appl. Energy* (submitted).

(6) **Farobie**, **O**.; Matsumura, Y. Effect of pressure on biodiesel production in supercritical tert-butyl methyl ether (MTBE). *J. Jpn. Inst. Energy* (submitted).

CHAPTER 1

Introduction

1.1. Introduction

In 1893, Rudolph Diesel firstly operated his new engines using vegetable oil (peanut oil) where petroleum was not available at that time. His first experiment has inspired many researchers to study further about biodiesel. Since then, biodiesel production is developed until now. However, the usage of vegetable oil directly for engine fuels has a problem due to high viscosity of this oil. Therefore, it is needed to reduce the viscosity of vegetable oil.

There are several techniques to reduce the viscosity of vegetable oil such as dilution (Schwab et al., 1987), microemulsion (Ziejewski et al., 1984), pyrolysis (Maher and Bressler, 2007), and transesterification (Freedman et al., 1984; Ma et al., 1998.). In dilution process, vegetable oil is mixed directly or diluted with diesel fuel to improve the viscosity. This method is able to overcome the problems regarding high viscosity of vegetable oil in compression ignition engines. It was reported in 1980 that Caterpillar Brazil used a 10% mixture of vegetable oil to maintain total power without any adjustment to the engine. A blend of 20% vegetable oil and 80% diesel fuel was also successfully used (Singh, SP and Singh, D, 2007). Another approach to reduce the viscosity of the vegetable oils is by microemulsion in which butanol, hexanol, and octanol are usually used as a solvent (Jain and Sharma, 2010). Pyrolysis has also been used to reduce the viscosity of oil by employing elevated temperature with the addition of the catalyst without air or oxygen. Schwab et al. (1987) found that even though the viscosity of the pyrolysed soybean oil (10.2 cSt at 37.8 ºC) was higher than that of the ASTM specified range for diesel fuel, it is acceptable as still well below the viscosity of soybean oil.

However, the above-mentioned methods still faced the problems due to carbon deposition and contamination (Sharin et al., 2007). Transesterification has been well known to be the best techniques due to physical and chemical similarity with conventional diesel fuel and forming little or no deposits once used in diesel engines. In this transesterification process, three consecutive reversible reaction steps occur. Triglyceride (TG) is firstly converted to diglyceride (DG) and followed by the conversion of diglyceride to monoglyceride (MG). The next step involves the conversion of monoglyceride to glycerol. Each reaction step produces a fatty acid alkyl ester. Consequently, a total of three fatty acid alkyl esters are obtained in the transesterification process (Ma and Hanna, 1999). The complete chemical reaction of biodiesel production is shown in **Fig. 1.1**.

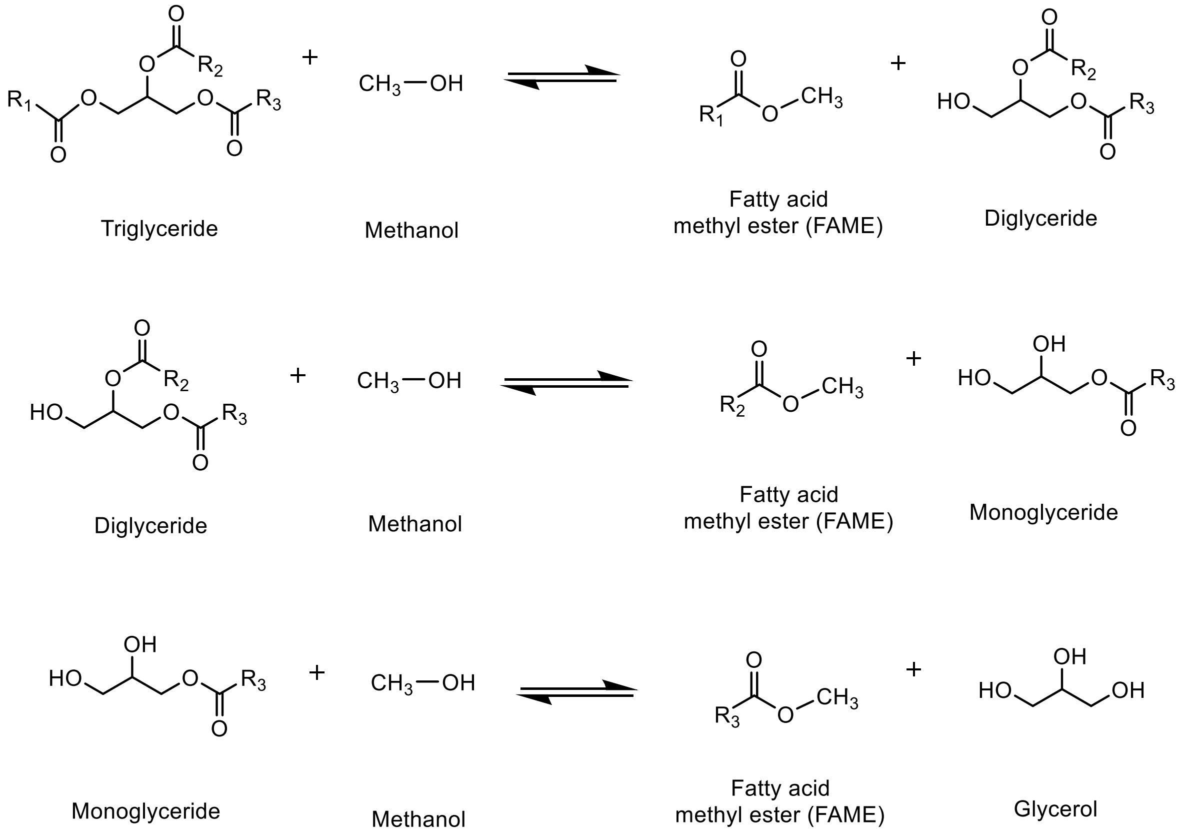


Fig. 1.1. Chemical reaction of biodiesel production using methanol.

Biodiesel is a liquid biofuel generated by chemical processes, well known as transesterification from vegetable oils such as canola oil with an alcohol that can be used in diesel engines. Comparing with conventional diesel fuel, biodiesel has many advantages such as biodegradability and low toxicity (Zhang et al., 1998; Pasqualino et al., 2006; Sendzikiene et al., 2007), low particulate matter and CO exhaust emissions (McCormick et al., 2001; Knothe et al., 2006; Tat et al., 2007; Krahl et al., 2009),high flash point (> 130°C) (Guo et al., 2009), low sulfur and aromatic content (Knothe et al., 2006 and Ma et al., 1999), and inherent lubricity that extends the life of diesel engines (Sharp et al., 1996; Goodrum et al., 2004; Munoz et al., 2011). Nevertheless, biodiesel also has some disadvantages, namely slightly higher nitrous oxide (NOx) emissions and freezing point than diesel fuel. It must be noted that these drawbacks are significantly reduced when biodiesel is used in blends with diesel fuel (Knothe et al., 2005).

This chapter focused on the fundamentals of biodiesel production (biodiesel feedstock and biodiesel production process). In addition, the topic regarding biodiesel production under supercritical conditions was also discussed in this chapter.

1.2. Biodiesel production

1.2.1. Introduction

Up to now, many countries in the world have been looking for renewable energy due to some environmental reasons such as air pollution, global warming, and exhaustible fossil fuel. Biodiesel, which is ordinarily produced by transesterification of vegetable oils, animal fats, waste oils or microalgae with alcohol, has been considered as one of the most promising renewable energy to substitute conventional diesel fuel (Bezergianni and Dimitriadis, 2013). Biodiesel is commonly produced from a transesterification reaction of triglyceride with alcohol, with or without catalyst, to form fatty acid alkyl esters.

In this process, triglyceride from vegetable oil or animal fat reacts with alcohol (usually methanol or ethanol) in the presence of a catalyst (acid or base) to generate fatty acid alkyl esters. **Fig. 1.2** depicts the overall chemical reaction to produce biodiesel.

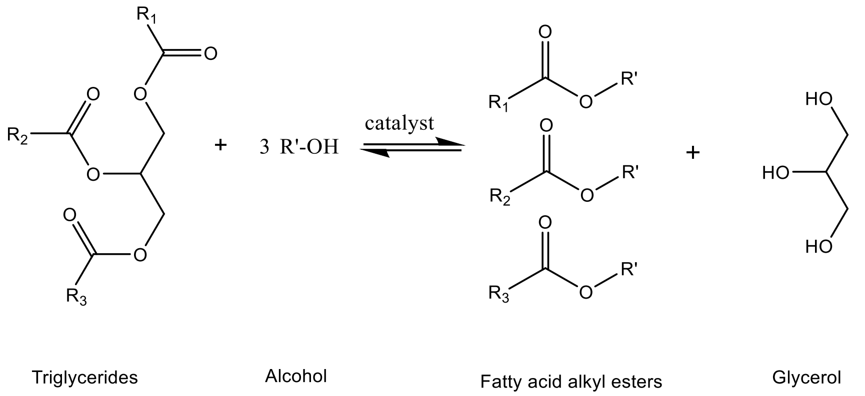


Fig. 1.2. Overall chemical reaction to produce biodiesel.

Biodiesel in Indonesia is commonly produced from oil palm due to the abundance of this feedstock. Oil palm tree can produce approximately 12 to 20 fresh fruit bunches (FFB) per year, and this FFB contains more than 1,000 fruitlets. After pressing and other physical treatments, crude palm oil (CPO) is obtained. Crude palm oil then reacts with straight alcohol (methanol or ethanol) through transesterification reaction to generate biodiesel. This biodiesel can be utilized for transportation after blending with diesel fuel. The vehicles release carbon dioxide gas (CO_2), and this gas is used further for the photosynthesis process as shown in **Fig. 1.3**. There is no CO_2 release into atmosphere in this process, so it is called as neutral carbon. This is one of the superiority of biodiesel over conventional diesel fuel.

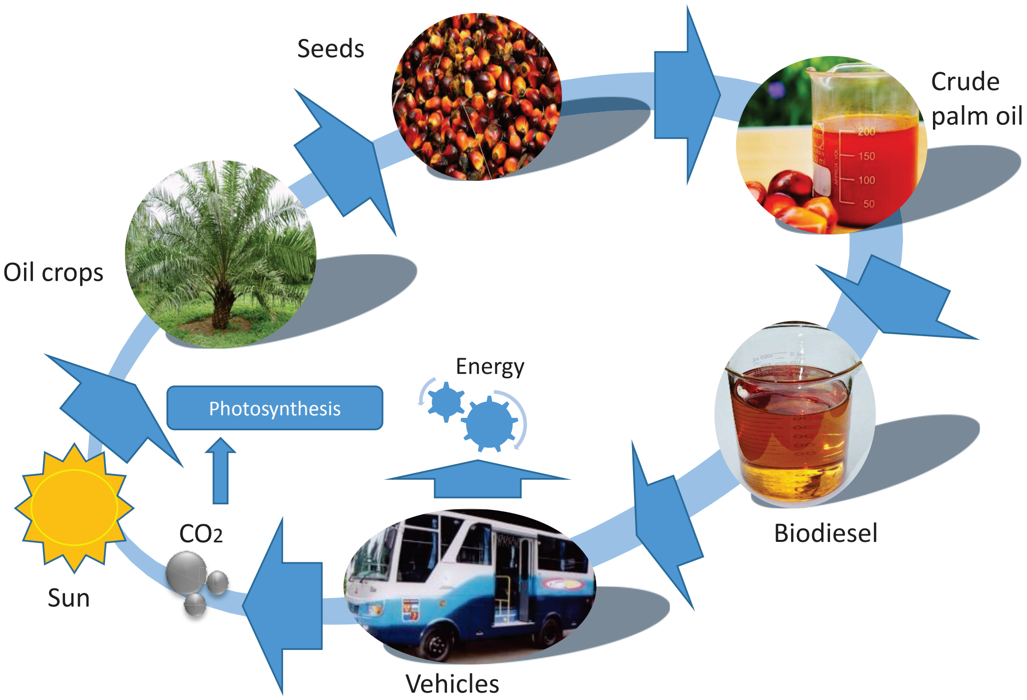


Fig. 1.3. The illustration of biodiesel cycle.

1.2.2. Biodiesel feedstock

Biodiesel can be obtained from a great variety of feedstock. According to Lim and Teng (2010), the cost of feedstocks accounts for about 75% of the total of biodiesel production (**Fig. 1.4**). Therefore, selection of an appropriate feedstock for biodiesel production is important to ensure a low biodiesel production cost. The primary potential feedstocks for the biodiesel production from various countries in the world are provided in **Table 1.1**.

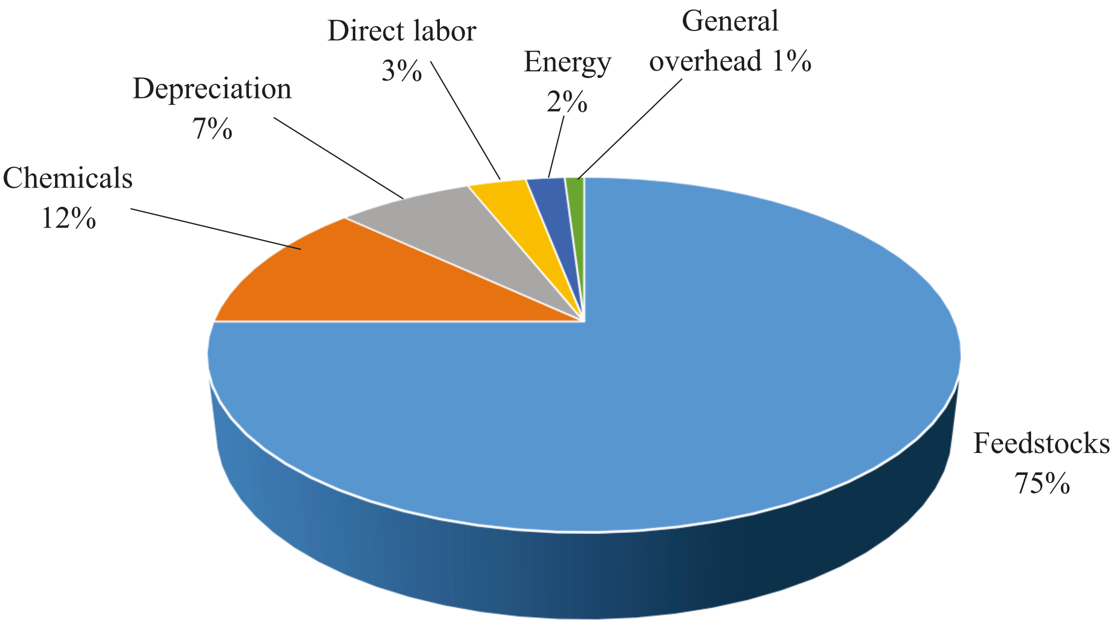


Fig. 1.4. General biodiesel production cost (Lim and Teng, 2010).

Table 1.1. The primary potential feedstock of biodiesel in different countries

Country	Feedstock	Reference
Argentina	Soybean	Sharma and Singh (2009); Jayed et al. (2011)
Belgium	Rapeseed, animal fat	Sharma and Singh (2009); Bomb et al. (2007)
Brazil	Soybean, palm, sunflower, castor, cotton	Sharma and Singh (2009); Jayed et al. (2011); Atabani et al. (2012)
Canada	Rapeseed, animal fat, soybean, yellow grease, tallow, mustard	Atabani et al. (2012)
China	Jatropha, waste cooking oil, rapeseed	Atabani et al. (2012)
European Union	Rapeseed, sunflower	Kondilia and Kaldellis (2007)
France	Rapeseed, sunflower	Atabani et al. (2012)
Germany	Rapeseed, animal fat	Sharma and Singh (2009); Bomb et al. (2007); Atabani et al. (2012)
Greece	Rapeseed, sunflower, cotton	Panoutsou et al. (2008), Atabani et al. (2012)
Hungary	Rapeseed, sunflower	Kondilia and Kaldellis (2007)
India	Jatropha, karanja, soybean, rapeseed, peanut	Sharma and Singh (2009); Atabani et al. (2012)
Indonesia	Palm oil, jatropha, coconut	Sharma and Singh (2009); Jayed et al. (2011); Atabani et al. (2012)
Ireland	Frying oil, animal fat	Atabani et al. (2012)
Italy	Rapeseed, sunflower	Atabani et al. (2012)
Japan	Waste cooking oil	Atabani et al. (2012)
Latvia	Rapeseed, sunflower	Kondilia and Kaldellis (2007)
Lithuania	Rapeseed, sunflower	Kondilia and Kaldellis (2007)
Malaysia	Palm oil, jatropa	Sharma and Singh (2009); Jayed et al. (2011)
Mexico	Animal fat, waste cooking oil	Atabani et al. (2012)
Netherlands	Soybean	Sharma and Singh (2009); Jayed et al. (2011)
New Zealand	Waste cooking oil, tallow	Atabani et al. (2012)
Philippines	Coconut, jatropha	Atabani et al. (2012)
Poland	Rapeseed, sunflower	Kondilia and Kaldellis (2007)
Singapore	Palm oil	Atabani et al. (2012)
Spain	Rapeseed	Sharma and Singh (2009); Grau et al. (2010)
Sweden	Rapeseed	Atabani et al. (2012)
Taiwan	WVO, sunflower, soybean	Huang and Wu (2008)
Thailand	Palm oil, coconut, waste cooking oil, animal fat	Phalakornkule et al. (2009)
UK	WVO, rapeseed	Bomb et al. (2007); Atabani et al. (2012)
USA	Soybean, waste oil, peanut	Sharma and Singh (2009); Jayed et al. (2011); Atabani et al. (2012)

The biodiesel feedstock generally can be divided into four types, namely edible oil, non-edible oil, waste oil, and algae (**Fig. 1.5**). Some researchers have investigated biodiesel production from edible oil such as oil palm (Kalam and Masjuki, 2002; Ooi et al., 2004; Sumathi et al., 2008; Canakci et al., 2009; Kansedo et al., 2009), coconut

(Kumar et al., 2010; Nakpong and Wootthikanokkhan, 2010; Jiang and Tan, 2012; Riberio et al., 2012; Tupufia et al., 2013), sunflower (Antolín et al., 2002; Georgogianni et al., 2008; Pereyra-Irujo et al., 2009; Porte et al., 2010; Ghanei et al., 2011), canola (Dizge and Keskinler, 2008; Ilgen, 2011; Jang et al., 2012; Liang et al., 2013; Boz et al., 2013), peanut (Kaya et al., 2009; Nguyen et al., 2010; Moser, 2012), soybean (Liu et al., 2008; Yin et al., 2008; Georgogianni et al., 2009; Yu et al., 2010; Silva et al., 2010;Guo et al., 2012), rapeseed (Georgogianni et al., 2009; Koda et al., 2010; Abo El-Enin et al., 2013; Wang et al., 2013; Meng et al., 2013), and rice bran (Zullaikah et al., 2005; Sinha et al., 2007, Lin et al., 2009; Gunawan et al., 2011; Zhang et al., 2013; El Boulifi et al., 2013).

The production of biodiesel from non-edible oil has also been investigated over the past few years. Some of these non-edible oil crops include *Jatropha curcas* (Tiwari et al., 2007; Ganapathy et al., 2009; Deng et al., 2011; Mofijur et al., 2012; Kartika et al., 2013), castor (Ramezani et al., 2010; Sousa et al., 2010; López et al., 2011; Dias et al., 2012; Dias et al., 2013), linseed (Demirbas, 2009; Dixit et al., 2012; Kumar et al., 2013), tobacco (*Nicotiana tabacum* L.) (Usta, 2005; Veljkovic et al., 2006), karanja (*Pongamia pinnata*) (Naik et al., 2008; Agarwal and Rajamanoharan, 2009; Das et al., 2009; Kamath et al., 2011; Thiruvengadaravi et al., 2012), mahua (*Madhuca indica*) (Ghadge and Raheman, 2005; Puhan et al., 2005; Raheman and Ghadge, 2007), rubber (*Hevea brasiliensis*) (Ikwuagwu et al., 2000; Ramadhas et al., 2005; Morshed et al., 2011; Widayat et al., 2013; Gimbun et al., 2013), neem (*Azadirachta indica*) (Rao et al., 2008; Karmakar et al., 2012; Dhar et al., 2012; Ali et al., 2013). Due to the high price of vegetable oil, cheaper waste oil such as used cooking oil (Zhang et al., 2003; Phan and Phan, 2008; Demirbas, 2009; Chen et al., 2009; Hingu et al., 2009; Patil et al., 2010; Lam et al., 2010; Gude and Grant, 2013) and animal fats (Tashtoushet al., 2004;

Canakci, 2007; Gürü et al., 2009; Encinar et al., 2011; Ito et al., 2012; Dias et al., 2012; Awad et al., 2013; Cunha et al., 2013) from households and restaurants are attracting attention as possible feedstocks. Another promising feedstock used to produce biodiesel is microalgae (Sánchez et al., 2011; Amaro et al., 2011; Halim et al., 2011; Zhang et al., 2012; Rawat et al., 2013; Wang et al., 2013; Lam and Lee, 2013; Zhang et al., 2013; Dong et al., 2013). A microalgae, the third generation of biodiesel feedstock became one of the most promising feedstocks for biodiesel production owing to its higher productivity and grow faster than conventional crops (Minowa T et al., 1995).

The choice of biodiesel feedstock is determined by characteristic of oil. It has to be considered that different feedstock types have different chemical properties. The chemical properties of oil are mainly characterized by saturation and the fatty acid content. The fatty acid compositions of some vegetable oils are summarized in **Table 1.2**. Meanwhile, a list of fatty acid mostly found in biodiesel is shown in **Table 1.3**.

Biodiesel derived from highly saturated oils such as palm oil and coconut oil has high cetane number and good oxidative stability. However, it is not suitable to be applied in countries that have a winter season since it performs poorly at low temperatures. Thus, feedstock with a high degree of saturation is more appropriate in warmer climates. Selection of this feedstock also mainly depends on its availability (regional production and productivity) and cost. For instance, USA and European countries have a surplus amount to export edible oils such as soybean and rapeseed, so these feedstocks are used to produce biodiesel in USA and Europe, respectively (Sharma and Singh, 2009). Meanwhile, some South East Asian countries such as Malaysia, Indonesia, and Thailand are utilizing edible oils such as palm oil and coconut oil for biodiesel production. However, the main feedstocks used in India is a non-edible oil, *Jatropha curcas* oil (Sohpal et al., 2011).

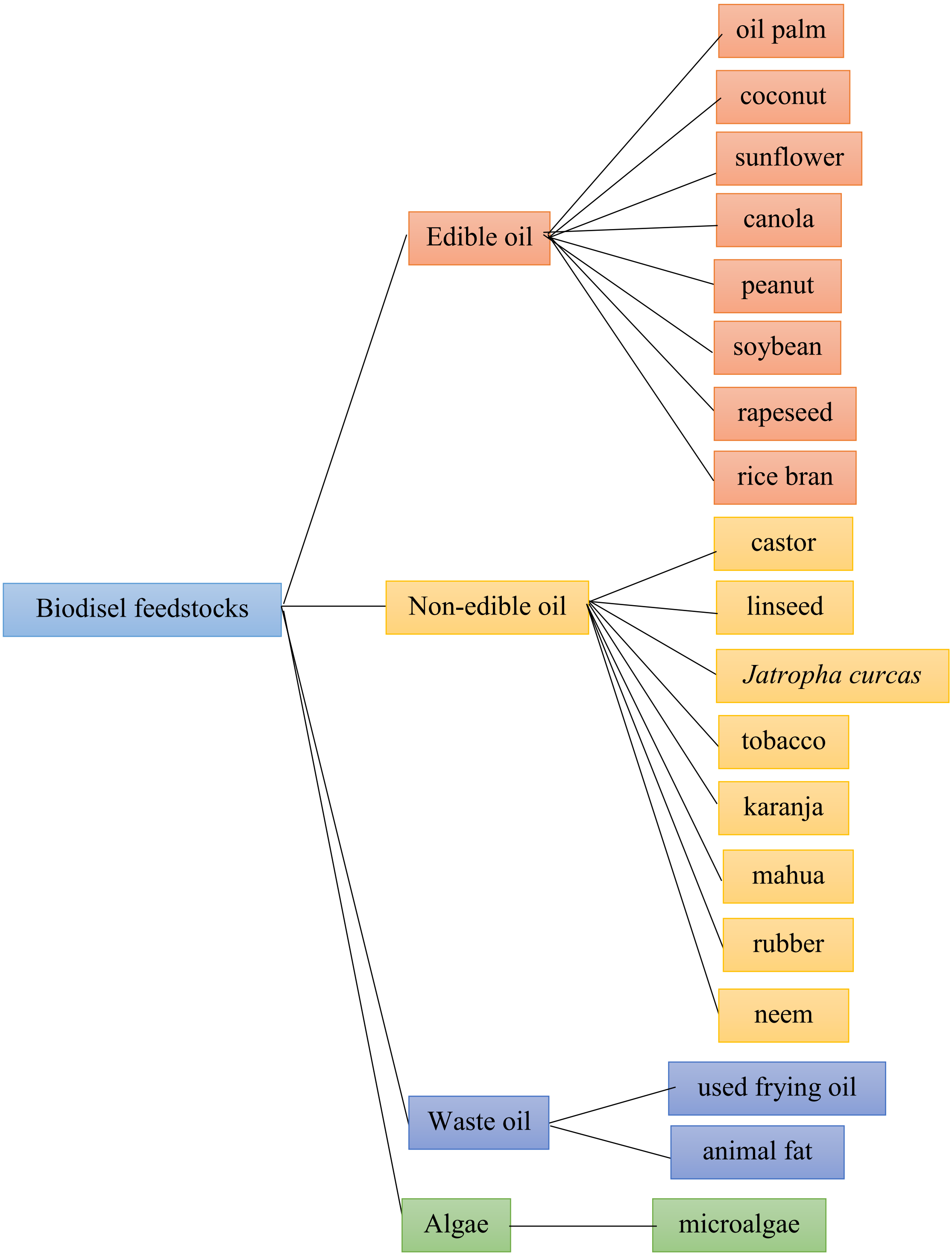


Fig. 1.5. Types of biodiesel feedstocks.

Table 1.2. Typical fatty acid (FA) groups found in biodiesel (shaded compounds are most common) (Hoekman et al., 2012)

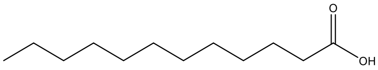
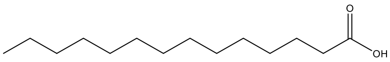
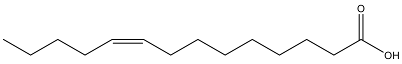
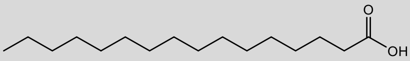
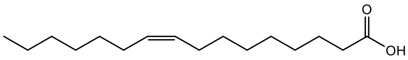
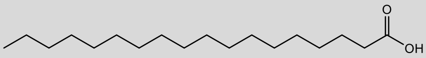
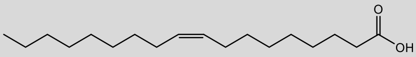
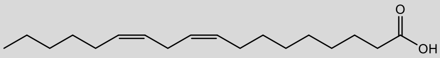
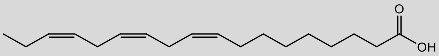
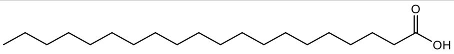
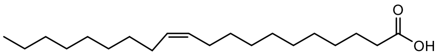
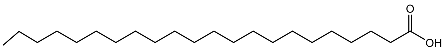
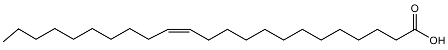
Common name	Formal name	Abbreviation	Molecular formula	Molecular structure
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$	
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$	
Myristoleic acid	*cis*-9-Tetradecanoic acid	14:1	$C_{14}H_{26}O_2$	
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$	
Palmitoleic acid	*cis*-9-Hexadecanoic acid	16:1	$C_{16}H_{30}O_2$	
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$	
Oleic acid	*cis*-9-Octadecanoic acid	18:1	$C_{18}H_{34}O_2$	
Linoleic acid	*cis*-9,12-Octadecadienoic acid	18:2	$C_{18}H_{32}O_2$	
Linolenic acid	*cis*-9,12,15-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$	
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$	
Gondoic acid	*cis*-11-Eicosanoic acid	20:1	$C_{20}H_{38}O_2$	
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$	
Erucic acid	*cis*-13-Docosanoic acid	22:1	$C_{20}H_{42}O_2$	

Table 1.3. Fatty acid compositions of some vegetable oils.

Vegetable oil	Fatty acid composition, % by weight											
	C 14:0	C 16:0	C 18:0	C 20:0	C 22:0	C 24:0	C 16:1	C 18:1	C 20:1	C 22:1	C 18:2	C 18:3
Canola	0.10	3.50	1.50	0.60	0.30	0.00	0.20	60.10	1.40	0.20	20.10	9.60
Corn	0.00	11.67	1.85	0.24	0.00	0.00	0.00	25.16	0.00	0.00	60.60	0.48
Cottonseed	0.00	28.33	0.89	0.00	0.00	0.00	0.00	13.27	0.00	0.00	57.51	0.00
Crude palm oil	1.10	43.70	4.50	0.00	0.00	0.00	0.20	40.20	0.00	0.00	9.80	0.50
Jatropha curcas	0.00	14.20	6.90	0.00	0.00	0.00	1.40	43.10	0.00	0.00	34.40	0.00
Peanut	0.00	11.38	2.39	1.32	2.52	1.23	0.00	48.28	0.00	0.00	31.95	0.93
Rapeseed	0.00	3.49	0.85	0.00	0.00	0.00	0.00	64.40	0.00	0.00	22.30	8.23
Soybean	0.00	11.75	3.15	0.00	0.00	0.00	0.00	23.26	0.00	0.00	55.53	6.31
Sunflower	0.00	6.08	3.26	0.00	0.00	0.00	0.00	16.93	0.00	0.00	73.73	0.00

Source: Ma and Hanna (1999); Tan et al., (2009); Koh and Ghazi (2011)

Some potential feedstocks for biodiesel production in Indonesia are oil palm, coconut, and *Jatropa curcas*. Therefore, these kinds of feedstocks are discussed in this section. In addition, since canola oil is used in this study, this feedstock is discussed as well.

1.2.2.1 Oil palm

Oil palm, also known as *Elaeis guineensis*, is originated from coastal regions of West Africa but is now planted in all tropical countries. In addition, it has become the most leading industrial crops, especially in some South East Asia countries such as Indonesia, Malaysia, and Thailand. The color of oil palm fruits is reddish and grows in large bunches. One bunch usually weighs about 10-40 kg. Each fruit consists of a single seed, also known as the palm kernel, and surrounded by a soft oily pulp. The oil is extracted from both pulps of the fruit that can be used as edible oil, and kernel, which is utilized mainly in soap-manufacturing industries.

According to Abdullah (2003), palm oil tree can be harvested when the palm starts to bear fruit three years after planting. Currently, palm oil has become world's largest source of edible oil with amount of 38.5 million tonnes or 25% of the world total edible oil and fat production as presented in **Fig. 1.6** (MPOC, 2008). Therefore, oil palm has now become principal economic crops in a large number of countries that triggered expansion of plantation area around the world (Yusoff, 2006).

It was reported by USDA (2007) that Indonesia is the largest producer of palm oil over the world, producing 15.9 million tonnes of oil or approximately 44% of the total world supply, followed by Malaysia that produces approximately 15.88 million tonnes as shown in **Fig. 1.7**.

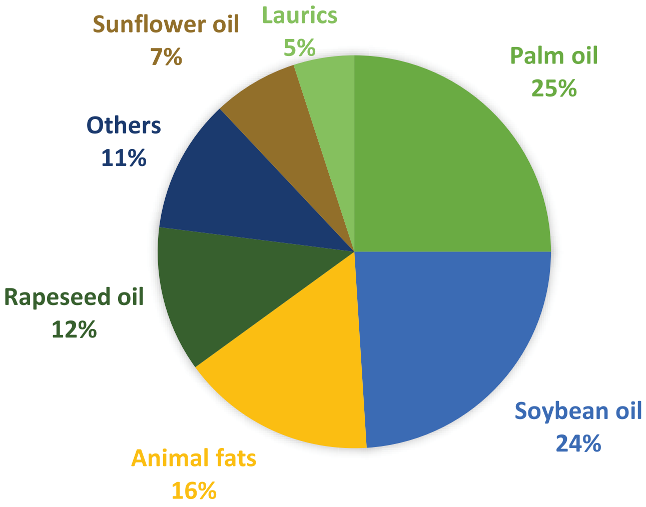


Fig. 1.6. World's oil production in 2007 (MPOC, 2008).

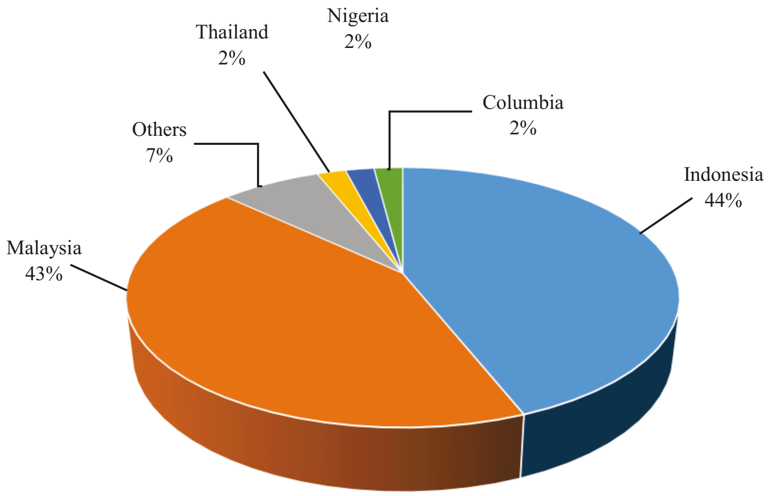


Fig. 1.7. World producer of oil palm in 2006 (USDA, 2007).

Lam et al. (2009) reported that oil palm is a perennial crop, meaning the production of oil is continuous and uninterrupted. The production yield of oil palm is much higher than that of soybean, sunflower, and rapeseed (Mekhilef et al., 2011) as shown in **Fig. 1.8**. Therefore, in the South East Asia countries, especially in Indonesia, Malaysia and Thailand, palm oil is one of the most promising feedstock for biodiesel production.

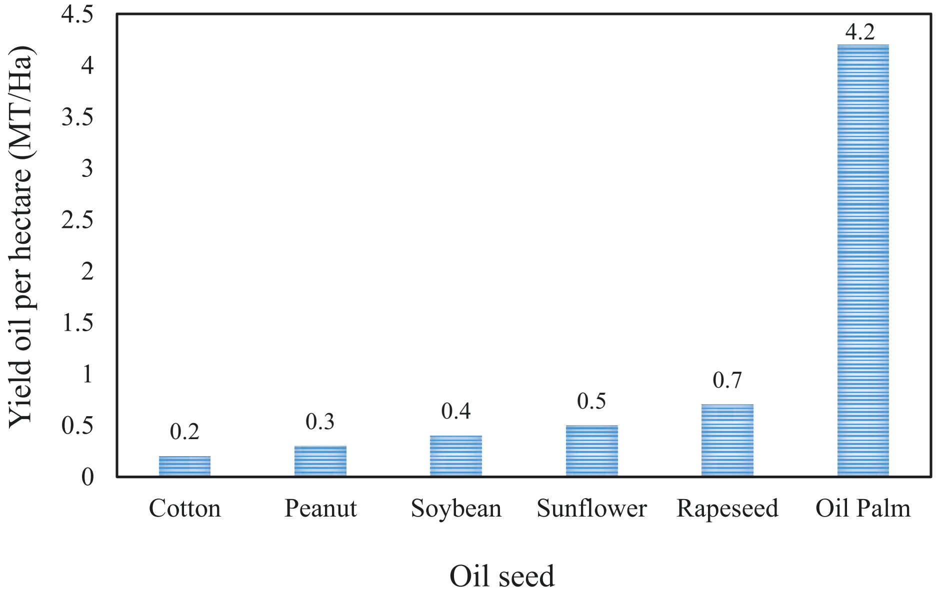


Fig. 1.8. Yield comparison of major oilseeds (Adapted from Mekhilef et al., 2011).

1.2.2.2 Coconut

The coconut palm, *Cocos nucifera*, belongs to Plant Kingdom under Magnoliphyta Division, Class Liliopsida, Order Arecales, Family Arecaceae and Genus Cocos (Yokoyama and Matsumura, 2008). They also reported that coconut plant is widely spread throughout Asia, Latin America, Africa, the Caribbean and the Pacific region. In 2008, Indonesia was the world's largest producer of coconut with 21.5 million tonnes or approximately 34.9% of the total world supply. It is then followed by Philippines with the production of 15.6 million tonnes or 25.4% of the total world coconut production as shown in **Fig. 1.9** (FAO, 2009).

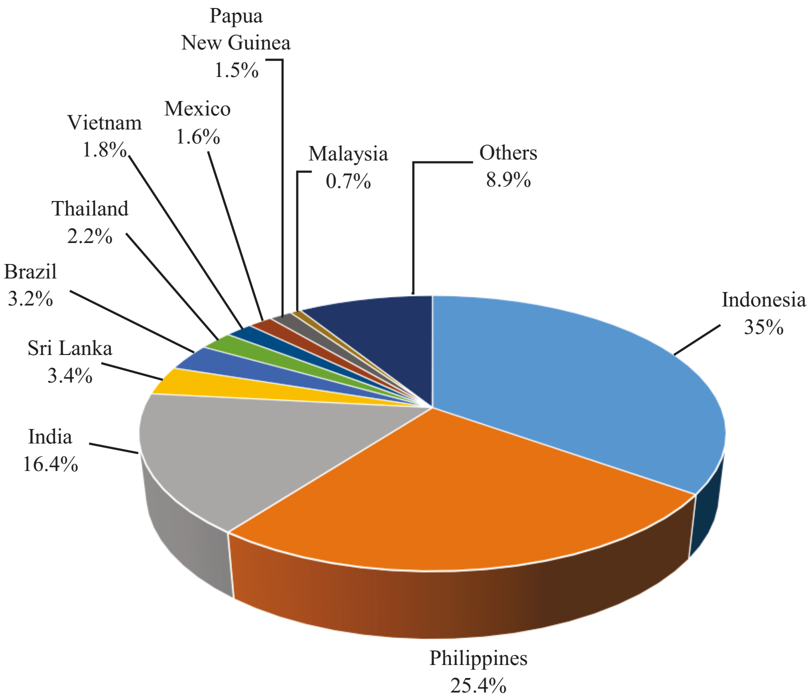


Fig. 1.9. World coconut production in 2008 (FAO statistics, 2009).

The coconut palm can grow well to a wide range of soil types. The ideal pH range is 5.5-7, but it can tolerate in soil with the pH range from 4.5 to 8. This sun-loving plant requires sunlight for photosynthesis and raising the temperature of the air. This plant can grow best at temperature about 27 ºC and rainfall of 1,300 to 2,300 mm per year. It may even grow well at 3,800 mm or more if the drainage of the soil is good. It grows well in humid climate. The best soil for coconut palm to grow is a deep mellow soil like sandy or silt loam or clay with granular structure (Yokoyama and Matsumura, 2008).

It is common in some tropical countries to utilize each part of the coconut palm become the value-added products. The kernel (endosperm) can be used as copra, oil, cake, and milk. The husk (mesocarp) can be used for fuel, mulch, coir, and peat. The hard shell enclosing the seed is utilized for producing charcoal, handicraft, flour, and activated charcoal.

The physicochemical properties of coconut oil have been investigated by some researchers using several techniques (Kamariah et al., 2008; Marina et al., 2009; Mansor et al., 2012). The main components of coconut oil that affect the characteristics of oil are fatty acids, triacylglycerols, phospholipids, tocopherols, sterols, trace metals, mono and diacylglycerols. There are approximately 90% of the fatty acids are saturated and consists mainly of lauric, myristic, and palmitic acid with lauric acid predominating (48.6%) as shown in **Table 1.4**.

Table 1.4. Fatty acid composition of coconut oil

Fatty acid	Composition (wt%)
Caprylic acid (C 8:0)	7.7
Capric acid (C 10:0)	6.4
Lauric acid (C 12:0)	48.6
Myristic acid (C 14:0)	17.8
Palmitic acid (C 16:0)	8.9
Stearic acid (C 18:0)	2.2
Oleic acid (C 18:1)	6.8
Linoleic acid (C 18:2)	1.6

Source: Lin and Tan (2013)

1.2.2.3 *Jatropha curcas*

Jatropha curcas belonging to family *Euphorbiaceae* is a non-edible bioenergy plant for the production of biodiesel. According Openshaw (2000) *Jatropha* plant produces seeds containing non-edible oil that can be converted into biodiesel. The biodiesel production from *Jatropha curcas* oil has been studied by some researchers using several techniques as presented in **Table 1.5**.

Jatropha usually grows at altitudes of 0–6,000 ft (0–2,000 m) and optimum temperature ranges of 20-40° C (Misra and Misra, 2010). Dagar et al. (2006) reported that this plant thrives on different types of soil, including infertile, sandy, gravelly, and saline soils. The pH ranging for growing *Jatropha* is about 5.5 to 9.0. (Foidl et al., 1996). The production of Jatropha tree starts from 9-12 months after germination, but optimum yields can be obtained after 4-5 years.

Like coconut palm, each part of *Jatropha* can be utilized to be the value added products. The seeds of *Jatroph*a contain viscous oil that can be used for candle or soap, diesel or paraffin substitute or extender (Kumar and Sharma, 2008). The oil is mainly used as biodiesel. The seed cake can be used for animal feed (after detoxification), biomass feedstock to power electricity plants, biogas, or high quality of organic fertilizer (Wani et al., 2006; Achten et al., 2008). The uses of *Jatropha* curcas is presented in **Fig. 1.10.**

Table 1.5. Comparisons of biodiesel production from *Jatropha curcas* oil

Methods	Reaction conditions				Biodiesel Yield (%)	Reference
	Catalyst	Temp (ºC)	Reaction time	Molar ratio of reactant to oil		
Homogeneous alkali-catalyzed biodiesel	KOH 1 wt %	50	120 min	Methanol to oil: 6:1	97	Berchmans et al. (2010)
	NaOH 1 wt %	60	90 min	Methanol to oil: 5.6:1	98	Chitra et al. (2005)
	NaOH 0.8 wt %	45	30 min	Methanol to oil: 9:1	96	Tapanes et al. (2008)
	NaOH 0.8wt %	250	28 min	Methanol to oil: 24:1	90.5	Tang et al. (2007)
Heterogeneous acid and alkali-catalyzed biodiesel	CaO 1.5 wt %	70	150 min	Methanol to oil: 9:1	93	Zhu et al. (2006)
	KNO_3/Al_2O_3 6 wt %	70	360 min	Methanol to oil: 12:1	87	Vyas et al. (2009)
	KSF clay&Amberlyst 15 5 wt %	160	6 h	Methanol to oil: 12:1	70	Zanette et al. (2011)
	SO_4^{2-}/SnO_2-SiO_2 3 wt%	180	2 h	Methanol to oil: 15:1	97	Kafuku et al. (2010)
Two-step transesterification	H_2SO_4/KOH 0.55 wt %	60	88/24 min	Methanol to oil: 4:1	99	Tiwari et al. (2007)
	H_2SO_4/NaOH 1.4 wt %	65	60/120 min	Methanol to oil: 6.7:1	90	Berchmans and Hirata (2008)
	H_2SO_4/KOH 4.5 wt %	60	120/120 min	Methanol to oil: 9:1	90-95	Patil and Deng (2009)
	(SO_4^{2-}/TiO_2)/KOH 1.3 wt %	64	120/20 min	Methanol to oil: 6:1	98	Lu et al. (2009)
	H_2SO_4/NaOH 1.0 wt%	50	180/180 min	Methanol to oil: 9.6:1	90	Jain and Sharma (2010)
	SiO_2.HF/NaOH 1.0 wt %	60	120/120 min	Methanol to oil: 6:1	99.5	Corro et al. (2010)
Enzymatic-catalyzed biodiesel	*Pseudomonas cepacia* lipase immobilized on celite	50	8 h	Methanol to oil: 4:1	98	Shah and Gupta (2007)
	Novozyme 435 (*Candida antarctica* lipase B)	45	24 h	Methanol to oil: 5:1	98	Su and Wei (2008)
	Enterobacter aurogenes lipase	55	48 h	Methanol to oil: 4:1	68	Kumari et al. (2009)
	Rhizopus oryzae lipase	30	60 h	Methanol to oil: 3:1	80	Tamalampudi et al. (2008)
Supercritical condition	No catalyst	400	32 min	Methyl acetate to oil: 50:1	78	Niza et al. (2013)
	No catalyst	320, 8.4 MPa	4 min	Methanol to oil: 43:1	100	Hawash et al. (2009)
	No catalyst	400, 9.5 MPa	30 min	Methanol to oil: 16:1	99.67	Lim and Lee (2013)
	No catalyst	300, 9 MPa	15 min	Dimethyl carbonate to oil: 40:1	97	Ilham and Saka (2010)

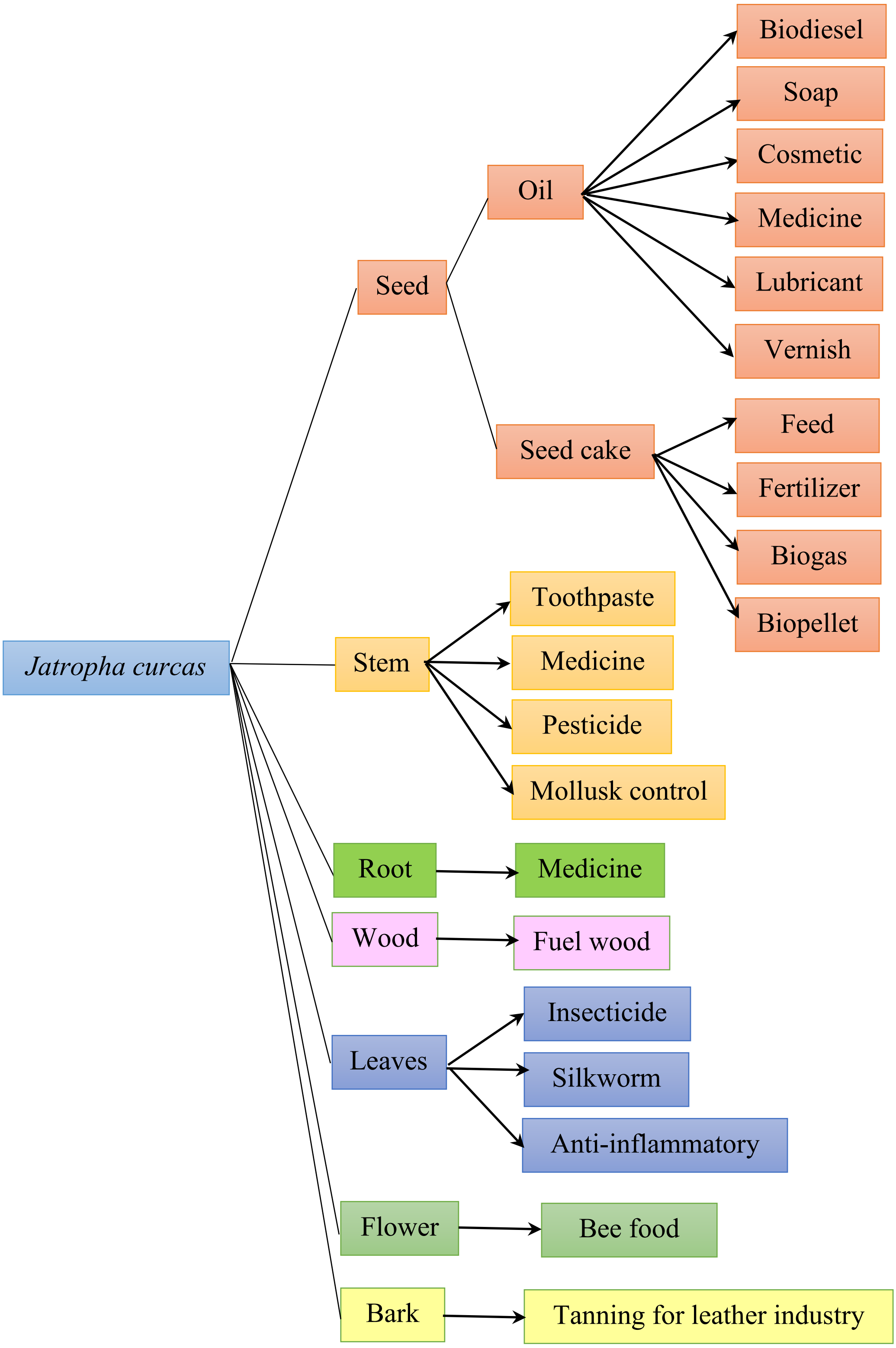


Fig. 1.10. The uses of *Jatropha curcas* (adapted from Heller, 1996, Openshaw, 2000; Kumar and Sharma, 2008).

1.2.2.4 Canola

Canola is a part of the Brassica family with the taxonomy name is *Brassica napus* L. Canola plant grows from 1 to 2 m and produces yellow flowers. Canola oil is obtained from the crushed seeds of this plant. Since the oil content of canola seed is high enough, approximately 40% (based on the seed dry), canola oilseeds are used for oil and meal consumption (Kimber and McGregor, 1995). Mag (1999) reported that canola oil primarily consisted of triglycerides. Canola oil analysis shows that the triglycerides constitute 94.4 to 99.1% of the total lipid (Mag, 1990). The typical composition of canola oil is presented in **Table 1.6**.

Table 1.6. Chemical composition of canola oil

Component	Value
Triglycerides (%)	94.4-99.1
Free Fatty Acids (%)	0.4-1.2
Unsaponifiables (%)	0.5-1.2
Crude oil	up to 2.5
Water-degummed	up to 0.6
Acid-degummed	up to 0.1
Tocopherols (ppm)	700-1200
Chlorophylls (ppm)	5 -35
Sulfur (ppm)	3 - 15

Source: Mag (1990)

The most common fatty acid found in canola oil methyl esters was oleic acid (62.33), and followed by linoleic acid (19.13) as shown in **Table 1.7**.

Table 1.7. Fatty acid composition of canola methyl ester

Fatty acid	Composition (wt%)
Palmitic	4.21
Stearic	2.03
Oleic	62.33
Linoleic	19.13
Linolenic	9.18
Eicosenoic	1.26
Erucic	1.87
Total	100

Source: Dmytryshyn et al., 2004

Canola oil can be utilized as bio-lubricant (Madankar et al., 2013), polyurethane (Kong et al., 2012), nutrition and pharmacy (Carvalho et al., 2006), and biodiesel (Lee et al., 2010). Biodiesel production from canola oil can be proceeded by using homogeneous, heterogeneous, enzymatic catalytic transesterificaiton as well as non-catalytic biodiesel production under supercritical conditions. The comparison of biodiesel production technologies from canola oil is shown in **Table 1.8**.

Table 1.8 Summary of reported experiment data of biodiesel production using canola oil

Methods	Reaction conditions				Biodiesel Yield [%]	Additional information	Reference
	Catalyst	T [ºC]	Reaction time	Methanol to oil ratio [mol/mol]			
Homogeneous alkali-catalyzed transesterification	$AlCl_3$ or $ZnCl_2$ 5 wt%	110	18 h	24:1	98	THF as co-solvent	Sariano Jr. et al. (2009)
	KOH 0.7 wt %	67.5	50 min	5:1	99	using ultrasonic irradiation (20 kHz)	Thanh et al. (2010)
Heterogeneous acid and alkali-catalyzed transesterification	Dolomite 3 wt %	70	3 h	6:1	91.78	catalyst calcined at 850 ºC	Ilgen (2011)
	Nanopowder CaO 3 wt %	65	2 h	9:1	99.85		Zhao et al. (2013)
	MgCoAl-layer double hydroxide (LDH)	200	5 h	14:1	98		Li et al. (2009)
	Potassium-supported TiO_2 6 wt %	55	7 h	54:1	99	catalyst calcined at 700 ºC	Salinas et al. (2012)
	Brønsted acidic ionic liquids based on 1-benzyl-1H-benzimidazole 5 wt %	60	5 h	9:1	99		Ghiaci et al. (2011)
	Calcium bentonite impregnated with 40 wt% KF	65	7 h	6:1	98.2		Boz et al. (2013)
Enzymatic-catalyzed transesterification	Lipase from *T. lanuginosus*	50	24 h	6:1	97	enzyme immobilize onto hydrophobic microporous styrene-divinylbenzene copolymer	Dizge et al. (2009)
Supercritical condition	No catalyst	270	45 min	20:1	102	pressure of 10 Mpa	Lee et al. (2012)
	No catalyst	420-450	4 min	11-45:1	100	pressure of 40 Mpa	Iijima et al. (2002)

1.2.3 Biodiesel production process

Biodiesel is mainly produced from vegetable oils or animal fats by transesterification process. The primary components of vegetable oils and animal fats are triacylglycerols (often called as triglycerides) (**Fig. 1.11**). The fundamental reaction of biodiesel production includes the transesterification between triglycerides (TG) and short chain alcohol such as methanol, generating biodiesel and glycerol (Freedman et al., 1984; Ma and Hanna, 1999; Vicente et al., 2004; Sharma et al., 2008). Diglyceride and monoglyceride are the intermediate compounds in this process. The chemical structures of diglyceride and monoglyceride are shown in **Fig. 1.12** and **1.13**, respectively.

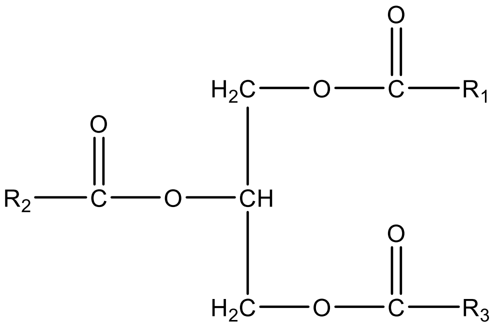


Fig. 1.11. Chemical structure of triglyceride.

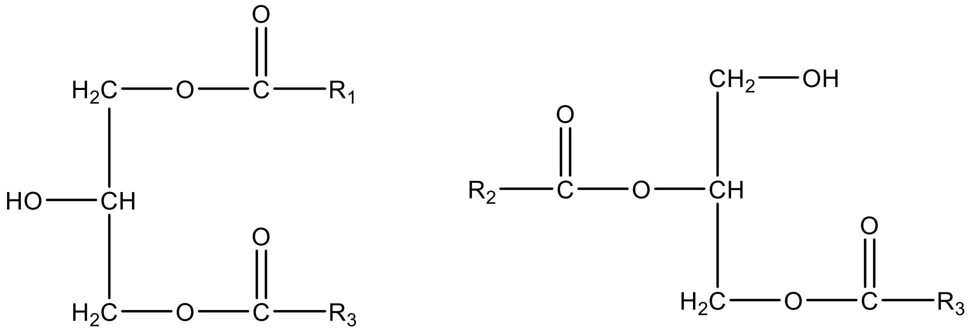


Fig. 1.12. Chemical structure of diglyceride.

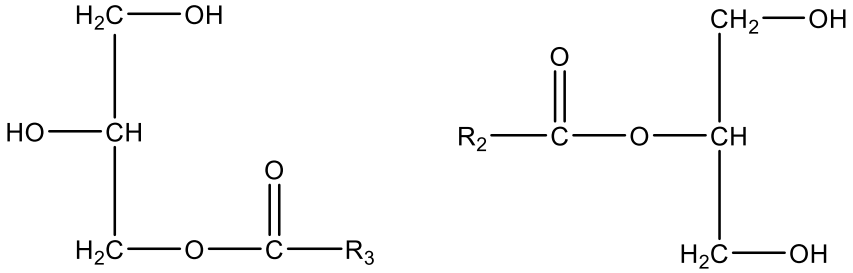


Fig. 1.13. Chemical structure of monoglyceride.

Biodiesel is commonly produced by homogeneous alkali-catalyzed transesterification. The mechanism of homogeneous alkali-catalyzed transesterification is described in **Fig. 1.14.** In the pre-step, methanol reacts with a catalyst (usually KOH or NaOH) to generate methoxide ion. This methoxide ion attacks the carbon atom of carbonyl functional groud from triglyceride molecule, which results in the formation of tetrahedral intermediate compound. The reaction of this intermediate compound with methanol produces the methoxide ion in the second step. In the last step, the rearrangement of the tetrahedral intermediate compound generates diglyceride and alcohol. This reaction will proceed continuously to produce monoglyceride and fatty acid methyl ester (Ma and Hanna, 1999).

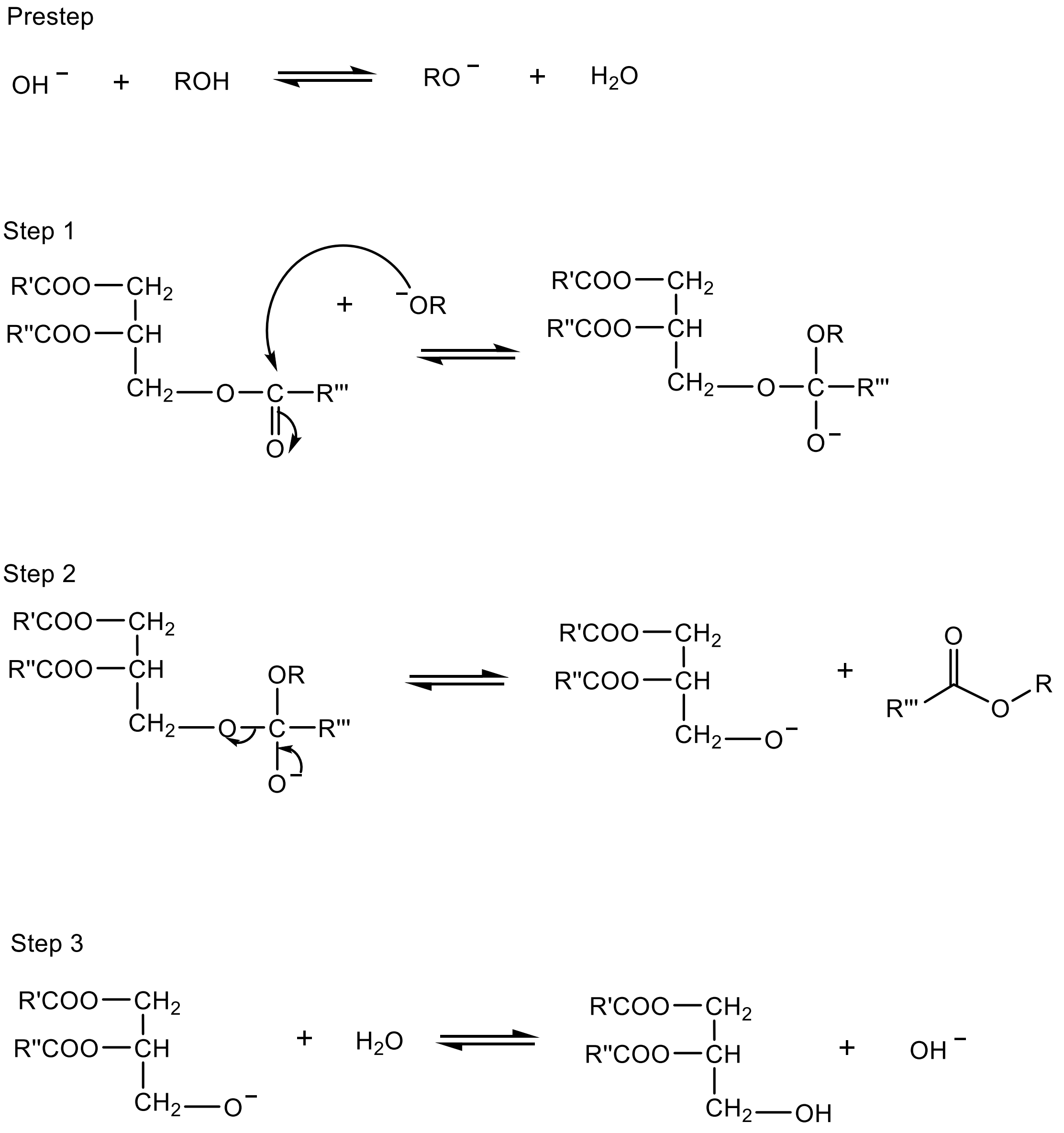


Fig. 1.14. Mechanism of transesterification with base catalyst (Demirbas A, 2005).

Up to now, one of the leading research center in Indonesia, Surfactant and Bioenergy Research Center (SBRC), Bogor Agricultural University, is still producing biodiesel using homogenous alkali-catalyzed transesterification. The flow chart of biodiesel production developed in this research center is shown in **Fig. 1.15**. If the feedstock has free fatty acid (FFA) value more than 2 wt%, the esterification reaction is required. Meanwhile, if the FFA of feedstock is less than 2 wt%, it can be directly proceeded via transesterification process. The catalyst usually used in this process is potassium hydroxide (KOH). This process is performed at 55 ºC for 2 hours.

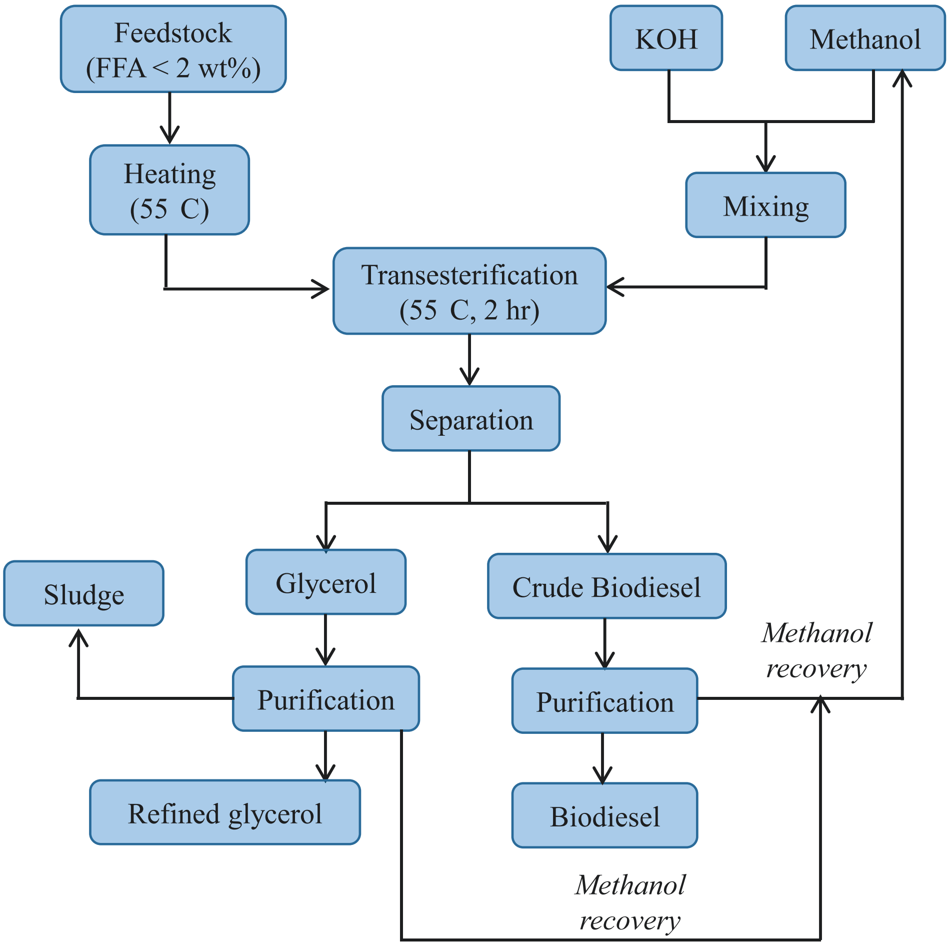


Fig. 1.15. Flow chart of biodiesel production developed in surfactant and bioenergy research center (SBRC), Bogor Agricultural University.

Biodiesel production using homogeneous alkali-catalyzed transesterification method has some drawbacks such as feedstock should have lower acid value and water content, the possibility to form soap from the reaction between catalyst and FFA, and the anhydrous material is required. These drawbacks can be solved by using biodiesel production in supercritical conditions. Therefore, the supercritical technology is selected in this study.

1.2.4 Biodiesel production under supercritical conditions

Biodiesel production under supercritical conditions is a non-catalytic method to produce biodiesel under elevated temperature and high pressure. This technology is firstly invented by Saka and Dadan from Kyoto University, Japan. They found that biodiesel production can be synthesized in supercritical methanol without the addition of catalysts. Comparing with the conventional methods, this process is a much simpler, particularly in the purification step and no catalyst requirement. The schematic process to produce biodiesel in supercritical methanol developed by Saka and Dadan is shown in **Fig. 1.16**.

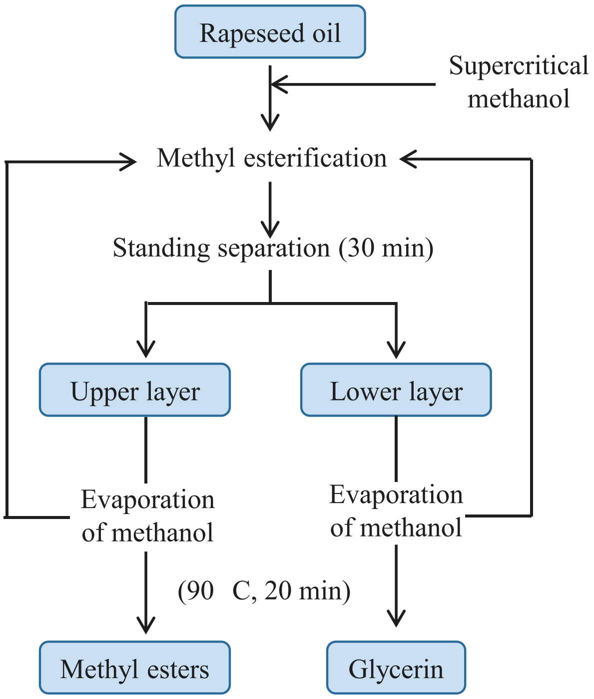


Fig. 1.16. Schematic process of biodiesel production in supercritical methanol developed by Saka and Dadan (adapted from Saka and Dadan, 2001).

The reaction between triglyceride and methanol under supercritical conditions can be explained by two reasons, one is that the polarity of methanol decreased at high temperature and high pressure (Saka and Dadan, 2001), and the other one is that the solubility of triglyceride increased with temperature and pressure increase (Makareviciene et al., 2005). Because of these reasons, a mixture of triglyceride and methanol becomes single phase at elevated temperature and high pressure. Consequently, triglyceride can be well dissolved in methanol under supercritical conditions.

The optimum conditions for biodiesel production in supercritical methanol was found at 350 °C, 20 MPa, oil-to-methanol molar ratio of 1:42 for 4 min (Saka and Dadan, 2001). In order to reduce the severity of operating conditions, Kusdiana and Saka (2004) proposed two-stage process, namely hydrolysis of triglycerides under subcritical water conditions and esterification of the fatty acids under supercritical methanol conditions. In this process, a biodiesel production was proceeded under milder operating conditions (270 °C, 7-20 MPa) compared to the previous one step (350 °C, 20-50 MPa). These reaction conditions certainly reduce energy consumption. However, this process has a significant disadvantage, namely need to heat up large amount of water in the hydrolysis process. Thus, it reduces the energy efficiency of the process. The flow diagram of two-step biodiesel production proposed by Kusdiana and Saka is shown in **Fig. 1.17**.

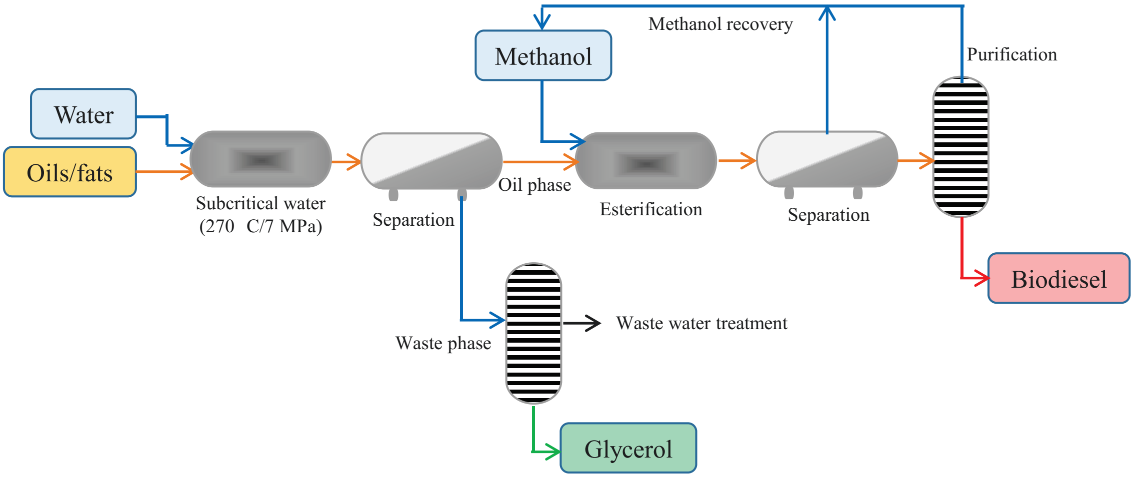


Fig. 1.17. Two-step preparation for catalyst-free biodiesel fuel production (Kusdiana and Saka, 2004).

CHAPTER 2

Literature Review

2.1. Introduction

American Society for Testing and Materials (ASTM) defines biodiesel as a monoalkyl ester of fatty acids derived from renewable feedstocks such as vegetable oils, animal fats, waste cooking oil, and microalgae via transesterification process. Since biodiesel is a good candidate to substitute petroleum diesel fuel owing to its biodegradability and similar flow and combustion properties with conventional diesel fuel, biodiesel has attracted a considerable amount of interest with comprehensive emergence of researches during the past few years. There are numerous methods to produce biodiesel, namely homogeneous acid and alkali-catalyzed transesterification, heterogeneous acid and alkali-catalyzed transesterification, enzymatic-catalyzed transesterification, non-catalytic supercritical conditions, and microwave and ultrasound assisted transesterification.

This literature review provided a thorough analysis and background study on the biodiesel production process that have been achieved previously. The reviews are divided into several parts. The first reviews are focused on comparisons of biodiesel production process including homogeneous acid and alkali-catalyzed transesterification, heterogeneous acid and alkali-catalyzed transesterification, enzymatic-catalyzed transesterification, non-catalytic biodiesel production under supercritical conditions, and microwave and ultrasound-assisted transesterification. This profound review is vital to give better understanding on current biodiesel production process. The further reviews are focused on the biodiesel production process under several reactants. To the best our knowledge, there are numerous studies on biodiesel production under various supercritical reactants such as methanol, ethanol, methyl acetate, and dimethyl carbonate. This review is also necessary to provide understanding regarding the reaction characteristics between triglyceride and some reactants including methanol, ethanol, methyl acetate, and dimethyl carbonate. The last reviews are focused on main factors affecting biodiesel production. In this section, the main factors affecting biodiesel yield such as temperature, pressure, reaction time, and oil-to-reactant molar ratio were intensely discussed.

2.2. Comparisons of biodiesel production process

Biodiesel is mainly produced by reacting triglyceride with short chain alcohol such as methanol and ethanol through transesterification process. As mentioned previously, there are numerous methods to produce biodiesel, namely homogeneous acid and alkali-catalyzed transesterification, heterogeneous acid and alkali-catalyzed transesterification, enzymatic-catalyzed transesterification, non-catalytic supercritical conditions, and microwave and ultrasound assisted transesterification as presented in **Fig. 2.1**. Each method has advantages and drawbacks and is explained thoroughly in this section.

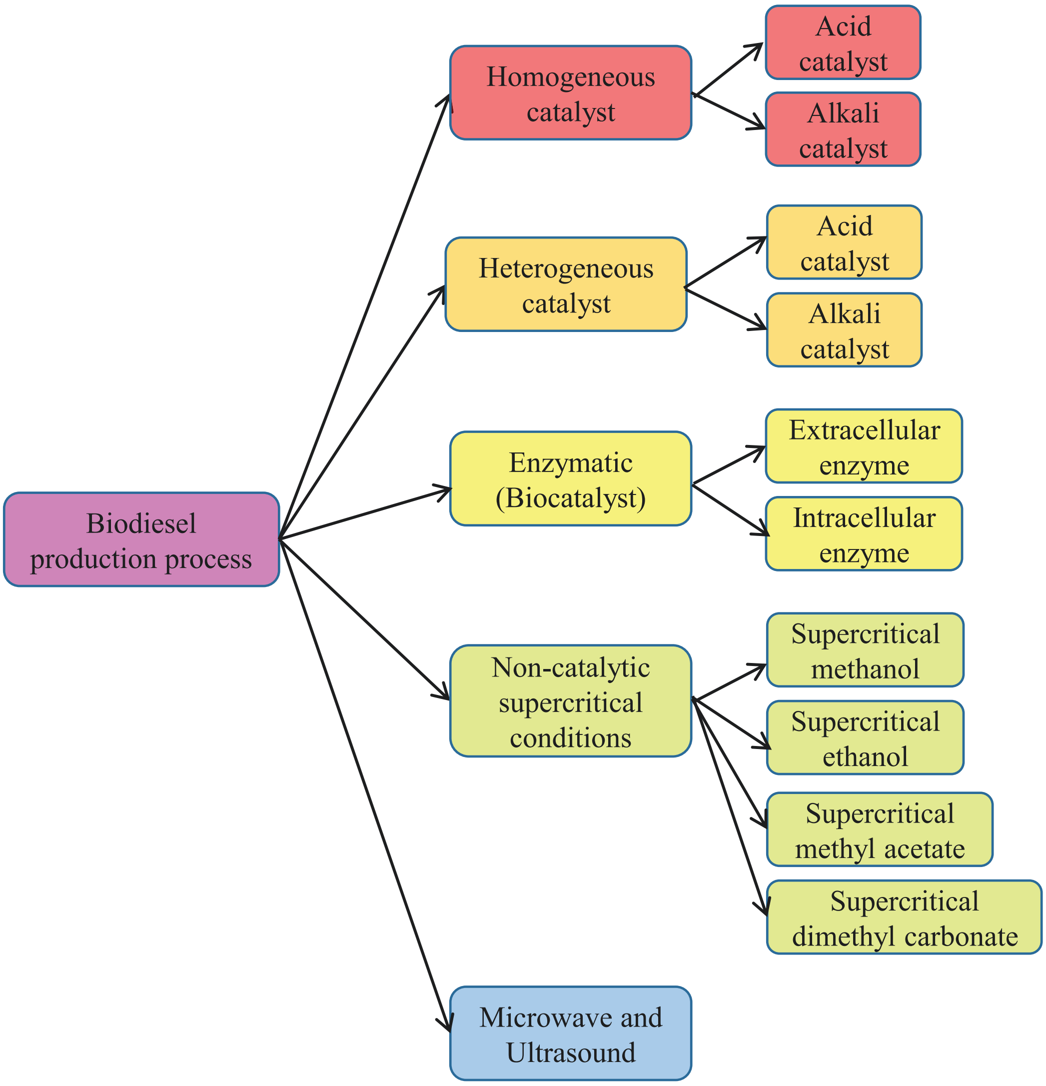


Fig. 2.1. Several methods to produce biodiesel.

2.2.1. Homogeneous catalysts for biodiesel production

The following section describes biodiesel production by using homogeneous catalysts. There are mainly two homogeneous catalysts for biodiesel production process, namely homogeneous acid catalyst and heterogeneous alkali catalyst.

2.2.1.1. Homogeneous acid-catalyzed transesterification

So far, hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) are the most commonly used catalysts for acid-catalyzed transesterification process. Comparing with the alkali-catalyzed system, the advantages of this method are acid catalyst can proceed esterification and transesterification simultaneously (Jacobson et al., 2008), not sensitive to the presence of FFAs in the feedstock (Kulkarni and Dalai, 2006), and can be applied for low-cost lipid feedstocks such as waste cooking oil (Canakci and Van Gerpen, 1999). Zhang et al., (2003) reported that acid catalysis gave the better performance when the amount of FFA in the feedstock is greater than 1 wt%.

Fig. 2.2 shows the mechanism of homogeneous acid-catalyzed transesterification process for biodiesel production using methanol. This mechanism includes the protonation of the carbonyl group by the acid catalyst, nucleophilic attack of the methanol to produce a tetrahedral intermediate compound, and proton migration and breakdown of the intermediate. This sequencing process is repeated twice to generate biodiesel and glycerol.

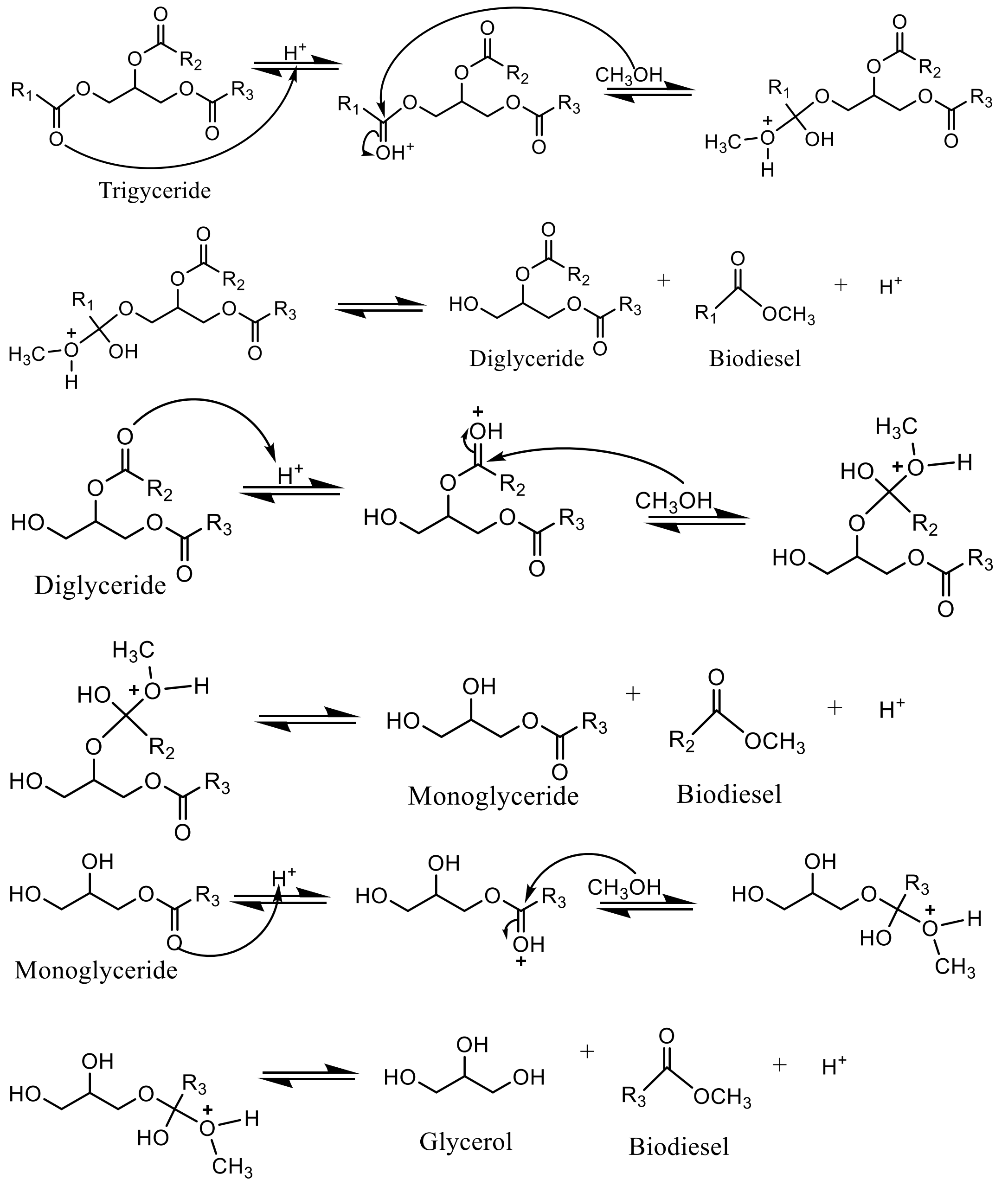


Fig. 2.2. Reaction mechanism for homogeneous acid-catalyzed transesterificaiton of triglyceride.

Even though this catalyst is insensitive to the presence of FFAs, this process requires more severe reaction conditions over alkali-catalyzed transesterification. Therefore, it is not a feasible to be applied for industrial application. Besides, this process requires high reaction temperature and high oil-to-alcohol molar ratio, takes slower reaction rate, and causes an environmental problem due to the corrosion (Goff et al., 2004, Jacobson et al., 2008). It was explained in some previous studies that the conversion of waste cooking oil was achieved more than 90% after 10 h reaction time, the addition of 4 wt% H_2SO_4, and oil-to-methanol molar ratio of 1:20 (Wang et al., 2006). Freedman et al. (1984) also investigated the biodiesel production using H_2SO_4-catalyzed transesterification. They observed that 99% oil conversion was obtained within 69 h reaction time by using 1 mol% catalyst and oil-to-methanol molar ratio of 1:30. These previous studies proved that the acid-catalyzed transesterification requires severe reaction conditions.

2.2.1.2. Homogeneous alkali-catalyzed transesterification

Nowadays, biodiesel is generally produced using homogeneous alkali-catalyzed transesterification due to the fact that this process promises some advantages such as catalyst is widely available, transesterification process is performed under milder reaction conditions (low reaction temperature and atmospheric pressure), high conversion can be achieved in shorter time than acid-catalyzed transesterification (Fukuda et al., 2001, Lotero et al., 2005). The most commonly used catalysts in this process are sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Meher et al., 2006, Felizardo et al., 2006). Fukuda et al. (2001) identified that homogeneous alkali-catalyzed transesterification reaction rate performs 4000 times faster over acid-catalyzed transesterification process. Nevertheless, this process has limitation such as sensitive to the presence of free fatty acid (FFA) of feedstock. Ma and Hanna (1999) concluded that the FFA content in vegetable oil should be less than 1 wt% for alkali-catalyzed transesterification process. When the feedstock contains an enormous amount of FFA, the saponification will occur as a result of a reaction between FFA and alkali catalyst as shown in **Fig. 2.3**. This saponification reaction is certainly undesirable since it will deactivate the catalyst to enhance the transesterification process and the vast amount of soap can inhibit the purification of biodiesel and reduce the biodiesel yield (Kulkarni and Dalai, 2006, Yan et al, 2009).

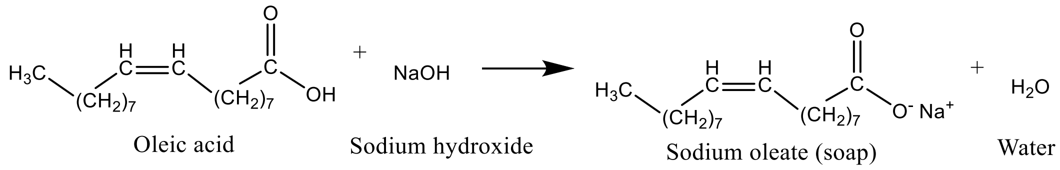


Fig. 2.3. Saponification as a result of reaction between oleic acid and sodium hydroxide.

Another shortcoming of alkali-catalyzed transesterification process is that this reaction is sensitive to the presence of water since it can hydrolyze triglycerides to form diglycerides and FFA as shown in **Fig. 2.4**. Thus, in industrial application, the FFA and water content of the feedstock must be strictly maintained in order to obtain high-quality biodiesel.

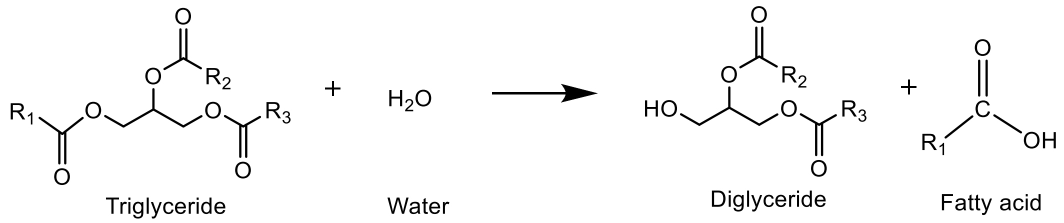


Fig. 2.4. Hydrolysis of triglyceride to produce diglyceride and fatty acid.

Fig. 2.5 shows the mechanism of homogeneous alkali-catalyzed transesterification process for biodiesel production using methanol. This mechanism includes the production of methoxide, nucleophilic attack of methoxide to carbonyl group on triglycerides forming a tetrahedral intermediate compound, breakdown of intermediate, and regeneration of catalyst. This sequencing process is repeated twice in which in the first repetition, biodiesel and monoglyceride are obtained and in the second repetition, biodiesel and glycerol are obtained.

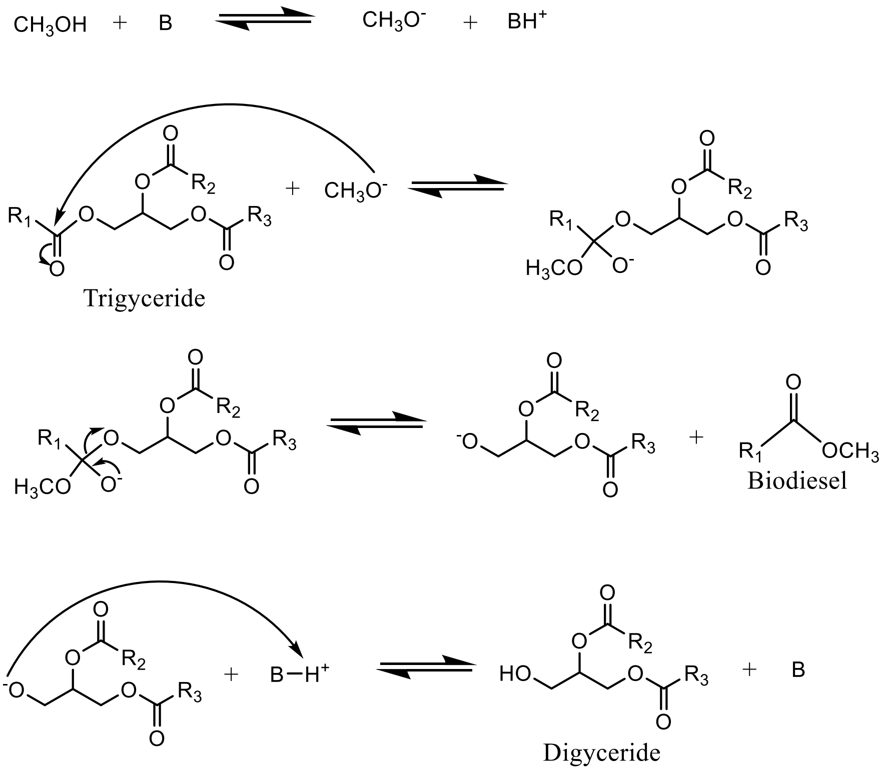


Fig. 2.5. Reaction mechanism for homogeneous alkali-catalyzed transesterificaiton of triglyceride.

2.2.2. Heterogeneous catalysts for biodiesel production

Like homogeneous catalytic method, biodiesel production by using heterogeneous catalyst is also divided into two parts, namely heterogeneous acid-catalyzed transesterification process and heterogeneous alkali-catalyzed transesterification process. In comparison with homogeneous acid and alkali-catalyzed transesterification, this method provides some advantages such as easy separation, reusable of catalyst, and no saponification reaction.

Besides that, the heterogeneous catalyst for biodiesel production process is more environmentally friendly and can be used in either batch or continuous-flow reactor over homogeneous one (Yan et al., 2010; Endalew et al., 2011).

2.2.2.1. Heterogeneous acid-catalyzed transesterification

Even though heterogeneous acid-catalyzed transesterification has lower activity, this method has been applied for industrial processes due to some reasons such as ability to catalyze both esterification and transesterification process simultaneously, the catalyst is less toxic and corrosive than homogeneous acid catalyst, insensitive to FFA content, eliminate the washing step of biodiesel, contain a variety of acid sites with different strength of Bronsted or Lewis aciditity, easy separation of the catalyst from the reaction medium, resulting in lower product contaminant, and easy regeneration and recycling of catalyst (Jitputti et al., 2006, Kulkarni and Dalai, 2006, Patil and Deng, 2009). However, the heterogeneous acid-catalyzed transesterification also has the drawbacks, namely slow reaction rate and possible undesirable side reactions.

Some heterogeneous acid catalysts that have been utilized to produce biodiesel are zirconium oxide (ZrO_2), tin oxide (SnO_2), titanium oxide (TiO_2), zeolite, and sulfonic ion-exchange resin including Amberlyst-15, Amberlyst-35, and Nafion-NR50. Among these solid catalysts, Nafion-NR50 gave higher selectivity to produce biodiesel and glycerol because of its acid strength (Carvero e al., 2008; Antunes et al., 2008). Nevertheless, it has a limitation due to expensive and lower activity over liquid acid catalyst (Lopez et al., 2007).

Some researchers have used zirconium oxide (ZrO_2) as heterogeneous acid catalyst for biodiesel production due to its strong surface acidity. This catalyst is commonly used by impregnating with acidic solution such as sulfuric acid (H_2SO_4) to form sulfated zirconia, SO_4^{2-}–ZrO_2 (Miao and Gao, 1997) or by combining with alumina, Al_2O_3 to become ZrO_2–Al_2O_3 or even with tungsten oxide (WO_3). There is a different activity while this catalyst was applied with or without impregnation. It was reported in the previous study that when this catalyst impregnated with sulfuric acid (SO_4^{2-}–ZrO_2), the yield of biodiesel after transesterification of palm kernel oil and crude coconut oil could be achieved as high as 90.3 and 86.3%, respectively. Meanwhile, when this catalyst was not impregnated, merely 64.5 and 49.3% of biodiesel were achieved for transesterification of palm kernel oil and crude coconut oil, respectively (Jitputti et al., 2006). Thus, it could be confirmed that the modification of metal oxide surface acidity is the key point to obtain high biodiesel yield. Besides that, Jacobson et al., (2008) discovered that the combination of this catalyst with alumina and tungsten oxide (ZrO_2–Al_2O_3–WO_3) could enhance mechanical strength and the acidity of the catalyst.

Fig. 2.6 shows the proposed reaction mechanism of SiO_2/ZrO_2-catalyzed transesterification for biodiesel production using methanol. Initially, a carbonyl oxygen from triglyceride attacks zirconium to produce intermediate compound. The intermediate compound is then attacked by methanol, forming a new C-O bond. Lastly, rearranging the intermediate compound results in biodiesel and catalyst. As mentioned previously, this catalyst is reusable.

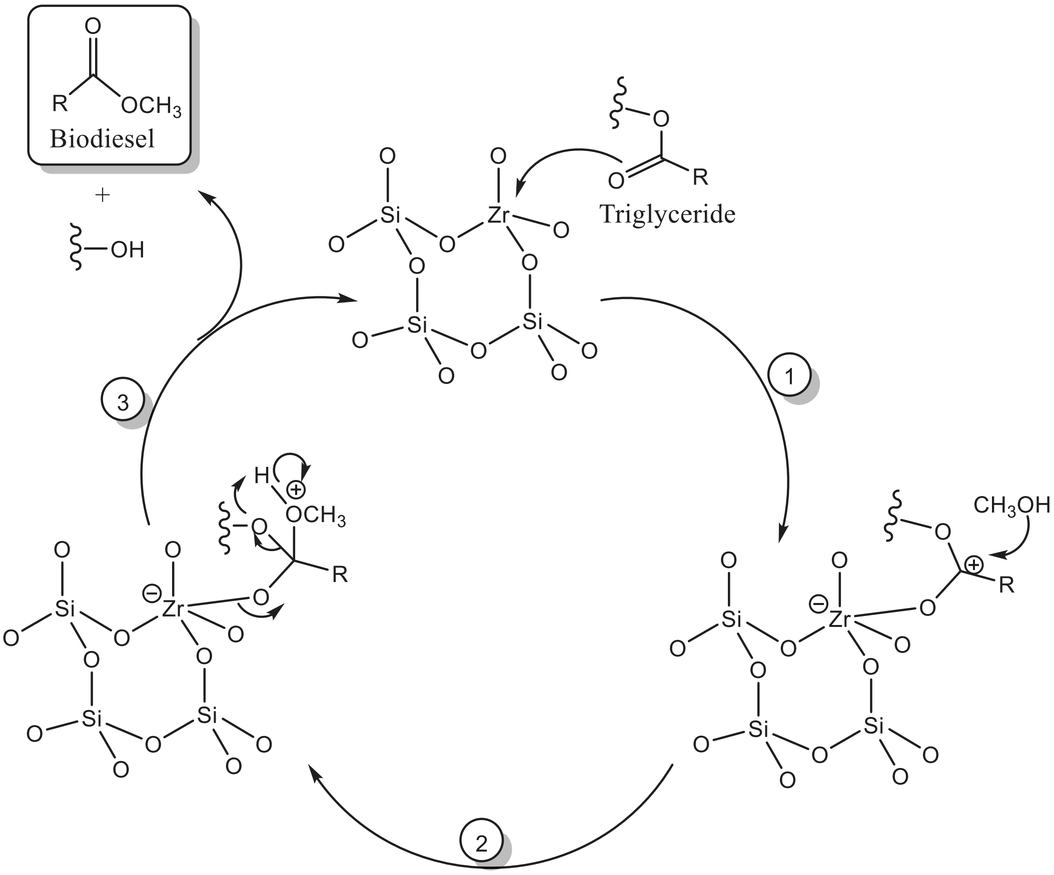


Fig. 2.6. Proposed reaction mechanism of SiO_2/ZrO_2-catalyzed transesterification (adapted from Faria et al., 2009).

Tin oxide (SnO_2) also has been used as heterogeneous acid catalyst for biodiesel production, but the study about this is still limited since the preparation method of this catalyst is complicated. The usage of this catalyst is also the same with ZrO_2 in which this catalyst should be impregnated with the strong acid such as sulfuric acid to form SO_4^{2-}–SnO_2. Furuta et al. (2004) deduced that the acid strength of SO_4^{2-}–SnO_2 is higher than that of SO_4^{2-}–ZrO_2. Thus, for esterification of n-octanoic acid with methanol at temperature below 150 °C, the catalytic activity of SO_4^{2-}–SnO_2 was observed more superior than that of SO_4^{2-}–ZrO_2. However, again, since the pretreatment of this catalyst is complicated due to the difficulty in obtaining oxide gels from its salt, this catalyst is rarely used for biodiesel production (Matsuhashi, 2001, and Khder et al., 2008).

Another heterogeneous acid catalyst ever used for biodiesel production is titanium oxide (TiO_2). Even though the study about utilization of this catalyst for biodiesel production is still limited, this metal oxide catalyst has good acidic properties. Chen et al. (2007) reported that the transesterification of cotton oil by employing SO_4^{2-}/TiO_2 and SO_4^{2-}/ZrO_2 is proportional to the specific surface area. It was found that biodiesel yields of 90% and 85% were obtained for transesterificaiton of cotton oil using SO_4^{2-}/TiO_2 with a specific surface area of 99.5 m^2/g and using SO_4^{2-}/ZrO_2 with a specific surface area of 91.5 m^2/g, respectively. Nevertheless, this catalyst still has the shortcoming such as this catalyst requires more severe reaction condition (high reaction temperature of 230 °C) over homogeneous one. de Almaeda et al. (2008) found that a FAME yield of 40% was obtained after transesterification for 1 h at 120 °C using this catalyst. In another study, Peng et al. (2008) examined that the activity of SO_4^{2-}/TiO_2 catalyst was able to be enhanced by introducing a secondary metal, SiO_2 to generate $SO_4^{2-}/TiO_2–SiO_2$. It was discovered that the specific surface area of the catalyst increased to 258 m^2/g by adding SiO_2 to SO_4^{2-}/TiO_2. The optimum yield of biodiesel (90%) was achieved at 200 °C, catalyst loading of 3 wt%, oil-to-methanol molar ratio of 1:9, after 3 h reaction time.

Zeolite has also been used as heterogeneous acid catalyst for biodiesel production in the previous studies because it contains silicon (Si), aluminium (Al), and oxygen (O) in its framework. The advantageous of biodiesel production using zeolite is that this catalyst can be obtained naturally, cheap, and the acid strength can be controlled by changing aluminosilicate framework. However, according to Kiss et al., (2006), this catalyst has low activity in transesterification process due to the diffusion limitation of bulky reactants, in this case, triglyceride into the microporous structure of zeolite. It was discovered by Brito et al. (2007) that biodiesel yield was only obtained about 26.6% for transesterification of waste cooking oil at high reaction temperature of 460 °C, after 22 min reaction time, and oil-to-methanol ratio of 1:6. In recent study, Kusuma et al. (2013) notified that to enhance the activity of zeolite, the potassium hydroxide should be added. It was found in their study that the highest yield of biodiesel (95.09%) was obtained at 60 °C, impregnation of zeolite with 100 g/100 mL KOH, palm oil-to-methanol molar ratio of 1:7, the addition of catalyst of 3wt%, after 2 h reaction time. They also proposed reaction mechanism for transesterification of triglycerides using KOH-impregnated zeolite catalyst as presented in **Fig. 2.7**. The reaction mechanism is almost the same with the homogeneous alkali-catalyzed transesterification. Initially, the reaction between an active site of catalyst (K_2O) with methanol results in methoxide ion (CH_3O^-). This methoxide ion then attacks the carbonyl carbon of triglyceride, forming the tetrahedral intermediate compound. This intermediate compound then rearranges to produce diglyceride anion and biodiesel. The formation of diglyceride molecule is from the reaction between H^+ with diglyceride anion. Besides that, there is a possibility of reaction between diglyceride anion with methanol to produce diglyceride and methoxide anion. This process will repeatedly occur twice.

Apart from that, sulfonic ion-exchange and sulfonic modified mesostructure silica have also been utilized as heterogeneous acid catalyst for biodiesel production. Amberlist-15, Amberlist-35, Amberlist-15 DRY, and Nafion SAC-13 are the common types of sulfonic ion-exchange and have been used by some researchers (de Rezende et al., 2008, Mo et al., 2008, Chang and Bae, 2011). The advantages of using such kind of catalyst for biodiesel production are this catalyst provides excellent catalytic activity in the esterification reaction. However, the shortcomings of biodiesel production process using this catalyst as reported by Lotero et al. (2005) are:

- Catalyst gives low performance in transesterification process.
- This type of catalyst requires very high oil-to-alcohol molar ratio.
- It has low thermal stability and become unstable at the temperature above 140 °C.
- It needs high reaction temperature (150–200 °C) to achieve fast reaction rate.

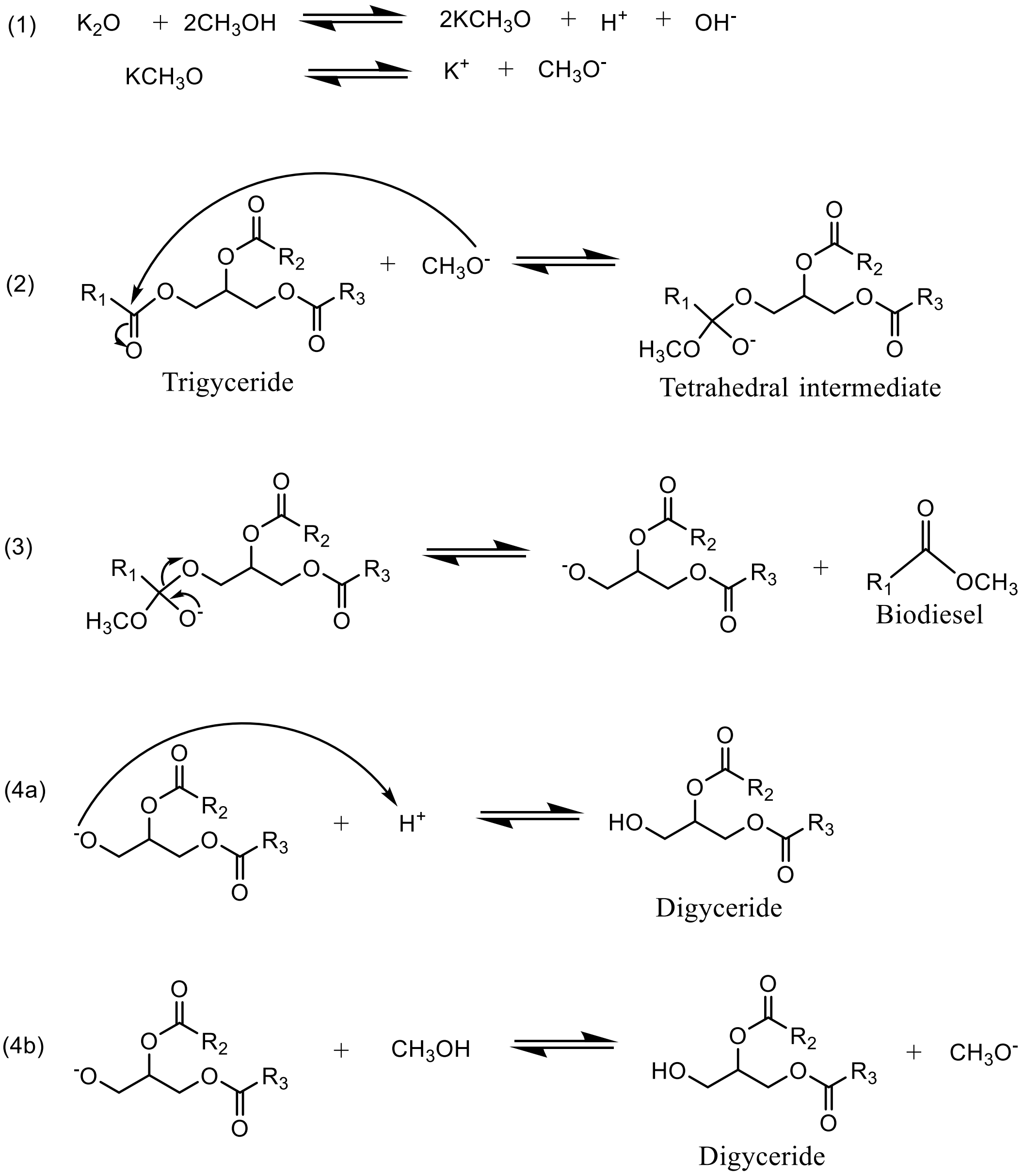
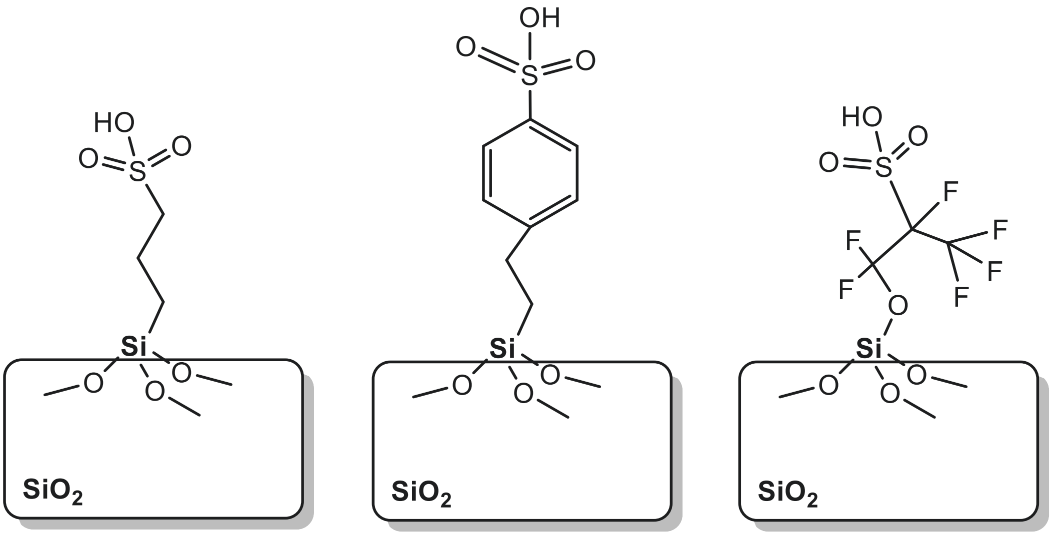


Fig. 2.7. Proposed reaction mechanism for transesterification of triglycerides using KOH-impregnated zeolite catalyst (adapted from Kusuma et al., 2013).

Vicente et al. (1998) reported that the FAME yield of only 0.7% was obtained using Amberlist-15 at atmospheric pressure and oil-to-methanol molar ratio of 1:6 after 8 h reaction time. In addition, Dos Reis et al. (2005) notified that to increase the biodiesel yield, the oil-to-methanol molar ratio should be increased. The biodiesel yield of 80% was achieved at 60 °C and oil-to-methanol molar ratio of 1:100 after 8 h reaction time. Besides that, the common types of sulfonic modified mesostructure silica are porpylsulfonic acid-modified SBA-15, arenesulfonic acid-modified SBA-15, and perfluorosulfonic acid-modified SBA-15 as shown in **Fig. 2.8**. According to Mbaraka and Shanks (2006), these catalysts have large mesopores compared to the sulfonic ion-exchange, thus the diffusion problem faced by reactants to approach the active site of catalyst can be reduced. However, the use of this catalyst for biodiesel production is still limited since there is a possibility of accumulation of organic compound on the catalyst surface that can inhibit the active site.



Propylsulfonic acid-modified SBA-15

Arenesulfonic acid-modified SBA-15

Perfluorosulfonic acid-modified SBA-15

Fig. 2.8. Organosulfonic acid-modified mesostructure silica (adapted from Lam et al., 2010).

2.2.2.2. Heterogeneous alkali-catalyzed transesterification

Heterogeneous alkali-catalyzed transesterification is formerly expected to be able to overcome the problem faced in homogeneous alkali-catalyzed transesterification. There are several advantages when heterogeneous alkali catalyst was employed for biodiesel production. Some of them are (1) catalyst is reusable, (2) more environmentally benign than homogeneous alkali catalyst, (3) catalyst can be synthesized from cheap sources such as limestone or calcium hydroxide, (4) the amount of alkali waste water is only a few, and (5) the activity of this catalyst is almost the same with a homogeneous one at the same operating condition (Kim et al., 2004). However, this method is still facing some limitations such as (1) catalyst needs to be activated through calcination process using high temperature, (2) reaction rate is slower than homogeneous alkali catalyst method, and (3) there is a possibility of side reaction as a result of reaction between catalyst and glycerol to generate calcium diglyceroxide (Kouzu et al., 2008a) as shown in **Fig. 2.9.**

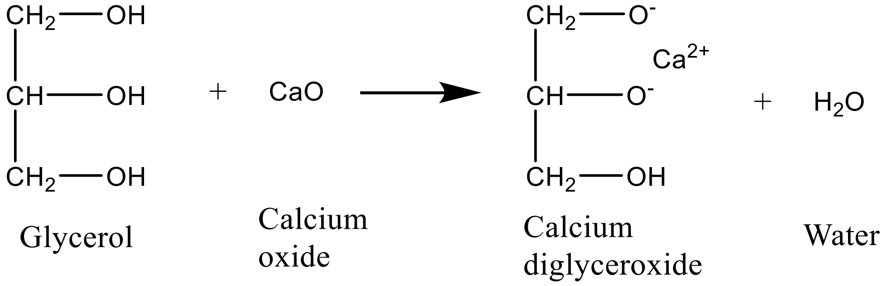


Fig. 2.9. The reaction between glycerol and calcium oxide forming calcium diglyceroxide and water.

Some heterogeneous alkali-catalysts that were previously used for biodiesel production are calcium oxide (CaO), magnesium oxide (MgO), strontium oxide (SrO), and hydrotalcites ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$). According to Zabeti et al. (2009), calcium oxide is the most attractive heterogeneous alkali-catalyst owing to low solubility in methanol and the strongest basic activity over alkaline earth metal oxide. In the previous study by Kouzo et al. (2008b), it was observed that biodiesel yield of 93% was found after 1 h transesterification process at methanol reflux temperature with oil-to-methanol ration of 1:12 using CaO catalyst which was formerly obtained from calcinations of pulverized limestone ($CaCO_3$) at 900 °C for 1.5 h.

In addition, Kazembe-Phiri et al. (2010) also observed that biodiesel yield of 88.81% was obtained for transesterification of ground nut after 2 h transesterification reaction time with oil-to-ethanol molar ratio of 1:9 using 1 wt% CaO catalyst calcined at 900 °C for 1.5 h. Meanwhile, Di Serio et al. (2006) discovered that a FAME yield of only 20% was obtained after transesterification of soybean oil at 100 °C. All previous studies agreed that the activity of magnesium oxide is much lower than that of calcium oxide. To enhance the activity of magnesium oxide, Xie et al. (2006) notified that the mixed magnesium-alumina (Mg-Al) oxide calcined at high temperature and using hydrotalcites ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) as precursor could perform useful activity. It was found that a FAME yield more than 90% was obtained by employing magnesium-alumina oxide as a catalyst despite using high reaction temperature (Di Serio et al., 2006).

Fig. 2.10 shows reaction mechanism for calcium oxide-catalyzed transesterification of triglyceride using methanol as a reactant. This reaction mechanism is following several steps: (1) the formation of methoxide ion as a result of abstraction of proton from methanol by the basic site of CaO, (2) methoxide anion then attacks the carbon atom of carbonyl functional group in a triglyceride compound to generate alkoxycarbonyl intermediate compound, (3) rearrangement of alkoxycarbonyl intermediate results in the more stable compounds consisted of biodiesel and diglyceride anion, and (4) calcium hydroxide cation is then attacked by diglyceride anion forming diglyceride and CaO. As shown in this figure, the catalyst is obtained again after process. In addition, this reaction mechanism is continuously repeated twice until biodiesel and glycerol are obtained.

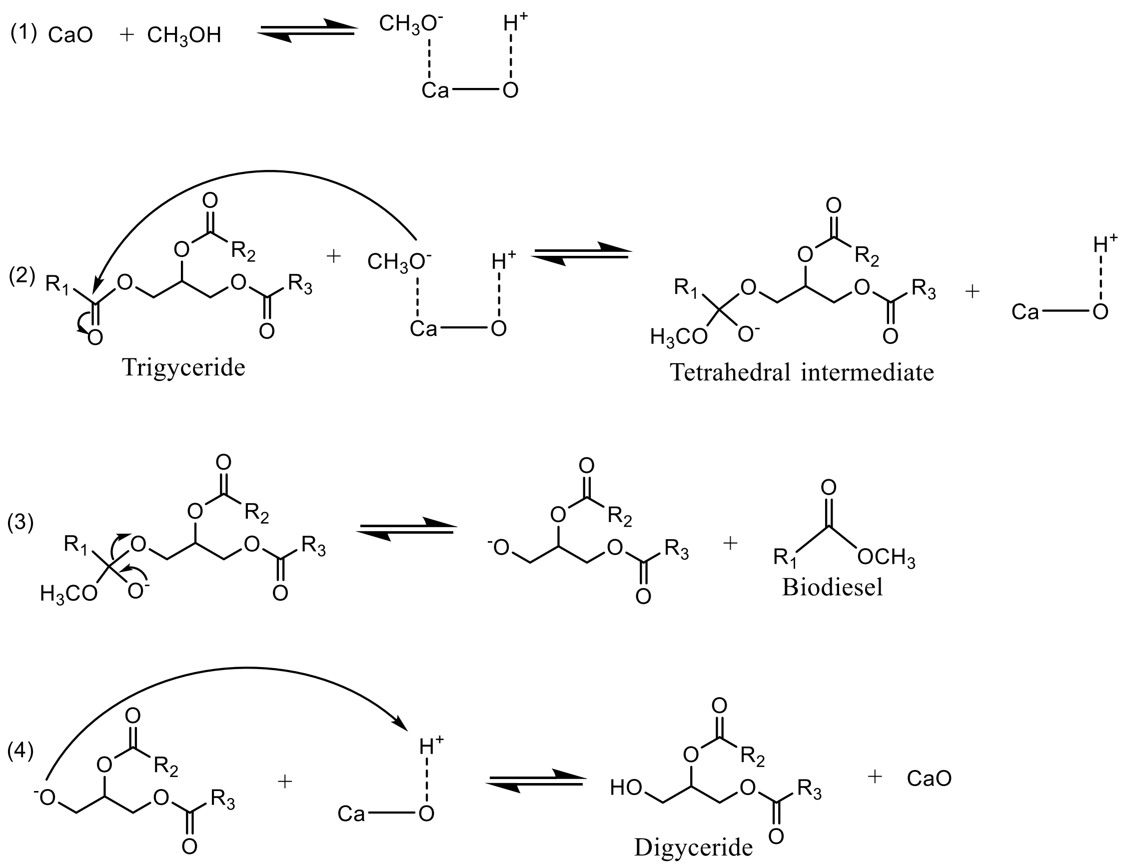


Fig. 2.10. Reaction mechanism for heterogeneous alkali-catalyzed transesterificaiton of triglyceride.

2.2.3. Enzymatic-catalyzed biodiesel production

Due to the drawbacks associated with waste water treatment, environmentally unfriendly process, and difficulties to recover glycerol from catalyst faced by chemicals-catalyzed transesterification, some researchers have proposed green method to produce biodiesel by employing enzyme as a catalyst, as well known as biocatalyst.

Figs. 2.11 and **2.12** show the difference in downstream operation for biodiesel production using alkali catalyst and using an enzyme. As shown in these figures, enzymatic-catalyzed transesterification process is superior to alkali-catalyzed transesterification process due to the ability to eliminate the downstream operation required for alkali-catalyzed transesterification. Thus, biodiesel product obtained has high purity.

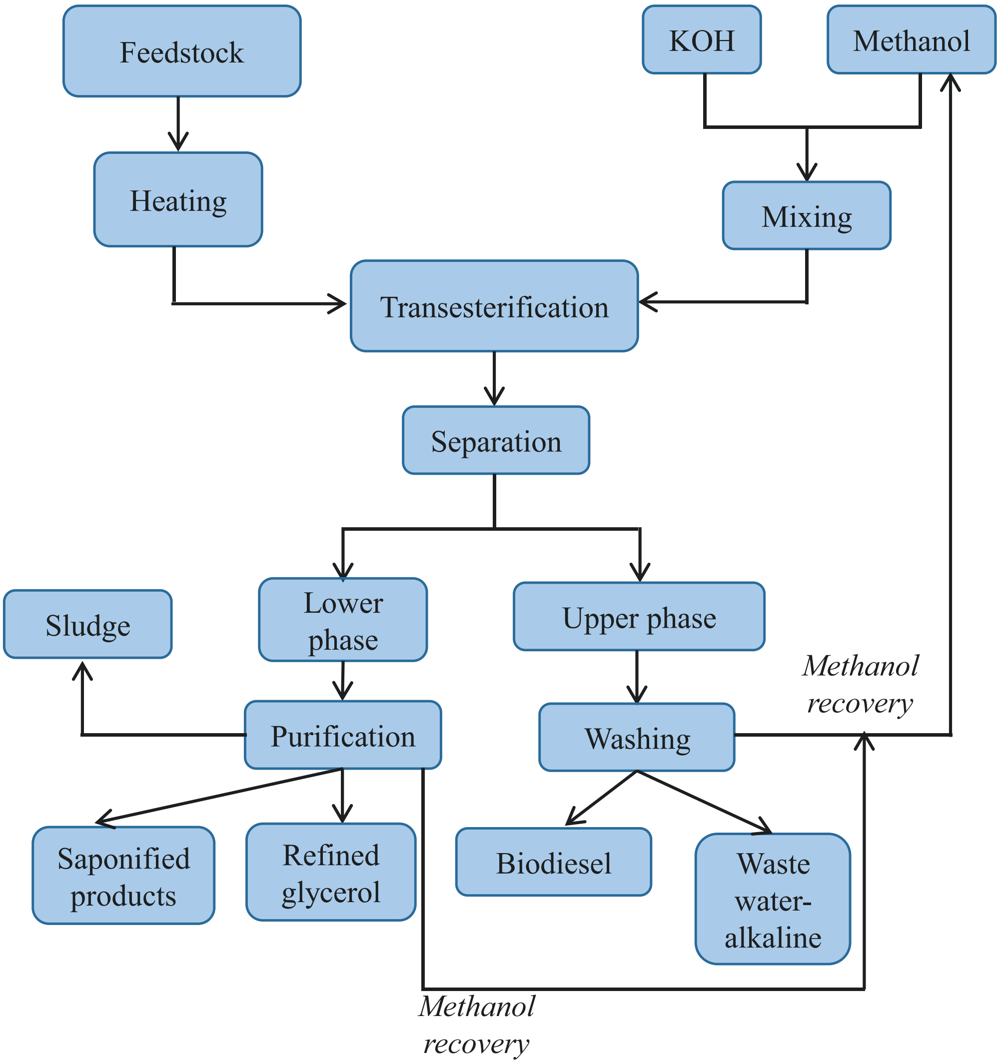


Fig. 2.11. Biodiesel production using alkali-catalyzed transesterification process.

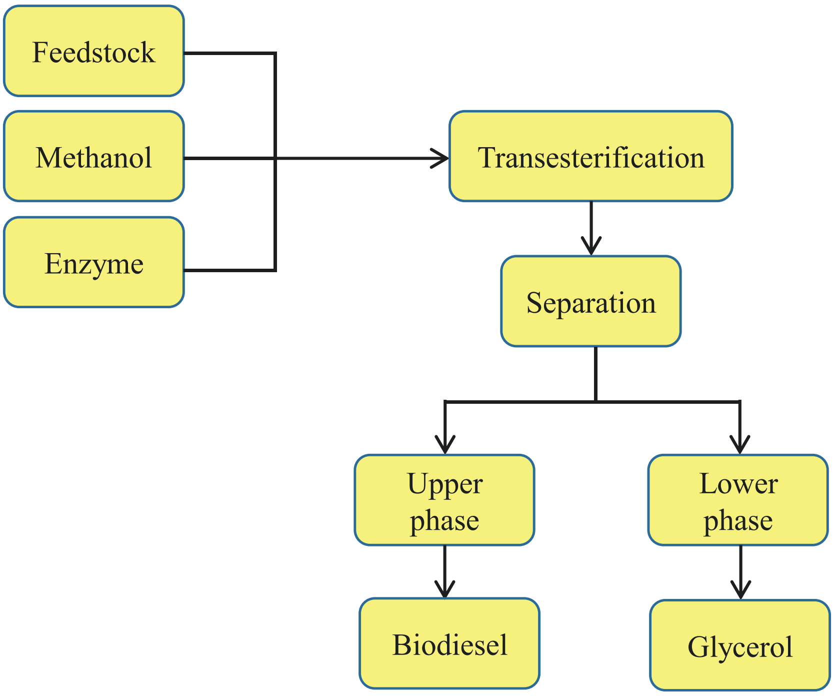


Fig. 2.12. Biodiesel production using enzymatic-catalyzed transesterification process.

Besides that, another advantages of biodiesel production using enzymatic-catalyzed transesterification route over the chemical-catalyzed transesterification route are as follows (Fukuda et al., 2001, Hama et al., 2004, Oda et al., 2004, Kulkarni and Dalai, 2006, Fukuda et al., 2008, Marchetti et al., 2008, Atadashi et al., 2011):

- Generation of zero by-products.
- Use of moderate reaction temperatures (35–45 °C).
- Easier separation and recovery of product.
- High selectivity of esterification-transesterification process towards substrate.
- Insensitive to high free fatty acid (FFA) or water content of the feedstock.
- Avoidance of side reactions such as saponification or hydrolysis.
- Lower oil-to-alcohol molar ratio required.
- High possibility of enzyme to reuse.
- The ability to convert FFA and triglyceride to biodiesel simultaneously.
- Biodegradability of enzyme.

Despite the attractiveness of enzymatic-catalyzed transesterification process, it is still facing some constrains, especially for industrial application (Fukuda et al., 2001, Meher et al., 2006, Bajaj et al., 2010, Macaira et al., 2011) such as:

- High production cost of enzyme.
- Higher reaction times compared to the alkali-catalyzed transesterification route.
- Enzyme inhibition by methanol.
- Enzyme deactivation.
- Regeneration of enzyme is limited with an extended operation time.

During the past few years, some researchers have utilized lipase produced from microorganisms including fungi, bacteria, and yeasts. Lipase-producing fungi that were used in the previous study are *Alternaria brassicicola, Aspergillus fumigates, Aspergillus japonicas*, *Aspergillus nidulans*, *Aspergillus*, *Candida antarctica*, *Fusarium heterosporum*, *Humicola lanuginose*, *Mucor miehei*, *Oospora lactis*, *Penicillium cyclopium*, *Rhizomucor miehei*, *Rhizopus chinensis* and *Rhizopus microsporous*, *Rhizopus niveus*, *Rhizopus nodosus*, *Rhizopus oryzae*, *Streptomyces cinnamomeus*, *Streptomyces exfoliates*, *Streptomyces fradiae*, *Streptomyces* sp., *Rhizopus arrhizus*, *Thermomyces lanuginous*. Meanwhile, the lipase-producing bacteria are *Achromobacter lipolyticum, Acinetobacter radioresistens, Acinetobacter calcoaceticus, Acinetobacter pseudoalcaligenes*, *Aeromonas hydrophila*, *Archaeglobus fulgidus*, *Bacillus acidocaldarius*, *Bacillus pumilus*, *Burkholderia glumae*, *Chromobacterium viscosum, Staphylococcus aureus*, *Pseudomonas mendocina, Bacillus megaterium, Bacillus stearothermophilus*, *Bacillus subtilis*, *Bacillus thermoleovorans*, *Chromobacterium visosum*, *Enterococcus faecalis*, *Micrococcus freudenreichii, Pasteurella multocida*, *Propionibacterium avidium* and *Propionibacterium granulosum*, *Pseudomonas aeruginosa*, *Pseudomonas cepacia*, *Pseudomonas alcaligens*, *Pseudomonas putida,* *Psychrobacter immobilis, Serratia marcescens, Staphylococcus canosus*, *Staphylococcus epidermidis, Staphylococcus haemolyticus*, *Staphylococcus hyicus, Staphylococcus warneri*, *Statphylococcus stolonifer*. In addition, the lipase-producing yeasts previously used are *Candida deformans*, *Candida parapsilosis*, *Candida rugosa*, *Candida quercitrusa*, *Geotrichum candidum*, *Pichia burtonii* and *Pichia sivicola*, *Pichia xylose, Saccharomyces lipolytica*, and *Yarrowia lipolytica* NRRL YB-423 (Christopher et al., 2014).

Among lipase-producing microorganisms mentioned above, *Candida* sp., *Pseudomonas* sp., and *Rhizopus* sp. are the most frequently reported enzyme sources for biodiesel production (Benjamin et al., 1998). *Candida antartica* or it is well known as Novozym 435 was firstly used by Nelson et al. (1996) for biodiesel production using tallow as a feedstock. They found that the biodiesel yield of 96.4% was obtained at 45 °C, tallow-to-alcohol molar ratio of 1:3, reaction time of 16 h, and stirring speed of 200 rpm. In addition, it was found that the addition of water with the amount of 6 mol% based on tallow into the system could improve ester production when secondary alcohol was employed. It is because water is an essential element to enhance activity of the enzyme. However, the addition of an enormous amount of water could reduce the yield of biodiesel since the hydrolysis of triglyceride generates FFA and diglyceride. It was reported by several researchers that *Candida antartica* immobilized on acrylic resin was the most useful lipase among extracellular enzymes by using methanol as acyl acceptor employed for transesterification process of vegetable oils (Shimada et al., 1999, Xu et al., 2003, Du et al, 2004). Other than Novozym 435, *Pseudomonas cepacia* (PS 30) also has been used to produce biodiesel, but the catalytic activity of this enzyme was small. Nelson (1996) invetigated that biodiesel yield obtained from transesterification of tallow by using primary alcohol such as methanol, ethanol, and isobutanol is merely

13.9–28.8%, whereas, by using secondary alcohol such as isopropanol, biodiesel yield of 44.1% was obtained. The reaction conditions used in that previous study are reaction time of 5 h, reaction temperature at 45 °C, 0.34 molar of triglyceride in hexane, oil-to-methanol molar ratio of 1:3, 12.5-25 wt% enzyme, and stirring speed of 200 rpm. In another previous study, Noureddini et al. (2005) also reported that biodiesel yield of 67% was obtained from catalytic conversion of 10 g soybean oil using immobilized *Pseudomonas cepacia* at 35 °C, reaction time of 1 h, oil-to-methanol molar ratio of 1:7.5, 475 mg enzyme, and containing 50 g kg^{-1} water. In addition, *Rhyzopus oryzae* was also one of the most commonly used lipase-producing microorganisms for biodiesel production. Chen et al. (2006) discovered that biodiesel yield in the range of 88-90% was obtained for enzymatic conversion of waste cooking oil at 40 °C, pressure of 1 atm, reaction time of 30 h, oil-to-methanol molar ratio of 1:4, and immobilized lipase-to-oil weight ratio of 30%. They applied a three-step batch transesterification and stepwise process under these conditions.

Based on the immobilization method, enzymatic biodiesel production is divided into two possible methods, namely extracellular enzyme and immobilized whole cell (intracellular enzyme). Comparisons of steps involved using both extracellular enzyme and immobilized whole cell (intracellular enzyme) are presented in **Fig. 2.13**. As shown in this figure, immobilized whole cell (intracellular enzyme) technique is more efficient than extracellular enzyme because in the extracellular lipase, separation and purification are required before immobilization of enzyme.

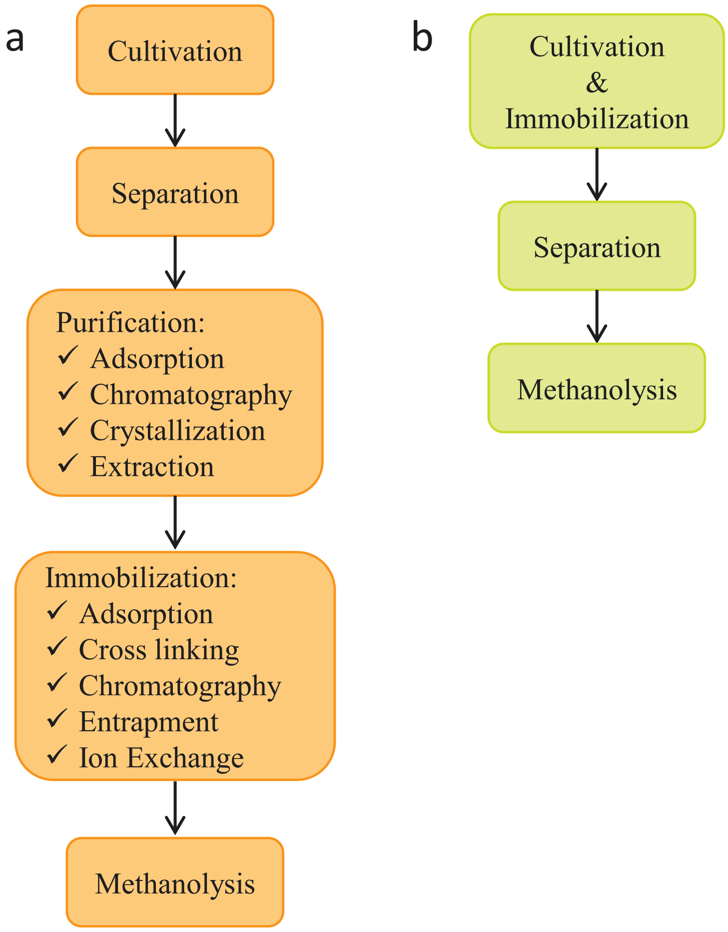


Fig. 2.13. Steps involved in enzyme-catalyzed biodiesel production for (a) extracellular enzyme and (b) immobilized whole cell (intracellular enzyme) (adapted from Ranganathan et al., 2008).

Immobilization of enzyme is a vital part for enzymatic-catalyzed biodiesel production. In this process, enzymes are attached physically to a solid support through various methods such as adsorption (Rathi et al., 2001), cross-linking (Lee et al., 2006), entrapment (Lee et al., 2009), or ion exchange (Yang et al., 2006). The solid supports used can be either natural or synthetic supports. According to Chawla et al. (2012) and Datta et al. (2013), the support and technique selection are based on the nature of substrate, enzyme nature, and the type of reaction. Compared to free enzyme, the immobilized enzymes provide some advantages such as stabilization of enzyme as a result of binding to support, rapid termination of the enzyme-substrate reaction, and no contamination (Raghuvanshi and Gupta, 2010).

Matsumoto et al. (2011) developed the whole cell enzyme for biodiesel production by immobilizing *Rhyzopus oryzae* cells. It was reported that biodiesel content of 71% was observed at 37 °C after 165 h reaction time. In this study, three stepwise methanolysis of plant oil without addition of solvent and water was employed. In another study, Ban et al. (2011) reported that a high conversion of 90% to biodiesel was obtained with stepwise methanol and addition of 15% water content using immobilized whole cell *Rhyzopus oryzae*. They also found that several substrate related compounds, especially olive oil and oleic acid could enhance the methanolysis activity of the immobilized cells. In addition, the same researchers, Ban et al. (2012) also examined the effectiveness of cross-linking treatment with the addition of 0.1% glutaraldehyde in order to stabilize *Rhyzopus oryzae*. They observed that a conversion to biodiesel was only obtained 50% in the stepwise addition without cross-linking treatment, whereas, the conversion to biodiesel was obtained 72-83% with cross-linking treatment after six batch cycles for both conditions. Biodiesel production by utilizing whole cell enzyme treated with lower alcohols has been patented by Fukuda and Kondo (2003). It was reported that the reaction rate of biodiesel production using cells treated with lower alcohols increased 350-600 times compared to untreated cells.

Effect of alcohols on enzymatic activity for biodiesel production was also studied by some researchers. Stoichiometrically, biodiesel production using alcohol as reactant required three moles of alcohol for each mol of triglyceride. The addition of an excess amount of alcohol is a common for conventional biodiesel production to shift the equilibrium to biodiesel formation due to the fact that transesterification proceed on a reversible reaction (Vyas et al., 2011). However, in enzymatic biodiesel production, the decrement of biodiesel yield was observed with the addition of high concentration methanol since the polar short chain of alcohol might inhibit the enzyme activity and interfere the separation of glycerol (Encinar et al., 2002, Mata et al., 2012). Thus, it is noted that the enzymatic biodiesel production requires lower alcohol to oil ratio than chemical-catalyzed biodiesel production (Narasimharao et al., 2007, Tamalampudi et al., 2008). According to some previous studies, it is common to add alcohol with the oil-to-alcohol molar ratio of 1:3 and 1:6 for enzymatic biodiesel production (Bernardes et al., 2007, Demirbas, 2008, Mata et al., 2012).

Some researchers investigated the effect of oil-to-methanol molar ratio on biodiesel yield catalyzed by immobilized lipase using vegetable oil. Du et al. (2003) reported that FAME yields of 75, 92, and 80% were obtained for *Thermomyces lanuginose* IM lipase methanolysis treated by employing oil-to-methanol molar ratio of 1:3, 1:4, and 1:5, respectively in a solvent-free system. In addition, the maximum yield of biodiesel (95%) was achieved by immobilized *C. antartica* lipase reaction at oil-to-methanol molar ratio of 1:3 (Shimada et al., 1999). Another study by Garlapati et al., (2013) revealed that a maximum yield of biodiesel (91.5%) was obtained by methanolysis of *Simarouba glauca* oil using a fungal immobilized lipase at oil-to-methanol molar ratio of 1:1. Moreover, Li et al., (2006) observed that a methanolysis of lipase-catalyzed transesterification produced a maximum yield of 95% biodiesel using rapeseed oil and oil-to-methanol molar ratio of 1:4. Thus, from these previous studies, it is confirmed that a maximum yield of biodiesel for enzymatic-catalyzed biodiesel production could be achieved by employing oil-to-methanol molar ratio in the ranges of 1:1 and 1:5.

In the previous studies, some alcohols such as methanol, ethanol, propanol, n-butanol, isopropanol, and isobutanol have been used as the reaction medium for biodiesel production. Among them, methanol is the most frequently used reactant for enzymatic-catalyzed transesterification due to high reactivity and lower cost than other alcohols. However, it was elucidated by Nelson et al., (1996) that the short chain alcohols are easier to inactive enzyme than longer aliphatic alcohol. To overcome the problem regarding the inhibition of methanol addition in enzymatic biodiesel production, some researchers have suggested some strategies such as: (1) stepwise addition of methanol (Shimada et al., 1999, Watanabe et al., 2000, Matasolli et al., 2009, Shimada et al., 2002), (2) use of solvent (Yu et al., 2013), and (3) use of alternative acyl acceptors such as alkyl esters or longer chain alcohols (Li et al., 2007).

Stepwise addition of methanol in order to circumvent the problem due to the inhibition of reactant have been carried out by several researchers. Shimada et al. (1999) reported that a biodiesel yield of 95% was achieved through stepwise addition of methanol even after 50 cycles of operation. The same researchers, Shimada et al. (2002) obtained conversion to biodiesel above 90% via stepwise addition of methanol using waste cooking oil as a feedstock. In another study, Watanabe et al. (2000) also observed that an optimum yield of biodiesel (90%) was achieved by conducting experiment on two-step batch wise addition of methanol and three-step continuous addition of methanol, and the yield was maintained even after 100 batches of operation. Similarly, a biodiesel yield of 97% was achieved through three-step wise addition of 0.3 M equivalent of methanol using plant oil as feedstock (Samukawa et al., 2000). The usage of regiospecific lipase (intolerant to the inhibition of methanol such as *R. oryzae*) and non-regiospecific lipase (tolerant to the inhibition of methanol such as *C. rugosa*, *P. cepacia* and *P. fluorescens*) have been used by Kaida et al. (2000). It was established that biodiesel yields with the range of 80-90% were obtained with stepwise addition of methanol using regiospecific lipase in the presence of 4-30% water. Therefore, it was confirmed that the inhibition effect of methanol to enzyme activity can be minimized by employing stepwise addition of methanol.

Apart from that, the use of organic solvent such as hexane, n-heptane, t-butanol, 1.4-dioxane, benzene, and chloroform was also believed to be able to reduce the inhibition of methanol since it could give the positive effects includes: protect lipase from denaturation due to increased solubility of methanol, prevent inhibition of lipase due to increased solubility of glycerol, and creation of single phase (Royon et al., 2007, Liu et al., 2009). Soumanou and Bornscheuer (2003) studied the effect of organic solvent on alcoholysis of sunflower oil using *Pseudomonas fluorescens*. It was found that the highest conversion to biodiesel (80%) was achieved by adding n-hexane and petroleum ether. In another study, it was reported that the addition of t-butanol could enhance biodiesel in which a maximum yield of biodiesel (94%) was obtained at 55°C with t-butanol-oil volume ratio of 0.8:1 after 48 h of reaction time (Kumari et al., 2009). In addition, Linko and Yan (1996) reported that the addition of 2-ethyl-1-hexanol could improve the conversion of rapeseed oil to biodiesel up to 97%. Besides, it was observed that the use of alternative acyl acceptors to methanol such as isopropanol, t-butanol, octanol, methyl acetate and ethyl acetate can circumvent the inhibition effect of methanol (Iso et al., 2001, Du et al., 2004, Li et al., 2006, Modi et al., 2007).

2.2.4. Biodiesel production under supercritical conditions

As mentioned previously, chemical-catalyzed transesterification processes are still facing the problem such as a tremendous amount of waste water generated, sensitivity to high FFA and water content and difficulties in separation of downstream steps. Other drawbacks of this method are the formation of undesirable products, low glycerol purity and high cost of catalyst that make the process uneconomical. In addition, the removing traces of the catalyst from the system is also a necessity, so that it brings to complicated purification steps. Enzymatic-catalyzed transesterification process is firstly expected to be able to circumvent those problems due to more environmentally benign, milder reaction temperature, and higher biodiesel quality over chemical-catalyzed biodiesel production. However, again, this method still has some constrains to be applied in industrial scale due to expensive production of enzyme and long reaction time even more than one day. In addition, this enzyme is sensitive to the presence of organic solvent.

To circumvent the problems faced by chemical and enzymatic-catalyzed transesterification process, Saka and Dadan, proposed a novel method to produce biodiesel without the addition of any catalysts under supercritical conditions (Saka and Dadan, 2001). This new approach provides some advantages as follows:

- No need catalyst
- Fast reaction rate, typically at a few minutes level.
- Transesterification of triglyceride and esterification of FFA occur simultaneously.
- Higher production efficiency since it requires a smaller number of processing step.
- Environmentally benign benefits.
- Simpler separation and purification steps.

- More tolerant to the presence of free fatty acid (FFA) and water.
- Applicability to a wide variety of feedstock.
- Being simple and easy for continuous production.

Andrews (1869) first discovered the supercritical state of fluid. Supercritical condition is defined as the fluid's temperature and pressure above the supercritical state. For instance, supercritical methanol is a methanol above the critical state (T_c = 239.2 °C, P_c = 8.09 MPa). The diagram phase of methanol is presented in **Fig. 2.14**. It is well known that fluids demonstrate properties of both liquid and gas under supercritical conditions. Under such condition, small changes in temperature and pressure bring in a dramatic change in density of methanol leading to increasing the solubility properties and decrease mass-transfer limitations. Therefore, under supercritical methanol, the feedstock or triglyceride and methanol become a single phase due to an increase in density of methanol and decreasing of dielectric constant. There are two reasons how triglyceride and methanol can react under supercritical conditions. First, at high temperature and high pressure, the polarity of methanol diminish (Saka and Kusdiana, 2001). It is known that methanol is a polar compound and has hydrogen bonding between OH hydrogen and OH oxygen to generate methanol agglomerates as shown in **Fig. 2.15**. However, at high temperature and high pressure, the degree of hydrogen bonding reduces results in the decreasing polarity of methanol. Thus, the triglyceride that is a non-polar compound can be dissolved with the methanol under supercritical conditions to form a homogeneous phase. Second reason is that the solubility of triglyceride increases with increasing temperature and pressure as observed by Glisic and Skala (2010).

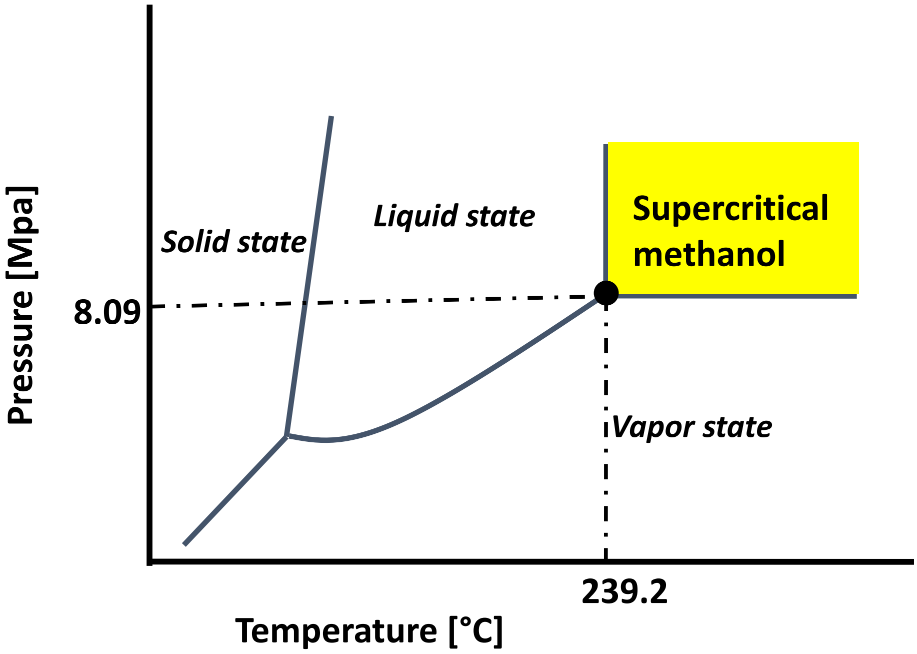


Fig. 2.14. Phase diagram of methanol.

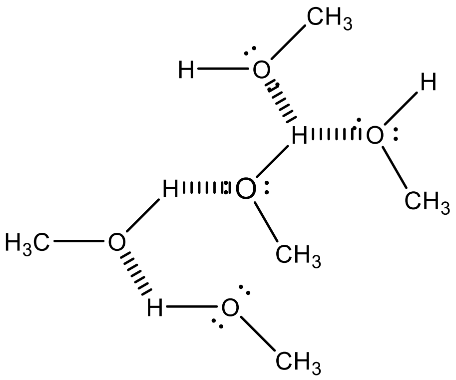


Fig. 2.15. Hydrogen bonding in methanol.

The phase transition of methanolysis of triglyceride under subcritical and supercritical conditions have been studied by Glisic and Orlovic (2012). It was reported that during the methanolysis of triglyceride, the distribution of methanol, triglyceride, biodiesel, and glycerol was changed depending on the temperature and pressure of the reaction. They divided the phase transition into three types; the first type is a phase transition for temperature below 270°C and pressure less than 1.5 MPa. The second type is a phase transition found at subcritical conditions (170–220 °C and 1.5–5.0 MPa), and the last type is a phase transition observed around supercritical point. The possible number of phases and phase composition at the different reaction temperature and pressure is schematically presented in **Fig. 2.16.**

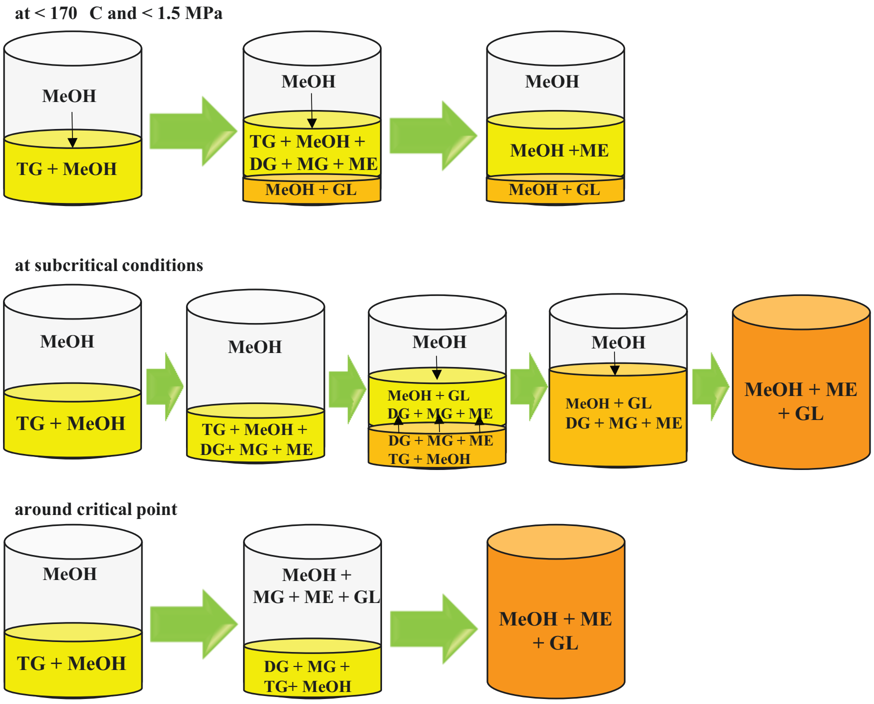


Fig. 2.16. The phase distribution and composition as a result of reaction between methanol and triglycerides at different reaction conditions (adapted from Glisic and Orlovic, 2012).

The reaction mechanism between triglycerides and methanol under supercritical conditions was firstly proposed by Kusdiana and Saka (2004a). Since at high temperature and high pressure methanol clusters will break to be a free monomer, this methanol can attack carbon atom of carbonyl functional group from triglycerides. This process results in intermediate compound via transfer of a methoxide moiety. The next step is rearrangement of intermediate compound to generate more stable compounds, namely biodiesel and diglyceride. In a similar way, this diglyceride will react with other methanol molecules forming biodiesel and monoglyceride. In the last step, the reaction between monoglyceride and methanol results in biodiesel and glycerol. The proposed reaction mechanism of triglycerides in supercritical methanol is presented in **Fig. 2.17**.

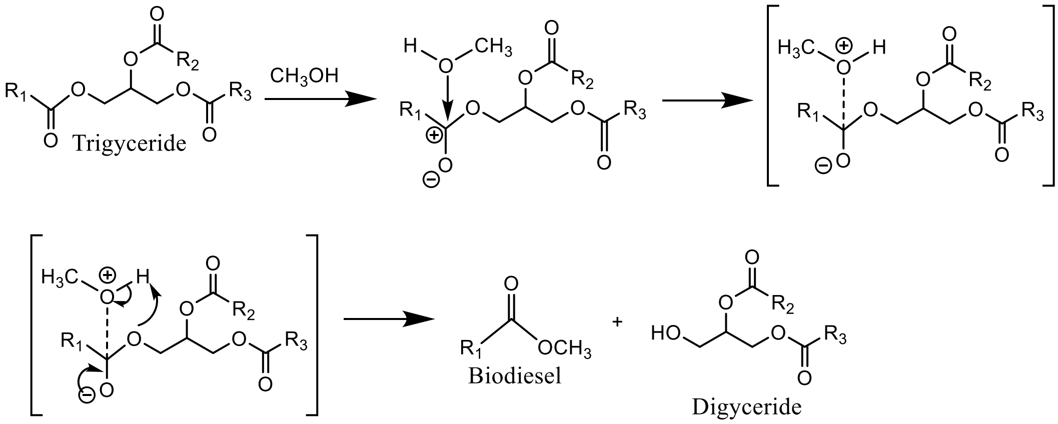


Fig. 2.17. The proposed reaction mechanism between triglyceride and methanol under supercritical conditions (adapted from Kusdiana and Saka, 2004a).

Despite the attractiveness of non-catalytic biodiesel production under supercritical conditions, this method is still facing some limitations such as a high oil-to-alcohol molar ratio and high temperature and pressure required. To circumvent the problem facing in non-catalytic biodiesel production under supercritical conditions, some researchers suggested the improvement method such as process modification, the addition of co-solvent, and the use of catalysts. Process modification was carried out using two-step processing. This method was proposed by Kusdiana and Saka (2004b). In the first step, triglycerides are hydrolyzed under subcritical water to generate free fatty acid and glycerol. In the second step, FFA is then esterified by employing lower oil-to-methanol molar ratio following the reaction as shown in **Fig. 2.18**. This technology certainly can reduce energy consumption due to milder operating conditions (270 °C, 7 MPa) compared to the last one-step biodiesel production (350 °C, 20-50

MPa). In addition, this method required the less oil-to-methanol molar ratio compared to the previous one.

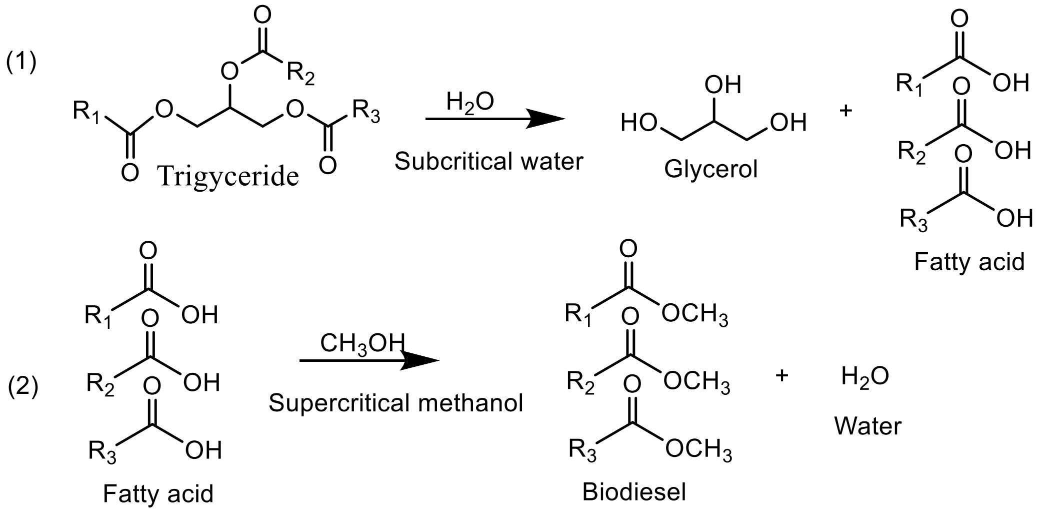


Fig. 2.18. Two-step processing for non-catalytic biodiesel production.

The addition of co-solvent has also been proposed to reduce the severity conditions for biodiesel production in supercritical methanol. The addition of co-solvent was assumed could increase the mutual solubility between triglycerides and methanol and might decrease the critical point of methanol. Consequently, biodiesel can be produced under milder conditions. Several co-solvents used for biodiesel production under supercritical conditions are propane, carbon dioxide, ethane, propane, n-butane, n-hexane, n-heptane, and tetrahydrofuran (THF). Cao et al. (2005) reported that the reaction temperature can be significantly reduced to 280 °C to obtain a complete conversion of biodiesel using propane as co-solvent with propane-to-methanol molar ratio of 0.1. Imahara et al. (2009) observed the addition of carbon dioxide as co-solvent increased the yield of biodiesel in the methanolysis of canola oil. However, it decreased by employing a higher molar of carbon dioxide, typically above 0.1 CO_2/methanol. By employing microtube reactor, Trentin et al. (2011) also investigated the effect of carbon dioxide addition on biodiesel yield under supercritical conditions. They found that a maximum yield of biodiesel was obtained with the addition of carbon dioxide-to-substrate mass ratio of 0.2:1. In addition, Tan et al. (2010) reported that the addition of 0.2 n-heptane-to-oil molar ratio gave a significant effect on palm oil conversion to biodiesel under supercritical methanol conditions. The effect of n-hexane addition as co-solvent was studied by Muppaneni et al. (2012), and the results showed that the maximum yield of biodiesel was achieved with the addition of 0.2 n-hexane-to-oil volume ratio.

Besides that, the addition of catalyst has also been proposed to improve biodiesel production under supercritical conditions. Demirbas (2007) investigated the effect of calcium oxide (CaO) addition on biodiesel yield conducted via supercritical method using sunflower as a feedstock. He reported that the biodiesel yield increased with CaO addition. In addition, it was found that the maximum yield of biodiesel was observed within 6 min at 525 K, oil-to-methanol molar ratio of 1:41 and the addition of 3wt% CaO. In addition, Yoo et al., (2010) also examined biodiesel production in supercritical methanol by adding several heterogeneous metal oxide catalysts such as SrO, CaO, ZnO, TiO_2, and ZrO_2. They discovered that the maximum yield of biodiesel (around 95%) was achieved by adding 1 wt% ZrO_2 at 250 °C and oil-to-methanol molar ratio of 1:40 within 10 min reaction time.

2.2.5. Microwave and ultrasound-assisted transesterification

Biodiesel also can be produced via microwave-assisted transesterification process. The advantages of this method include short reaction time and more environmentally friendly over conventional heating process. However, this method also has many constrains including high energy consumed, chemical catalysts needed, difficulties in scale-up due to unsafety operation, high temperature required, and sensitivity to FFA and water of feedstock as a result of reaction with catalyst. Thus, until now this technology cannot be used for commercial application.

During the past few years, many researchers have conducted an experiment on biodiesel production in laboratory scale via microwave-assisted transesterification process. Leadbeater and Stencel (2006) reported that the maximum yield of biodiesel (98%) was obtained at 323 K using 5% KOH or NaOH under 25 W microwave exit power and oil-to-methanol molar ratio of 1:6 for 1 min. Similarly, Azcan and Danisman (2008) used KOH as a catalyst, and they observed that the optimum conversion to biodiesel (93.7%) was achieved using 1.0% KOH at 313 K, for 1 min reaction time. In the same year, Reefat et al. (2008) investigated transesterification using KOH as a catalyst as well. They found that biodiesel production proceeded faster (2 min) in microwave irradiation compared with the conventional method (60 min). A year later, Zu et al. (2009) observed that the highest yield of biodiesel (96%) from yellow horn (*Xanthoceras sorbifolia* Bunge) oil was achieved at 60 C, 500 W power microwave irradiation, oil-to-methanol molar ratio of 1:6, and 1% wt catalyst for 6 min. Acid catalyst such as H_2SO_4/C was also used by Yuan et al. (2009) as a catalyst in microwave irradiation system. They found that the highest biodiesel yield (94%) was obtained at 338 K, oil-to-methanol molar ratio of 1:12, 5 wt% of catalyst for 60 min. In 2010, Sherbiny et al. (2010) studied the comparison between conventional and microwave irradiation for biodiesel production using *Jatropha* oil. They discovered that a complete conversion for microwave assisted transesterification could be obtained faster (2 min) compared with conventional method (60 min). Recently, this method has been applied to produce biodiesel from microalgae *Nannochloropsis* sp. by direct conversion (Koberg et al., 2011). They deduced that a direct transesterification using microwave irradiation gave a higher biodiesel yield (37.5%) compared to sonication method (20.9) within the same reaction time of 5 min.

Apart from that, ultrasound-assisted transesterification process has also been proposed as a technique to produce biodiesel, but the study about this is still limited. Due to the drawbacks associated with the downstream process and a tremendous amount of the chemical catalyst required, this method still cannot be applied for commercial purposes. Nishimura et al. (2003) investigated the biodiesel production from vegetable oil using low-frequency ultrasound (28-40 kHz). They found that a maximum yield of biodiesel (98%) was obtained at 25°C, 40 kHz, oil-to-methanol molar ratio of 1:6, 0.5% NaOH, and 20 min reaction time. Mootabadi et al. (2010) also examined transesterification of palm oil using ultrasound method with several alkali earth metal catalysts such as CaO, SrO, and BaO. They notified that the optimum yield of biodiesel, 95.2%, was obtained using oil-to-methanol molar ratio of 1:15 and 60 min reaction time for both BaO and SrO catalysts.

2.3. Biodiesel production under various supercritical reactants

Among methods explained above, biodiesel production under supercritical conditions is one of the most notable techniques in the future. Thus, in recent years, many researchers are focusing on the study of biodiesel production using this technology. So far, there are various reactants as well as the reaction medium used for non-catalytic biodiesel production under supercritical conditions, namely methanol, ethanol, methyl acetate, and dimethyl carbonate. The product and by-product obtained for each process are presented in **Fig. 2.19**. Some previous literatures regarding biodiesel production in supercritical methanol, ethanol, methyl acetate, and dimethyl carbonate are deeply discussed in this section.

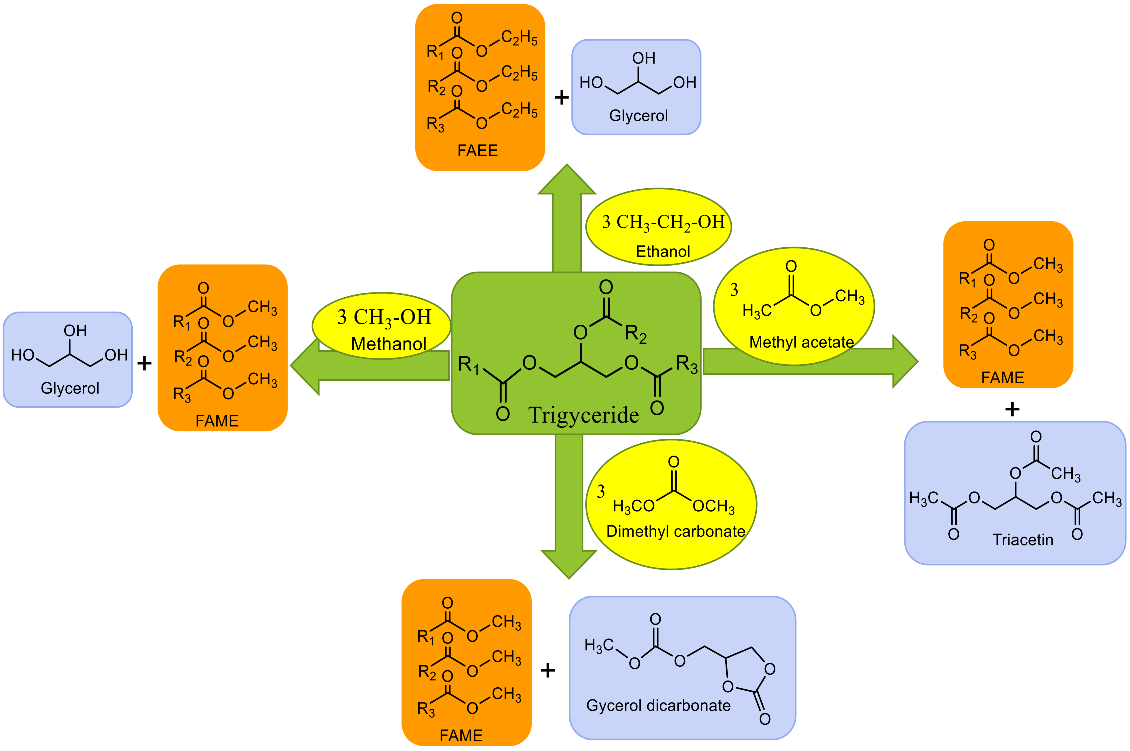


Fig. 2.19. Reaction of biodiesel production under various supercritical reactants.

2.3.1. Biodiesel production in supercritical methanol

As mentioned previously, biodiesel production in supercritical methanol was firstly studied by Saka and Dadan (2001) using batch type reactor. They concluded that the findings could answer the problem faced by chemical-catalyzed and enzymatic-catalyzed transesterification in which biodiesel could be produced in the shorter reaction time without the addition of any catalysts and simpler separation and purification in the downstream process.

A year later, Demirbas (2002) confirmed what Saka and co-workers found. He compared biodiesel production between conventional and non-catalytic supercritical methods using six vegetable oils, i.e., cottonseed, hazelnut kernel, poppy seed, rapeseed, safflower seed, and sunflower seed. He also observed that non-catalytic biodiesel production in supercritical methanol is superior over the conventional method in terms of reaction time required to produce biodiesel. Kusdiana and Saka (2001a) then elucidated the reaction behavior of free fatty acids (FFA) under supercritical methanol conditions without any catalysts. They found that FFA was successfully converted into biodiesel at 350 °C, and a complete conversion to biodiesel was found over 95%. This new finding proved that non-catalytic biodiesel production under supercritical condition can be applied for a wide variety of feedstock including waste cooking oil and waste lard which have high FFA.

In 2004, effect of water on biodiesel production in supercritical methanol was also discovered by the same researchers, Kusdiana and Saka (2004a). They noted that the presence of water did not affect so much on biodiesel yield. Meanwhile, a certain amount of water in the system could enhance the formation of biodiesel. They suggested that this water will hydrolyze triglyceride into FFA and glycerol, but FFA then reacts with methanol to generate biodiesel. Moreover, biodiesel under supercritical conditions has also been synthesized using bio-methanol prepared from wood gasification (Isayama and Saka, 2008). This bio-methanol contains some impurities such as ethanol, 1-butanol, methyl formate, water, and diisopropyl ether. They confirmed that the conversion to biodiesel was obtained with ethanol, 1-butanol, and methyl formate, whereas no conversion was made with diisopropyl ether.

Since the new finding of biodiesel production under supercritical methanol conditions was successfully investigated, this approach has attracted many researchers to conduct an experiment using this approach by employing various feedstocks. Song et al. (2008) investigated biodiesel production in supercritical methanol using batch reactor and RBD palm oil as a feedstock. They found that biodiesel production rate increase dramatically under supercritical conditions, but the FAME yield decreased above 350 °C due to thermal decomposition of RBD palm oil or biodiesel. The same derivative of oil palm, namely palm oil was also used as a feedstock for biodiesel production in supercritical methanol by Tan et al. (2009). They examined that more than 70% yield of biodiesel was obtained by employing non-catalytic supercritical methanol technology within 20 min. In addition, Kasim et al. (2009) discovered biodiesel production from low-cost materials such as rice bran and dewaxed degummed rice bran oil (DDRBO) oil using carbon dioxide as a co-solvent. They reported that *in situ* transesterification of rice bran with supercritical methanol under experimental conditions of 30 MPa, 300 and 5 min was not a promising way due to the low biodiesel yield (51.28%). *Jatropha curcas* L. seed has also been used as a feedstock for non-catalytic biodiesel production using supercritical fluid reactive extraction by Lim et al. (2010). They observed that optimum oil extraction efficiency of 105.3% and FAME yield of 103.5% w/w were observed at 300 °C, 240 MPa, 2.5 ml/g of n-hexane to seed ratio, and 10.0 ml/g methanol-to-solid ratio. Moreover, Patil et al. (2011) performed the optimization of single-step conversion of wet algal biomass (Inoculum *Nannochloropsis* sp., CCMP1776) containing about 90% water in supercritical methanol. They identified that optimum conditions for this process were met at 255 °C, 25 min and wet algae-to-methanol (wt/v) ratio of 1:9 based on the experimental data and response surface method (RSM) study. Biodiesel production from vegetable oil including sunflower, rapeseed, cottonseed, and camelina oils was also carried out in supercritical methanol by Anikeev and Yakovleva (2013). They concluded that the type of oil used did not affect significantly on the product yield and oil conversion value. Recently, Samniang et al. (2014) studied the comparison of biodiesel production from two different non-edible oils, namely crude *Jatropha* oil and *Krating* oil using this technique. Biodiesel yields of 90.4 and 84.6 % were obtained from transesterification of *Krating* and *Jatropha* oil, respectively at 320 °C, 15 MPa and oil-to-methanol molar ratio of 1:40 due to the higher FFA of *Krating* oil.

Low-grade feedstocks such as waste cooking oil and waste lard have also been used for biodiesel production in supercritical methanol. Demirbas (2009) studied the comparison of biodiesel production via base-catalytic and supercritical methanol transesterification using waste cooking oil. He found that supercritical methanol method was superior over base-catalytic transesterification providing the significant advantages such as FFA in the waste cooking oil was transesterified simultaneously and not sensitive in the presence of water and FFA. In addition, Shin et al. (2012) examined transesterification of waste lard in supercritical methanol using a batch-type reactor. They noted that a maximum yield of biodiesel (89.91 %) was obtained at 335 °C, 20 MPa, oil-to-methanol molar ratio of 1:45 within 15 min and an agitation speed of 500 rpm. Lee et al. (2012) also investigated biodiesel production from waste canola oil in supercritical methanol under relatively moderate conditions (240–270 °C/10 MPa).

They reported that the optimum yield of biodiesel made from this study was 102% that was obtained at 270 °C, 10 MPa, oil-to-methanol weight ratio of 2:1 for 45 min. Recently, Ghoreishi and Moein (2013) conducted the optimization of biodiesel production from waste vegetable oil in supercritical methanol using RSM. They evaluated that the optimum biodiesel yield (95.27%) was obtained at 271.1 °C, 23.1 MPa, oil-to-methanol molar ratio of 1:33.8 within 20.4 min reaction time using RSM.

Besides a batch mode reactor, some researchers also employed a continuous flow reactor to produce biodiesel under supercritical conditions. He et al. (2007a) investigated a continuous transesterification of soybean oil under supercritical methanol conditions. They found that the maximum yield of biodiesel was 77% obtained at 310 °C, 35 MPa, oil-to-methanol molar ratio of 1:40 after 25 min residence time. Similarly, Zhou et al. (2010) also examined continuous biodiesel production from soybean oil using vertical tubular reactor. They noted that a biodiesel yield as high as 92% was made at 375 °C after 1400 s at 15 MPa and a fixed oil-to-methanol molar ratio of 1:40. In addition, Macaira et al. (2011) also discovered transesterification of sunflower oil using a continuous reactor using supercritical methanol with the addition of dioxide mixtures as a co-solvent. They deduced that the reaction rate of biodiesel production using non-catalytic supercritical methanol is 20 time faster than that of conventional one, and the addition of co-solvent also could enhance the rate of the methanol supercritical transesterification. They also established that optimum yield of biodiesel (88%) could be achieved at 200 °C after 2 min reaction time.

In recent year, Tsai et al. (2013) performed non-catalytic biodiesel production of waste cooking oil with or without carbon dioxide addition using continuous reactor. Their finding is in contrary with the previous study of Macaira et al. (2011) in which they confirmed that the effect of carbon dioxide on biodiesel yield was negligible. The maximum yield of biodiesel (0.90) was obtained at 573.2 K within 13 min.

Reaction mechanism and kinetics of biodiesel production in supercritical methanol have also been reported in the previous studies. It is well known that the transesterification of triglyceride under supercritical methanol proceeds through three consecutive reaction steps. First, the reaction between triglyceride and methanol results in fatty acid methyl ester (FAME) and diglyceride. This intermediate compound, diglyceride then reacts with another methanol compound to generate FAME and monoglyceride. Finally, the reaction between monoglyceride and methanol gives FAME and glycerol. This reaction mechanism is presented in **Fig. 2.20**.

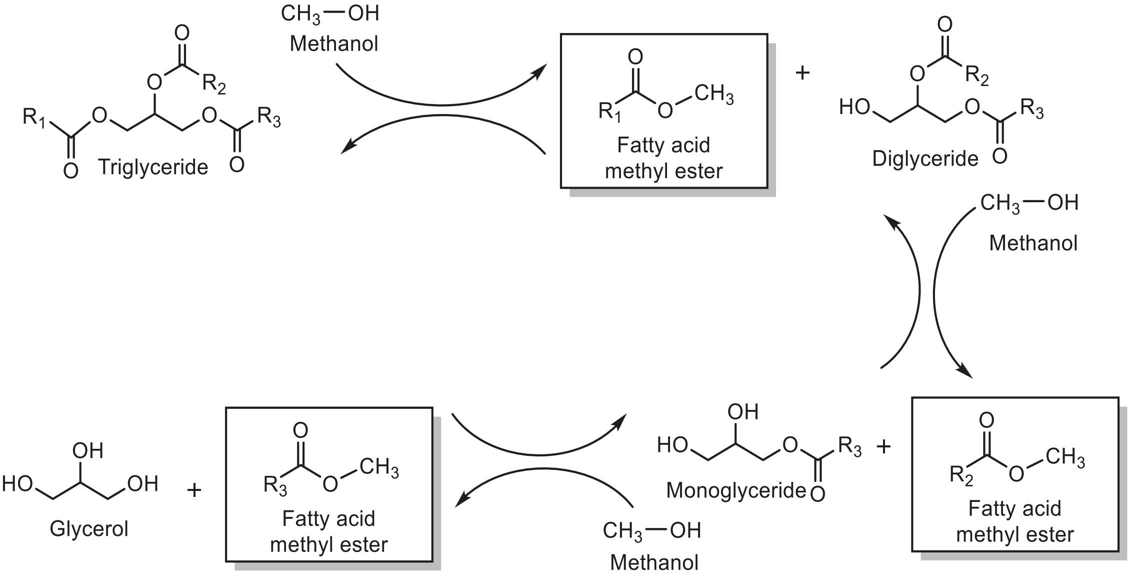


Fig. 2.20. Reaction mechanism of biodiesel production under supercritical methanol conditions.

He et al. (2007b) elucidated reaction kinetics of soybean oil conversion to biodiesel under supercritical methanol. The activation energy and the activation volume for transesterification of soybean oil under supercritical methanol were obtained approximately 56.0 kJ/mol and -206 cm3/mol, respectively. Similarly, Varma and

Madras (2007) also calculated activation energies for castor and linseed oil under conditions of 200–350 °C and 20 MPa. They determined activation energies of 35.00 and 46.50 kJ mol^{-1} for transesterification of castor and linseed oil in supercritical methanol, respectively. Recently, Choi et al. (2011) also deduced transesterification kinetics of palm olein oil at a reaction temperature of 350 °C, 35 MPa, oil-to-methanol molar ratio of 1:40 and a residence time of 20 min. They calculated activation energy, reaction activation volume, and entropy of activation of 81.37 kJ/mol, -175.35 J/molK, and -233.29 cm^3/mol, respectively.

2.3.2. Biodiesel production in supercritical ethanol

Since ethanol can be derived from biomass via fermentative process, some researchers are interested in exploring biodiesel production under supercritical ethanol conditions. In 2007, Silva et al. (2007) investigated biodiesel production from soybean oil under sub- and supercritical ethanol conditions using a tubular reactor. Experimental conditions were carried out at the temperature range of 473–648 K, pressure of 7–20 MPa, and oil to-ethanol molar ratio of 1:10 to 1:100. They found that under sub-critical conditions, fatty acid ethyl ester (FAEE) exhibited too low. Meanwhile, a biodiesel yield as high as 80% was observed at 623 K, 20 MPa, and oil-to-ethanol molar ratio of 1:40 within 15 min. A year later, Vieitez et al. (2008) also conducted an experiment on continuous production of soybean oil under supercritical ethanol conditions with the addition of water. Experiments were employed at 350 °C, 20 MPa, oil-to-ethanol molar ratio of 1:40. The results showed that biodiesel yields of 77.5 and 68.1% were obtained in a water-free system and 10 wt% of water addition, respectively. It demonstrated that the presence of water in the system gave an unconstructive to process efficiency. In 2009, Gui et al. (2009) performed the optimization of supercritical ethanol process for production using response surface methodology (RSM) by varying some parameters, namely temperature (300–400 °C), ethanol-to-oil molar ratio (5–50), and reaction time (2–30 min). It was reported in this study that optimum yield of biodiesel (79.2 wt%) was obtained at 349 °C, oil-to-ethanol molar ratio of 1:33 and reaction time of 30 min.

Recently, there is an interesting study of biodiesel production using this technology from 3rd generation of feedstock, i.e., microalgae *Nannochloropsis Salina* in which the authors transesterified wet algae by direct conversion without pretreatment (Reddy et al. 2014). They confirmed that the highest yield of biodiesel was 67% that could be made at 265 °C, dry algae-to-ethanol (w/v) ratio of 1:9 after 20 min.

One of the superiorities of biodiesel production under supercritical conditions over chemical and enzymatic-catalyzed transesterification is the easiness in producing biodiesel using continuous mode. There were several reports regarding continuous biodiesel production under supercritical ethanol conditions. da Silva (2010) conducted continuous production of biodiesel from soybean oil using microtube and tubular reactor. Experimental study was carried out in the temperature range of 523–598 K, pressure of 10–20 MPa and oil-to-ethanol molar ratio of 1:10–1:40 with the addition of carbon dioxide as co-solvent. They reported that the microtube reactor (inner diameter of 0.76 mm) could give higher biodiesel yield compared to the tubular reactor (inner diameter of 3.2 mm). It might be due to the mass transfer phenomenon. In addition, it was identified that the addition of co-solvent did not give a significant effect on biodiesel yield. In a similar way, Trentin et al. (2011) also investigated continuous biodiesel production under supercritical ethanol using micro-tube reactor, but there was no significantly different with the previous study conducted by da Silva (2010). In addition, Vieitez et al. (2011) performed continuous production of biodiesel from castor oil under supercritical ethanol conditions. They confirmed that a maximum yield of biodiesel was 74.2% obtained at 573 K, 20 MPa with addition of 5 wt% water, and feedstock flow rate of 0.8 ml min^{-1}.

Effect of FFA, co-solvent, and catalyst addition on biodiesel production in supercritical ethanol was also examined in the previous studies. Vietiez et al. (2012) investigated effect of FFA composition on the process efficiency of biodiesel production by a continuous supercritical ethanol using several feedstocks, namely soybean oil, rice bran oil, and high oleic sunflower oil. They noted that the addition of FFA on the system could enhance the efficiency of all vegetable oils conversion proven by higher biodiesel yield.

Effect of co-solvent such as n-hexane on biodiesel production in supercritical ethanol was reported by Muppaneni and co-workers using camelina oil (Muppaneni et al., 2012) and palm oil (Muppaneni et al., 2013) as feedstocks. They observed that the addition of co-solvent could improve biodiesel yield and reduce the severity of critical operational parameters. In addition, the optimum conditions obtained by employing RSM method were at 295 °C, oil-to-ethanol molar ratio of 1:45, n-hexane-to-oil ratio of 0.2% (v/v) within 20 min for camelina oil. Moreover, the optimum conditions for palm oil were established at 300 °C, oil-to-ethanol molar ratio of 1:33, n-hexane-to-oil ratio of 0.4% (v/v) within 30 min.

Few researchers elucidated a comparative study between methanol and ethanol under supercritical conditions. The first study was conducted by Warabi et al. (2004) using rapeseed oil in batch mode reactor. They established that the maximum yield of biodiesel (almost 100%) was obtained within 15 min in supercritical methanol, but it required 45 min in supercritical ethanol. In addition, Tan et al. (2010) performed optimization of biodiesel production in supercritical methanol and ethanol. They observed that the supercritical methanol could achieve a complete conversion about

85% at lower reaction time compared to supercritical ethanol with the biodiesel yield of 79.2%. Similarly, Vieitez (2010) also identified the same finding that oil conversion to biodiesel by methanolysis was higher than that by ethanolysis. A similar finding was reported by Santana et al. (2012) who examined a comparative study between methanol and ethanol in continuous mode reactor. They noted that supercritical methanol (SCM) gave biodiesel yield (90%) higher compared to supercritical ethanol (SCE) (80%) with residence time around 2 and 6 min for SCM and SCE, respectively. Newly, Kiss et al. (2014) also found the same report that SCM is superior to SCE in terms of reaction rate.

Similar to biodiesel production in supercritical methanol, reaction mechanism of triglyceride conversion to biodiesel under supercritical ethanol conditions also proceeds via three (3) steps reversible reaction as shown in **Fig. 2.21**.

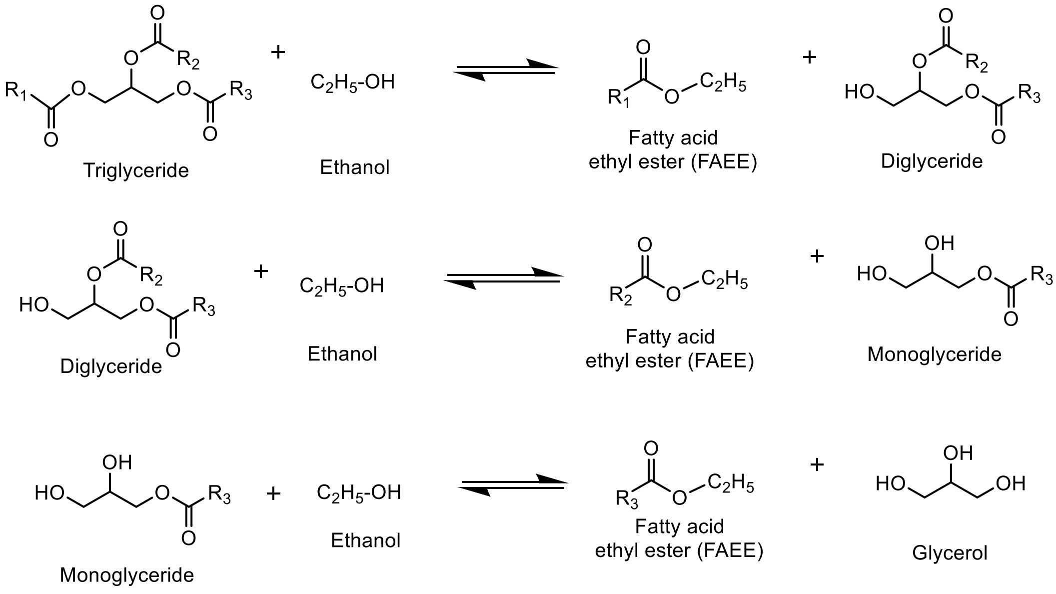


Fig. 2.21. Reaction mechanism of biodiesel production under supercritical ethanol conditions.

Some researchers elucidated the reaction kinetics of oil conversion to biodiesel under supercritical ethanol conditions. Velez et al. (2012) determined reaction kinetics of sunflower oil conversion to fatty acid ethyl ester (FAEE) under supercritical ethanol conditions in continuous mode reactor. They proposed a first-order kinetic model and calculated activation energy of 67.6 kJ/mol. In addition, Santana et al. (2012) also identified reaction kinetics of sunflower oil conversion to biodiesel in supercritical ethanol. They found that the activation energies of 104.82, 98.30, 91.69, 58.63, 125.99, and 139.95 kJ mol^{-1} were obtained for reaction conversion of TG to DG, DG to TG, DG to MG, MG to DG, MG to GL, and GL to MG, respectively. In another study by Silva et al. (2007), they calculated the reaction kinetics of transesterification of soybean oil in supercritical ethanol using a tubular reactor in a continuous mode, obtaining an activation energy of 78.7 kJ mol^{-1}.

2.3.3. Biodiesel production in supercritical methyl acetate

Due to an increasing of glycerol production as the main by-product of biodiesel synthesis process, some researchers proposed a new way of non-catalytic biodiesel production using supercritical methyl acetate method. Not only biodiesel but also triacetin that has higher added-value than glycerol was also obtained using this new approach. Reaction mechanism of biodiesel production in supercritical methyl acetate is presented in **Fig. 2.22**. Similar to the methanol route, transesterification of triglyceride in supercritical methyl acetate also proceeds through three reaction steps. In the first stage, reaction between triglyceride and methyl acetate results in fatty acid methyl ester and monoacetin diglyceride. In the same way, monoacetin diglyceride then reacts with another methyl acetate molecule forming fatty acid methyl ester and diacetin monoglyceride. In the last step, fatty acid methyl ester and triacetin are generated from diacetin monoglyceride and methyl acetate reaction. Overall, one molecule of triglyceride reacts with three molecules of methyl acetate to generate three molecules of biodiesel and one molecule of triacetin. However, since the reaction is reversible, it requires a tremendous amount of methyl acetate in order to obtain a complete conversion to biodiesel.

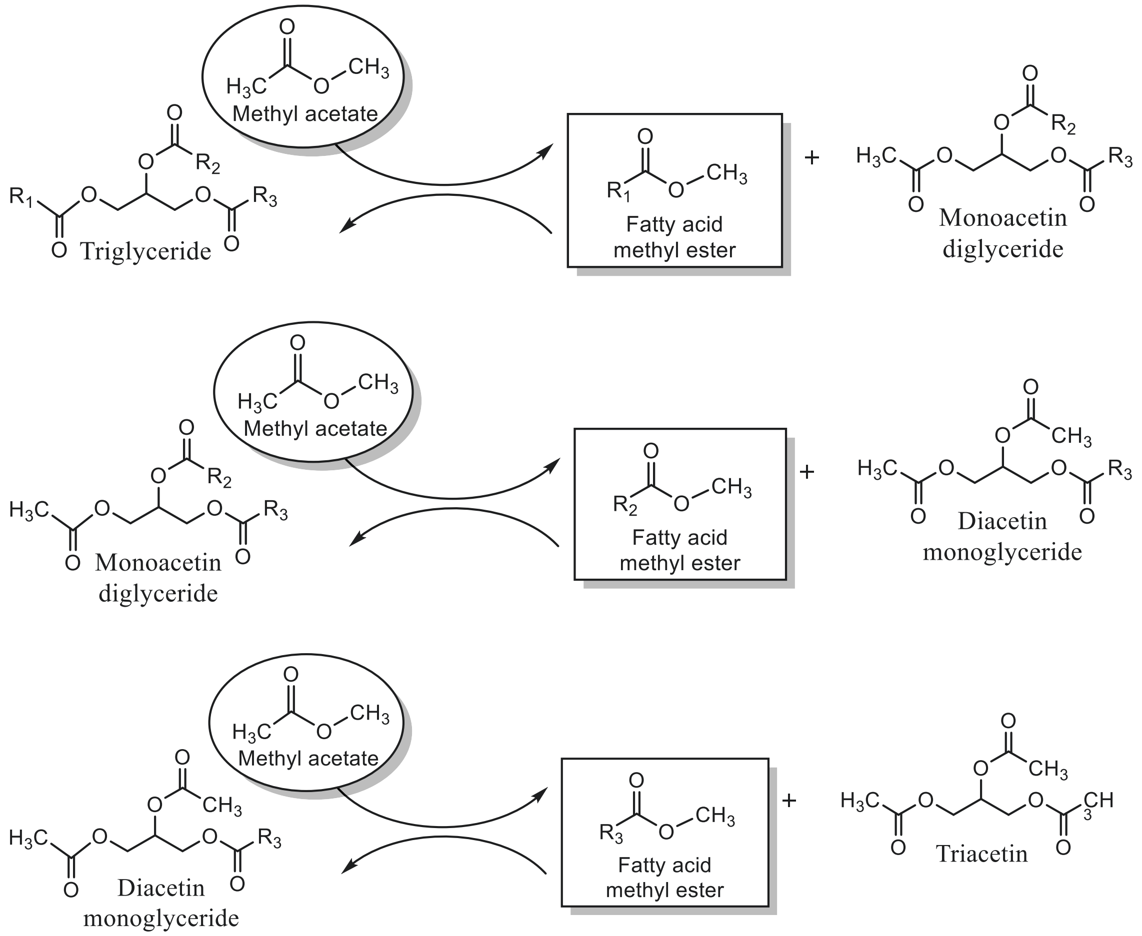


Fig. 2.22. Reaction mechanism of biodiesel production under supercritical methyl acetate conditions.

A new route of biodiesel production in supercritical methyl acetate was firstly invented by Saka and Isayama (2009). They investigated transesterification of rapeseed oil in supercritical methyl acetate at temperature range of 270–380 °C, reaction time of

10 to 120 min, a fixed pressure of 20 MPa, and oil-to-methyl acetate molar ratio of 1:42. It was reported that biodiesel fuel (BDF) composed of biodiesel and triacetin was successfully synthesized without producing glycerol with the yield of 105%. In addition, the study of BDF characteristics was proven that the addition of triacetin gave real effects on the drop point and oxidation characteristics.

A year later, Tan et al. (2010) followed what Saka and co-workers achieved. They conducted transesterification of palm oil in supercritical methyl acetate using batch-type tube reactor and optimized the experimental results by utilizing RSM approach. They discovered that the maximum yield of biodiesel (97.6%) was obtained at 399 °C, oil-to-methyl acetate molar ratio of 1:30 and reaction time of 59 min. Another study by the same researchers, Tan et al. (2011) performed supercritical methyl acetate method to produce biodiesel with the same method and the same feedstock. The different is only on the investigation of main factors affecting biodiesel under supercritical methyl acetate conditions in the latest report. They noted that the highest yield of biodiesel (99 wt%) was obtained at 400 °C/220 bar and oil-to-methyl acetate molar ratio of 1:30 for 60 min. An optimization of biodiesel production by supercritical methyl acetate was also carried out by Goembira and Shaka (2013). They examined four main factors to be considered to produce an optimum condition, namely temperature, reaction time, pressure, and oil-to-methyl molar ratio. They found that the optimum conditions of rapeseed oil conversion to biodiesel in supercritical methyl acetate was met at 350 °C/20 MPa/54 min/oil-to-methyl acetate molar ratio of 1:42. A FAME yield of 96.7 wt% and triacetin yield of 8.8 wt% were obtained under this condition.

Campanelli et al. (2010) also investigated biodiesel synthesis from soybean, sunflower, *J. curcas*, and waste soybean oil using this approach. They observed that the composition of oil or feedstock did not significantly affect biodiesel yield. In addition, it was found that a complete conversion to biodiesel was obtained at 345 °C, 20 MPa, oil-to-methyl acetate of 1:42 after 50 min for all feedstocks. In contrast, Dona et al. (2013) identified that the FFA content in the feedstock affected biodiesel yield. They examined biodiesel synthesis from two different types of feedstock, i.e. soybean and macauba oil under supercritical methyl acetate conditions using a tubular packed bed reactor. They reported that the highest biodiesel yield was merely 44% obtained for soybean conversion to biodiesel at 350 °C and oil-to-methyl acetate molar ratio of 1:5 for 45 min. Meanwhile, the maximum biodiesel yield of 83% was obtained at 325 °C, oil-to-methyl acetate molar ratio of 1:5 for 45 min. Biodiesel yield obtained from macauba oil is superior to soybean oil might be due to high free fatty acid content in macauba oil. They assumed that this free fatty acid reacts with methyl acetate to generate FAME and acetic acid following the reaction as presented in **Fig. 2.23**. In addition, they also concluded that acetic acid generated could act as an acid catalyst to enhance the transesterification process.

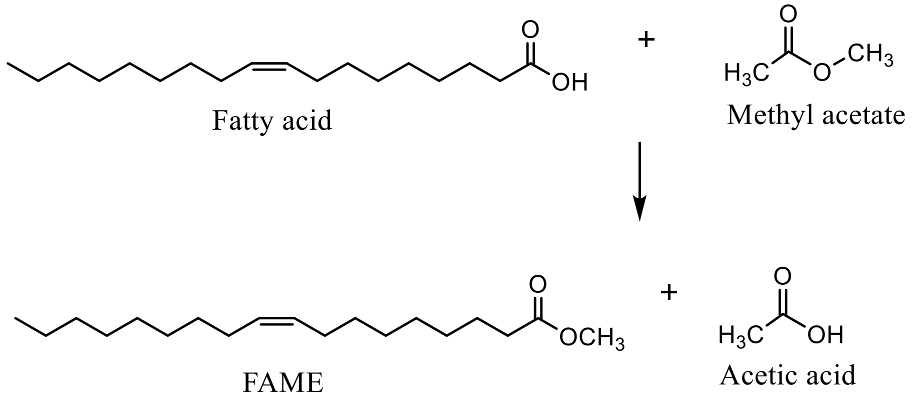


Fig. 2.23. Reaction between fatty acid and methyl acetate.

Biodiesel production using supercritical methyl acetate and methanol was also compared in the previous study. Niza et al. (2011) elucidated the different reaction behavior between methanol and methyl acetate under supercritical conditions using *J. curcas* oil. They reported that optimum yield of biodiesel in supercritical methanol of

89.4% was obtained under condition of 358 °C/27 min/oil-to-methanol molar ratio of 1:44. Meanwhile, the optimum yield of biodiesel in supercritical methyl acetate was 71.9% that was achieved under condition of 400 °C/32 min/oil-to-methanol molar ratio of 1:50. They also assumed that this difference could be attributed to reactivity and mutual solubility between oil and methanol or methyl acetate. In addition, thermal stability of biodiesel production in supercritical methyl acetate was studied by same researchers (Niza et al., 2013) in another paper. They discovered thermal stability of biodiesel production in supercritical methyl acetate at temperature range of 330–420 °C. They found that the decrement of thermal stability of poly-unsaturated methyl linoleate was observed with increasing temperature from 330 to 420 °C, whereas the thermal decomposition of methyl oleate was found above 390 °C.

Up to now, there is only one previous study determining reaction kinetics of transesterification under supercritical methyl acetate conditions. Campanelli et al. (2010) examined kinetics of soybean, sunflower, *J. curcas*, and waste soybean oil conversion to biodiesel at temperature range of 300 to 345 °C. They determined the activation energies of 373, 349, 364, and 369 kJ mol^{-1} for soybean, sunflower, *J. curcas*, and waste soybean oil, respectively.

Recently, effect of four additives (oleic acid, acetic acid, methanol, and water) on biodiesel production using supercritical methyl acetate method was published by Goembira and Saka (2014). They observed that the addition of acetic acid and water could enhance biodiesel yield, whereas the addition of oleic acid and methanol did not affect so much. At the milder reaction temperature, the higher biodiesel was obtained when the aqueous acetic acid was employed as additive. In addition, it was reported that the highest biodiesel under conditions of 300 °C/20 MPa/45 min was obtained by adding 10 wt% aqueous acetic acid. It was confirmed from this study that the addition of a potential additive could enhance the performance of biodiesel production using supercritical methyl acetate route.

Besides methyl acetate, other various carboxylate esters were also used as a reactant as well as the reaction medium for biodiesel production under supercritical conditions (Goembira et al., 2012). There are 12 carboxylate esters used in this study, namely methyl acetate, methyl propionate, methyl butyrate, ethyl acetate, ethyl propionate, ethyl butyrate, propyl acetate, propyl propionate, propyl butyrate, butyl acetate, butyl propionate, and butyl butyrate. As expected, among all carboxylate esters, supercritical methyl acetate gave the highest yield of biodiesel, i.e., 97.7 wt%. It should be due to the shorter chain of a carboxylate ester the more reactive to react with triglyceride.

2.3.4. Biodiesel production in supercritical dimethyl carbonate

Another new route to produce biodiesel is by employing dimethyl carbonate instead of using alcohol. By using this new method, biodiesel and glycerol dicarbonate are obtained. Different with the previous methods of supercritical methanol, ethanol, and methyl acetate, the reaction mechanism of biodiesel synthesis in supercritical dimethyl carbonate proceeds via two steps reversible reaction as presented in **Fig. 2.24**. Firstly, the reaction between triglyceride and dimethyl carbonate results in fatty acid methyl ester and fatty acid glycerol carbonate (FAGC). Secondly, FAGC then reacts with another molecule of dimethyl carbonate to generate another FAME molecule and glycerol dicarbonate. Thus, in the overall reaction, one molecule of triglyceride reacts with two molecules of dimethyl carbonate to generate three molecules of FAME and one molecule of glycerol dicarbonate.

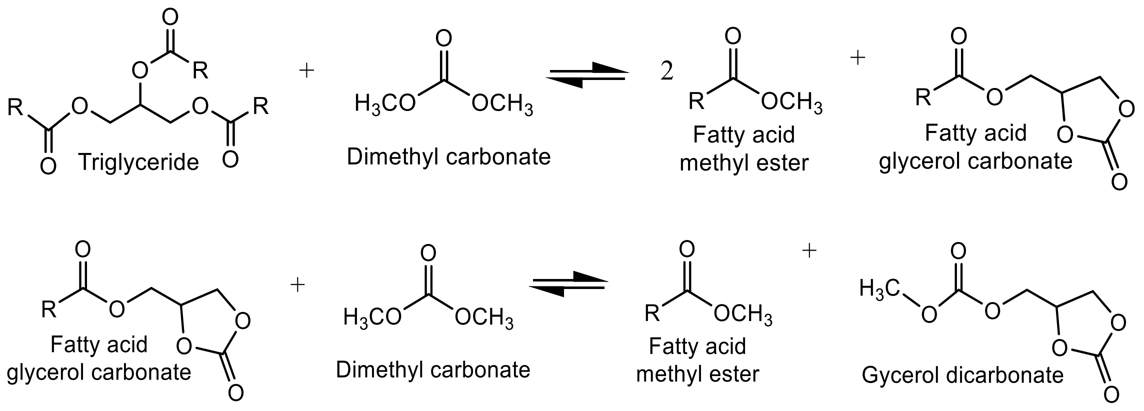


Fig. 2.24. Reaction mechanism of biodiesel production under supercritical dimethyl carbonate conditions.

Study about biodiesel production under supercritical dimethyl carbonate conditions is still limited. In addition, there is no previous report about reaction kinetics of oil conversion to biodiesel in supercritical dimethyl carbonate. It might be because reaction mechanism of biodiesel production in supercritical dimethyl carbonate is more complicated than supercritical alcohol and methyl acetate methods. Ilham and Saka (2009) firstly investigated biodiesel production from rapeseed oil in supercritical dimethyl carbonate using a batch type reactor (5 ml reaction vessel) made of Inconel-625. It was noted that the reaction between triglyceride and dimethyl carbonate under supercritical conditions gave fatty acid methyl ester, glycerol carbonate and citramalic acid. A complete conversion to biodiesel about 94% (w/w) was made at 350 °C, 20 MPa, oil-to-dimethyl carbonate molar ratio of 1:42 after 12 min. In addition, they observed that free fatty acid could react with dimethyl carbonate to generate FAME and glyoxal as presented in **Fig. 2.25**.

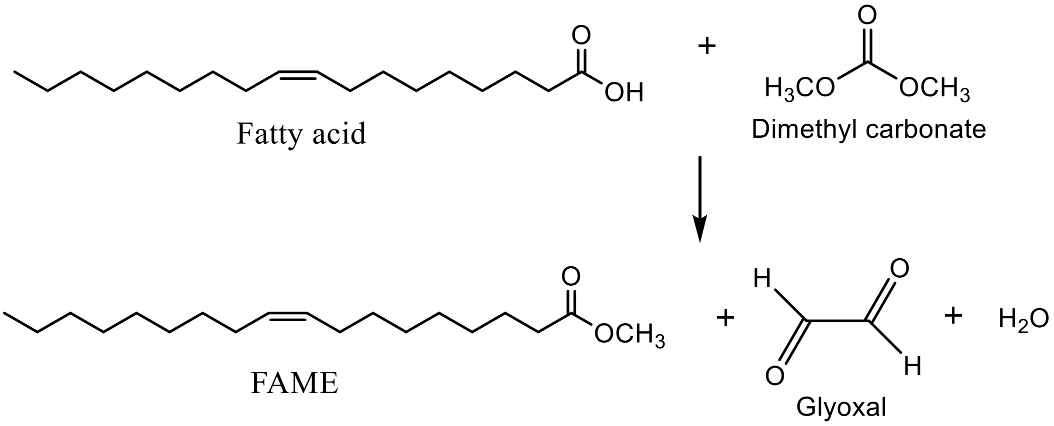


Fig. 2.25. Reaction between fatty acid and dimethyl carbonate.

A year later, the same researchers (Ilham and Saka 2010) also proposed two-step supercritical dimethyl carbonate method to produce biodiesel from *Jatropha curcas* oil. They reported that this study provided milder conditions than the previous one since triglyceride was firstly hydrolyzed under subcritical water and subsequently was esterified under supercritical dimethyl carbonate conditions. The reaction is shown in **Fig. 2.26**. It was found from this study that an optimum condition to produce FFA from triglyceride under subcritical water was 270 °C/27 MPa/25 min. Meanwhile, the optimum condition to produce biodiesel under supercritical dimethyl carbonate was 300 °C/9 MPa/15 min in which 97 wt% of biodiesel was obtained.

Optimization studies on biodiesel production using supercritical dimethyl carbonate method have also been carried out in the previous literatures. Tan et al. (2010) investigated the effect of important factors such as temperature, reaction time, and oil-to-dimethyl carbonate on biodiesel production from palm oil and optimized them using RSM analysis. They found that the optimum conditions for supercritical dimethyl carbonate process was obtained at 380 °C, 30 min and oil-to-dimethyl carbonate molar ratio of 1:39 achieving 91% yield of biodiesel. In another study by Ilham and Saka (2012), it was reported that the optimum condition for biodiesel production using supercritical dimethyl carbonate method was obtained at 300 °C, 20 MPa, 20 min reaction time, and oil-to-dimethyl carbonate molar ratio of 1:42, obtaining 97.4 wt% yield of biodiesel.

Recently, non-catalytic biodiesel production from coconut oil using dimethyl carbonate under ambient pressure was performed by Kwon et al. (2014). They conducted an experiment via a continuous flow mode using a tubular reactor. They reported that a complete conversion to biodiesel was achieved in a short reaction time of 1-2 min at 365–450 °C under ambient pressure, obtaining 98%.

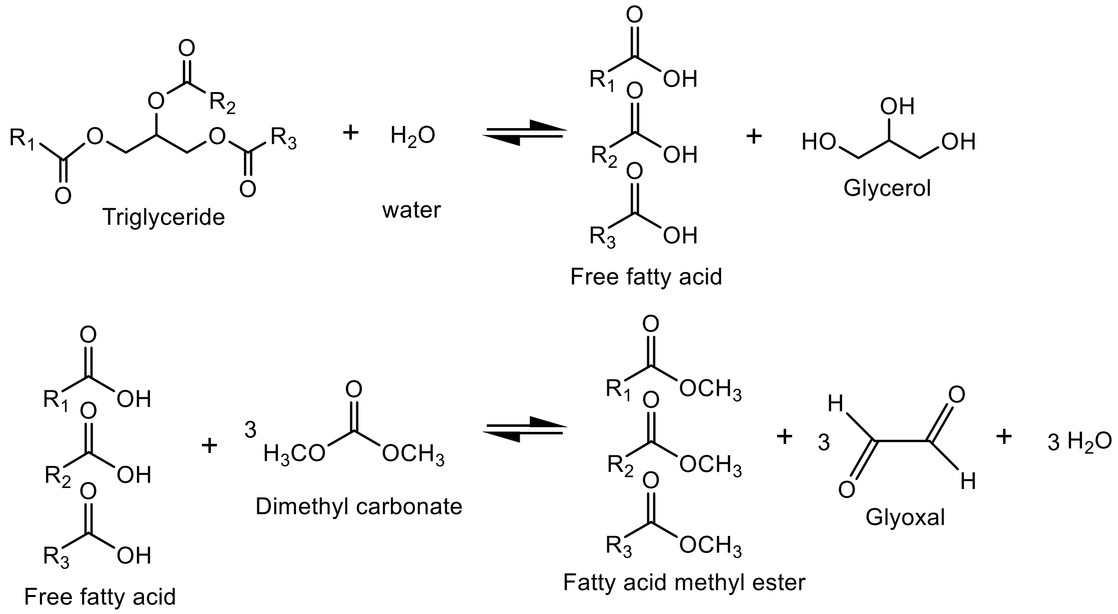


Fig. 2.26. Reaction mechanism of two-step supercritical dimethyl carbonate method for biodiesel production.

2.4. Main factors affecting biodiesel production

2.4.1. Temperature and reaction time

Reaction time together with temperature give an important role to determine reaction kinetics of oil conversion to biodiesel under supercritical conditions. In all reports addressing to supercritical methanol and ethanol, oil conversion to biodiesel mainly increased with reaction temperature and time. It was owing to an increase in the reaction rate constant based on Arrhenius equation and a change of alcohol properties at high temperature and high pressure. The effect of temperature on biodiesel yield in supercritical methanol was firstly investigated by Kusidana and Saka (2001b). They studied the effect of temperature at the temperature and pressure ranges of 200 °C/7 MPa to 487 °C/105 MPa. They reported that at 200 and 230 °C, the biodiesel yield is relatively low owing to the subcritical state of methanol. A complete conversion of rapeseed oil to biodiesel was found at 350 °C after 4 min obtaining 95 wt% of biodiesel. At 400 °C, a complete conversion was needed 2 min merely. However, thermal decomposition of biodiesel occurred at temperature above 400 °C.

The similar results were reported by Rathore and Madras (2007). They discovered that both grade groundnut oil and palm oil conversion to biodiesel increased with increasing temperature from 200 to 400 °C, but thermal decomposition was observed above 400 °C. In addition, Varma and Madras (2007) also found that both castor oil and linseed oil conversion to biodiesel increased with temperature. In addition, the highest yield of biodiesel was obtained at 350 °C after 40 min and oil-to-methanol molar ratio of 1:40. Song et al. (2008) also investigated the effect of temperature on biodiesel yield using RBD palm oil in batch reactor at a fixed reaction time of 5 min. They concluded that the biodiesel yield increased with temperature up to 350 °C, but it decreased above 375 °C for both oil-to-methanol molar ratio of 1:40 and 1:60.

Effect of temperature on biodiesel production in continuous flow mode was also studied. Zhou et al. (2010) investigated the effect of temperature on methyl ester yield at a fixed pressure and oil-to-methanol molar ratio of 15 MPa and 1:40, respectively. They observed that the reaction rate increased significantly with temperature resulting in an increased in biodiesel yield. Biodiesel yields of about 85% and 92% were obtained at temperature of 350 °C and 375 °C, respectively within 800 s reaction time. However, thermal decomposition was identified after 1400 s and 1200 s at 350 °C and 375 °C, respectively. Moreover, Choi et al. (2011) also examined the effect of temperature on methyl ester yield using palm olein oil in a plug flow reactor. Using a fixed pressure of 35 MPa and oil-to-methanol molar ratio of 1:40, FAME yield increased with increasing temperature from 270 to 350 °C.

In supercritical methyl acetate, Saka and Isayama (2009) investigated the effect of temperature on biodiesel production from rapeseed oil using batch reactor. A fixed pressure and oil-to-methyl acetate molar ratio of 20 MPa and 1:42, respectively was employed in this study. They explained that rapeseed oil conversion to biodiesel rapidly increased with increasing temperature from 300 °C to 380 °C, and thermal decomposition was observed after 45 min at 380 °C. In addition, Campanelli et al. (2013) also found similar finding that increasing temperature could enhance the biodiesel yield. Moreover, a complete conversion with the yield of 100% was obtained at 345 °C after 50 min reaction time. Furthermore, Tan et al. (2011) also concluded that biodiesel yield proportionally increased with temperature until 400 °C, and thermal decomposition was identified beyond the optimum temperature. In another study by Goembira and Saka (2013), oil conversion to biodiesel significantly increased with increasing temperature from 300 °C to 380 °C. However, above 380 °C and after 45 min, thermal decomposition occurred. Using tubular packed bed reactor, Dona et al.

(2013) also discovered similar trends in which temperature could increase reaction rate of biodiesel production.

In supercritical dimethyl carbonate, oil conversion to biodiesel was also favored with increasing temperature. Only one study by Ilham and Saka (2012) did report about temperature effect on biodiesel production in supercritical dimethyl carbonate. They investigated the effect of temperature and pressure simultaneously. It was reported that under low reaction pressure, i.e. 5 and 10 MPa, the increasing of temperature did not affect biodiesel yield so much. The significant change of canola oil conversion to biodiesel was observed at 20 MPa.

Even though biodiesel yield mainly increased with temperature, thermal decomposition of biodiesel occurred above 400 °C. Imahara et al. (2008) observed that methyl ester content decreased for methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate about 91%, 90%, 86%, 73%, and 15%, respectively. In addition, Lin et al. (2014) recently proposed reaction mechanism and kinetics of thermal decomposition for biodiesel production in supercritical methanol. Based on GC-FID and GC-MS analyses, there were 3 processes of thermal decomposition under supercritical conditions: isomerization at 275–400 °C, polymerization or Diels-Alder reaction at 300–425 °C, and pyrolysis reaction above 350 °C.

Besides, at higher temperature, usually above 400 °C, thermal cracking of triglyceride also occurred as reported by Marulanda et al. (2009). **Fig. 2.27** shows the products of thermal cracking of triglyceride under supercritical conditions.

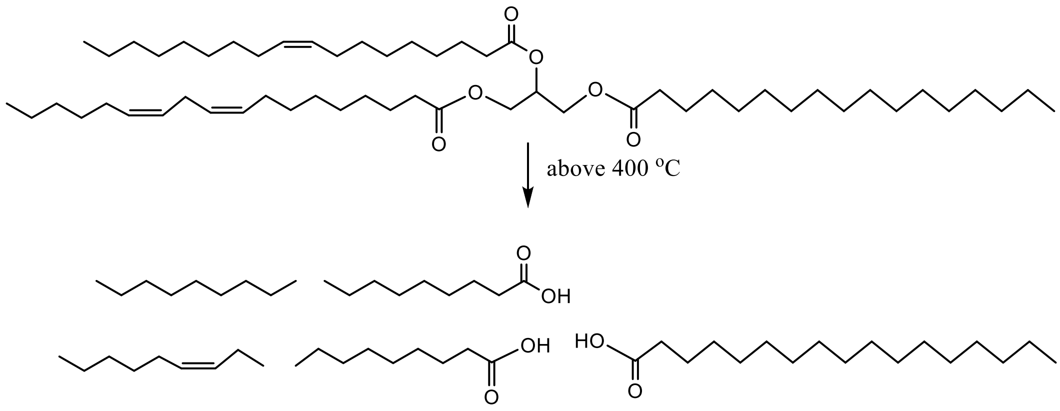


Fig. 2.27. Products obtained after thermal cracking of triglyceride under supercritical conditions.

2.4.2. Oil-to-reactant molar ratio

Stoichiometrically, transesterification of triglyceride required three molecules of methanol. However, since the transesterification process is reversible, an enormous amount of methanol is needed to achieve a complete conversion. The effect of oil-to-methanol molar ratio was firstly studied by Kusdiana and Saka (2001) in the ranges of 1:3.5 to 1:42. It was reported that at the lower methanol molar ratio (6 or less), incomplete conversion to biodiesel was observed resulting in lower yield of biodiesel. Meanwhile, at higher methanol molar ratio (42), a complete conversion was apparent with methyl ester yield of 95%. This should be due to higher molar ratio of methanol enhances the contact area between triglyceride and methanol and also eliminates the transition temperature, but at methanol molar ratio more than 50, it gave no benefits.

Varma and Madras (2007) also investigated the effect of oil-to-alcohol molar ratio on biodiesel conversion from castor and linseed oil in batch reactor. They explained that biodiesel increased with increasing the molar ratio of alcohol (methanol and ethanol) from 10 to 40, but it was relatively constant from 40 to 70. Similar results were reported by Song et al. (2008) who conducted the effect of molar ratio from RBD palm oil in batch reactor at a fixed temperature of 350 °C and a pressure of 40 MPa. They observed that biodiesel content increased significantly up to the molar ratio of 30 and was constant above 30. In continuous production of biodiesel from soybean oil, the effect of molar ratio was studied by He et al. (2007a). They found that methyl ester yield increased rapidly with the increased molar ratio from 5 to 40, but it was constant afterwards.

Under supercritical methyl acetate conditions, Goembira and Saka (2013) investigated the effect of oil-to-methyl acetate molar ratio on biodiesel production in batch reactor at a fixed temperature of 350 °C and a pressure of 20 MPa. They found that a higher molar ratio of methyl acetate resulted in the higher biodiesel yield. A highest yield of biodiesel was identified at oil-to-methyl molar ratio of 1:42, obtaining 96.5 wt% of biodiesel. Meanwhile, an increase in a molar ratio from 42 to 54, biodiesel yield was not significantly observed. Similar result was reported by Tan et al. (2011) who examined effect of molar ratio in supercritical methyl acetate at a fix temperature of 400 °C and reaction time of 60 min using a batch-type tube reactor. They discovered that biodiesel increased with increasing of molar ratio from 20 to 30, but it decreased thereafter. In addition, for supercritical dimethyl carbonate case, an optimum molar ratio to produce biodiesel was 42 (Ilham and Saka, 2012).

2.4.3. Pressure

Pressure also plays an important role on biodiesel production under supercritical conditions since it affects the supercritical fluid properties including hydrogen bound intensity, density, viscosity, etc. Shin et al. (2012) investigated effect of pressure on biodiesel content in batch reactor at a fixed temperature of 335 °C and oil-to-methanol molar ratio of 1:45. It was reported that an increase in pressure from 15 to 20 MPa resulted in a higher biodiesel yield, but it was relatively constant at pressure above 20 MPa. Recently, Samniang et al. (2014) also examined pressure effect on biodiesel production from crude *Jatropha* oil and *Krating* oil. They concluded that the biodiesel yield increased rapidly when the pressure increased from 8 to 16 MPa for *Krating* oil, but it was not significantly observed for *Jatropha* oil.

In continuous flow reactor, He et al. (2007b) investigated the effect of reaction pressure on conversion of soybean oil to biodiesel. They reported that the pressure has a significant effect on biodiesel yield in the pressure range from ambient pressure to 25 MPa. At pressure below 15.5 MPa, the increment of biodiesel yield was much higher than at pressure above 15.5 MPa. Biodiesel yields of 56.1 % and 81.7% were obtained at 8.7 MPa and 15.5 MPa, respectively. In addition, they found that the biodiesel yield increased merely 9% and 1% when the pressure increased from 15.5 to 25 MPa and from 25 to 36 MPa, respectively. In addition, Choi et al. (2011) also examined pressure effect on conversion of palm olein oil to biodiesel conducted at a fixed temperature of 350 °C and a residence time of 20 min. They observed that reaction pressure gave a great influence over a pressure range of 20–40 MPa, but this effect was negligible at a pressure above 35 MPa.

Similar trends were observed for biodiesel production in supercritical methyl acetate and dimethyl carbonate. Goembira and Saka (2013) investigated the effect of pressure on biodiesel production from rapeseed oil in supercritical methyl acetate using a flow-type reaction system at a fixed oil-to-methyl molar ratio of 1:42 and 350 °C. It was reported that there was no biodiesel and triacetin discovered at reaction pressure of 5 MPa. Biodiesel yield was initially found at 10 MPa, and an increased in pressure from 10 to 20 MPa resulted in increasing biodiesel and triacetin. However, the increasing of biodiesel yield was insignificant at reaction pressure of 30 MPa.

In supercritical dimethyl carbonate, Ilham and Saka (2012) examined the effect of pressure together with temperature on biodiesel yield using a flow-type reaction system at a fixed temperature of 300 °C. They explained that the biodiesel yield merely 40 wt% was obtained at 5 MPa. Increasing pressure to 10 and 20 MPa could increase biodiesel to 78 wt% and 96 wt%, respectively. However, at 40 MPa, the increment of biodiesel yield was not significantly identified.

From this pile of study, it can be concluded that 20 MPa is the optimum pressure to conduct biodiesel production for supercritical methanol, ethanol, methyl acetate, and dimethyl carbonate. In addition, the effect of pressure on biodiesel production under supercritical conditions is much more significant at high temperature since density of fluids increased with pressure.

CHAPTER 3

Aim and Objectives

3.1. Research motivation

An alternative energy derived from biomass such as biodiesel is receiving extensive interest due to the world facing the challenges caused by the depletion of fossil fuel resources, global warming issues, and the increased demand for energy. Biodiesel becomes one of the most notable alternative fuels owing to biodegradability and low toxicity. In addition, it is derived from renewable feedstocks such as vegetable oil, animal fats, microalgae, or even insect. In addition, it has low toxicity, low particulate matter and CO emissions. Besides, the flow and combustion properties are similar to petroleum-based diesel, and low sulfur and aromatic content compared to conventional diesel fuel.

Biodiesel production is commonly synthesized via homogeneous alkali-catalyzed transesterification since these catalysts are widely available. However, this method has caused the problem regarding waste generated from purification of products in the downstream step. To purify glycerol, acid solution such as phosphoric acid should be added, so that this process could bring about a new environmental problem. Besides, this process also has led to the overproduction of glycerol in the market.

Thus, our strategy is how to produce biodiesel without generating glycerol, no waste water, no need catalyst, easier separation of product, and fast reaction rate. Among several methods of biodiesel production, supercritical method is the most promising one since it can be carried out without any catalyst. In addition, biodiesel can be synthesized within short reaction time and easier separation of products. In order to obtain biodiesel without producing glycerol, another reactant instead of methanol or ethanol should be selected. One of the most interesting reactants is MTBE since *tert*-butyl group can substitute the hydrogen atom in the hydroxyl group of glycerol generating glycerol *tert*-butyl ether (GTBE). This by-product has a higher added-value than glycerol owing to cetane improver and good blending property with diesel fuel. Therefore, a new approach of non-catalytic biodiesel production using supercritical MTBE method was proposed in this study. For this purpose, the effect of temperature and reaction time were studied in order to know reaction behavior between triglyceride and MTBE in more detail. In addition, the reaction mechanism as well as reaction kinetics of canola oil conversion to biodiesel under supercritical MTBE conditions were also determined. It is also important to compare reaction behavior of biodiesel production in this study with the previous studies which employed methanol, ethanol, methyl acetate and dimethyl carbonate as reactant.

Since high temperature and high pressure are required to conduct biodiesel production under supercritical conditions, heat recovery must be concerned for improvement of biodiesel production via supercritical method. So far, biodiesel production under supercritical conditions was performed using a batch or a conventional flow reactor. By employing these reactors, the heat could not be properly recovered. Thus, our next strategy is how to find a technology to produce biodiesel under supercritical conditions that, being able to recover the heat and being able to reduce the space. One possibility to overcome those mentioned problems is by employing a novel spiral reactor. The spiral reactor used in this study is composed of a parallel tube heat exchanger and high-temperature transesterification reactor. The parallel tube heat exchanger, where heat is recovered, is in turn composed of two tubes placed side-by-side in a spiral formation. The high-temperature transesterification reactor, where the reaction mainly takes place, consists of insulated tubing. In this study, ethanol was firstly selected as a reactant since it can be derived from renewable sources such as cellulose, starch, or sugar-based biomass. Temperature profile of spiral reactor was firsly presented. The different between spiral and batch reactors was also compared. In addition, effect of temperature and reaction time as well as reaction kinetics was also investigated in order to know the characteristics of the reactor.

Owing to a successful recovery of heat by employing spiral reactor and no previous study applying this reactor for biodiesel production using supercritical MTBE method, effectiveness of spiral reactor for supercritical MTBE method was further studied. To investigate the characteristics of spiral reactor, effect of temperature and residence time were elucidated. The conventional flow and spiral reactors were also compared to verify the expected advantage of the spiral reactor giving a higher yield as a result of the reaction in the heat exchanger. In addition, the heat recovery characteristics were also examined.

Effect of pressure is one of the most factors affecting biodiesel production under supercritical conditions. However, this effect on biodiesel production using supercritical MTBE method has not been studied previously. Therefore, it is also vital to examine the effect of pressure on product composition as well as reaction kinetics.

Considering above issues, a study on new approach of biodiesel production using supercritical MTBE and alcohols is proposed. The title of this study is as follows "Biodiesel Production Using Supercritical tert-Butyl Methyl Ether (MTBE) and Alcohols".

3.2. Aim and objectives

The aim of this work is to carry out a detailed study on biodiesel production using supercritical MTBE and alcohols. For this purpose, the detailed objectives of this study are as follows:

1. To propose the kind of new biodiesel production.
2. To elucidate reaction characteristics between oil and MTBE.
3. To obtain the fundamental characteristics of spiral reactor for biodiesel production.
4. To examine the effectiveness of the spiral reactor on supercritical MTBE biodiesel production by elucidating the effects of temperature and reaction time on FAME yields.
5. To obtain a better understanding of the effect of pressure on biodiesel yield using supercritical MTBE.
6. To elucidate the difference of reaction behavior of biodiesel production using supercritical methanol, ethanol, and MTBE by examining temperature and residence time effects as well as reaction kinetics.

CHAPTER 4

Experimental Method

4.1. Introduction

The details of the experimental setup and procedures used in the experimental work are thoroughly described in this chapter. Furthermore, the details of product analysis, materials, chemical compounds as well as experimental conditions employed in this work are also discussed in this chapter.

4.2. Experimental Setup and Procedures

There are two different experimental apparatus employed in this experimental work. To give better understanding, both experimental apparatus and procedures are described in more details in this chapter. Experimental apparatus 1 is a conventional flow reactor that consisted of 1/8 inch piping made of stainless-steel tubing (SS316) with the length of 1.5 m. Meanwhile, experimental apparatus 2 is a spiral reactor made of the same material with the apparatus 1. The length of the reactor and heat exchanger was 10.0 and 2.5 m, respectively. Both experimental apparatuses are capable of achieving high temperature and high pressure under supercritical conditions with temperature range of 250–600 °C and pressure range of 10–30 MPa.

4.2.1. Apparatus 1: Conventional flow reactor

Conventional flow reactor is used for the study featured in Chapter 5 entitled "New Approach of Biodiesel Production in Supercritical MTBE". This reactor was designed to be suitable for high temperature and high pressure with a temperature range from 250 °C to 600 °C and pressure range from 10 MPa to 30 MPa.

The experimental apparatus for supercritical MTBE method is schematically illustrated in **Fig. 4.1**. The reactor and heat exchanger were made of stainless steel (SS 316) with the inner and outer diameter of 1.00 mm and 1.59 mm, respectively. The length of this reactor was 1.5 m. Firstly, feedstocks consisted of canola oil and MTBE were fed into the reactor. Subsequently, the temperature was set up at the desired temperature. Having achieved the desired temperature, the pressure was increased to 10 MPa using a back-pressure regulator. Before samples are collected, the feedstock was fed into the reactor for at least 30 min to ensure a steady-state condition. Products were cooled in the heat exchanger and then were removed from the reactor after passing them through a filter and a back-pressure regulator.

The residence time was determined using Eq. 4.1, taking into consideration of the density of canola oil and MTBE at the reaction temperature, mass flow rate of canola oil and MTBE, and the reactor volume. It was assumed that there is no change of volume caused by mixing.

$$\text{(Residence time [min])} = \frac{(\text{Reactor volume } [\text{cm}^3])}{\frac{(\text{Mass flow rate of oil [g/min]})}{(\text{Density of oil } [\text{g/cm}^3])} + \frac{(\text{Mass flow rate of MTBE [g/min]})}{(\text{Density of MTBE } [\text{g/cm}^3])}} \quad (4.1)$$

Meanwhile, the density of canola oil at certain temperature and pressure was calculated using equation as shown in Eq. 4.2 (Hartung and Philadelphia, 1914). In addition, the density of ethanol and MTBE under supercritical condition was determined from previous literatures (Bazaev et al., 2007; Ihmels and Gmehling, 2002).

$$\rho = \frac{\rho o\left(1+\frac{42.8\times10^{-6}\times\Delta P}{P^{0.25}\vartheta^{0.0385}}\right)}{1+\frac{\left(\frac{23.2}{p^{0.25}}+0.421\right)10^{-4}\Delta T}{\rho o^{2}\left(1+\frac{42.8\times10^{-6}\times\Delta P}{P^{0.25}\vartheta^{0.0385}}\right)^{2}}} \quad (4.2)$$

where;

ρ = density of oil at certain temperature and pressure (g/mL)

ρ_o = density of oil at room temperature = 0.9 g/mL

ΔP = P-P_0, where P is actual pressure and P_0 is pressure at room temperature (Psi)

ΔT = T-T_0, where T is actual temperature and T_0 is room temperature (°F)

ϑ = viscosity of oil at 37.8 °C; i.e., 44.34 cSt.

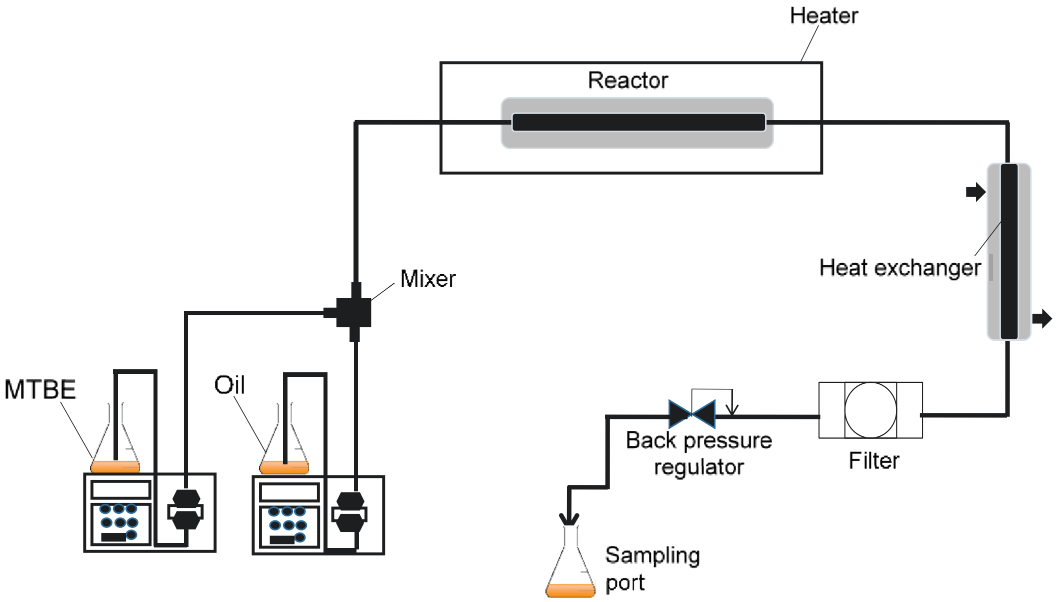


Fig. 4.1. Experimental apparatus 1 for Chapter 5.

4.2.2. Apparatus 2: Spiral reactor

Spiral reactor is used for the experimental investigations featured in Chapter 6, 7, 8, and 9. Like conventional flow reactor, this reactor was also set up to be suitable for high temperature and high pressure with the temperature range from 250 °C to 600 °C and pressure range from 10 MPa to 30 MPa.

The experimental apparatus used for Chapter 6, 7, 8, and 9 as well as a detailed schematic of the spiral reactor is schematically illustrated in **Fig. 4.2**. This experimental apparatus consisted of a pump, the spiral reactor, heat transfer cement, a ceramic microheater, thermocouples, a thermal insulator, a filter, and a back-pressure regulator.

The spiral reactor was made of stainless-steel tubing (SS316) with an inner and outer diameter of 2.16 mm and 3.17 mm, respectively. This reactor consisted of a heat exchanger and the reactor. The heat exchanger was a pair of tubes placed side-by-side and connected to each other, whereas the reactor was a single tube that was thermally controlled by an electric heater. Thermocouples, connected with a tee union fitting, were used to measure temperatures inside the spiral reactor. The lengths of the reactor and the heat exchanger were 10.0 and 2.5 m, respectively.

Initially, a mixture of canola oil and MTBE was fed to the spiral reactor at the desired temperature. Subsequently, the pressure was increased to the desired pressure using a back-pressure regulator. Having achieved the desired experimental conditions and a steady state, the obtained products were removed from the reactor after passing through the filter and back-pressure regulator.

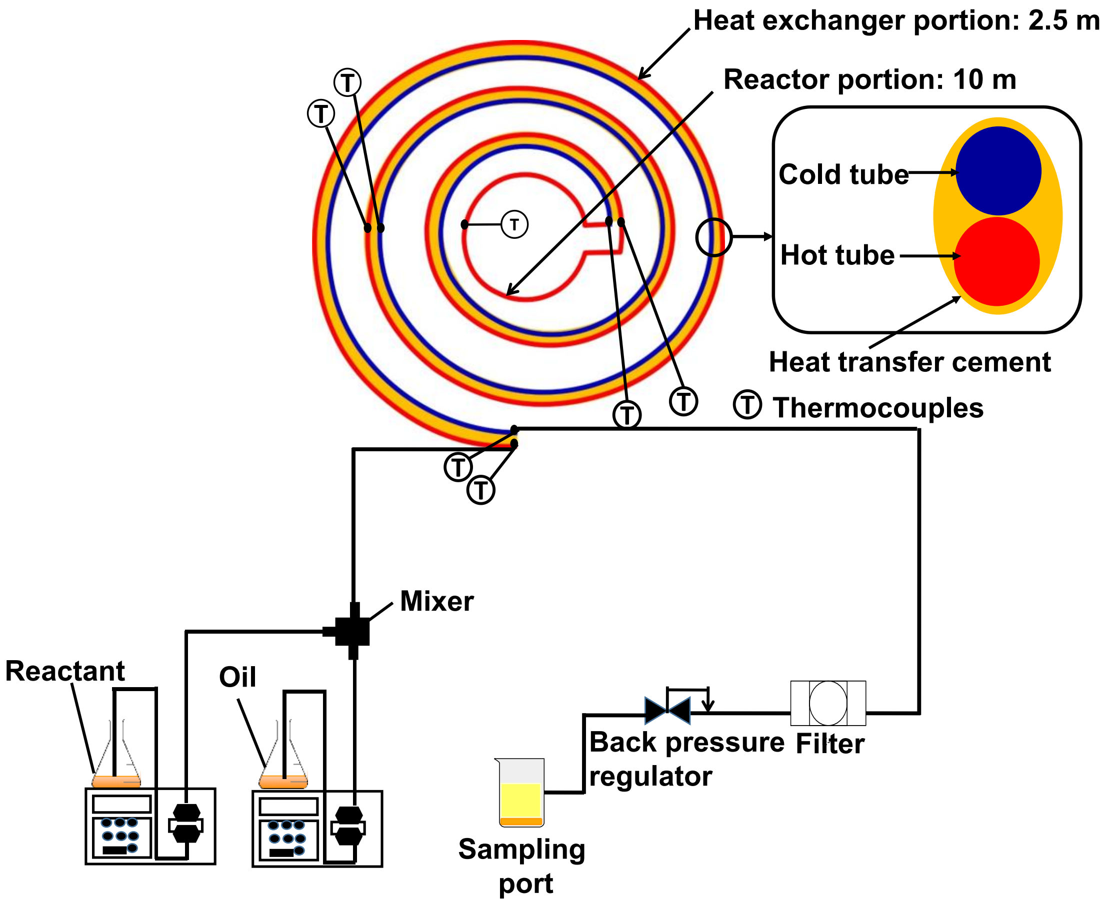


Fig. 4.2. Experimental apparatus 2 for Chapter 6, 7, 8, and 9.

4.3. Product analysis

The details of product analysis have been reported in our previous paper (Farobie et al., 2014). Briefly, the obtained products were analyzed using gas chromatography (GC-390B; GL Sciences), which employed a column (MET-Biodiesel, with an integrated 2 m guard column, Sigma Aldrich, Supelco, 28668-U) and a flame ionization detector (FID). **Fig. 4.3** shows photographs of GC-390B, GL Sciences.

Fig. 4.3. Photographs of GC-390B, GL Sciences.

Argon was used as the carrier gas. In details, the temperature program began at 50 °C, which was held constant for 1 min. Then, the temperature was raised at 15 °C/min to 250 °C and was held constant for 10 min. Finally, the temperature was increased to 380 °C at a rate of 15 °C/min, and 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 1 μL, and peak identification was achieved by comparing the retention times between the standard and sample compounds. An internal standard used in this study was tricaprin (IUPAC name: 2,3-di(decanoyloxy)propan-2-

yl decanoate). The methyl ester content was calculated using a calibration curve on the basis of peak areas. **Table 4.1** shows the types of standard and samples detected by GC and its respective retention time.

Table 4.1. The types of standard and samples detected by GC-390B and its respective retention time.

No.	Compound name	Chemical formula	Retention time (min)
1	MTBE	$C_5H_{12}O$	0.295
2	Ethanol	C_2H_6O	0.473
3	Triolein	$C_{57}H_{104}O_6$	31.12
4	Diolein	$C_{39}H_{72}O_5$	22.75
5	Monoolein	$C_{21}H_{40}O_4$	12.57
6	Glycerol	$C_3H_8O_3$	5.03
7	GTBE	$C_{15}H_{32}O_3$	6.13
8	Tricaprin	$C_{33}H_{62}O_6$	14.51
9	Methyl oleate	$C_{19}H_{36}O_2$	9.05
10	Methyl linoleate	$C_{19}H_{36}O_2$	9.27
11	Methyl linolenate	$C_{19}H_{32}O_2$	9.45
12	Methyl palmitate	$C_{17}H_{34}O_2$	8.22
13	Methyl stearate	$C_{19}H_{38}O_2$	8.47

Experimental biodiesel yields were calculated by dividing the moles of biodiesel product by the moles of fatty acid groups in the initial triglyceride (TG) as shown in Eq. 4.3.

$$\text{(Product yield)} = \frac{\text{(Molar amount of product biodiesel)}}{\text{(Molar amount of fatty acid group in initial TG)}} \qquad (4.3)$$

4.4. Experimental Conditions

Tables 4.2–4.6 show the experimental conditions for the studies as discussed in Chapter 5–9, respectively.

Table 4.2. Experimental conditions for study in Chapter 5 entitled “New approach of biodiesel production in supercritical MTBE”

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3-15 min
Oil-to-MTBE molar ratio	1:40
Temperature	200-500 °C
Pressure	10 MPa
Reactor length	1.5 m

Table 4.3. Experimental conditions for study in Chapter 6 entitled “Biodiesel production in supercritical ethanol using a novel spiral reactor”

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3–30 min
Oil-to-ethanol molar ratio	1:40
Temperature	270–400 °C
Pressure	20 MPa
Reactor length	10 m

Table 4.4. Experimental conditions for study in Chapter 7 entitled "Effectiveness of spiral reactor for biodiesel production in supercritical MTBE"

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	6–30 min
Oil-to-MTBE molar ratio	1:40
Temperature	250–400 °C
Pressure	10 MPa
Reactor length	10 m

Table 4.5. Experimental conditions for study in Chapter 8 entitled "Effects of pressure on biodiesel production in supercritical MTBE"

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3–30 min
Oil-to-MTBE molar ratio	1:40
Temperature	300–400 °C
Pressure	10–30 MPa
Reactor length	10 m

Table 4.6. Experimental conditions for study in Chapter 9 entitled "A comparative study of biodiesel production in supercritical methanol, ethanol, and MTBE"

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3–30 min
Oil-to-MTBE molar ratio	1:40
Temperature	270–400 °C
Pressure	20 MPa
Reactant	Methanol, ethanol, and MTBE

4.5. Materials

All reagents were used without further treatment. The canola oil feedstock was a commercial one produced by J-Oil Mills (Tokyo), Higashi-Hiroshima, Japan. Methanol (99.5%), ethanol (99.5%) and MTBE (99.5%) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Standard compounds of fatty acid methyl esters including methyl oleate (99.9%), methyl linoleate (min. 97%), methyl linolenate (min. 95%), methyl palmitate (min. 95%), and methyl stearate (min. 90%) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan). Standard compounds of fatty acid ethyl esters were also purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan). Triolein (99.9%), diolein (99.9%), and monoolein (> 40%) standards were purchased from Nacalai Tesque, Inc. (Kyoto, Japan), Sigma-Aldrich, Co. (Japan), and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively. To prepare GC standard solutions, all chemicals (tricaprin and n-hexane) used were of analytical grades.

CHAPTER 5

New approach of biodiesel production in supercritical MTBE

5.1. Introduction

Biodiesel or a mixture of fatty acid alkyl ester (FAAE) is an environmentally benign fuel derived from biomass such as vegetable oil, animal fat, or microalgae with short chain alcohols via a transesterification reaction. Nowadays, homogeneous alkali-catalyzed transesterification is the most common method to produce biodiesel in industrial scale owing to the abundance and low cost of the alkali catalyst (Van Kesteren and Nisworo, 2007). However, this process requires high purity of feedstock since alkali catalyst is very sensitive to the presence of free fatty acids (FFAs) and water. It has led to undesirable side reactions such as saponification and lower biodiesel yield

(Kusdiana and Saka, 2004; Cao et al., 2005). According to Hajek and Skopal (2010) to purify glycerol from biodiesel production process, acid or alkali should be added to neutralize the catalyst, forming a vast amount of waste water and salt. Thus, the separation and purification of products in the downstream step is not only complicated and costly, but it has also led to a new environmental pollution problem.

Apart from that, since biodiesel production increases rapidly in recent years because of exhaustible of fossil fuel, the overproduction of the main by-product glycerol is unavoidable. It has caused the price of glycerol to decrease significantly in market (Johnson and Taconi, 2007). To overcome these problems, biodiesel production without generating glycerol as a main by-product as well as without producing waste water is needed. Thus, our strategy is to produce biodiesel under supercritical conditions by using MTBE as a reactant instead of using alcohol.

Since there has been no previous study employing supercritical MTBE method for biodiesel production, it would be interesting to determine the applicability of this reaction to produce biodiesel. In addition, it would provide a new process of biodiesel production that does not produce glycerol as a by-product. However, the reaction behavior between oil and MTBE has not been studied well. Therefore, the purpose of this study is to elucidate the reaction characteristics of canola oil and MTBE. For this purpose, the effects of temperature and residence time on biodiesel production in supercritical MTBE were investigated. In order to know the reaction behavior between oil and MTBE in more detail, reaction kinetics of oil conversion to biodiesel was also determined. In addition, the biodiesel yields obtained in this study were compared with the previous study which employed supercritical methanol, ethanol, methyl acetate, and dimethyl carbonate method.

5.2. Experimental procedures

Supercritical MTBE method was carried out using flow reactor that has been described in Chapter 4 (Section 4.2.1). In brief, a mixture consisted of the feedstock and MTBE was fed into the reactor at the desired temperature. Subsequently, the pressure was raised into the target pressure, i.e. 10 MPa. After achieving a steady state condition, the obtained products were collected from the reactor after passing them through a filter and a back pressure regulator. According to Han et al. (2013), the critical temperature and pressure of MTBE are 223.85 °C and 3.448 MPa, respectively. Thus, biodiesel production was carried out at temperature range of 200–500 °C and a pressure of 10 MPa. Oil-to-MTBE molar ratio used in this study was fixed at 1:40 since it was reported in some previous studies by He et al. (200); Silva et al. (2007); Varma and Madras (2007); Velez et al. (2012) that the optimum oil-to-reactant for biodiesel production under supercritical conditions is 1:40. Canola oil was used as a feedstock.

5.3. Experimental conditions

The experimental conditions for this study is presented in **Table 5.1**.

Table 5.1. Experimental conditions for this chapter

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3-15 min
Molar ratio of oil to MTBE	1:40
Reactor type	Flow reactor
Temperature	200-500 °C
Pressure	10 MPa

5.4. Results and Discussion

5.4.1. Temperature and pressure effects on FAME yield

Reaction temperature and pressure can significantly affect biodiesel production under supercritical conditions. Thus, it is crucial to investigate temperature and pressure effects on FAME yields. The effects of temperature on FAME yields were examined by varying temperature from 200 to 500 °C with a pressure of 10 MPa and a fixed oil-to-MTBE molar ratio of 1:40. Theoretically, higher reaction temperature and reaction time result in higher reaction rates, leading to higher FAME yields.

The time change of FAME yields for each temperature is presented in **Fig. 5.1**. It was observed that at the transesterification reaction time of 12 min, the FAME yields of 0.18, 0.34, 0.37, 0.44, 0.94, 0.70, and 0.13 were obtained at temperature condition of 200, 250, 300, 350, 400, 450, and 500 ºC, respectively, clearly demonstrating the effects of temperature on the reaction behavior. It was found that FAME yields increased with temperature from 200 to 400 °C, whereas it significantly decreased above 400 °C. It should be due to FAME decomposition at temperature above 400 °C. This result is supported by the previous study by Kusdiana and Saka (2001) who reported that decomposition of biodiesel occurred above 400 °C. In addition, in another study by He et al. (2007), it was found that the thermal decomposition of biodiesel from unsaturated fatty acids was observed at 300 °C for a reaction time longer than 25 min. Similar results were reported by many researchers in the previous works (Madras et al. 2004; Demirbas, 2006; Song et al. 2008; Hawash et al. 2009; Vietez et al. 2009).

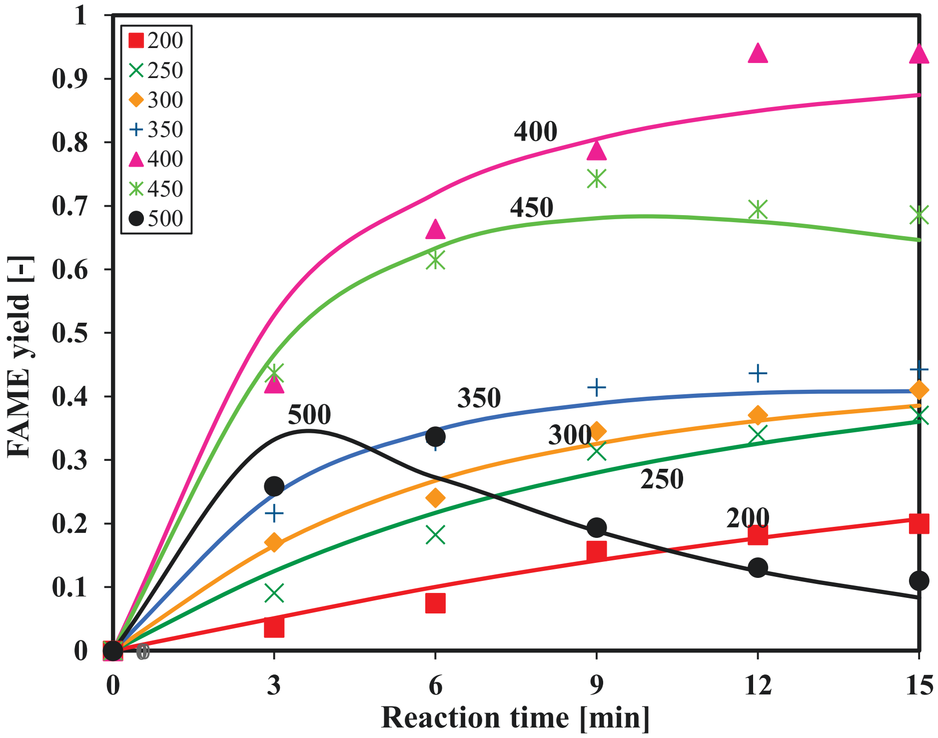


Fig. 5.1 Effect of temperature on FAME yield in supercritical MTBE (experimental conditions: 10 MPa, oil-to-MTBE molar ratio of 1:40).

Fig. 5.2 shows the effect of pressure on FAME yield at a reaction time of 5 min and a fixed temperature of 350 °C. The FAME yield slightly increased with pressure from 6 to 8 MPa, but it was relatively constant at the pressures higher than 8 MPa. This result is consistent with the previous study on biodiesel production in supercritical methanol by Kusdiana and Saka (2004). They reported that at the low pressure (less than 10 MPa), the reaction rate had a linear influence, whereas at higher pressures (more than 10 MPa), the conversion of oil to biodiesel did not significantly change so much. Similarly, in another study by Bunyakiat et al. (2006), it was found that the effect of pressure on transesterification conversion of coconut oil in supercritical methanol was negligible. On the other hand, it was discovered by He at al. (2007), increasing of pressure from 10 to 40 MPa resulted in increasing FAME yield from 43 % to 77 %, but that effect became insignificant at higher pressures.

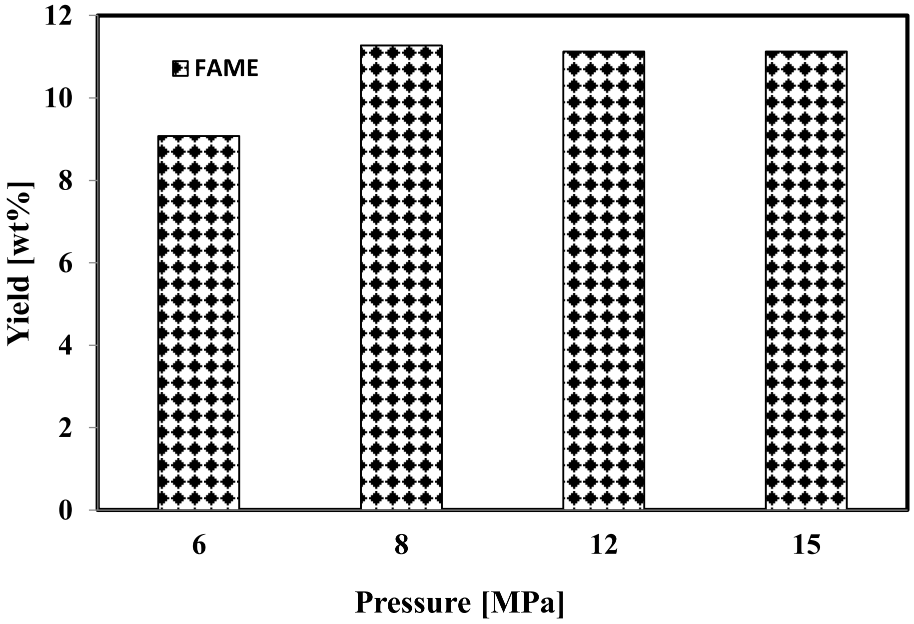


Fig. 5.2. Effect of pressure on FAME yield in supercritical MTBE (Experimental conditions: 350 °C, oil-to-MTBE molar ratio of 1:40, and 5 min).

5.4.2. Reaction time effect on FAME yield

The reaction behavior of biodiesel production in supercritical MTBE was further studied by investigating the effect of reaction time. For this purpose, the effect of reaction time on FAME yields was examined at various temperatures of 200 °C-500 °C with a fixed pressure of 10 MPa and oil-to-MTBE molar ratio of 1:40. **Fig. 5.3** shows the effect of reaction time on FAME yield and triglyceride consumption at 200 °C. As shown in this figure, the conversion of canola oil to FAME is relatively small due to subcritical state of MTBE. Under this reaction condition, the FAME yield slightly increased with reaction time. FAME yields of merely 0.037, 0.075, 0.16, 0.18, and 0.20 were obtained after transesterification reaction of 3, 6, 9, 12, 15 min, respectively. Meanwhile, the concentration of TG gradually decreased.

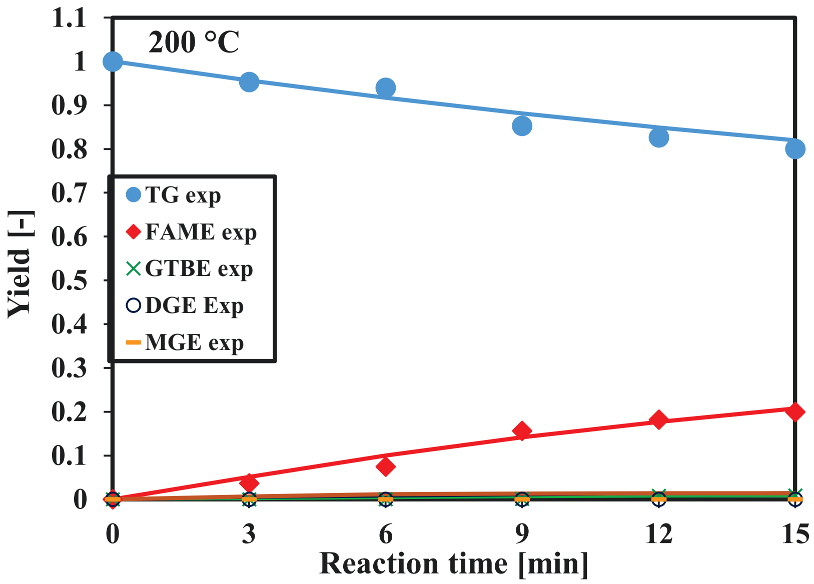


Fig. 5.3. Effect of reaction time on FAME yield and triglyceride consumption at 200 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

Fig. 5.4 shows the effect of reaction time on FAME yield and the triglyceride consumption at 250 °C. At temperature just above critical temperature of MTBE, 250 °C, FAME yield obtained was still relatively low. The FAME yields of 0.091, 0.18, 0.31, 0.34, and 0.37 were obtained after reaction time of 3, 6, 9, 12, 15 min, respectively.

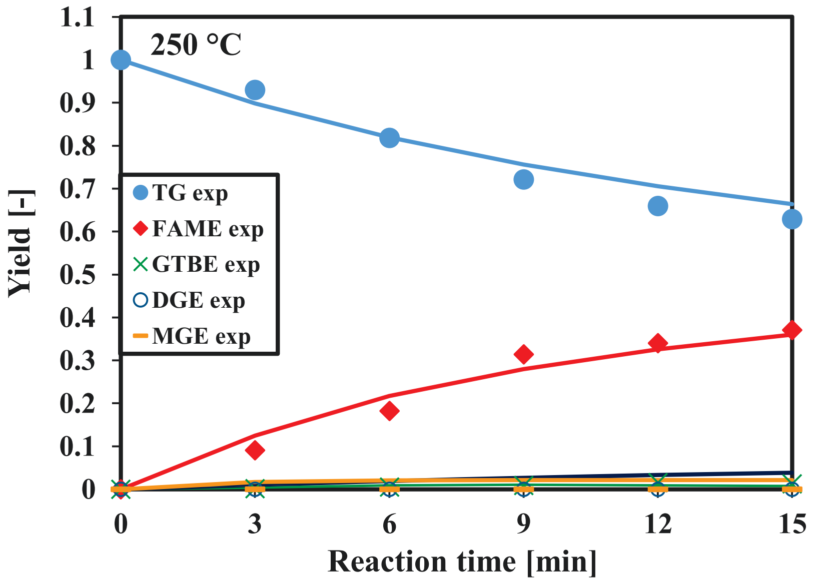


Fig. 5.4. Effect of reaction time on FAME yield and triglyceride consumption at 250 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

The reaction time effect on FAME yield and the triglyceride consumption at 300 °C is presented in **Fig. 5.5**. As observed in this figure, the conversion of oil to FAME is higher than that at 200 and 250 °C. The FAME yields of 0.17, 0.24, 0.35, 0.37, and 0.41 were obtained after transesterification reaction of 3, 6, 9, 12, 15 min, respectively.

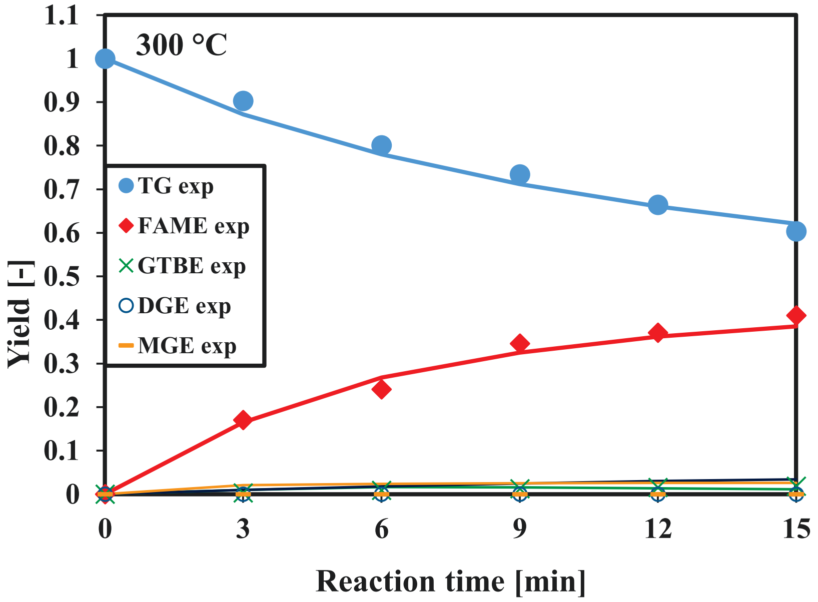


Fig. 5.5. Effect of reaction time on FAME yield and triglyceride consumption at 300 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

Fig. 5.6 shows the effect of reaction time on FAME yield and triglyceride consumption treated at 350 °C. Under this condition, a substantial change of canola oil to FAME was observed at reaction time of 9 min. A half of canola oil conversion was almost achieved after 9 min. The FAME yields of 0.41, 0.44, and 0.44 of FAME were obtained after reaction time of 9, 12, and 15 min, respectively.

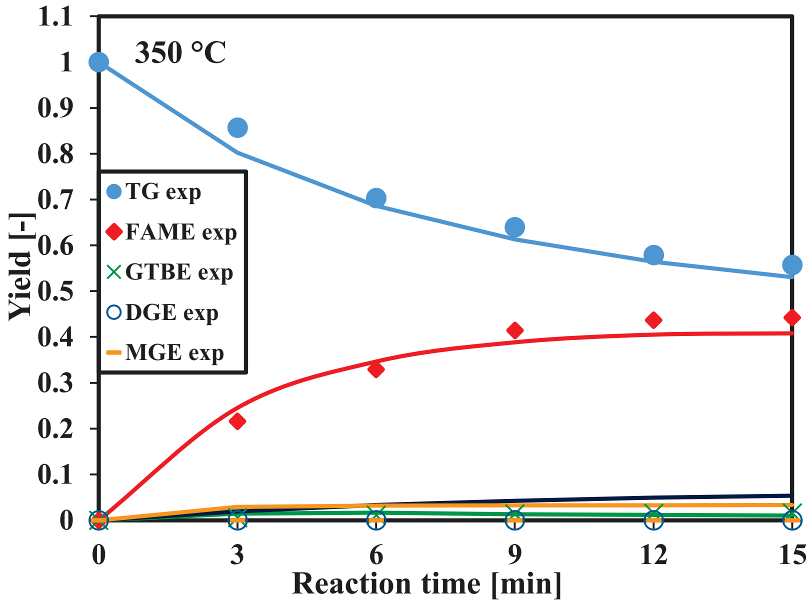


Fig. 5.6. Effect of reaction time on FAME yield and triglyceride consumption at 350 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

At 400 °C, the FAME yield significantly increased with reaction time as presented in **Fig. 5.7**. After 12 min, the transesterification reaction was almost completed, converting most of the canola oil to FAME with a yield of 0.94. Therefore, it was confirmed that 400 °C is the most favorable temperature condition for the supercritical MTBE production route. This result is different with the supercritical methanol method in which 350 °C was the best temperature to perform transesterification reaction as reported by Kusdiana and Saka (2001), Madras et al. (2004), and Silva et al. (2007). There are two reasons why biodiesel yield in supercritical MTBE completely achieved at 400 °C. The first reason might be because the reactivity of MTBE is lower than that of methanol. It was reported in the previous finding by Boer and Bahri (2011) that in supercritical methanol, the decrease of hydrogen bonding due to a supercritical state makes methanol a much stronger nucleophile. Thus, this compound is much more reactive in attacking the carbon atom of carbonyl functional group in triglyceride. In contrast, the molecular structure of MTBE is bulkier compared with that of methanol. Therefore, a higher temperature is required to enable the transesterification reaction to proceed completely. The second reason might be due to lower pressure employed in this study, i.e.; 10 MPa compared with the previous works in supercritical methanol studies which employed 20 MPa. Thus, it is interesting to examine the effect of pressure on biodiesel yield in more details for the next study. Furthermore, it is noted that the triglyceride consumption and GTBE yield obtained at 400 °C were both much higher than those obtained at 200–350 °C.

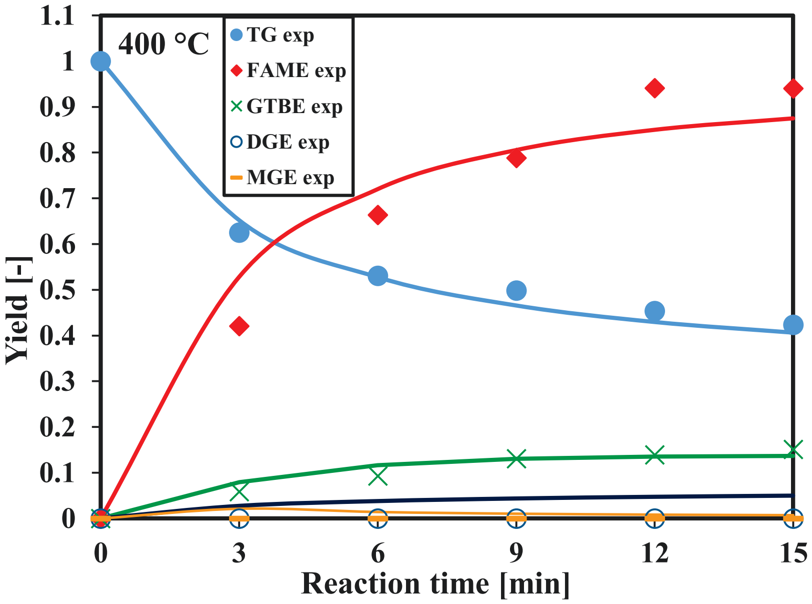


Fig. 5.7. Effect of reaction time on FAME yield and triglyceride consumption at 400 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

The optimum yield of FAME (0.94) obtained from this study is comparable with that of a previous reports. In supercritical methanol method, Ayhan (2002) found that FAME yield of 0.95 was achieved for transesterification of hazelnut oil at 350 °C after 5 min of reaction time and using an oil-to-methanol molar ratio of 1:42. In addition, in another study by Silva et al. (2007), they observed that a maximum yield of biodiesel from ethanolysis of soybean oil under supercritical conditions at 350 °C, 20 MPa, and after 15 min of reaction was 0.80. Under supercritical dimethyl carbonate (DMC) conditions, Ilham and Saka (2009) found that an ester yield of 0.80 was obtained at 300 °C, 9 MPa, and an oil-to-DMC molar ratio of 1:40 for 15 min. In supercritical methyl acetate method, Niza et al. (2011) discovered transesterification reaction of jatropha oil at 400 °C, under 20 MPa, and after 32 min of reaction, obtaining an ester yield of 0.72. As obtained from this study and also as reported by several previous studies, it was confirmed that biodiesel could be achieved in the shorter reaction time by employing supercritical method. **Table 5.2** shows some references to biodiesel yields obtained under supercritical conditions.

Fig. 5.8 shows the effect of reaction time on biodiesel yield and TG consumption at 450 °C. As indicated in this figure, the FAME yields under this condition were higher than those at 400 °C for the short transesterification reaction times of 3–9 min. Meanwhile, the prolonging reaction time, the significant decrement of FAME yields was observed due to thermal decomposition.

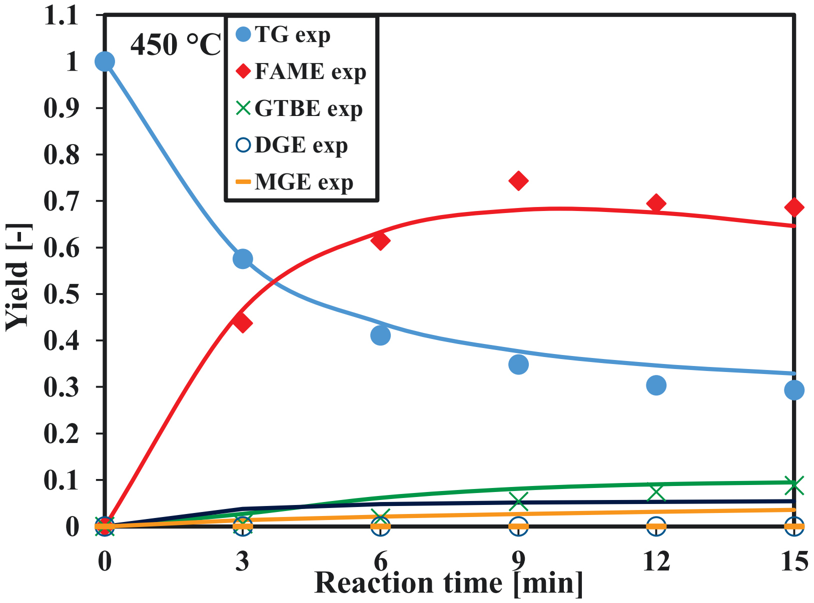


Fig. 5.8. Effect of reaction time on FAME yield and triglyceride consumption at 450 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

Table 5.2. Biodiesel yields obtained under various supercritical conditions

Feedstock	Reactant	Oil-to-reactant molar ratio	Temperature and pressure	Reaction time	Biodiesel yield (%)	Refs.
Sunflower oil	Methanol	1:40	350 °C, 20 MPa	40 min	96	(Madras et al., 2004)
Rapeseed oil	Methanol	1:42	350 °C, 45 MPa	4 min	95	(Saka and Kusdiana, 2001)
Hazelnut oil	Methanol	1:42	350 °C, N/A	5 min	95	(Ayhan, 2002)
Jatropha oil	Methanol	1:40	350 °C, 20 MPa	40 min	90	(Rathore and Madras, 2007)
Coconut and palm oil	Methanol	1:42	350 °C, 19 MPa	400 s	95-96	(Bunyakiat et al., 2006)
Soybean oil	Methanol	1:40	310 °C, 13 MPa	12 min	96	(Sawangkeaw et al., 2010)
Palm oil	Ethanol	1:33	349 °C, 20 MPa	30 min	79.2	(Gui et al., 2009)
Soybean oil	Ethanol	1:40	350 °C, 20 MPa	15 min	80	(Silva et al., 2007)
Carmelina oil	Ethanol	1:45	295 °C, 10 MPa	20 min	85	(Muppaneni et al., 2012)
Jatropha oil	Dimethyl carbonate	1:40	300 °C, 9 MPa	15 min	97	(Ilham and Saka, 2009)
Palm oil	Dimethyl carbonate	1:39	380 °C, 20 MPa	30 min	91	(Tan et al., 2010)
Soybean oil	Methyl acetate	1:50	350 °C, 20 MPa	45 min	44	(Campanelli et al., 2010)
Macauba oil	Methyl acetate	1:50	325 °C, 20 MPa	45 min	83	(Tan et al., 2010)
Rapeseed oil	Methyl acetate	1:42	350 °C, 20 MPa	45 min	96.7	(Goembira et al., 2012)
Soybean, sunflower, jatropha oil	Methyl acetate	1:42	345 °C, 20 MPa	50 min	100	(Campanelli et al., 2010)
Jatropha oil	Methyl acetate	1:50	400 °C, 20 MPa	32 min	71.9	(Niza et al., 2011)
Palm oil	Methyl acetate	1:30	399 °C, 20 MPa	59 min	97.6	(Tan et al., 2010)
Canola oil	MTBE	1:40	400 °C, 10 MPa	12 min	95.36	This study

At 500 °C, a decrease in FAME yields starts earlier: after 6 min of reaction time as presented in **Fig. 5.9**. As mentioned previously, the conversion of TG to FAME increases with increasing temperature, but at temperatures above 400 °C, the thermal decomposition of FAME occurs. It was reported in several studies (Minami and Saka, 2006; Bunyakiat et al., 2006; He et al., 2007) that product degradation was taken place at higher temperature, typically above 400 °C, leading to small biodiesel yields. Furthermore, Imahara et al., (2008) discovered thermal decomposition of biodiesel in supercritical methanol in more details. They found that poly-unsaturated FAMEs (methyl linoleate, C18:2 and methyl linolenate, C18:3) were significantly decomposed at 350 °C/43 MPa, accompanied by the isomerization of *cis*-type double bonds into *trans*-type bonds. Under supercritical methyl acetate conditions, Niza et al. (2013) also observed the thermal stability of biodiesel. They concluded that at temperatures ranging from 330 °C to 360 °C, the mono-unsaturated FAME was relatively stable, and prolonging the reaction time did not cause severe decomposition at these temperatures. However, at 420 °C, significant degradation of mono-unsaturated FAME compounds was clearly observed. Recently, the thermal decomposition mechanisms of biodiesel was proposed by Line et al. (2013). They noted that thermal decomposition of biodiesel occurred in the temperature ranges of 275–400 °C, 300–425 °C, and >350 °C corresponding to isomerization, polymerization (Diels-Alder reaction), and pyrolysis reactions, respectively. Thus, it could be concluded that in order to obtain a maximum yield of biodiesel and to avoid thermal decomposition, the temperature condition for biodiesel production under supercritical conditions should be maintained below 400 °C.

Notably, GTBE yield increased with temperature from 200 to 400 °C, but it decreased when the temperature was increased above 400 °C. At 500 °C, no more GTBE was observed due to the onset of thermal decomposition.

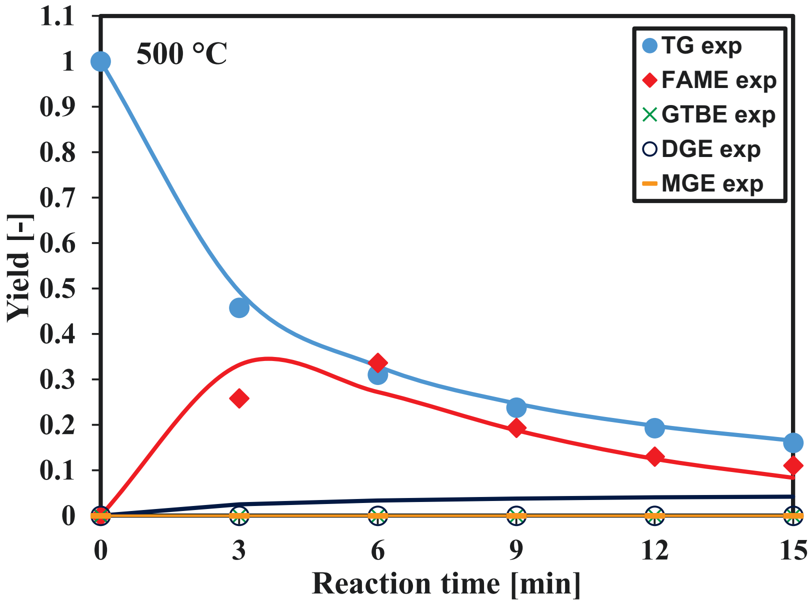


Fig. 5.9. Effect of reaction time on FAME yield and triglyceride consumption at 500 °C (Experimental conditions: 10 MPa and oil-to-MTBE molar ratio of 1:40).

5.4.3. Comparisons of supercritical MTBE with previous studies

Biodiesel production under supercritical conditions was firstly proposed by Saka and Kusdiana (2001). They observed that under supercritical conditions, methanol can convert triglyceride (TG) in rapeseed oil into FAME without any catalysts, following three consecutive reversible reactions. Firstly, triglycerides (TGs) are converted to diglycerides (DGs), DGs are then converted to monoglycerides (MGs), and lastly, MGs are then converted to glycerol in the final step. Since each reaction step produces one mole of FAME, three FAMEs are generated in the transesterification process as shown in **Fig. 5.10**.

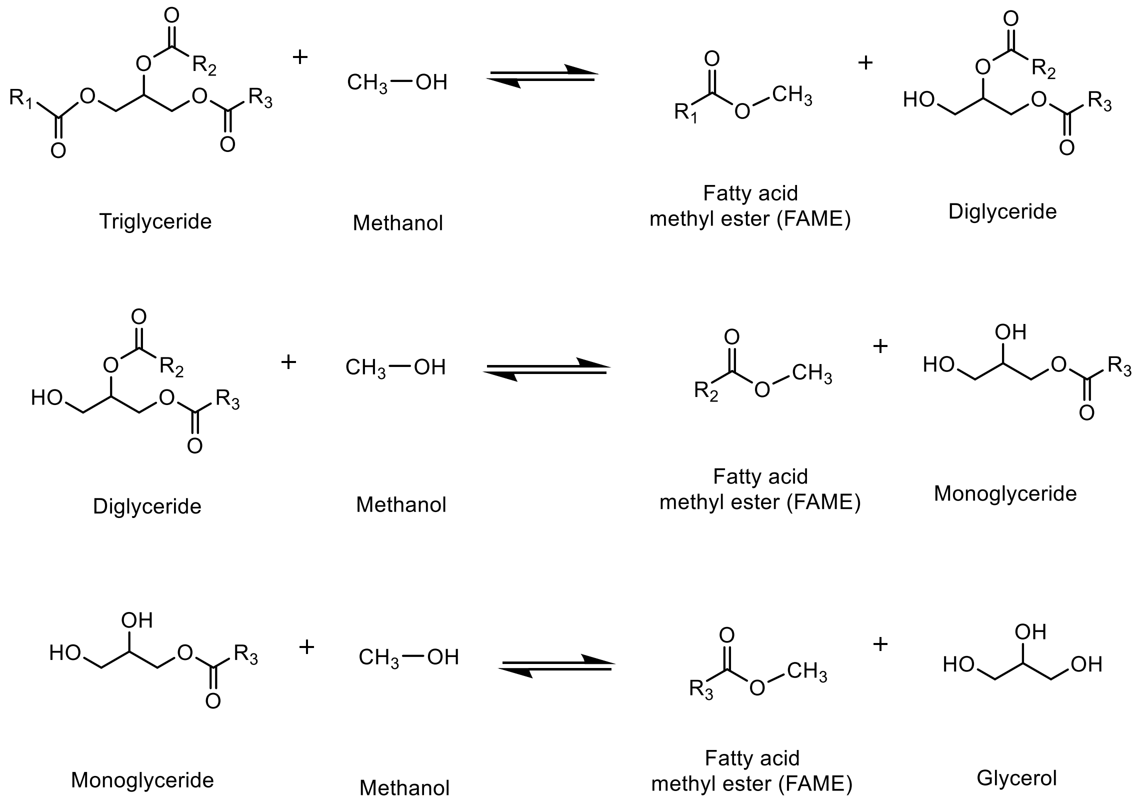


Fig. 5.10. Scheme of the reaction mechanism in supercritical methanol.

In similar way, in supercritical MTBE, the reaction mechanism of transesterification also comprises three consecutive reversible reactions. Initially, TG reacts with MTBE to produce FAME and intermediate compound of diglyceride mono *tert*-butyl ether (DGE). This intermediate moiety further reacts with another molecule of MTBE in the second step to generate FAME and monoglyceride di *tert*-butyl ether (MGE). FAME and GTBE as by-products are finally produced from a reaction of MGE and MTBE in the final step. This series of reaction is presented in **Fig. 5.11**.

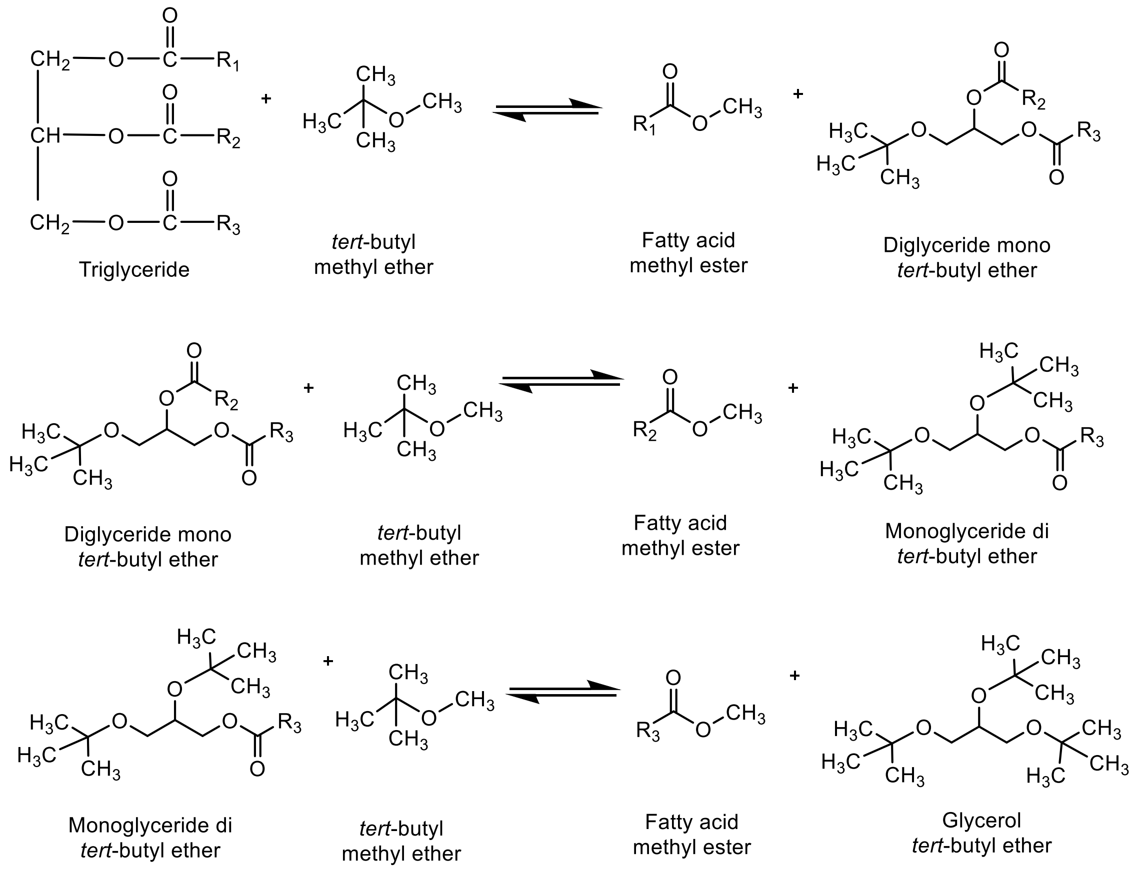


Fig. 5.11. Scheme of the reaction mechanism in supercritical MTBE.

A comparison of biodiesel yields as produced in continuous mode reactor under supercritical methanol (375 °C/15 MPa) (Zhou et al., 2010), ethanol (350 °C/20 MPa) (Silva et al., 2007), methyl acetate (350 °C/20 MPa) (Dona et al., 2013), and MTBE (400 °C/10 MPa) is shown in **Fig. 5.12**. Supercritical methanol method exhibited the highest biodiesel yields among others. Over the same reaction conditions, the yield of FAME in supercritical MTBE route was lower than that of the supercritical methanol process in spite of a higher temperature of the supercritical MTBE route (400 °C). Nevertheless, a significant change to biodiesel in supercritical MTBE was observed at the residence time of 12 min, obtaining 95.4 wt% of biodiesel that was nearly the same as those obtained using the supercritical methanol route. Interestingly, the yield of biodiesel using supercritical MTBE route was higher than that of the supercritical methyl acetate method. It might be because MTBE has a lower polarity than methyl acetate so that it is more able to miscible with triglyceride compared to methyl acetate at room temperature and pressure. At this point, the solubility effect gave an advantage for MTBE to circumvent the mass transfer problem faced by polar compounds such as methanol, ethanol, or methyl acetate.

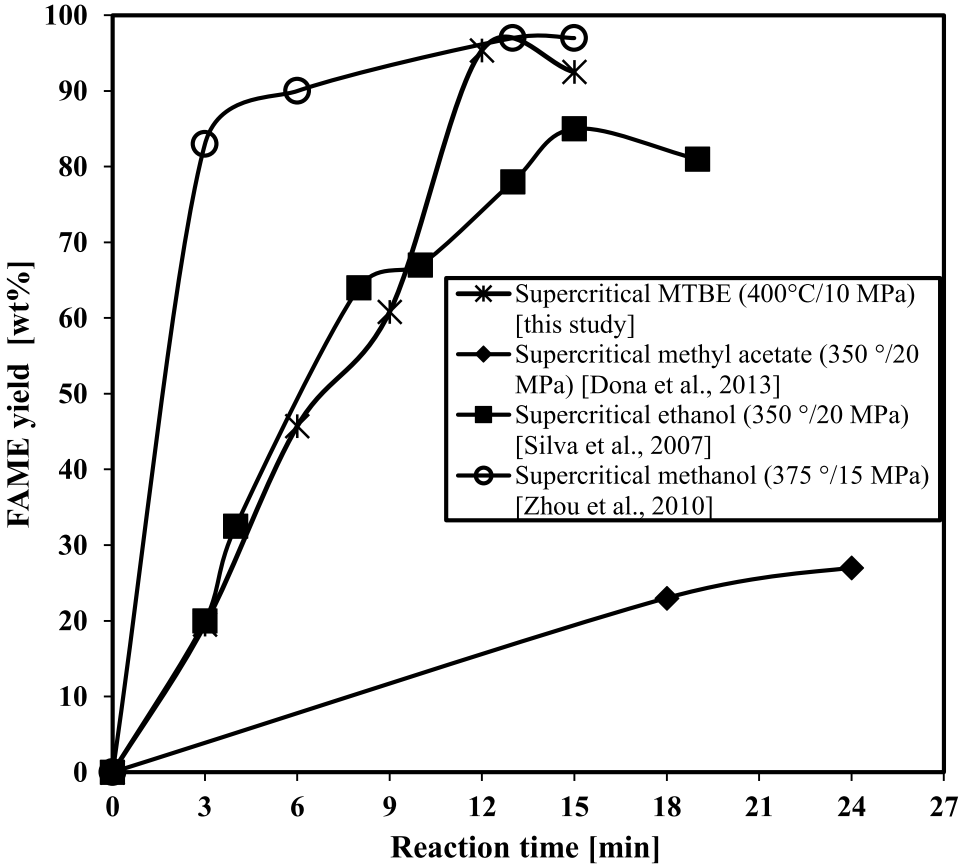
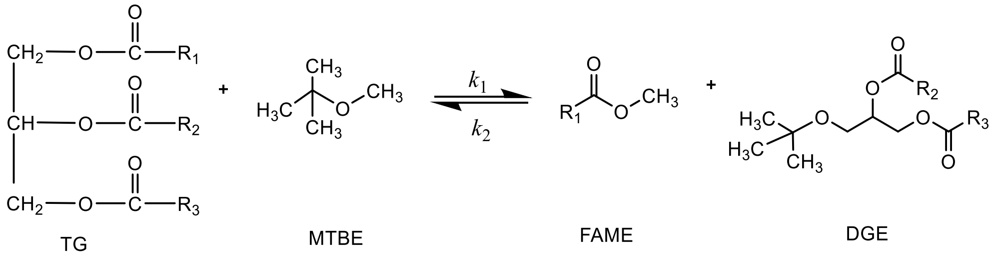


Fig. 5.12. Comparison of FAME yield under various supercritical conditions.

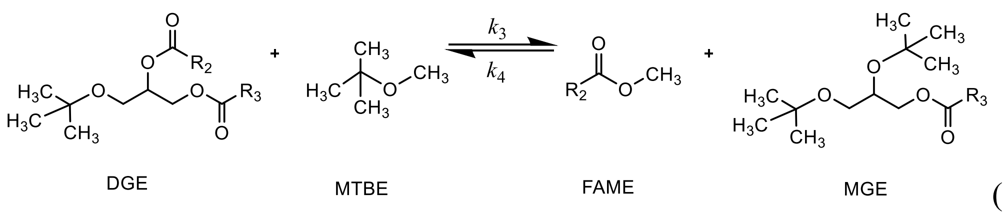
Comparing with the biodiesel production using the conventional method, these final FAME yields were almost the same as those reported by previous studies. In the previous study by Endalew et al. (2011), a biodiesel yield of 94% was obtained by transesterification using Mg-Al-hydrotalcites catalyst after 3 h reaction time. Meanwhile, Umer and Farooq (2008) reported that a biodiesel yield of 96% was achieved by potassium hydroxide-catalyzed transesterification of rapeseed oil after 2 h of reaction time. Having compared the results obtained in this study with those of the previous reports, it was confirmed that the non-catalytic supercritical process utilizing MTBE is another effective route to produce biodiesel. In other words, MTBE is a good candidate to be utilized as a reactant, as well as a reaction medium in the supercritical biodiesel production process.

5.4.4. Reaction kinetics

Reaction kinetics of canola oil conversion to FAME under supercritical MTBE conditions is finally determined. As proposed previously, the reaction between triglyceride and MTBE follows a scheme of multiple reactions, consisting of three consecutive and reversible reaction steps. In the first step, the reaction of TG and MTBE results in FAME and DGE (Eq. 5.1). In the second step, the intermediate DGE then reacts with MTBE to produce FAME and MGE (Eq. 5.2). Finally, in the third step, FAME and GTBE are generated from the reaction between MGE and MTBE (Eq. 5.3).



(5.1)



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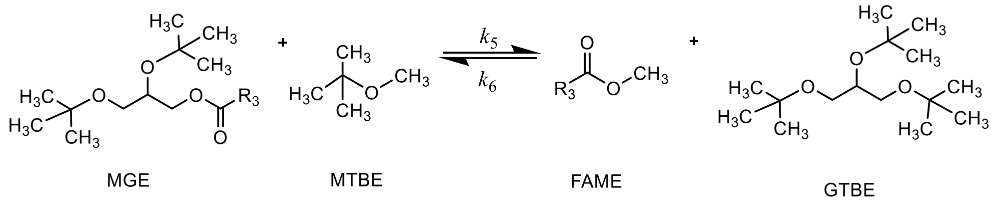


(5.3)

Having deduced the reaction steps described in Eq. (5.1)–(5.3), the rate of change in the concentration of each reaction component can be described by the following differential rate equations:

$$\frac{d[\mathrm{TG}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] + k_2\,[\mathrm{FAME}]\,[\mathrm{DGE}] \tag{5.4}$$

$$\frac{d[\mathrm{DGE}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] - k_2\,[\mathrm{FAME}]\,[\mathrm{DGE}] - k_3\,[\mathrm{DGE}]\,[\mathrm{MTBE}] + k_4\,[\mathrm{FAME}]\,[\mathrm{MGE}] \tag{5.5}$$

$$\frac{d[\mathrm{MGE}]}{dt} = k_3\,[\mathrm{DGE}]\,[\mathrm{MTBE}] - k_4\,[\mathrm{FAME}]\,[\mathrm{MGE}] - k_5\,[\mathrm{MGE}]\,[\mathrm{MTBE}] + k_6\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \tag{5.6}$$

$$\frac{d[\mathrm{FAME}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] - k_2\,[\mathrm{FAME}]\,[\mathrm{DGE}] + k_3\,[\mathrm{DGE}]\,[\mathrm{MTBE}] - k_4\,[\mathrm{FAME}]\,[\mathrm{MGE}] + k_5\,[\mathrm{MGE}]\,[\mathrm{MTBE}] - k_6\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \tag{5.7}$$

$$\frac{d[\mathrm{MTBE}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] + k_2\,[\mathrm{FAME}]\,[\mathrm{DGE}] - k_3\,[\mathrm{DGE}]\,[\mathrm{MTBE}] + k_4\,[\mathrm{FAME}]\,[\mathrm{MGE}] - k_5\,[\mathrm{MGE}]\,[\mathrm{MTBE}] + k_6\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \tag{5.8}$$

$$\frac{d[\mathrm{GTBE}]}{dt} = k_5\,[\mathrm{MGE}]\,[\mathrm{MTBE}] - k_6\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \tag{5.9}$$

where;

[TG] = triglyceride yield [-],

[DGE] = diglyceride mono *tert*-butyl ether yield [-],

[MGE] = monoglyceride di *tert*-butyl ether yield [-],

[MTBE] = *tert*-butyl methyl ether yield [-],

[FAME] = fatty acid methyl ester yield [-],

[GTBE] = *tert*-butyl glycerol ether yield [-],

k_i = rate constants [min^{-1}], and

t = residence time [min].

Since the decomposition of FAME was observed in this study at temperature above 400 °C, it is important to derive the rate equation for this FAME decomposition. The reaction rate of FAME decomposition is derived from the following reaction.

$$\text{FAME} \xrightarrow{k_7} \text{Decomposition product} \tag{5.10}$$

$$\frac{d[\text{Decomposition}]}{dt} = k_7\,[\text{FAME}] \tag{5.11}$$

After incorporating Eq. (5.11) with Eq. (5.7), the rate equation becomes as follows:

$$\begin{aligned}\frac{d[\text{FAME}]}{dt} = {} & k_1\,[\text{TG}]\,[\text{MTBE}] - k_2\,[\text{FAME}]\,[\text{DGE}] + k_3\,[\text{DGE}]\,[\text{MTBE}] \\ & - k_4\,[\text{FAME}]\,[\text{MGE}] + k_5\,[\text{MGE}]\,[\text{MTBE}] - k_6\,[\text{FAME}]\,[\text{GTBE}] \\ & - k_7\,[\text{FAME}]\end{aligned} \tag{5.12}$$

The reaction rate constants were calculated by the least squares of error (LSE) method that gave the best fitting between the experimental and calculated values (Eq. 5.13).

$$\mathrm{LSE} = \min_{\chi}\left(\Sigma([\mathrm{exp}] - [\mathrm{cal}]_{\chi})^2\right) \qquad (5.13)$$

where;

[exp] = Experimental yield [-]

[cal] = Calculated yield estimated by set of kinetic parameters χ [-]

The parity plot comparing experimental and calculated FAME yield is presented in **Fig. 5.13**. As observed in this figure and as suggested by the high r^2 (coefficient of determination) of 0.9736, the model could reproduce the trends of almost the FAME yield in terms of variation in the temperature and residence time.

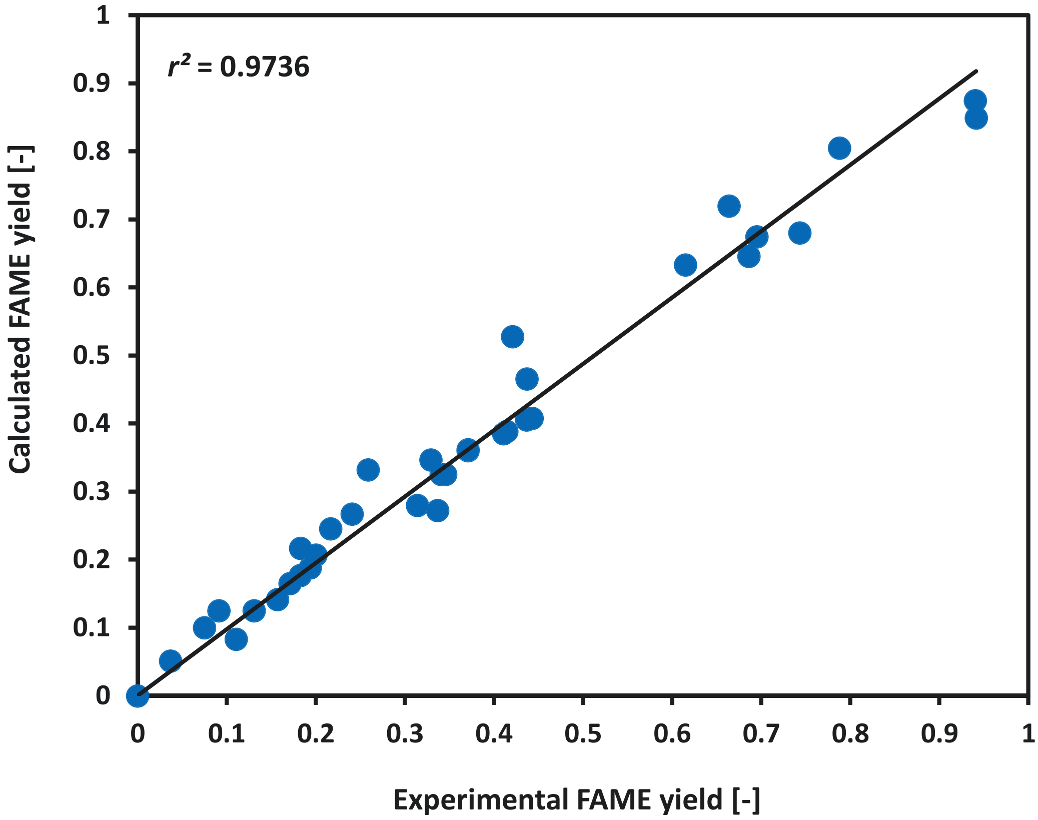


Fig. 5.13. Comparison of experimental and calculated FAME yields in supercritical MTBE (experimental conditions: 200–500 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

Table 5.3 shows the reaction rate constants determined for biodiesel in supercritical MTBE at temperature range of 200–500 °C and reaction time of 3–15 min. The reaction rate constants increase with temperature and reaction time, as expected.

Table 5.3. Kinetic parameters obtained from the first order model for biodiesel production in supercritical MTBE (experimental conditions: 200–500 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

Kinetic parameters	Reaction	Temperature [°C]						
		200	250	300	350	400	450	500
k_1	Eq. (1)	0.0152	0.0381	0.0503	0.0861	0.2036	0.2529	0.3380
k_2	Eq. (1)	0.0159	0.0303	0.0489	0.0721	0.0103	0.0120	0.0014
k_3	Eq. (2)	0.1505	0.3106	0.4512	0.7001	0.9820	0.0907	N/A
k_4	Eq. (2)	6.4084	7.8489	8.9567	10.5912	8.7196	0.1381	3.1469
k_5	Eq. (3)	0.1044	0.1961	0.3843	0.4492	2.0817	2.1084	3.2822
k_6	Eq. (3)	0.7027	1.0896	1.4051	1.7300	0.0148	0.1134	0.1715
k_7	Eq. (10)	0.0012	0.0038	0.0106	0.0237	N/A	0.0293	0.2414

After the corresponding reaction rate constants were determined, the temperature dependence reaction rate constant is calculated by Arrhenius equation as shown in Eq. 5.14. **Fig. 5.14** presents the Arrhenius plots of the individual rate constant for biodiesel production in supercritical MTBE. Expectedly, the logarithm of the overall reaction rate constants versus the inverse temperature is linear. It can be confirmed that transeterification reaction of canola oil to FAME in supercritical MTBE obeys the Arrhenius behavior.

$$k_i(T) = Ae^{-Ea/RT} \qquad (5.14)$$

where,

k_i is reaction rate constant [min^{-1}], A is Pre-exponential factor [min^{-1}], Ea is Activation energy [kJ mol^{-1}], R is Universal molar gas constant [kJ mol^{-1} K^{-1}], T is Temperature [K].

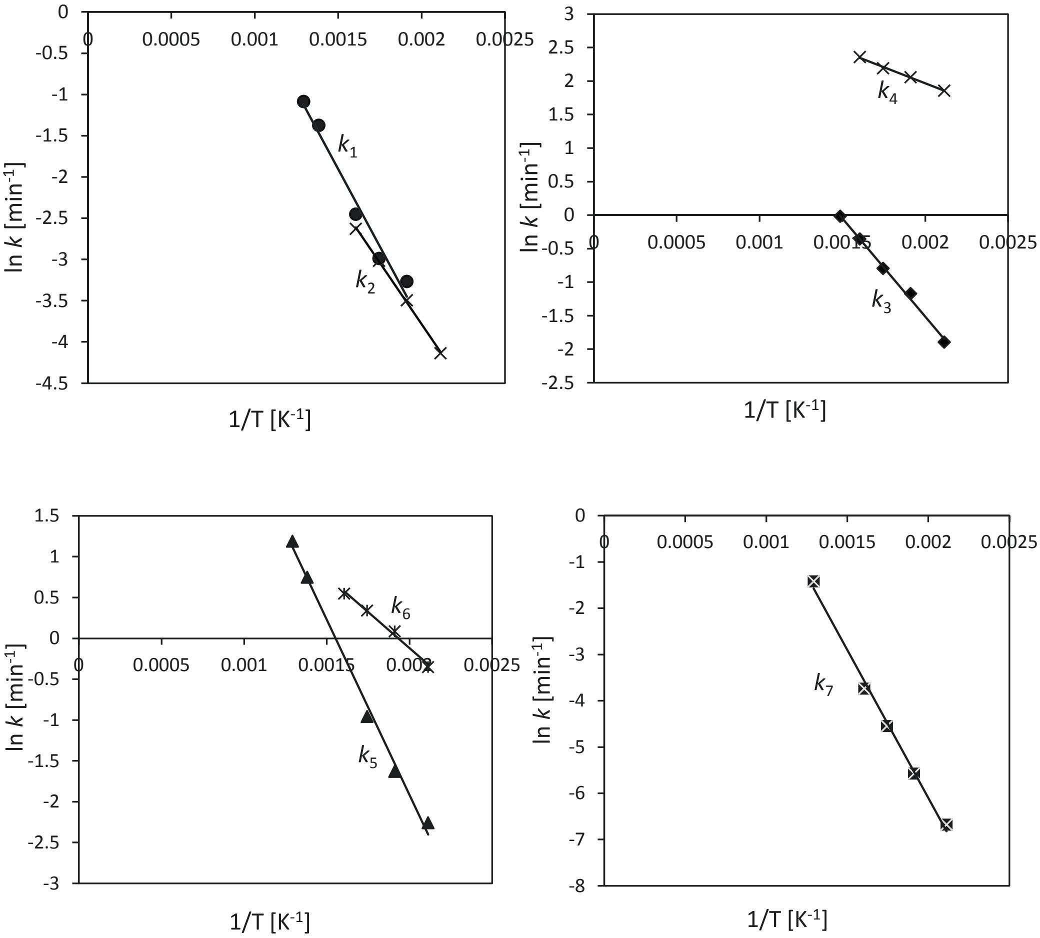


Fig. 5.14. Arrhenius plots of the individual rate constant of biodiesel production treated in supercritical MTBE (experimental conditions: 200–500 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

From the Arrhenius plots above, the activation energy (Ea) and pre-exponential factor (A) for the detailed kinetic analysis were determined as shown in **Table 5.4**. Activation energy between 14.63 to 53.19 kJ/mol were determined for biodiesel production in supercritical MTBE from the calculation in this study. The activation energy obtained in supercritical MTBE method is comparable with the supercritical methanol and ethanol. Kusdiana and Saka (2001) calculated the activation energy for the transesterification in supercritical methanol. They reported that the activation energy of 38.5 kJ/mol was obtained in the temperature range 200–270 °C. In another previous study by Varma and Madras (2007), the activation energies for the transesterifications of castor and linseed oils in supercritical methanol at 200–350 °C were 35.0 and 46.5 kJ mol^{-1} for castor and linseed oil, respectively. In addition, He et al. (2007) determined the activation energies for the transesterifications of soybean oil and palm oil. Activation energies of 1.2 and 14.9 kJ mol^{-1} were obtained for soybean oil and palm oil, respectively at temperature range 210–230 °C. Moreover, under the same supercritical methanol conditions, Ghoreishi and Moein (2013) investigated the activation energy for the transesterification of waste vegetable oil at temperature range 240–280 °C. They obtained the activation energy value of 31.7 kJmol^{-1}. Activation energies values obtained from this study are in a good agreement with the above reported literature values.

Table 5.4. Activation energies and pre-exponential factors (experimental conditions: 200–500 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

Reaction direction	Equations	Rate constants [min^{-1}]	Activation energy (*Ea*) [kJ mol^{-1}]	Pre-exponential factor (*A*) [min^{-1}]	r^2
TG → DGE	Eq. (1)	k_1	31.26	41.86	0.97
DGE → TG	Eq. (1)	k_2	24.63	8.51	0.99
DGE → MGE	Eq. (2)	k_3	24.36	77.14	0.99
MGE → DGE	Eq. (2)	k_4	8.03	49.32	0.99
MGE → GTBE	Eq. (3)	k_5	35.68	785.88	0.99
GTBE → MGE	Eq. (3)	k_6	14.63	29.97	0.99
FAME → Decomposition product	Eq. (10)	k_7	53.19	811.59	0.99

For transesterification in supercritical ethanol, Santana et al. (2012) determined the activation energies for the consecutive transesterification reaction of sunflower oil at

150–200 °C. They found that activation energies values of 104.8, 98.3, 91.7, and 58.6 kJ mol^{-1} were calculated for the transformation reaction of triglyceride (TG) to diglyceride (DG), DG to TG, DG to monoglyceride (MG), and MG to DG, respectively. In another study by Silva et al. (2007), the activation energy of 78.7 kJ mol^{-1} was obtained for the kinetics of transesterification of soybean oil in supercritical ethanol in temperature range 275–348 °C. In addition, Velez et al. (2012) also determined the kinetics of transeterification of sunflower oil in supercritical ethanol at 300–345 °C. The activation energy examined from this calculation was 67.6 kJ mol^{-1}. The activation energy for biodiesel production using supercritical MTBE route is lower than that of supercritical ethanol method, but it shows similarity with supercritical methanol method.

Campanelli et al. (2010) have also investigated the kinetics of transesterification of oil in supercritical methyl acetate. They used soybean oil, sunflower oil, *Jatropha curcas* oil, and waste soybean as feedstocks. They reported that the activation energies of 373, 349, 364, and 369 kJ mol^{-1} were obtained with their calculation technique for transterification of soybean oil, sunflower oil, *J. curcas* oil, and waste soybean oil, respectively. Since activation energy in supercritical MTBE is lower than that in supercritical methyl acetate, it can be confirmed that transterification process in supercritical MTBE is much faster than that in supercritical methyl acetate.

5.5. Conclusion

The non-catalytic supercritical MTBE method was proposed as a new route to produce biodiesel. The results revealed that MTBE could react with triglyceride under supercritical conditions, generating fatty acid methyl ester (FAME) and glycerol tert-butyl ether (GTBE). Under these reaction conditions, there was no glycerol discovered as a by-product. The FAME yield increased with temperature from 200 to 400 °C, but it decreased above 400 °C due to thermal decomposition of FAME at higher temperature. This result was consistent with the previous studies that thermal decomposition of biodiesel mainly occurs at temperature above 400 °C. The effect of pressure investigated here was negligible. The highest biodiesel yield of 0.94 was obtained at 400 °C, 10 MPa, with an oil-to-MTBE molar ratio of 1:40 in the short reaction time of 12 min. The activation energies of 14.63–53.19 kJ mol^{-1} were obtained for transesterification of canola oil in supercritical MTBE at 200–500 °C, 10 MPa, and reaction time of 3–15 min. The calculation results of activation energy obtained from this study was close to the value for the transesterification of canola oil in supercritical methanol.

CHAPTER 6

Biodiesel production in supercritical ethanol using a novel spiral reactor

6.1. Introduction

Presently, research on biodiesel production technologies has attracted a large amount of interest as a consequence of the depletion of fossil fuel reserves. The research and development on biodiesel production have improved year by year.

Biodiesel can be synthesized through various methods, i.e. homogeneous acid and alkali-catalyzed transesterification (Marchetti and Errazu, 2008; Suwannakarn et al., 2009; Vicente et al., 2004), heterogeneous acid and alkali-catalyzed trensesterification (Kim et al., 2004; Kouzu et al., 2009; Park et al.; 2010; Pesaresi et al., 2009; Kazembe-

Phiri et al., 2010) as well as biocatalyst or enzymatic transesterification (Bajaj et al., 2010).

All above mentioned methods are still facing the challenges such as low FFA and water content of feedstock requirements, longer reaction time, undesirable reaction generation, pre-treatment compulsion, strict reaction conditions, and catalyst or biocatalyst necessity. To overcome these drawbacks, non-catalytic transesterification under supercritical conditions was proposed. This technology provides some advantages such as no catalyst requirement, a higher reaction rate, and applicability to various feedstocks without pre-treatment. Besides, there is no waste water generated in downstream process and easier separation and purification of products (Saka and Kusdiana, 2001; Kusdiana and Saka, 2001; Kusdiana and Saka, 2004).

However, this technology is also still facing the challenges regarding heat recovery that has still problematic in terms of its application for commercial uses. To circumvent this problem, a novel spiral reactor was proposed in this study. This spiral reactor composed of high-temperature transterification reactor and a parallel tube heat exchanger. The high-temperature transterification reactor consisted of insulated tubing that allows transesterification reaction occurs. Meanwhile, the parallel tube heat exchanger consisted of two tubes place side-by-side in a spiral formation that is able to recover the heat.

The purpose of this work is to obtain the fundamental characteristics of spiral reactor for biodiesel production in supercritical ethanol. To meet this goal, temperature and reaction time effect on biodiesel production was investigated. In addition, energy efficiency of biodiesel production in supercritical ethanol using conventional flow and spiral reactor was also compared.

The originality of this study highlights the utility of the novel spiral reactor for biodiesel production under supercritical ethanol conditions, which, to the best of our knowledge, is not available in the previous study. Ethanol was used as a reaction medium in this experiment since biodiesel obtained from ethanol–fatty acid ethyl esters (FAEEs)–has a higher cetane number and heating value compared to fatty acid methyl esters due to the greater number of carbon atoms contained in ethanol (Bouaid et al., 2007; Encinar et al., 2007) and ethanol can be derived from renewable resources (Ĉernoch et al., 2010; Joshi et al., 2010; Oliveira et al., 2010; Pisarello et al., 2010).

6.2. Experimental procedures

Biodiesel production in supercritical ethanol using spiral reactor was carried out in the temperature range of 270–400 °C since the critical temperature and pressure of ethanol are 241.56 °C and 6.268 MPa, respectively (Bazaeve et al., 2007). A pressure used in this study was 20 MPa since some previous studies reported that optimum condition of biodiesel production in supercritical ethanol could be achieved at 20 MPa (Silva et al., 2007; Santana et al., 2012; Trentin et al., 2011; da Silva et al., 2010; Vieitez et al., 2011; Varma and Madras, 2007). The oil-to-ethanol molar ratio employed in this study was fixed at 1:40 since some references (Silva et al., 2007; Velez et al., 2012) concluded that the optimum molar ratio of oil to reactant for biodiesel production under supercritical conditions is 1:40. The transesterification reaction was performed over 3 to 30 min and were made in triplicates. Samples were collected after achieving a steady state. The experimental apparatus used in this research is schematically illustrated in Fig. 4.2 (chapter 4).

Residence time was determined using Eq. 6.1, taking into consideration mass flow rate of oil and ethanol and also density of oil and ethanol. Product concentration was calculated using calibration curve on the basis of peak area.

$$t = \frac{V}{m_1 / \rho_1 + m_2 / \rho_2} \tag{6.1}$$

where; t is residence time [min], V Reactor volume [36.65 mL], m_1 is mass flow rate of oil [g/min], ρ_1 is density of oil [g/mL], m_2 is mass flow rate of ethanol [g/min], and ρ_2 is density of ethanol [g/mL].

FAEE yields from the experimental results were calculated by dividing the moles of product FAEE by moles of fatty acid group in the initial TG as shown in Eq. 6.2.

$$\text{Product yield} = \frac{\text{mol of product FAEE}}{\text{mol of fatty acid group in initial TG}} \tag{6.2}$$

6.3. Experimental conditions

The experimental conditions for this corresponding study is shown in **Table 6.1**.

Table 6.1. Experimental conditions for this corresponding study

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3-30 min
Oil-to-ethanol molar ratio	1:40
Reactor type	Spiral reactor
Temperature	270-400 °C
Pressure	20 MPa

6.4. Results and Discussion

6.4.1. Fundamental characteristics of spiral reactor

To investigate the fundamental characteristics of spiral reactor, the temperature profile of spiral reactor was presented. **Fig. 6.1** reveals the temperature profile at each position of the spiral reactor for the target temperatures of 270, 300, 350, and 400 °C. As observed in this figure, the feedstocks were rapidly heated up to the reaction temperature in the heat exchanger part and were maintained at the desired reaction temperature in the reactor part. In addition, the temperatures of the hot and cold tubes in the heat exchanger were almost equal, indicating that heat recovery is conducted as expected.

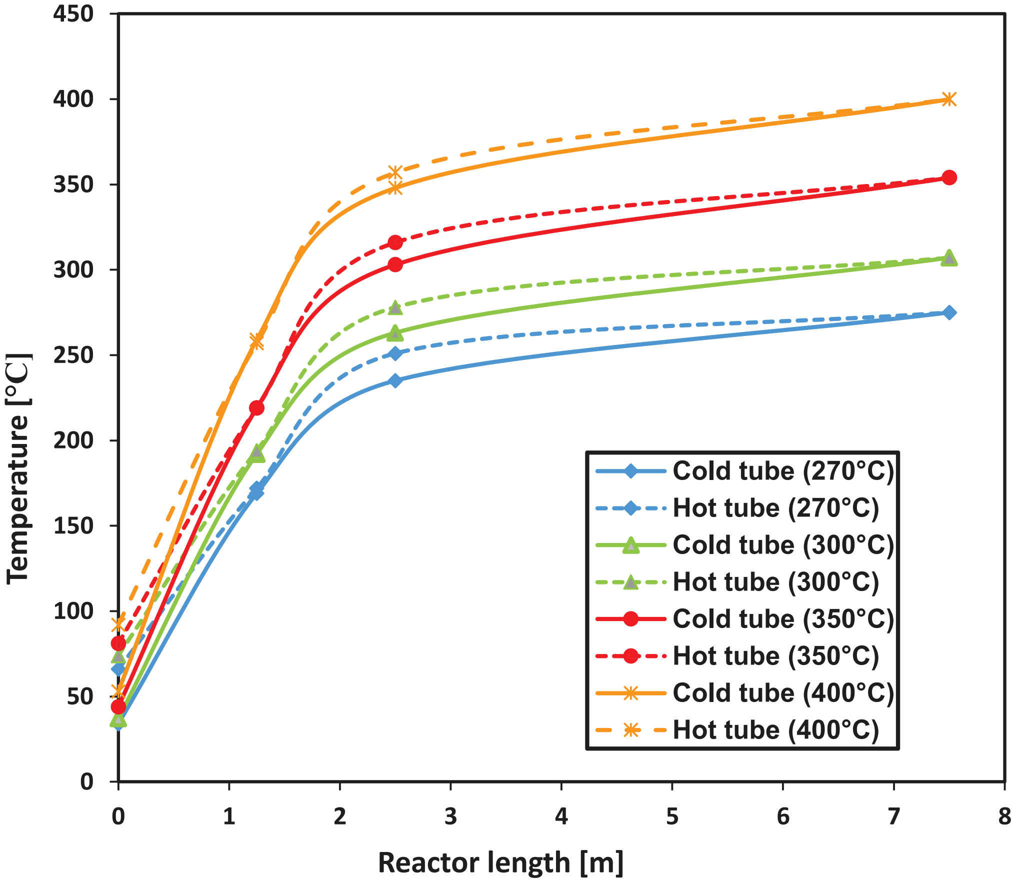


Fig. 6.1. Temperature profile of spiral reactor.

6.4.2. Temperature effect on FAEE yield

To investigate the effect of temperature on FAEE yields using the spiral reactor in more detail, the transesterification of canola oil and ethanol in this study was carried out in the temperature range of 270–400 °C at a fixed oil-to-ethanol molar ratio of 1:40 and pressure of 20 MPa. Theoretically, higher reaction temperatures would result in higher reaction rates, which consequently corresponds to higher FAEE yields for the same reaction time. **Fig. 6.2** shows the change in FAEE yield with temperature and reaction time. As observed in this figure, the yield of FAEE obviously increased with a change in reaction temperature from 270 to 400 °C as expected. This result is consistent with the previous work of Madras et al. (2004), who reported that the conversion of oil to FAEE in supercritical ethanol increased with the increase in temperature from 200 to 400 °C.

As observed in **Fig. 6.2**, a high FAEE yield could be achieved over a short reaction time using supercritical ethanol, which is the important feature of biodiesel production under supercritical conditions. Santana et al. (2012) obtained a biodiesel yield of 80 % within a relatively short reaction time of around 6 min under supercritical ethanol conditions using carbon dioxide as a cosolvent. Muppaneni et al. (2012) reported FAEE yields as high as around 85 % within 20 min at 295 °C for the ethanolysis of camelina oil. Rathore and Madras (2007) achieved a very high conversion above 80 % for the transesterification of various kinds of oil (palm, groundnut, *Pongamia pinnata*, and *Jatropha curcas* oil) in supercritical methanol and ethanol within a reaction time of 10 min.

It can also be noticed from **Fig. 6.2** that complete conversions of canola oil to FAEE at 400 °C were achieved in less than 10 min, while reaction times of 20 min were required for complete conversions at 350 °C. Meanwhile, the complete conversion of canola oil could not be achieved at 270 °C even after 30 min. This result is in complete agreement with the previous works of Rathore and Madras (2007), who observed that the conversions of oil to biodiesel are significant after 40 min at lower temperatures and after 10 min at high temperatures. In addition, Silva et al. (2007) investigated the continuous production of FAEE from soybean oil in supercritical ethanol under similar operating conditions, using a tubular reactor. They achieved an ester content of around 65 % at 20 MPa and 350 °C with an ethanol-to-oil molar ratio of 40:1 and a residence time of 10 min. Thus, the trends in the results obtained in this study are also in agreement with that of their report (Silva eta l., 2007).

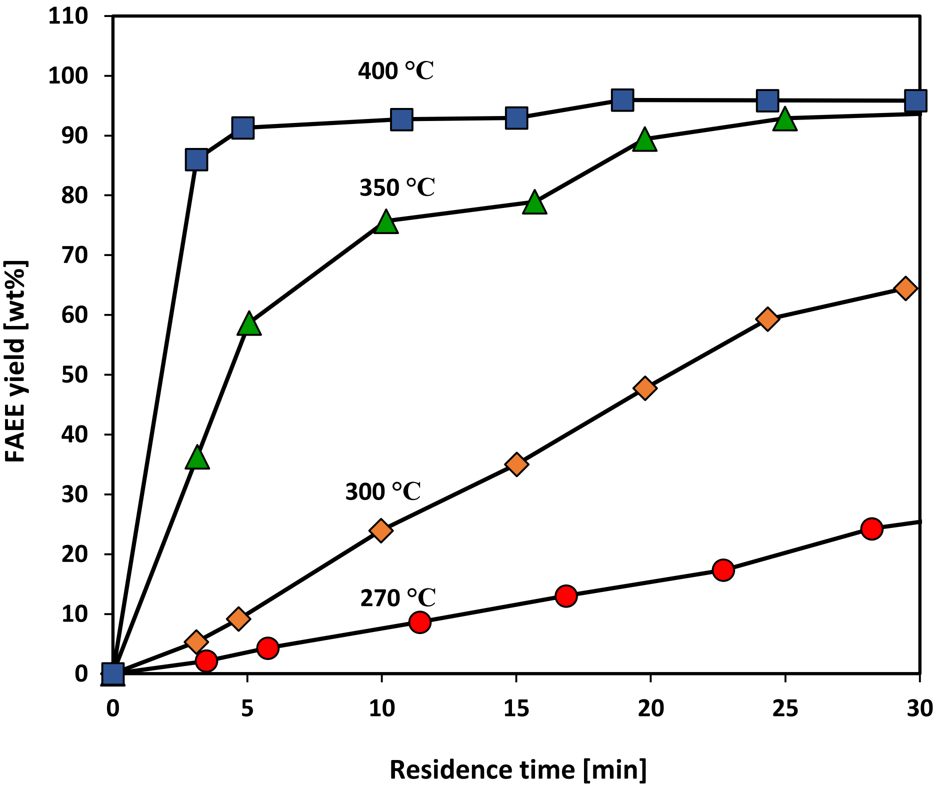


Fig. 6.2. Effect of temperature on FAEE yield (experimental conditions: 20 MPa, ethanol-to-oil molar ratio of 40:1).

6.4.3. Residence time effect on product yield

The changes in feedstock TG concentration, yields of final product FAEE, and other observed intermediates were investigated under various temperatures from 270 to 400 °C. The oil-to-ethanol molar ratio was fixed at 1:40 and the pressure was kept at 20 MPa. The changes in yields at 270, 300, 350, and 400 °C are shown in **Figs. 6.3**, **6.4**, **6.5**, and **6.6**, respectively.

At 270 °C, the yield of FAEE was relatively low. The DG yield increased up to 10 min, but decreased after reaction times greater than 10 min. Meanwhile, the trends in MG and glycerol production tended to increase with reaction time.

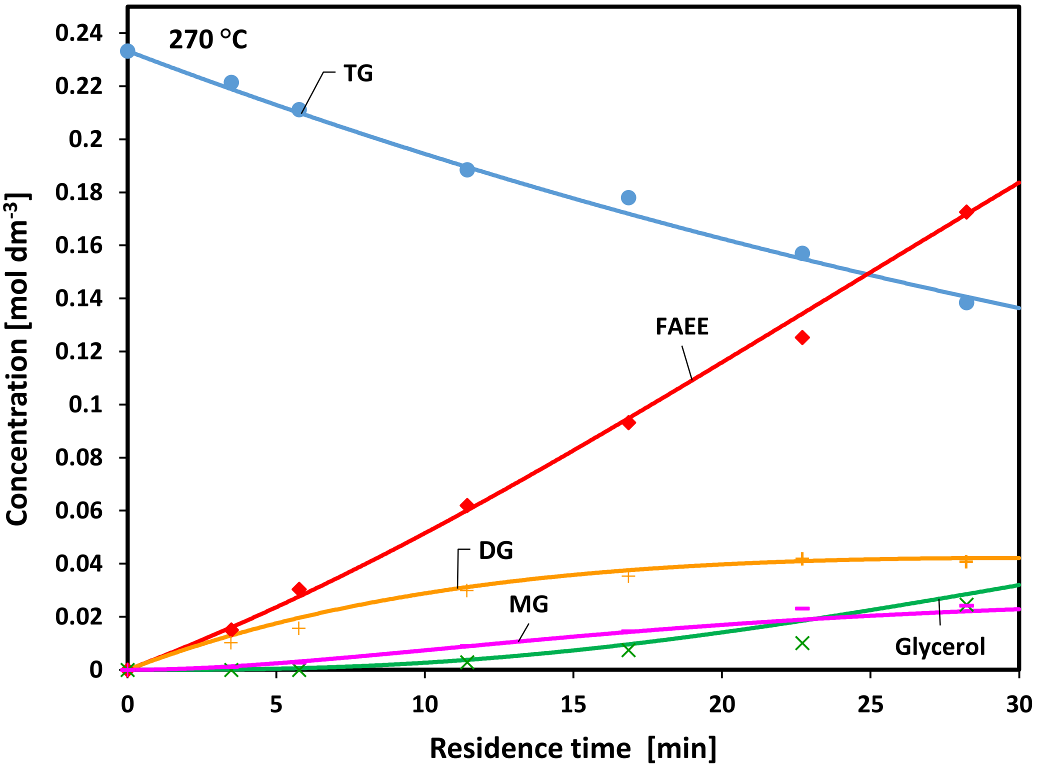


Fig. 6.3. Effect of residence time on FAEE concentration and triglyceride consumption (experimental conditions: 270 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

At 300 °C, the conversion of canola oil is higher than that at 270 °C, but it is still relatively low.

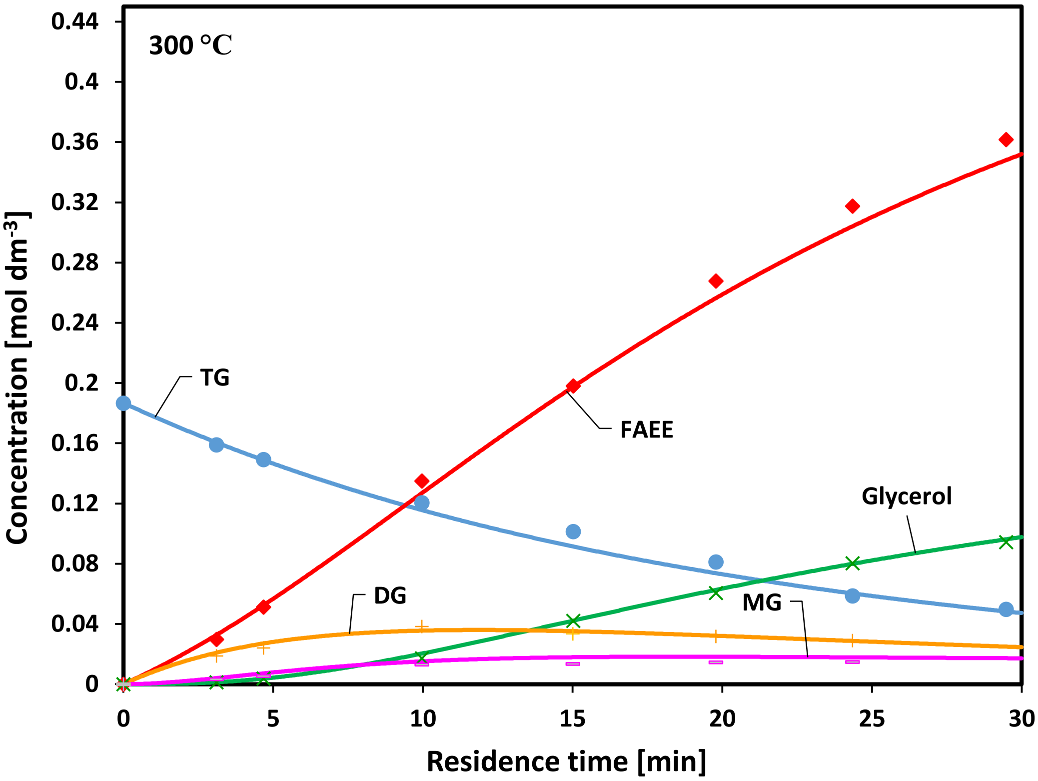


Fig. 6.4. Effect of residence time on FAEE concentration and triglyceride consumption (experimental conditions: 300 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

At 350 °C, a significant change in the conversion of canola oil to FAEE was noted at a reaction time of 10 min. FAEE yields of about 0.894 and 0.937 mol/mol (concentration of 0.361 and 0.378 mol dm^{-3}) were obtained after transesterification reaction times of 20 and 30 min, respectively. In particular, transesterification was almost complete within 30 min, converting almost all canola oil to FAEE. It is to be noted that Silva et al. [13] reported that 350 °C is the best temperature to carry out transesterification reactions in continuous mode under supercritical ethanol conditions. Moreover, similar results have been reported by Kusdiana and Saka [11], Madras et al. [30], and Warabi et al. [33] who carried out transesterification reactions in a batch reactor under supercritical methanol conditions.

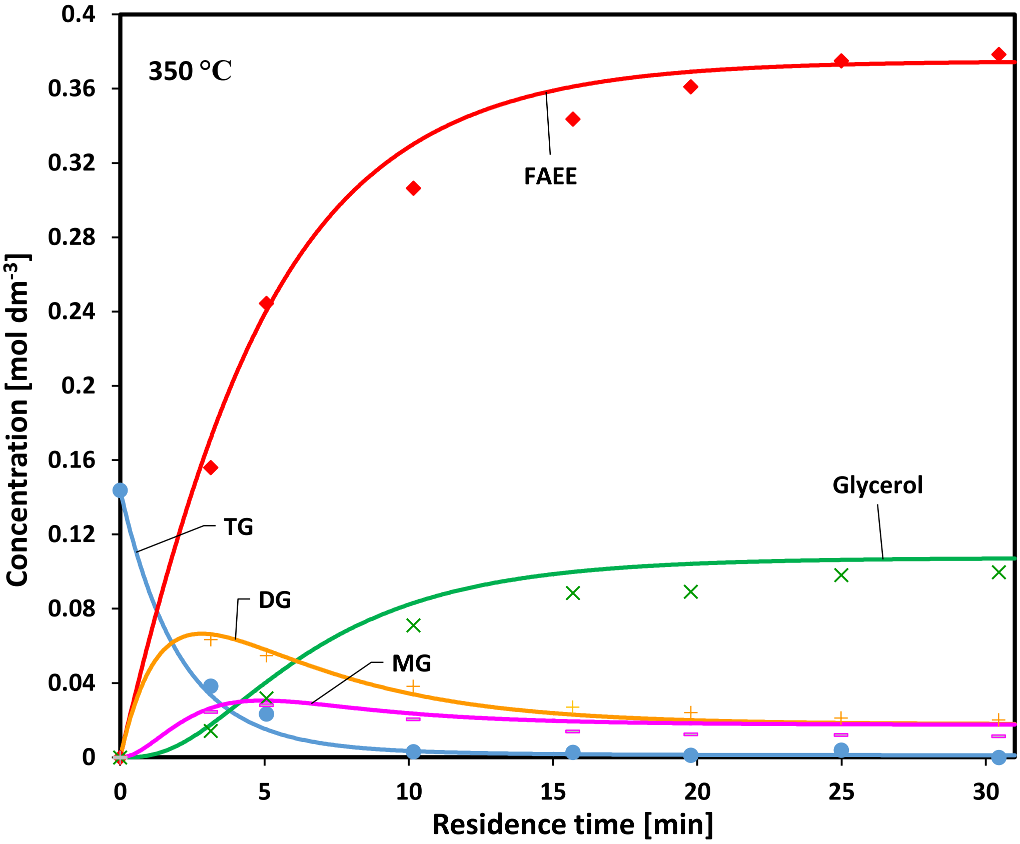


Fig. 6.5. Effect of residence time on FAEE concentration and triglyceride consumption (experimental conditions: 350 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

At 400 °C, the FAEE yield increased significantly from 3 min to 10 min; however, after 10 min of reaction time, this yield was relatively constant. Reaction temperature was found to directly affect the reaction rate of other components including intermediate compounds such as DG and MG. As expected, consumption of TG was favored with increasing temperature; the concentration of TG after 3 min were approximately 0.222, 0.159, 0.038, and 0.001 mol dm^{-3} at 270, 300, 350, and 400 °C, respectively. From these results, increasing the reaction temperature was much more effective compared to elongated reaction times for improving FAEE yields.

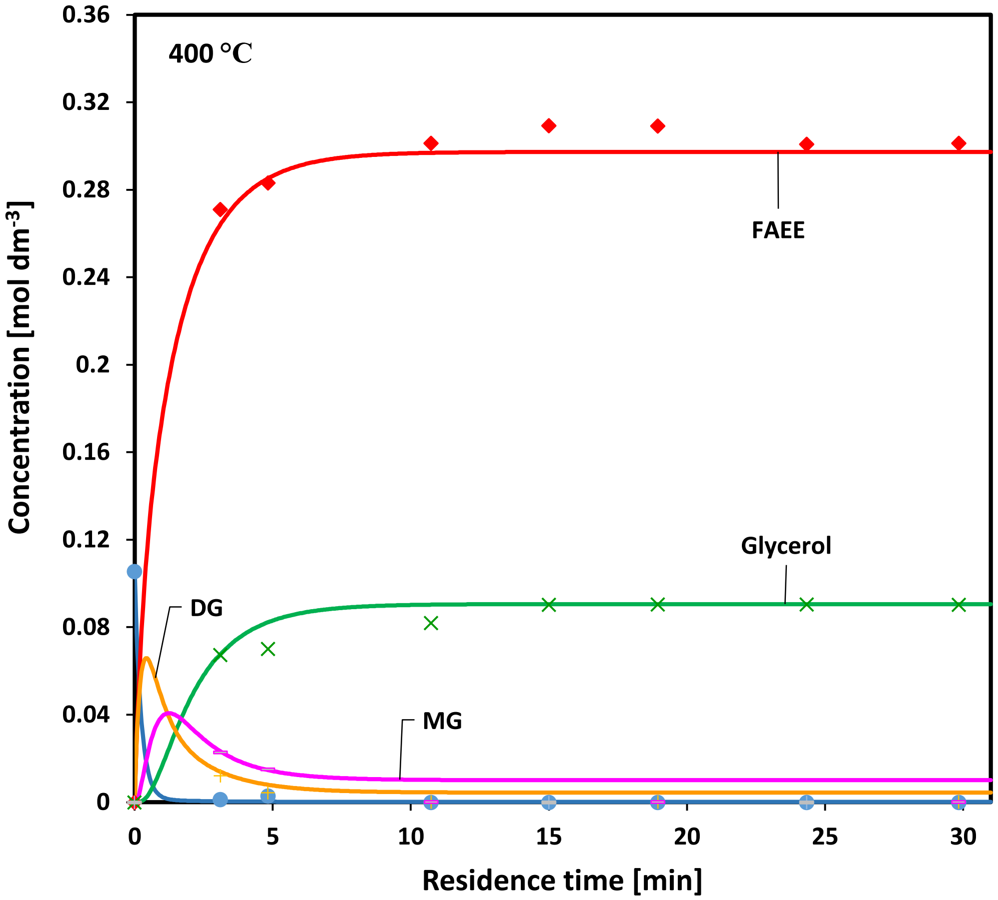


Fig. 6.6. Effect of residence time on FAEE concentration and triglyceride consumption (experimental conditions: 400 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

The high concentration of intermediate compounds, DG and MG, were observed in the initial reaction time examined, demonstrating the evident formation and consumption of both compounds as the reaction proceeded. This result is in complete agreement with the previous findings of da Silva et al. (2010), who conducted the continuous production of biodiesel in a microtube reactor under supercritical ethanol conditions. Meanwhile, the glycerol yield increased with reaction time, as reported in the previous works of da Silva et al. (2010), Aimaretti et al. (2009), and Anitescu et al. (2008).

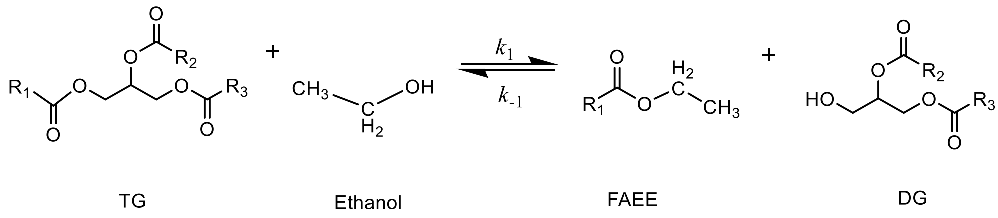
As mentioned previously, an interesting characteristic of biodiesel production conducted under supercritical conditions is the short reaction time. In this study, the highest FAEE yield at 350 °C was 0.937 mol/mol (98.1 %) at 30 min using an oil-to-ethanol molar ratio of 1:40 under a pressure of 20 MPa. This high yield matches the previous report by Warabi et al. (2004), who reported an FAEE yield of 95 % for the transesterification of rapeseed oil in supercritical ethanol at 350 °C in 45 min using a batch reactor, and that obtained by Silva et al. (2007), who achieved a maximum of 80 % for the supercritical ethanolysis of soybean oil using a tubular reactor at 350 °C, 20 MPa, and 15 min reaction time. In addition, Muppaneni et al. (2012) used a microreactor for the transesterification of carmelina oil, obtaining an FAEE yield of 85 % at 400 °C, 20 MPa, and 32 min reaction time. Some of the reports of FAEE yields obtained in transesterification reactions in supercritical ethanol using different reactors are summarized in **Table 6.2**.

Table 6.2. Comparison of FAEE yield obtained in supercritical ethanol using various kinds of reactor

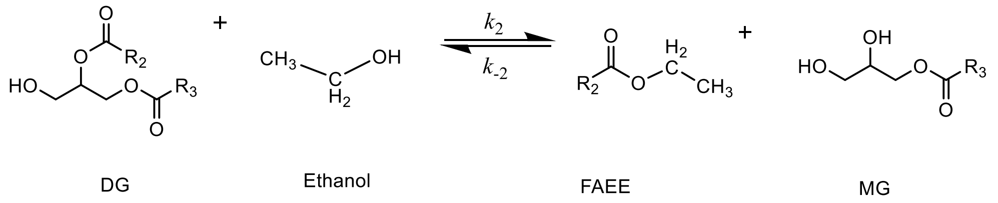
Feedstock	Reaction conditions					Yield/ conversion [%]	Reference
	Temperature [°C]	Pressure [MPa]	Reaction time [min]	Ethanol to oil ratio	Type of reactor		
Canola oil	350	20	30.45	40	Spiral reactor	98	This study
Rapeseed oil	350	15	45	42	Batch reactor	95	Warabi et al. (2004)
Sunflower oil	400	20	30	40	Batch reactor	95	Madras et al. (2004)
Carmelina oil	295	10	20	45	Microreactor	85	Muppaneni et al. (2012)
Soybean oil	350	20	15	40	Tubular reactor	80	Silva et al. (2007)
Palm oil	349	20	30	33	Tubular reactor	79.2	Gui et al. (2009)
Linseed oil	250	NA	8	41	Batch reactor	90	Demirbas (2009)
Linseed oil	300	20	40	40	Batch reactor	90	Varma and Madras (2007)
Castor oil	300	20	30	40	Batch reactor	95	Varma and Madras (2007)

6.4.4. Kinetics of transesterification in supercritical ethanol

The kinetics of transesterification of canola oil and ethanol to FAEE were analyzed in order to quantify the effects of temperature and reaction time investigated above. The transesterification reaction of canola oil with ethanol consists of multiple reactions, each consisting of a number of reversible reactions. The transesterification reaction occurs in three consecutive steps as follows: in the first step of Eq. 6.3, the reaction of TG and ethanol produces FAEE and DG. In the second step of Eq. 6.4, the intermediate DG then reacts with ethanol to generate FAEE and MG. Lastly, in the third step of Eq. 6.5, the reaction between MG and ethanol produces FAEE and glycerol.



(6.3)



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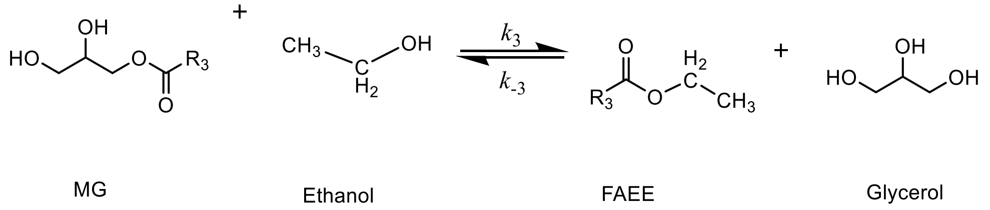


(6.5)

Having determined the reaction steps above, the next step is to fit the experimental data with a kinetic model with the aim of elucidating its kinetic parameters. Kinetic modeling is important for the determination of the relative kinetic rates based on the reaction pathway. Each reaction shown above is assumed to follow the second-order kinetics; and the rate of change in concentration can thus be expressed by the differential rate equations shown in Eqs. 6.6–6.11.

$$\frac{d[\mathrm{TG}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{Ethanol}] + k_{-1}\,[\mathrm{FAEE}]\,[\mathrm{DG}] \tag{6.6}$$

$$\frac{d[\mathrm{DG}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{Ethanol}] - k_{-1}\,[\mathrm{FAEE}]\,[\mathrm{DG}] - k_2\,[\mathrm{DG}]\,[\mathrm{Ethanol}] + k_{-2}\,[\mathrm{FAEE}]\,[\mathrm{MG}] \tag{6.7}$$

$$\frac{d[\mathrm{MG}]}{dt} = k_2\,[\mathrm{DG}]\,[\mathrm{Ethanol}] - k_{-2}\,[\mathrm{FAEE}]\,[\mathrm{MG}] - k_3\,[\mathrm{MG}]\,[\mathrm{Ethanol}] + k_{-3}\,[\mathrm{FAEE}]\,[\mathrm{GL}] \tag{6.8}$$

$$\frac{d[\mathrm{FAEE}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{Ethanol}] - k_{-1}\,[\mathrm{FAEE}]\,[\mathrm{DG}] + k_2\,[\mathrm{DG}]\,[\mathrm{Ethanol}] - k_{-2}\,[\mathrm{FAEE}]\,[\mathrm{MG}] + k_3\,[\mathrm{MG}]\,[\mathrm{Ethanol}] - k_{-3}\,[\mathrm{FAEE}]\,[\mathrm{GL}] \tag{6.9}$$

$$\frac{d[\mathrm{Ethanol}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{Ethanol}] + k_{-1}\,[\mathrm{FAEE}]\,[\mathrm{DG}] - k_2\,[\mathrm{DG}]\,[\mathrm{Ethanol}] + k_{-2}\,[\mathrm{FAEE}]\,[\mathrm{MG}] - k_3\,[\mathrm{MG}]\,[\mathrm{Ethanol}] + k_{-3}\,[\mathrm{FAEE}]\,[\mathrm{GL}] \tag{6.10}$$

$$\frac{d[\mathrm{GL}]}{dt} = k_3\,[\mathrm{MG}]\,[\mathrm{Ethanol}] - k_{-3}\,[\mathrm{FAEE}]\,[\mathrm{GL}] \tag{6.11}$$

where; [TG] is triglyceride concentration [mol dm^{-3}], [DG] is diglyceride concentration [mol dm^{-3}], [MG] is monoglyceride concentration [mol dm^{-3}], [Ethanol] is ethanol concentration [mol dm^{-3}], [FAEE] is fatty acid ethyl ester concentration [mol dm^{-3}],

[GL] is glycerol concentration [mol dm^{-3}], k_i is rate constants [dm^3 mol^{-1} min^{-1}], and t is residence time [min].

The rate constants were determined using the non-linear regression with the least-squares-error (LSE) method (i.e., the difference between the experimental and calculated values) to fit the model with the experimental data. **Fig. 6.7** reveals the parity plot comparing the experimental data for FAEE yields with the value calculated by the model using the LSE method. Based on the graph and as suggested by the high r^2 (coefficient of determination) value, the model predictions appear to fit the experimental data fairly well.

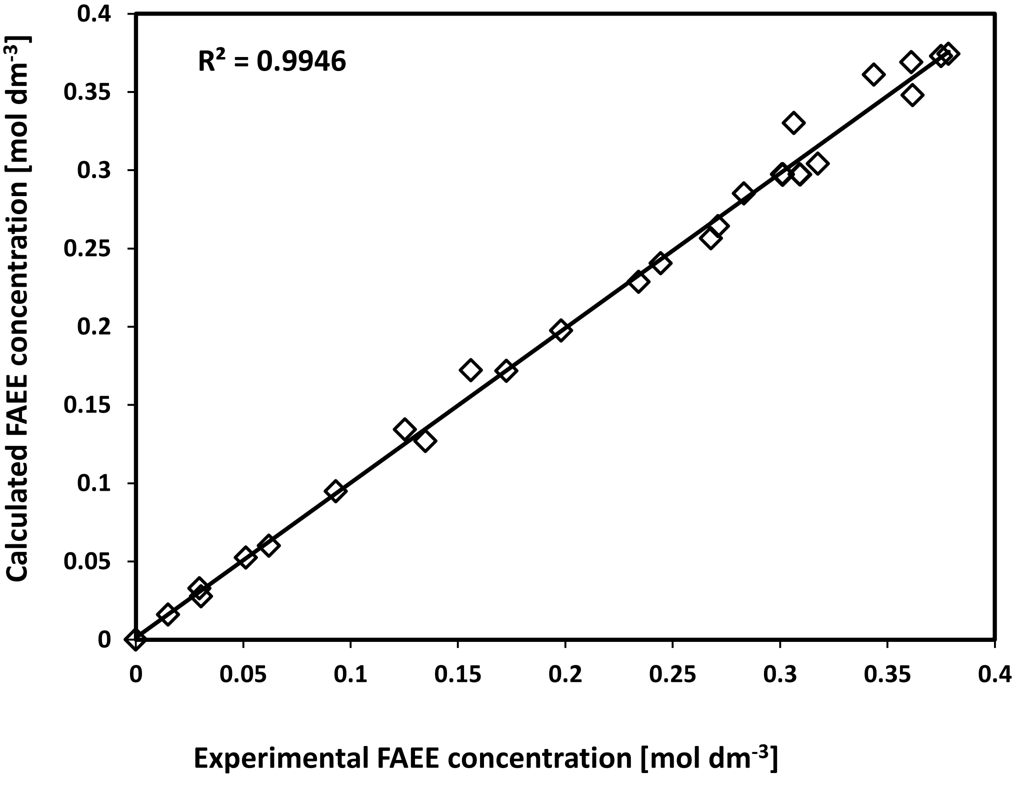


Fig. 6.7. Comparison of experimental and calculated FAEE concentration in supercritical ethanol using spiral reactor (Experimental conditions: 270–400 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

Based on the results of biodiesel yield as a function of reaction time and temperature, the corresponding reaction rate constants were calculated. The reaction rate constants obtained from the second-order model in the temperature range of 270–400 °C are presented in **Table 6.3.** Having calculated reaction rate constants at different temperatures, the temperature dependence on the rate coefficient is modeled by the Arrhenius equation. The Arrhenius plots of the individual rate constants for the transesterification reaction of canola oil to FAEE are shown in **Fig. 6.8**. Expectedly, the logarithm of the overall reaction rate constants was linear with the inverse temperatures, demonstrating that the transesterification reaction of canola oil to FAEE in supercritical ethanol obeys the Arrhenius equation.

Table 6.3. Kinetic parameters obtained from the second order model for biodiesel production in supercritical ethanol using spiral reactor (Experimental conditions: 270–400 °C, 20 MPa, ethanol-to-oil molar ratio of 40:1).

Kinetic parameters [$dm^3\ mol^{-1}\ min^{-1}$]	Denotation	Temperature [°C]			
		270	300	350	400
k_1	TG → DG	2.38×10^{-3}	6.83×10^{-3}	8.83×10^{-2}	9.08×10^{-1}
k_{-1}	DG → TG	8.00×10^{-3}	2.08×10^{-2}	7.38×10^{-2}	3.49×10^{-1}
k_2	DG → MG	8.03×10^{-3}	2.10×10^{-2}	5.80×10^{-2}	2.81×10^{-1}
k_{-2}	MG → DG	4.00×10^{-2}	1.34×10^{-1}	7.86×10^{-1}	1.62
k_3	MG → GL	1.25×10^{-2}	3.92×10^{-2}	8.60×10^{-2}	2.04×10^{-1}
k_{-3}	GL → MG	3.00×10^{-2}	5.19×10^{-2}	1.88×10^{-1}	3.00×10^{-1}

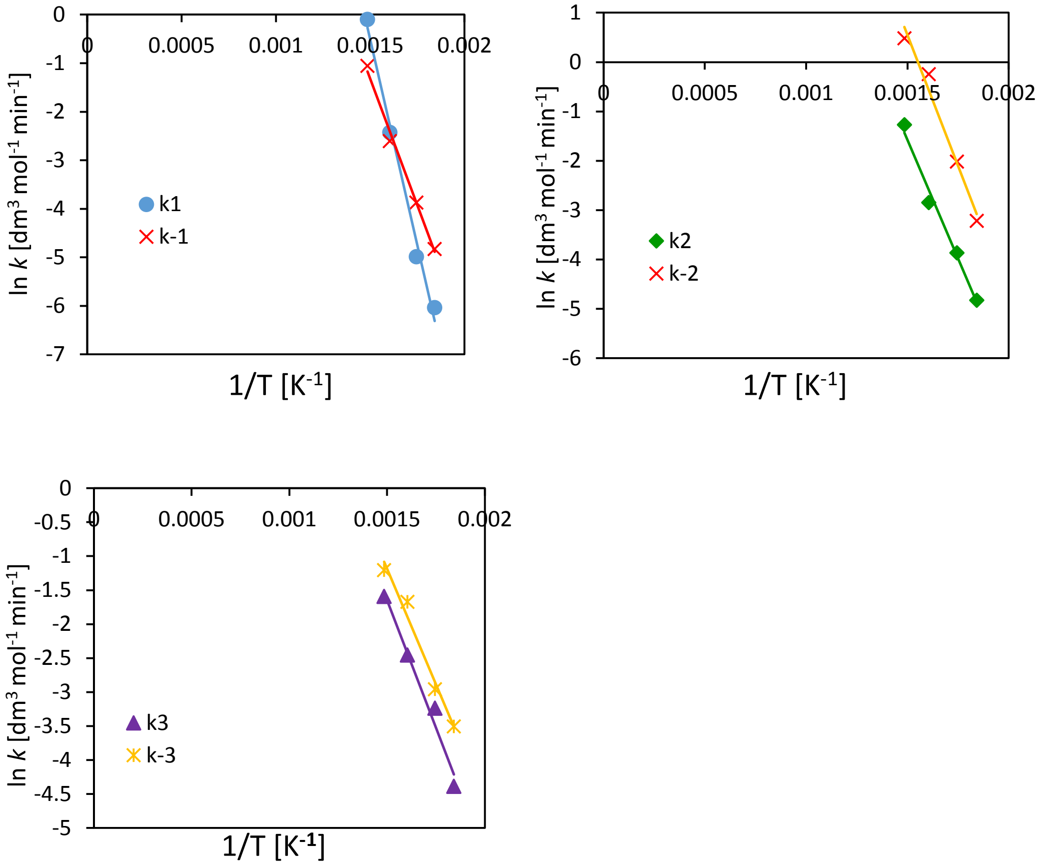


Fig. 6.8. Arrhenius plots of the individual rate constant for the transeserification reaction of canola oil to FAEE in supercritical ethanol using spiral reactor (experimental conditions: 20 MPa, ethanol-to-oil molar ratio of 40:1).

The activation energy (*Ea*) and pre-exponential factor (*A*) for the detailed kinetic analysis are presented in **Table 6.4**. As observed in this table, activation energies between 56.59 and 141.28 kJ mol^{-1} were determined. Santana et al. (2012) determined the activation energy for the transesterification of sunflower oil in supercritical ethanol at 150–200 °C using CO_2 as cosolvent. Activation energies for the transformation ranged from 59 to 140 kJ mol^{-1}. Their study was conducted using a fixed-bed reactor in continuous mode. Silva et al. (2007) also calculated the kinetics of transesterification of soybean oil in supercritical ethanol at 275–348 °C using a tubular reactor, obtaining an activation energy of 78.7 kJ mol^{-1}. Furthermore, Velez et al. (2012) obtained an activation energy of 67.6 kJ mol^{-1} for the transesterification of sunflower oil in supercritical ethanol at 300–345 °C, using a batch-type tubular reactor. The activation energy values obtained in this study are consistent with those of the previous works described above. Thus, it can be confirmed that even though different reactors were used to produce biodiesel in the same supercritical ethanol condition, the activation energies obtained were almost equal.

Table 6.4. Activation energies and pre-exponential factors

Reaction direction	Reaction rate constant [$dm^3\ mol^{-1}\ min^{-1}$]	Activation energy, *Ea* [kJ mol^{-1}]	Pre-exponential factor, *A* [$dm^3\ mol^{-1}\ min^{-1}$]	r^2
TG → DG	k_1	141.28	1.67×10^6	0.99
DG → TG	k_{-1}	86.76	7.03×10^{10}	0.99
DG → MG	k_2	80.31	4.09×10^5	0.98
MG → DG	k_{-2}	88.64	1.54×10^7	0.98
MG → GL	k_3	62.55	1.54×10^4	0.98
GL → MG	k_{-3}	56.69	8.48×10^3	0.98

6.4.5. Comparison between conventional flow and spiral reactors

To quantitatively prove the superiority of spiral reactor, energy supply needed for biodiesel production in spiral reactor was compared with that in conventional flow reactor. The calculation was made based on the spiral reactor setup shown in **Fig. 6.9**. Experimental data for reaction at 350 °C was employed for the calculation.

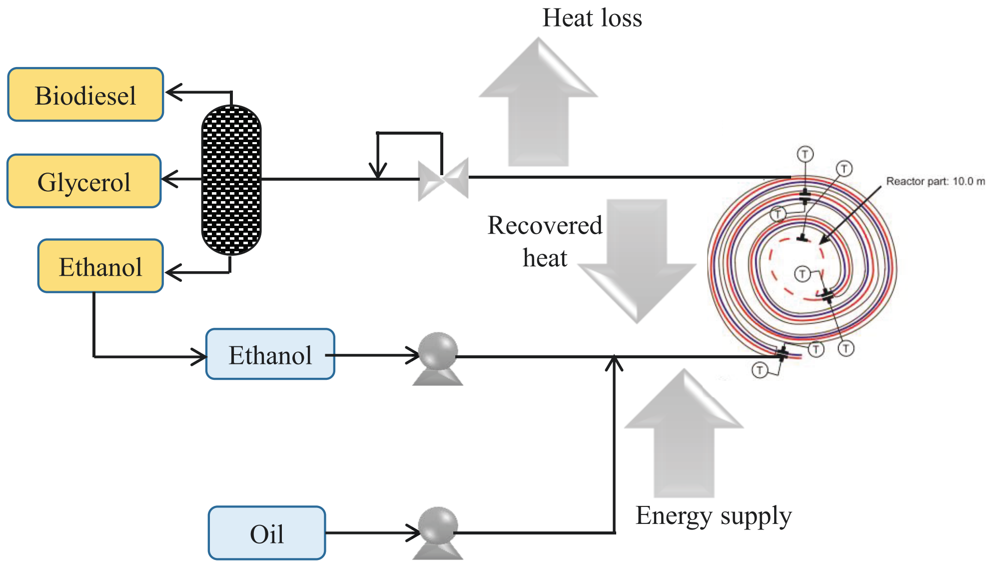


Fig. 6.9. Schematic diagram of biodiesel production in supercritical ethanol using spiral reactor.

First, energy required to achieve reaction temperature ($Q_{heating}$) was calculated using Eq. 6.12 to be 0.454 MJ/d.

$$Q_{heating} = m_{oil} C_{p,oil} \Delta T + m_{ethanol} C_{p,ethanol} \Delta T \qquad (6.12)$$

where; $Q_{heating}$ is energy required to achieve reaction temperature [MJ/d], m_{oil} is mass flow rate of canola oil (0.2066 kg/d), $C_{p,oil}$ is specific heat of canola oil (1.913 kJ/(kg K)), ΔT is the temperature difference between the inlet and outlet of cold tube of heat exchanger (310 °C), $m_{ethanol}$ is mass flow rate of ethanol (0.4352 kg/d), and $C_{p,ethanol}$ is specific heat of ethanol (2.46 kJ/(kg K)).

Then, the recovered heat from the system ($Q_{recovery}$) by the spiral reactor was calculated using Eq. 6.13 to be 0.388 MJ/d.

$$Q_{recovery} = m_{BDF} C_{p,BDF} \Delta T + m_{glycerol} C_{p,glycerol} \Delta T + m_{ethanol} C_{p,ethanol} \Delta T \qquad (6.13)$$

where; $Q_{recovery}$ is energy from the recovered heat [MJ/d], m_{BDF} is mass flow rate of biodiesel fuel (0.2033 kg/d), $C_{p,BDF}$ is specific heat of biodiesel fuel (1.80 kJ/(kg K)), ΔT is the temperature difference between the inlet and outlet of hot tube of heat exchanger

(269 °C), $m_{glycerol}$ is mass flow rate of glycerol (0.016 kg/d), $C_{p,glycerol}$ is specific heat of glycerol (2.41 kJ/(kg- K)), $m_{ethanol}$ is mass flow rate of remaining ethanol (0.4226 kg/d), and $C_{p,ethanol}$ is specific heat of ethanol (2.46 kJ/(kg K)).

The total energy supply for biodiesel production in the spiral reactor is obtained by subtracting recovered heat from heat required to achieve reaction temperature, and is calculated to be merely 0.066 MJ/d.

Fig. 6.10 shows the schematic diagram of biodiesel production under supercritical conditions using conventional reactor. Since there is no recovered heat for conventional reactor case, the energy supply of this system was only taken from energy required to achieve reaction temperature. The result of energy supply for biodiesel production in supercritical ethanol using conventional flow reactor was 0.454 MJ/d. This value is much higher than that of spiral reactor (0.0659 MJ/d), which indicates that spiral reactor is more efficient than that of conventional one.

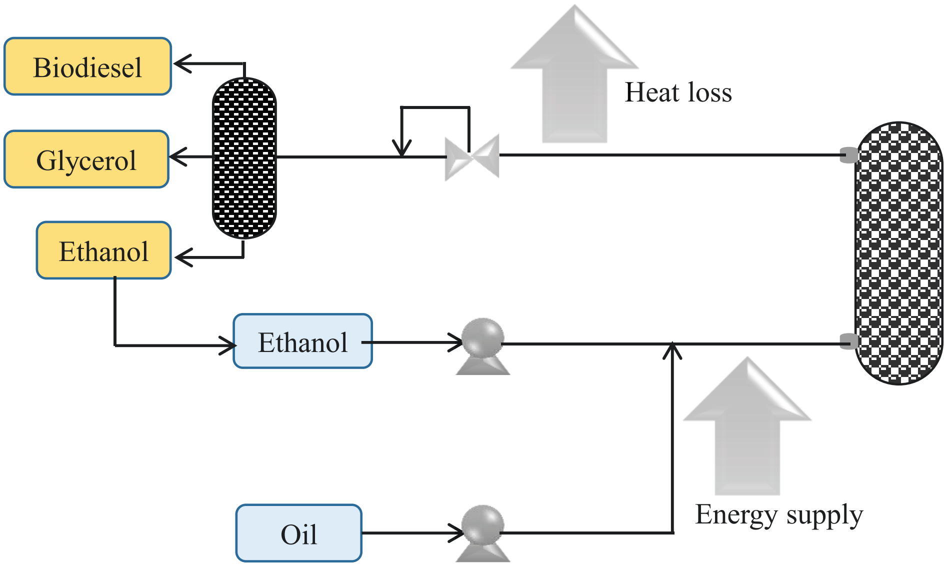


Fig. 6.10. Schematic diagram of biodiesel production in supercritical ethanol using conventional flow reactor.

The heat recovery efficiency of the spiral reactor employed in this study was determined using Eq. 6.14 to be 85.5 %.

$$Q_{eff} = \frac{Q_{recovery}}{Q_{heating}} \times 100\% \tag{6.14}$$

where; Q_{eff} is heat recovery efficiency [%], $Q_{recovery}$ is energy from recovered heat [MJ/d], and $Q_{heating}$ is energy to achieve reaction temperature [MJ/d].

To compare the differences in characteristics between conventional flow and spiral reactors, the study was performed by varying reaction temperatures using a fixed oil-to-ethanol molar ratio of 1:40 under a reactor pressure of 20 MPa. The effect of temperature on FAEE yield using the spiral reactor under the same reaction conditions (reaction time of 20 min, oil-to-ethanol molar ratio of 1:40, and pressure of 20 MPa) was compared with that for flow reactor (Velez et al., 2012) as shown in **Fig. 6.11**. Note that weight per cent unit is used here for the purpose of comparison with literature data. Good reproducibility was obtained, indicating that the spiral reactor is not only as effective as conventional reactor in terms of transesterification reactor but also was superior in terms of heat recovery.

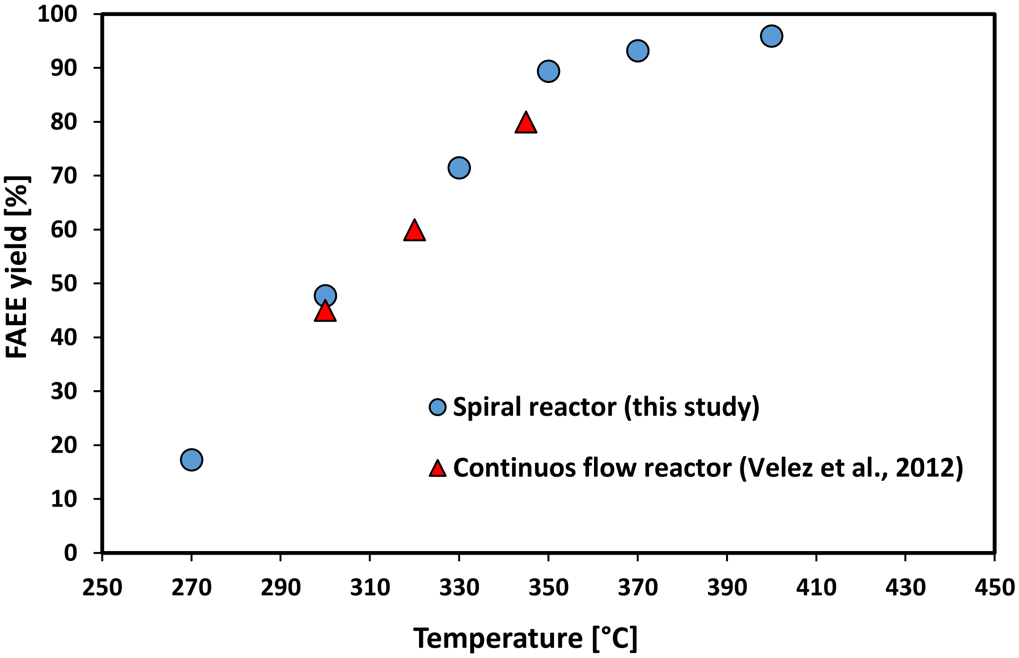


Fig. 6.11. Effect of temperature on FAEE yield in conventional flow and spiral reactors (experimental conditions: 20 MPa, 20 min, ethanol-to-oil molar ratio of 40:1).

6.5. Conclusion

The spiral reactor employed in this study was effective in the production of biodiesel under supercritical conditions with the successful recovery of heat. The effect of temperature and reaction time on biodiesel production using the spiral reactor was investigated. FAEE conversion increased with temperature. The spiral reactor was not only as effective as conventional reactor in terms of transesterification reactor but also was superior in terms of heat recovery. The quantitative analysis of the heat recovery efficiency was 85.5%. Utilization of this spiral reactor for biodiesel production in supercritical ethanol improves the biodiesel production process by reducing energy requirement from 0.4544 MJ/d to 0.0659 MJ/d owing to the heat recovery. Thus, it was concluded that spiral reactor is a good candidate of reactor for biodiesel production under supercritical conditions. A second-order kinetic model describing the transesterification of canola oil in supercritical ethanol using the spiral reactor was proposed; the reaction was observed to follow Arrhenius behavior. The corresponding second-order reaction rate constants and activation energies as well as pre-exponential factors were determined.

CHAPTER 7

Effectiveness of spiral reactor for biodiesel production in supercritical MTBE

7.1. Introduction

Research on biomass and renewable energy sources have attracted tremendous attention due to the ongoing depletion of fossil fuels and environmental pollution problems. Biodiesel is one of the most promising renewable energy derived from renewable lipid feedstocks such as vegetable oils (Demirbas, 2003; Xie et al., 2014), animal fats (Tashtoush et al., 2004), waste cooking oils (Abd Rabu et al., 2013; Patle et al., 2014), and microalgae (Demirbas and Demirbas, 2011; Wahidin et al., 2014).

Biodiesel production under supercritical conditions became one of the most notable technique to synthesize biodiesel since it enjoys a lot of merits including no catalyst requirement and short reaction time. In our laboratory, we have developed a novel method to produce biodiesel by using supercritical *tert*-butyl methyl ether (MTBE) (Farobie et al., 2014). The advantage of this method highlighted the production of glycerol *tert*-butyl ether (GTBE) as a by-product that has a higher added-value than glycerol. It was reported in the previous studies that GTBE is a good additive of diesel fuel owing to its good blending properties and high cetane number. In addition, it could reduce the particulate matter and carbon monoxide generation since it has oxygenated structure (Klepacova et al., 2007; Frusteri et al., 2009; Kiatkittipong et al., 2011).

In spite of these good merits, our biodiesel production method still has a drawback due to heat recovery. Since biodiesel production under supercritical conditions requires elevated temperatures and high pressures, tremendous amounts of heat are needed. In order to make the overall process is to be energetically efficient, this heat must be properly recovered.

In our previous study using supercritical ethanol method, it was found that a spiral reactor that could also serve as a heat exchanger was useful to circumvent this problem (Sasanami et al., 2014). This spiral reactor comprised a parallel-tube heat exchanger and transesterification reactor. The parallel tube heat exchanger, where heat is recovered, was made of stainless steel tubing with the length of 2.5 m. This heat exchanger part was composed of two tubes placed side-by-side in a spiral formation. Space between the tubes were filled with heat transfer cement for good heat transfer.

Effective heat recovery from the high temperature reactor effluent to the low temperature inlet flow was achieved in counter-flow mode. Meanwhile, the reactor part, where the transesterification reaction mainly took place, was made of the same material as the heat exchanger, but the length is longer, i.e., 10 m. This reactor part was designed as an insulated tubing for the high-temperature transesterification reaction to take place efficiently. It was reported that this spiral reactor was effective in the production of biodiesel using ethanol under supercritical conditions with the successful recovery of heat.

Since the spiral reactor properties for biodiesel production using supercritical MTBE have not been well characterized, it is interesting to investigate these characteristics. There are two expected advantages of biodiesel production using spiral reactor, i.e., (1) part of the reaction can take place in the heating section, improving the FAME yield and (2) the heat needed to achieve reaction temperature can be effectively recovered. The purpose of this study was to investigate the effectiveness of the spiral reactor on supercritical MTBE biodiesel production by elucidating the effects of temperature and reaction time on FAME yields.

7.2. Experimental procedures

Biodiesel production in supercritical MTBE using spiral reactor was carried out in the temperature range of 250–400 °C, a pressure of 10 MPa, and oil-to-MTBE molar ratio of 1:40. The transesterification reaction was investigated over 6 to 30 min. Samples were collected by passing through the filter and back-pressure regulator and after achieving a steady state. The liquid samples were analyzed by gas chromatography

(GC-390B; GL Sciences) equipped with a flame-ionization detector (FID) and MET-Biodiesel column (14 m × 0.53 mm × 0.16 μm film thickness) with an integrated 2 m guard column (Sigma Aldrich, 28668-U). The experimental apparatus used in this study is schematically illustrated in **Fig. 4.2** (chapter 4).

The thermal efficiency of the heat exchanger from spiral reactor part was calculated using Eq. 7.1.

$$\text{(Thermal efficiency)} = \frac{T_{\infty 2,o} - T_{\infty 2,i}}{T_{\infty 1,i} - T_{\infty 1,o}} \tag{7.1}$$

where;

$T_{\infty 1,i}$ is the temperature of the hot flow at the inlet of the heat exchanger;

$T_{\infty 1,o}$ is the temperature of the hot flow at the exit of the heat exchanger;

$T_{\infty 2,o}$ is the temperature of the cold flow at the exit of the heat exchanger; and

$T_{\infty 2,i}$ is the temperature of the cold flow at the inlet of the heat exchanger.

Experimental FAME yields were calculated by dividing the moles of FAME product by the moles of fatty acid groups in the initial triglyceride (TG), as shown in Eq. 7.2.

$$\text{(Product yield)} = \frac{\text{(Molar amount of product FAME)}}{\text{(Molar amount of fatty acid group in initial TG)}} \tag{7.2}$$

7.3. Experimental conditions

The experimental conditions for this study are summarized in **Table 7.1**.

Table 7.1. Experimental conditions for this corresponding chapter

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	6-30 min
Molar ratio of oil to MTBE	1:40
Reactor type	Spiral reactor
Temperature	250-400 °C
Pressure	10 MPa

7.4. Results and Discussion

7.4.1. Effect of temperature on FAME yield

The effect of temperature on FAME yield was studied first to examine the characteristics of the spiral reactor. The effect of temperature was investigated by varying reaction temperature from 250 °C to 400 °C at a fixed pressure of 10 MPa and oil-to-MTBE molar ratio of 1:40. The effect of temperature on FAME yield is presented in **Fig. 7.1**. An increase in the reaction temperature from 250 to 400 °C could enhance reactivity of MTBE, leading to higher FAME yields for the same residence time. Higher reaction temperatures generally would result in higher reaction rates, which would consequently correspond to higher FAME yields for the same residence times. These results are consistent with previous reports of biodiesel production using supercritical methanol, ethanol, dimethyl carbonate, and methyl acetate methods. For supercritical methanol and ethanol, Rathore and Madras (2007) observed that the biodiesel yield increased as the temperature rose from 200 to 400 °C. For supercritical dimethyl carbonate case, llham and Saka (2012) found that the conversion of rapeseed oil to biodiesel increased as the temperature rose from 270 to 385 °C at 10 MPa over 20 min. Similarly, in supercritical methyl acetate method, Goembira and Saka (2013) reported that the FAME yield increased with increasing temperature from 300 to 380 °C at 20 MPa and an oil-to-methyl acetate molar ratio of 1:42.

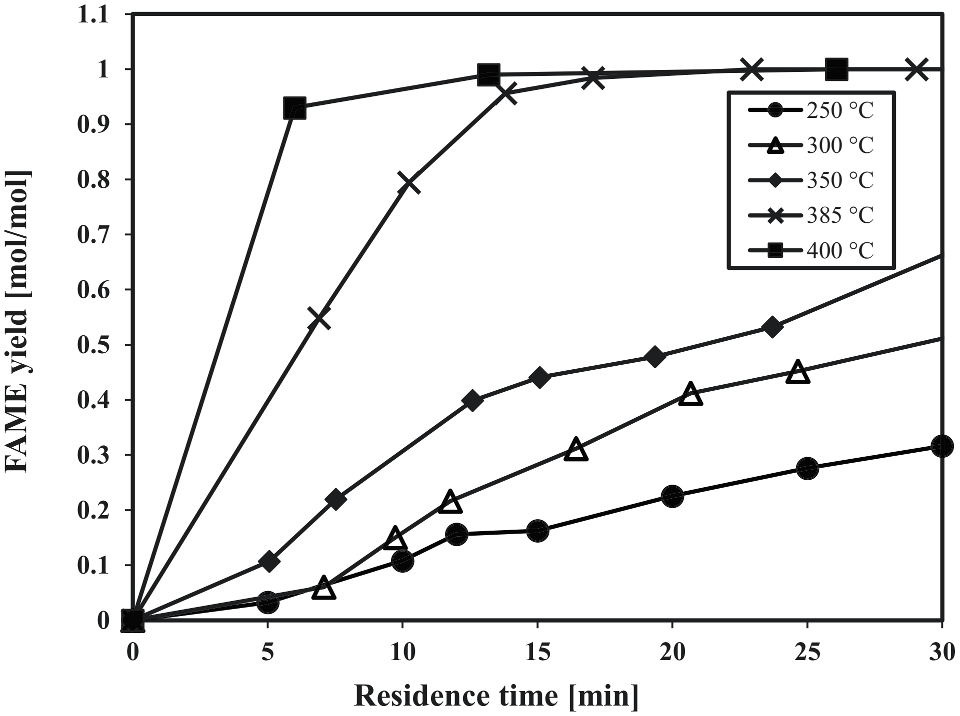


Fig. 7.1. Effect of temperature on FAME yield (experimental conditions: 10 MPa, oil-to-MTBE molar ratio of 1:40).

7.4.2. Effect of reaction time

To elucidate the reaction characteristics of supercritical MTBE in more detail, the effect of residence time on changes of feedstock TG conversion and yields of final product FAME and by-product GTBE were determined at 250, 300, 350, 385, and 400 °C. The results are presented in **Figs. 7.2**, **7.3**, **7.4**, **7.5**, and **7.6**, respectively. The unit for the yield in these figures is [mol dm^{-3}], which is appropriate for reaction rate calculation. A longer reaction time generally resulted in a higher FAME yield for all temperature employed in this study. This may be attributed to a longer reaction time could increase in contact time between the canola oil and MTBE, affording the higher FAME yield.

Even though the critical temperature of MTBE is 223.85 °C, the FAME yields obtained at 250 and 300 °C were relatively small. FAME yields of merely 0.31 and 0.53 mol/mol (concentrations of 0.1215 and 0.1289 mol dm^{-3}) were obtained after 30 min transesterification reaction at 250 and 300 °C, respectively. In addition, GTBE by-product was not observed at 250 °C, but it was found above 300 °C.

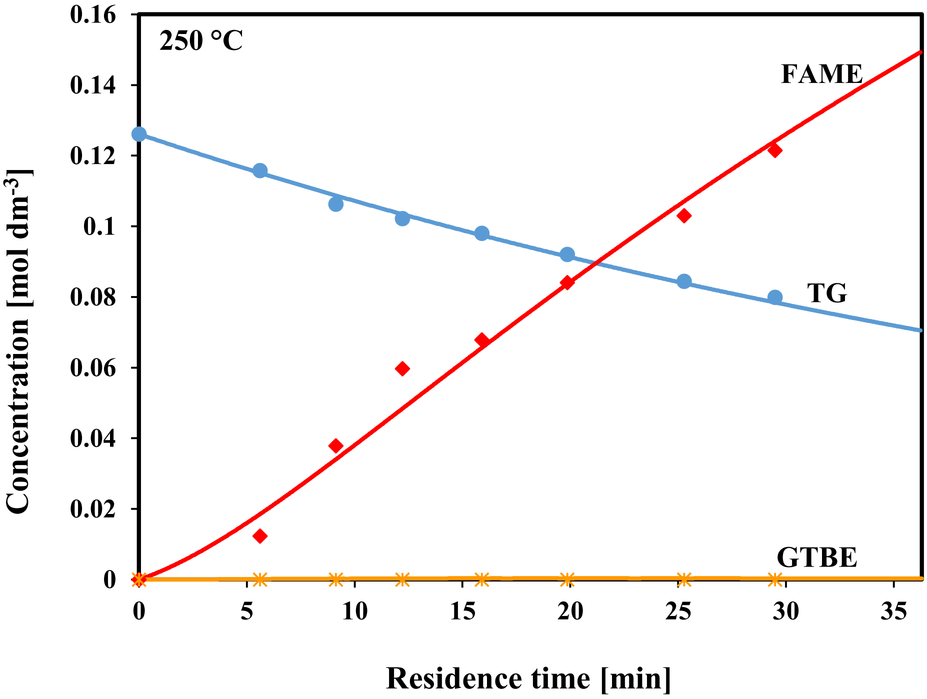


Fig. 7.2. Effect of residence time on FAME concentration and triglyceride consumption (experimental conditions: 250 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

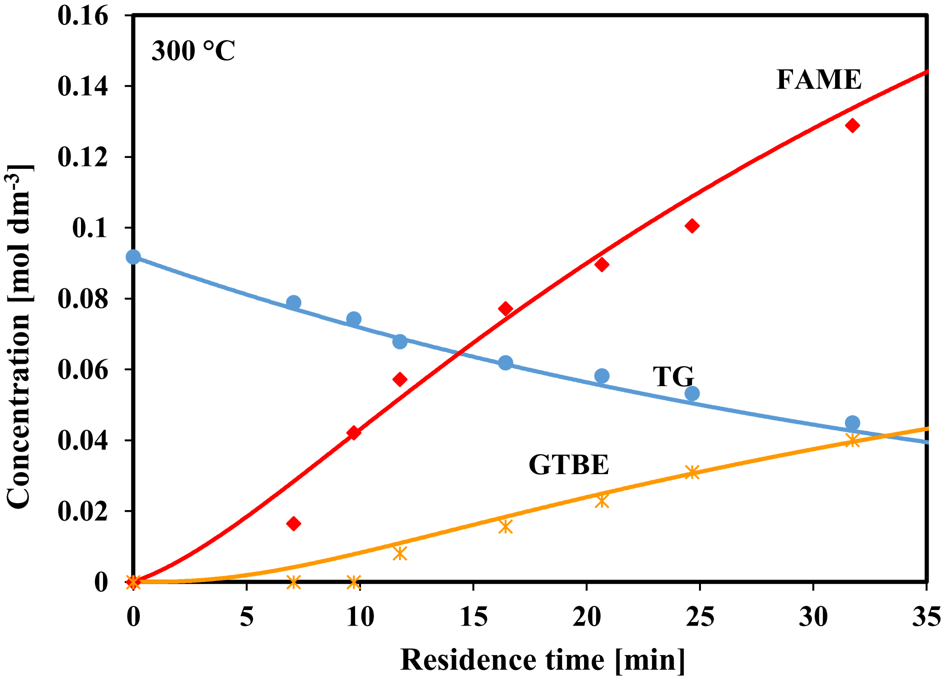


Fig. 7.3. Effect of residence time on FAME concentration and triglyceride consumption (experimental conditions: 300 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

Canola oil conversion to FAME at 350 °C was higher than at 250 and 300 °C, but it was still relatively low. Almost half of the TG was converted into FAME after 25 min. FAME yields of 0.53 mol/mol (concentration of 0.1667 mol dm^{-3}) and 0.67 mol/mol (concentration of 0.1727 mol dm^{-3}) were obtained after 25 and 30 min, respectively. GTBE yield obtained at 350 °C was also higher than that at 300 °C, as expected.

A significant change in the conversion of canola oil to FAME was found at 385 °C after transesterification reaction of 12 min. Under these conditions, FAME yields of approximately 0.95 and 0.98 mol/mol (concentrations of 0.3074 and 0.3230 mol dm^{-3}) were obtained after transesterification reaction times of 12 and 17 min, respectively. Transesterification of canola oil to FAME was complete within 20 min, with all the canola oil converted to FAME, generating FAME yield of 1.00 mol/mol (concentrations of 0.3321 mol dm^{-3}).

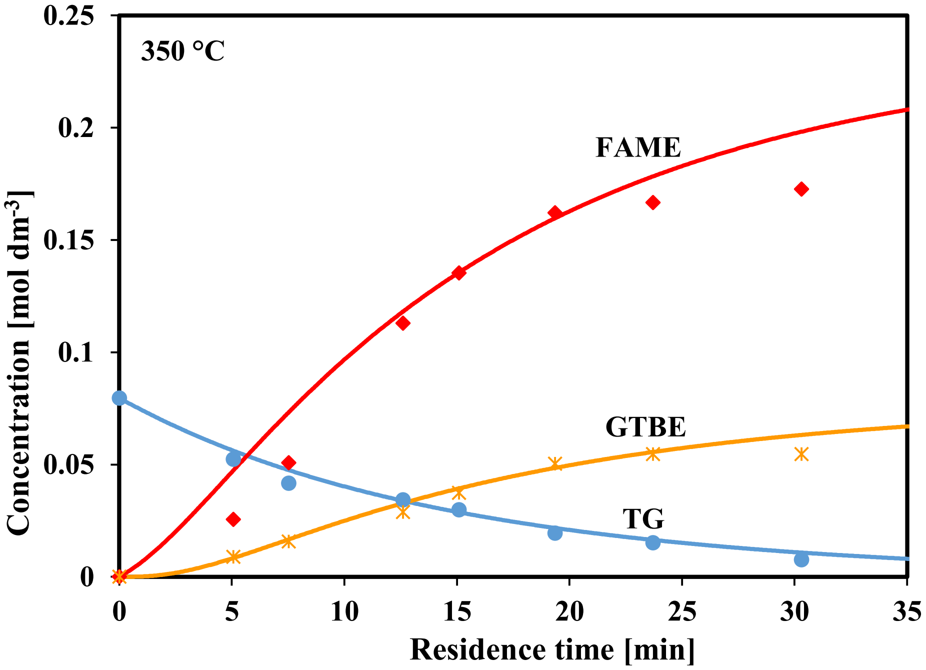


Fig. 7.4. Effect of residence time on FAME concentration and triglyceride consumption (experimental conditions: 350 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

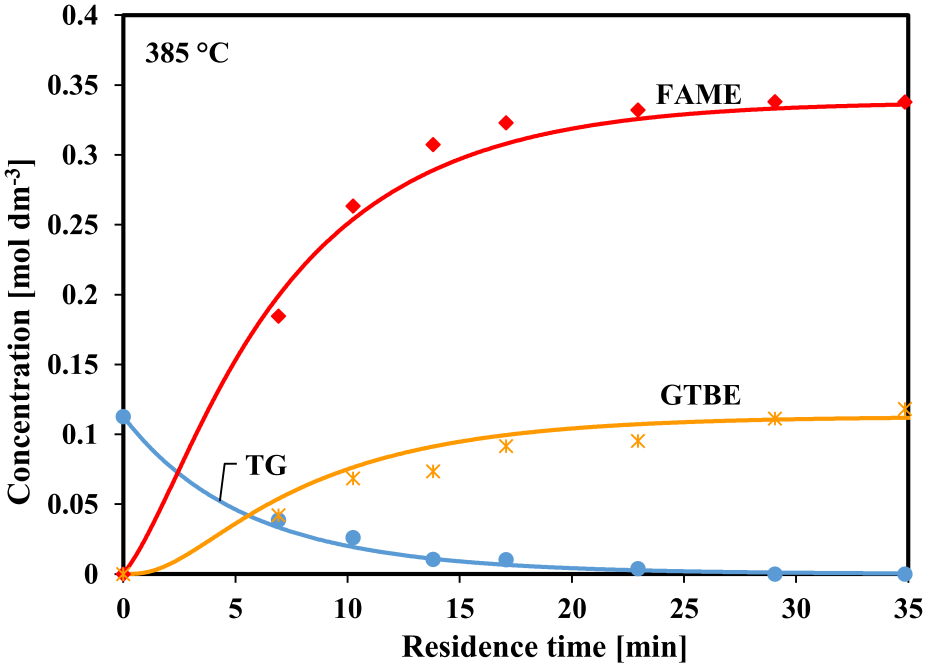


Fig. 7.5. Effect of residence time on FAME concentration and triglyceride consumption (experimental conditions: 385 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

At 400°C, the complete conversion of canola oil to FAME was observed in 12 min, but the yield was relatively constant thereafter. Under this condition, the all canola oil was completely converted in 12 min.

Apart from that, the reaction temperature and time were observed to directly affect the reaction rate of TG feedstock and GTBE by-product formation. In all cases, the GTBE yield increased with increasing temperature from 200 to 400 °C. Furthermore, the consumption of TG was favored with increasing temperature and reaction time, affording higher FAME and GTBE yields, expectedly.

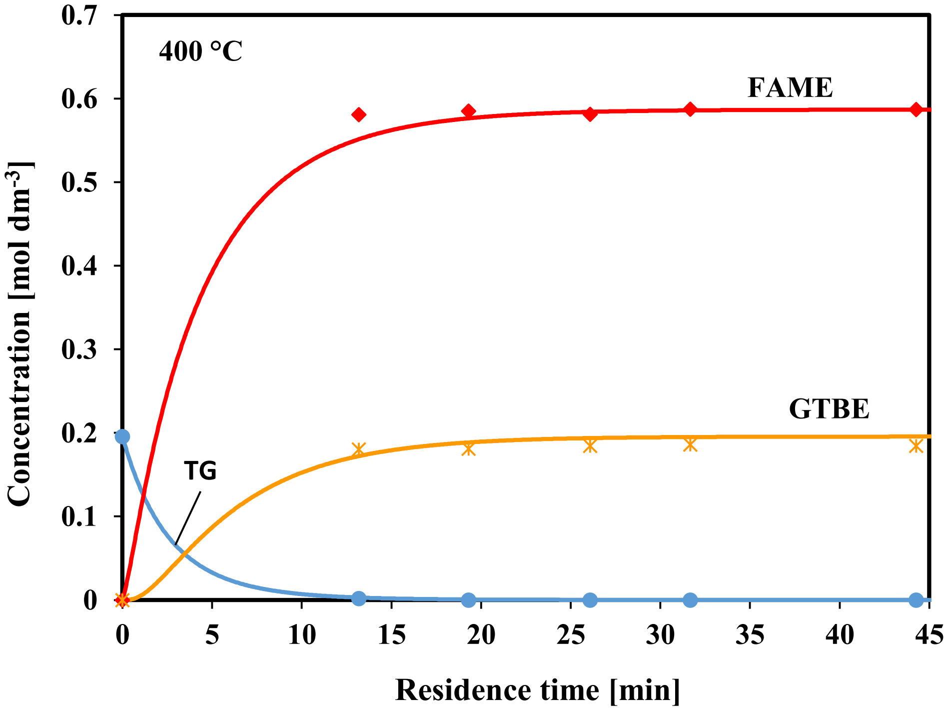


Fig. 7.6. Effect of residence time on FAME concentration and triglyceride consumption (experimental conditions: 400 °C, 10 MPa, oil-to-MTBE molar ratio of 1:40).

7.4.3. Comparison with conventional reactor

The first expected superiority of the spiral reactor over conventional flow reactor would be a higher FAME yield in consequence of the portion of reaction takes place in the heat exchanger. To confirm this, conventional flow and spiral reactors ware compared in this section. **Fig. 7.7** presents the FAME yields as a function of temperature for conventional flow and spiral reactors. Note that the residence time employed in the conventional reactor was similar to that in the reactor part of the spiral reactor. It can be observed from this figure that the spiral reactor produced a higher FAME yield compared to the conventional flow reactor. It could be attributed to because a portion of the reaction occurs in the heat exchanger. Note that the length of the heat exchanger is 2.5 m for the inlet flow side and 2.5 m for outlet flow side. This spiral reactor allows the reaction to proceed while hating even though the residence time employed at the reaction temperature is the same.

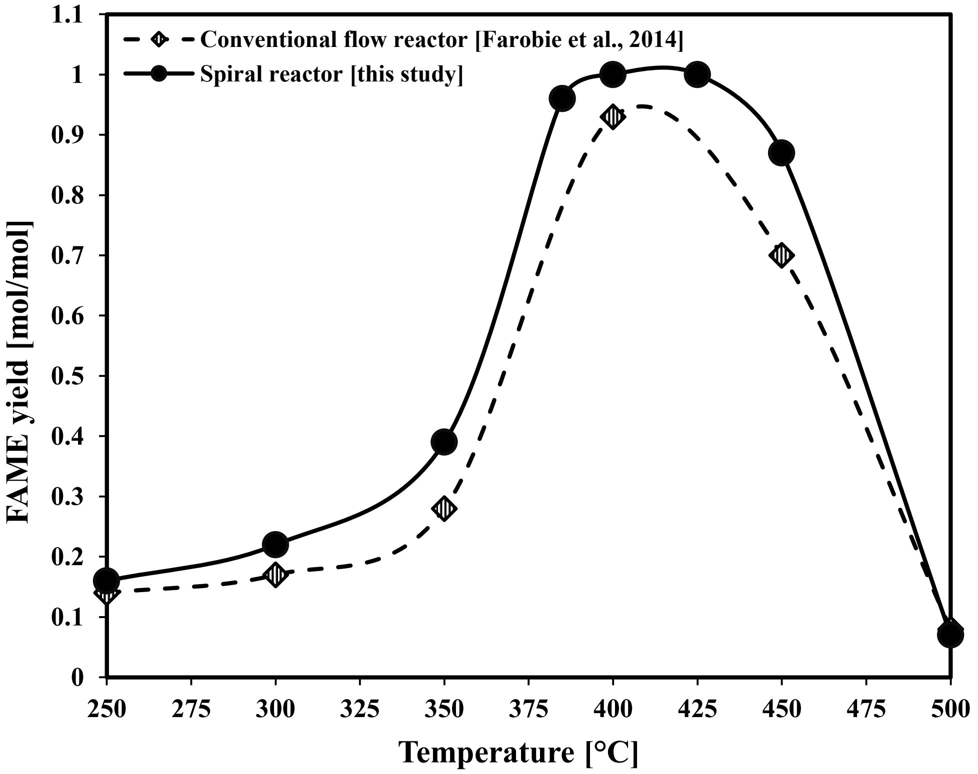


Fig. 7.7. The comparison of FAME yield for conventional flow and spiral reactors as a function of temperature (experimental conditions: 10 MPa, 12 min, oil-to-MTBE molar ratio of 1:40).

It could be noticed form **Fig. 7.7** that the decreased in FAME yields above 400 °C has been attributed to thermal decomposition. As reported by some previous studies, thermal decomposition of biodiesel takes place at higher temperature, typically above 400 °C. Niza et al. (2013) discovered the thermal decomposition of FAME in supercritical methyl acetate. They observed that mono-unsaturated FAME was relatively stable at the temperature range 330–360 °C, and longer reaction time did not lead to severe decomposition. The substantial decomposition of this compound was obviously observed at 420 °C. In another study by Imahara et al. (2008) who investigated thermal stability of biodiesel in supercritical methanol, it was reported that all FAMEs including poly-unsaturated FAME were stable at 270 °C/43 MPa. The decomposition of poly-unsaturated FAMEs such as methyl linoleate (C18:2) and methyl linolenate (C18:3) were widely decomposed at 350 °C/43 MPa. The decomposition mechanism can occur through isomerization reaction from *cis* double bonds into *trans* double bonds. In recent study, Lin et al. (2013) observed the complete thermal decomposition mechanisms of biodiesel under supercritical conditions. They presumed that in the temperature range of 275–400 °C, 300–425 °C, and >350 °C, FAMEs undergo the mechanism reaction through isomerization, polymerization (Diels-Alder reaction), and pyrolysis, respectively. These mechanisms also reduce the FAME yield in the spiral reactor, but the reaction in the heat exchanger helps to achieve higher FAME yields compared to the conventional reactor, especially in this high temperature range. The largest difference in FAME yield versus the conventional reactor, 0.17, was obtained at 450 °C. Thus, the advantage of a higher FAME yield due to the reaction in the heat exchanger has been confirmed experimentally.

7.4.4. Heat recovery characteristics

Another expected superiority of the spiral reactor over conventional flow reactor would be heat recovery. The temperature profile at each position of the spiral reactor for the target temperatures 250–400 °C is presented in **Fig. 7.8**. As observed in this figure, the feedstock consisted of canola oil and MTBE was quickly heated to the reaction temperature in the heat exchanger and maintained at that temperature in the reactor. Furthermore, the temperatures of the hot tube was similar to those of cold tube, demonstrating that heat recovery was occurring, as expected.

By employing Eq. 7.1, the heat exchanger efficiencies obtained from this calculation for the target temperatures of 250, 300, 350, 385, and 400°C were 0.92, 0.91, 0.90, 0.89, and 0.88, respectively.

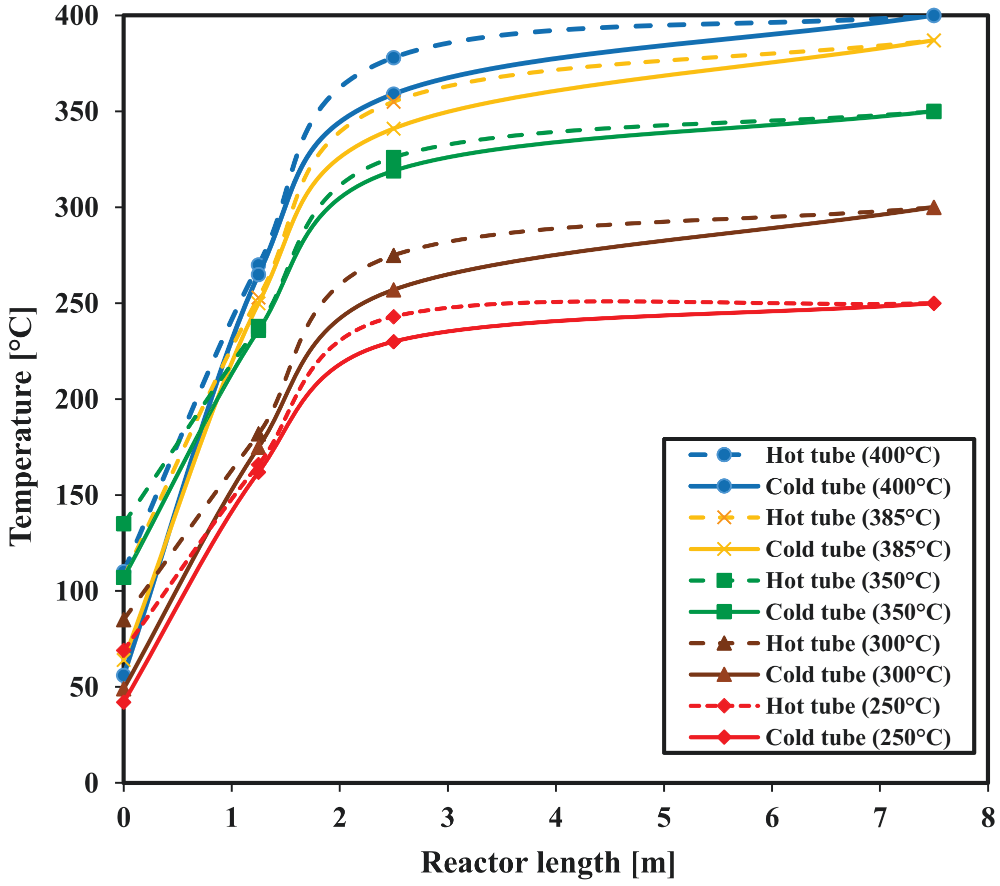


Fig. 7.8. Temperature profile of spiral reactor.

7.4.5. Comparison of biodiesel production with previous reports

Lastly, the characteristics of FAME production in supercritical MTBE using spiral reactor were compared with the previous studies of biodiesel production in supercritical methanol, ethanol, methyl acetate, and MTBE. Biodiesel production under supercritical conditions was firstly proposed by Saka and Kusdiana (2001) by employing methanol as reactant. Under this reaction conditions, FAME and glycerol were obtained. In similar way, FAEE and glycerol were also obtained when ethanol was employed as a reactant. Recently, a new route of biodiesel production under supercritical conditions was proposed by using methyl acetate and dimethyl carbonate as reactants. The by-product obtained by employing methyl acetate as a reactant was triacetin which has a higher added-value than glycerol. Meanwhile, by utilizing dimethyl carbonate as reactant, the by-product obtained was glycerol carbonate. 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 by-product is GTBE, which is the reaction system employed here. **Fig. 7.9** shows the chemical reaction for biodiesel production with various supercritical reactants.

The comparison of biodiesel yield produced under the optimum conditions of supercritical methanol (350 °C/43 MPa) (2001), ethanol (350 °C/20 MPa) (2007), methyl acetate (350 °C/17.8 MPa) (2012), dimethyl carbonate (380 °C/20 MPa) (2009), and MTBE (385 °C/10 MPa) (this study) is presented in **Fig. 7.10**. Note that weight percent unit is used here for the purpose of comparison. Biodiesel production in supercritical methanol route has similar trend with supercritical dimethyl carbonate method. However, the FAME yield obtained from this study by employing supercritical MTBE was lower than that for supercritical methanol and dimethyl carbonate methods at the same reaction time, in spite of the higher temperature of the supercritical MTBE method. Biodiesel yield in supercritical MTBE was observed the same with the supercritical methanol and dimethyl carbonate at a residence time of 15 min, obtaining 98.3 wt% of FAME. Interestingly, FAME yields for the supercritical method are higher than those for supercritical methyl acetate route at the same reaction time. It could be attributed to the solubility of MTBE with oil is much better than that of methyl acetate with oil. The solubility effect would be a merit for MTBE by which to overcome the mass transfer problem faced by more polar compounds.

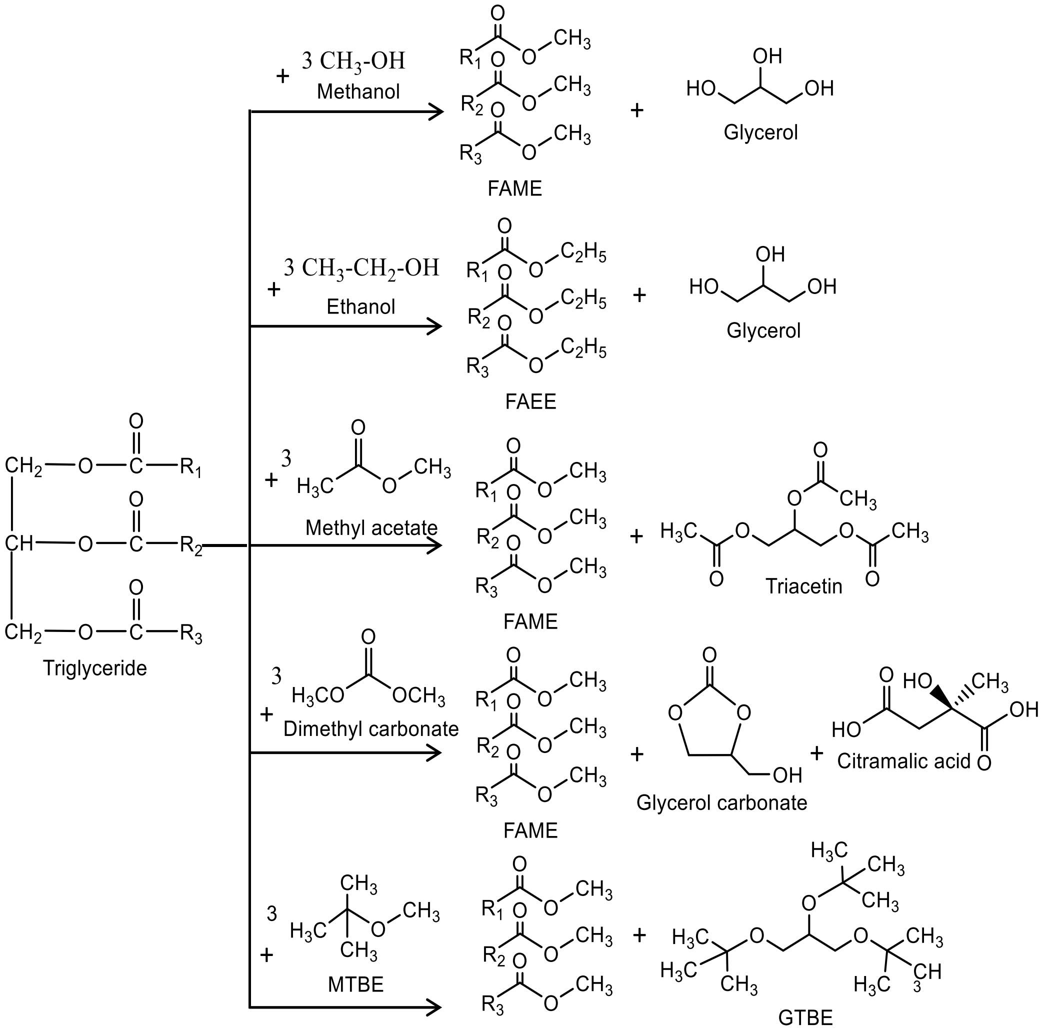


Fig. 7.9. The chemical reactions of biodiesel production under supercritical various reactants.

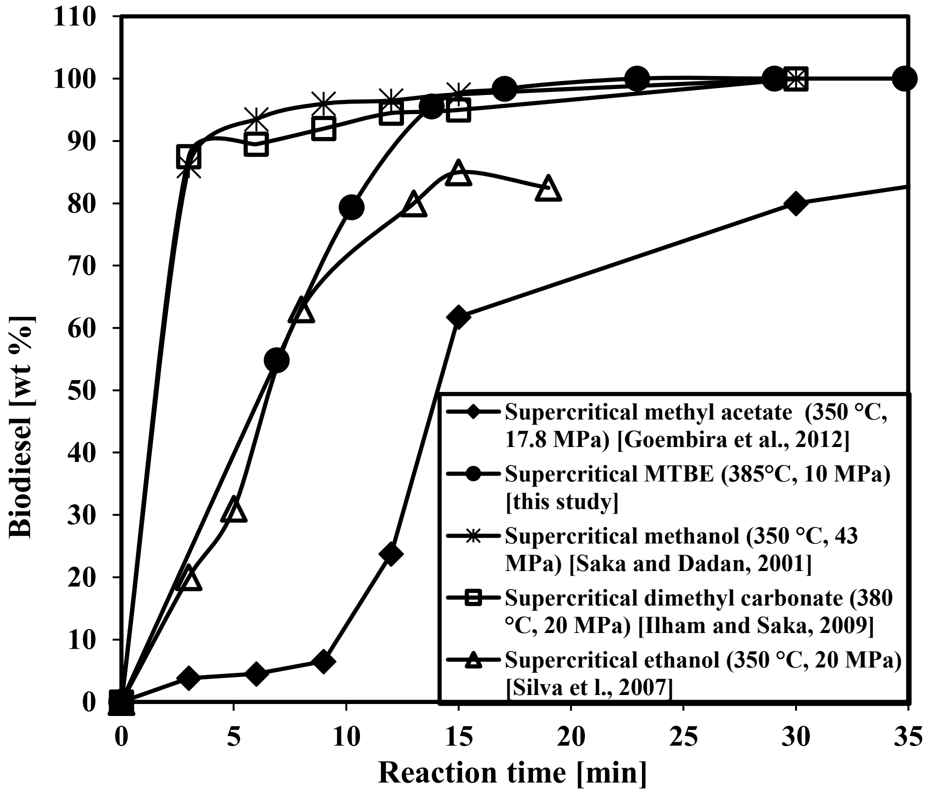


Fig. 7.10. Comparison of biodiesel under various supercritical reactants.

7.5. Conclusion

Biodiesel production in supercritical MTBE using spiral reactor was investigated. The effects of temperature and reaction time on FAME yield were studied. The comparison of FAME yields for conventional flow and spiral reactors as a function of temperature were also elucidated. The results revealed that the spiral reactor was superior to a conventional flow reactor since spiral reactor could lead to a higher FAME yield compared to the conventional flow reactor for the same residence time. This was partly as a result of the portion of the reaction that takes place in the heat exchanger. In addition, the spiral reactor employed here was effective for biodiesel production using MTBE under high temperature and high pressure conditions because of the successful recovery of heat. The complete conversion of oil to FAME (1.00 mol/mol) was rapidly observed at 385 °C under a reactor pressure of 10 MPa and an oil-to-MTBE molar ratio of 1:40 within 20 min.

CHAPTER 8

Effect of pressure on biodiesel production in supercritical MTBE

8.1. Introduction

Biodiesel production in some developing countries such as Indonesia and Thailand is mainly conducted via homogeneous alkali-catalyzed transesterification process. This is because these catalysts such as potassium and sodium hydroxide are widely available in developing countries. However, this method still has the constrain due to the sensitivity of these catalysts to the presence of water and free fatty acids (FFAs) of feedstock which results in saponification reaction and lower biodiesel yield (Kusdiana and Saka, 2004).

To overcome this problem, our laboratory has developed non-catalytic biodiesel production in supercritical *tert*-butyl methyl ether (MTBE) (Farobie et al., 2014). This novel method could not only answer the problem facing the feedstock, but also it could produce higher value by-product, i.e. glycerol *tert*-butyl ether (GTBE). This GTBE has higher value than glycerol since it has high cetane number and good blending property with the diesel fuel (Klepáčová et al., 2007; Frusteri et al., 2009).

However, the effect of pressure on biodiesel yield in supercritical MTBE has not been sufficiently examined. Considering pressure is one of the most affecting parameters for biodiesel production under supercritical conditions, the investigation of pressure effect is essential. Therefore, the purpose of this study is to obtain a better understanding of the effect of pressure on biodiesel yield in supercritical MTBE.

8.2. Experimental procedures

To investigate effect of pressure under supercritical conditions, transterificaiton was carried out in the pressure range of 10–30 MPa and temperature range of 300–400 °C. Oil-to-MTBE molar ratio used in this study was fixed at 1:40 and reaction time was varied from 3 min to 30 min. Samples were collected after achieving a steady state and after passing through the filter and back-pressure regulator. The liquid samples were analyzed by gas chromatography (GC-390B; GL Sciences) equipped with a flame-ionization detector (FID) and MET-Biodiesel column (14 m × 0.53 mm × 0.16 μm film thickness) with an integrated 2 m guard column (Sigma Aldrich, 28668-U). The experimental apparatus used in this study is schematically illustrated in Fig. 4.2 (chapter 4).

The residence time was determined using Eq. 8.1, taking into consideration reactor volume, the density of canola oil and MTBE at the reaction temperature and pressure, and mass flow rate of canola oil and MTBE. It was assumed that there was no volume change caused by mixing.

$$t = \frac{v}{m_1 / \rho_1 + m_1 / \rho_1} \qquad (8.1)$$

where;

t = residence time [min],

V = Reactor volume [36.65 mL],

m_1 = mass flow rate of oil [g/min],

ρ_1 = density of oil [g/mL],

m_2 = mass flow rate of MTBE [g/min],

ρ_2 = density of MTBE [g/mL].

Experimental FAME yields were calculated by dividing the moles of FAME product by the moles of fatty acid groups in the initial triglyceride (TG), as shown in Eq. 8.2.

$$\text{(Product yield)} = \frac{\text{(Molar amount of product FAME)}}{\text{(Molar amount of fatty acid group in initial TG)}} \qquad (8.2)$$

8.3. Experimental conditions

The experimental conditions for this study are presented in **Table 8.1**.

Table 8.1. Experimental conditions for chapter 8

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3-30 min
Molar ratio of oil to MTBE	1:40
Reactor type	Spiral reactor
Temperature	300-400 °C
Pressure	10-30 MPa

8.4. Results and Discussion

8.4.1. Effect of pressure on FAME yield

The effect of pressure on FAME yield for biodiesel production using supercritical MTBE was examined by varying pressure from 10 to 30 MPa at a fixed oil-to-MTBE molar ratio of 1:40 and the temperature range of 300–400 °C. **Figs. 8.1**, **8.2**, and **8.3** show the results for 10, 20, and 30 MPa, respectively.

A longer reaction time and a higher temperature resulted in a higher FAME yield was observed at 10 MPa. It can be discovered in **Fig. 8.1** that at 300 and 350 °C, FAME yields were still relatively small. The FAME yields of merely 0.41 and 0.48

mol/mol were obtained within 20 min at 300 and 350 °C, respectively. Meanwhile, at higher temperature of 400 °C, the complete conversion of canola oil to FAME was observed after 15 min.

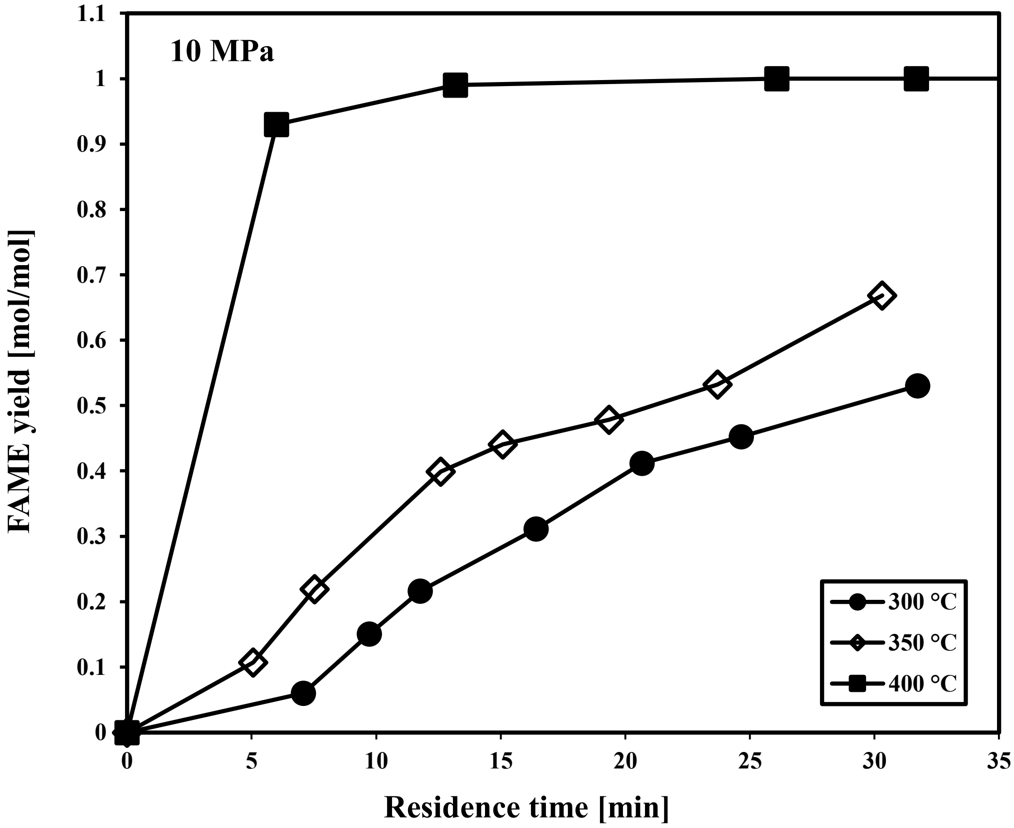


Fig. 8.1. FAME yield at 10 MPa (Experimental conditions: 10 MPa, oil-to-MTBE molar ratio of 1:40).

A slight change in the conversion of canola oil to FAME was observed at 20 MPa and at the milder temperature, i.e., 350 °C. Under these conditions (a pressure of 20 MPa and temperature of 350 °C), FAME yields of about 0.61 and 0.79 mol/mol were obtained after transesterification times of 15 and 20 min, respectively. After 30 min of residence time, transesterification was almost complete, with almost all canola oil converted to FAME. Under this pressure condition, the complete conversion was observed at 400 °C in the short reaction time of 10 min, and the yield was relatively constant thereafter.

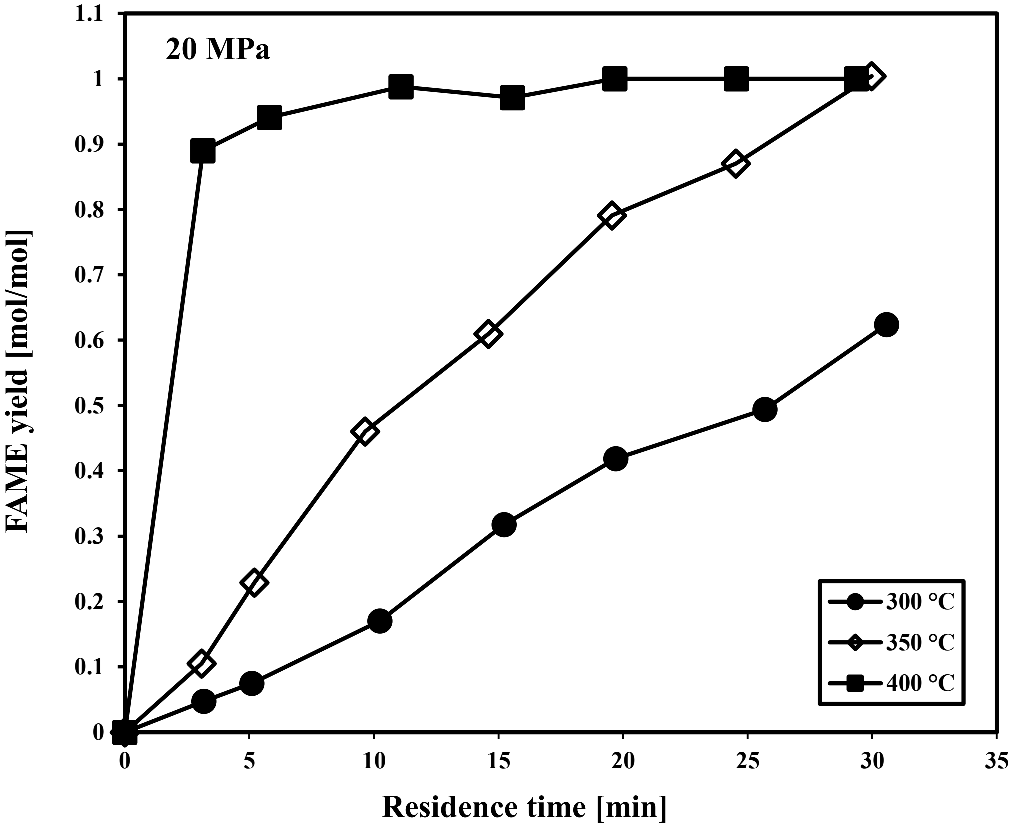


Fig. 8.2. FAME yield at 20 MPa (Experimental conditions: 20 MPa, oil-to-MTBE molar ratio of 1:40).

The FAME yields obtained at 30 MPa were almost the same as 20 MPa at the same temperature and residence time. The complete conversion was observed at 400 °C in the initial time of 5 min.

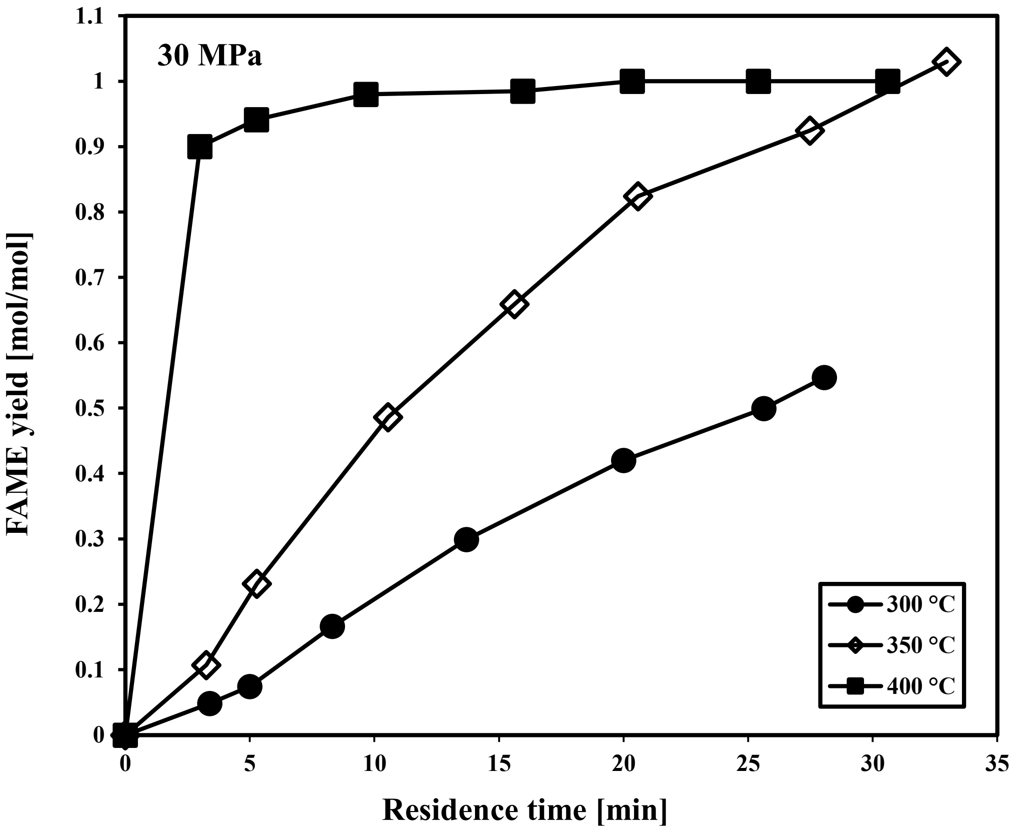


Fig. 8.3. FAME yield at 30 MPa (Experimental conditions: 30 MPa, oil-to-MTBE molar ratio of 1:40).

8.4.2. Effect of pressure on TG consumption and GTBE yield

The concentration change over time was discussed here in order to quantitatively evaluate the effect of pressure. **Figs. 8.4, 8.5**, and **8.6** show concentration changes of TG, GTBE, and FAME at 300, 350, and 400 °C, respectively. As observed in all figures, TG concentration decreases with residence time, while that of GTBE and FAME increases. At any temperature, the effect of pressure is not clearly observed. This is because the density of MTBE does not change so much when pressure changes. In fact, the density change of MTBE corresponding to the pressure change employed here is at most 6 %. This explains why the pressure effect was not observed in this study.

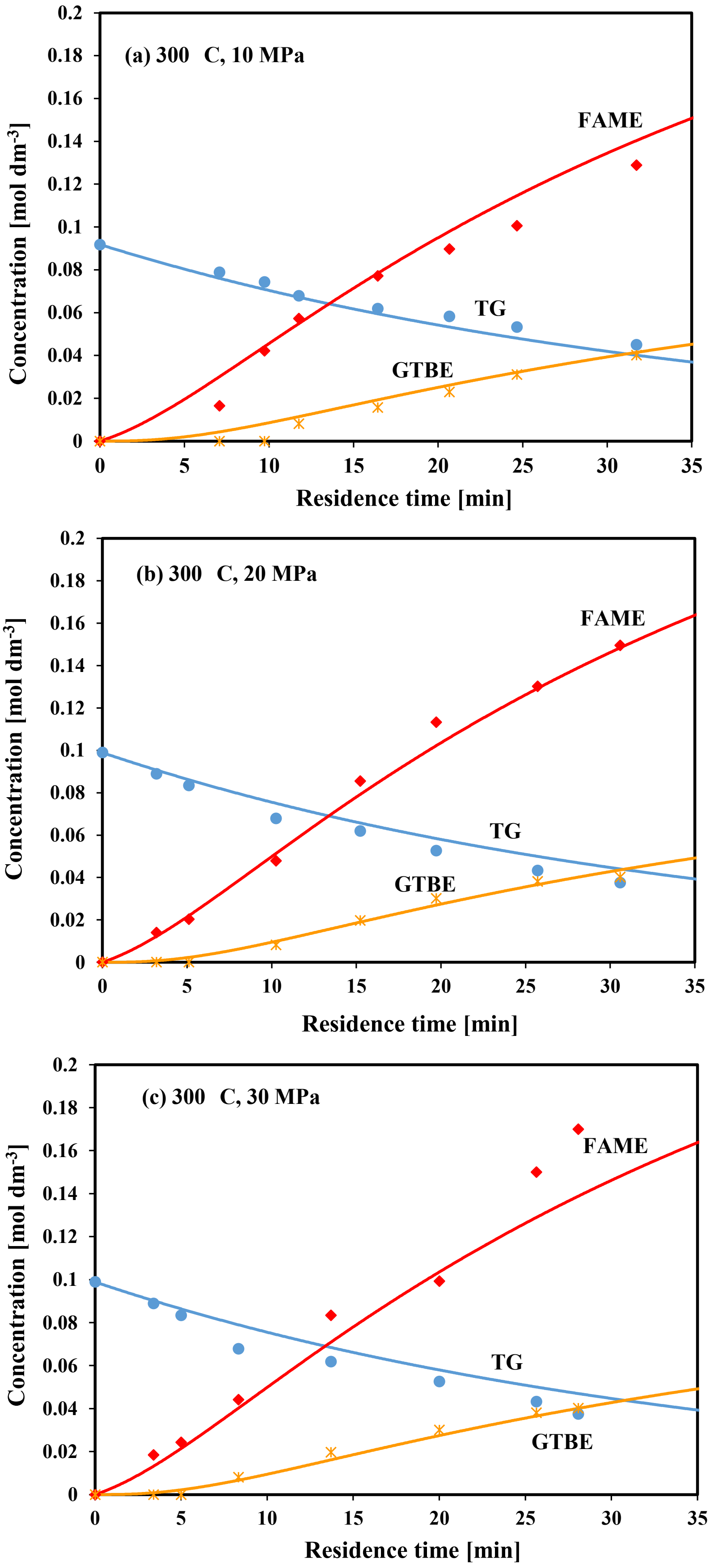


Fig. 8.4. Effect of pressure on TG consumption and GTBE yield at 300 °C.

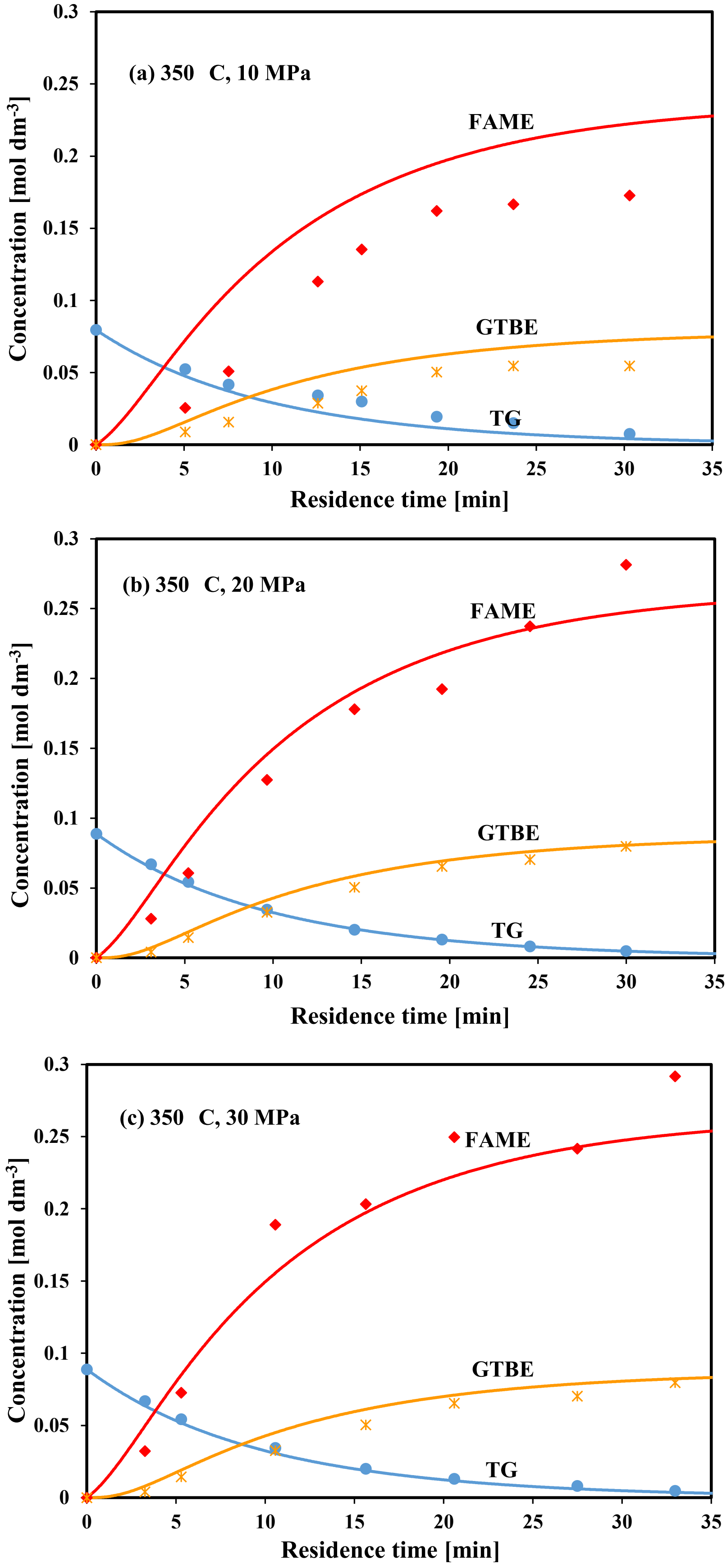


Fig. 8.5. Effect of pressure on TG consumption and GTBE yield at 350 °C.

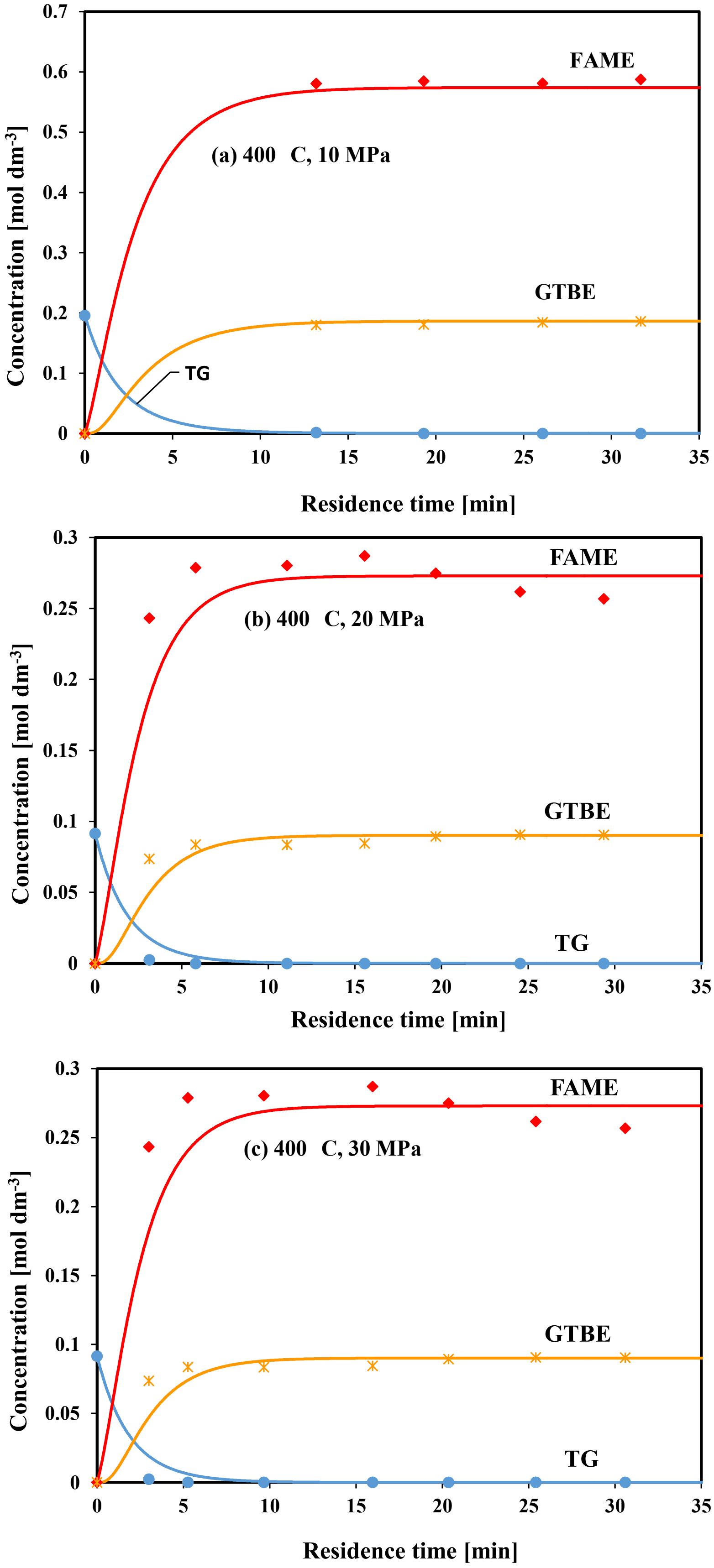


Fig. 8.6. Effect of pressure on TG consumption and GTBE yield at 400 °C.

8.4.3. Effect of pressure on reaction kinetics

Reactiokn kinetics of transesterification of canola oil with MTBE had been deduced in our previous report (Farobie et al., 2014). However, the effect of pressure on reaction kinetics has not been determined yet. In brief, the transesterification of canola oil with MTBE is assumed to occur in three consecutive reactions as shown in **Fig. 8.7**. In the first step, TG reacts with MTBE to generate FAME and DGE. The intermediate DGE then reacts with MTBE to generate FAME and MGE. Finally, the reaction of MGE and MTBE results in FAME and GTBE.

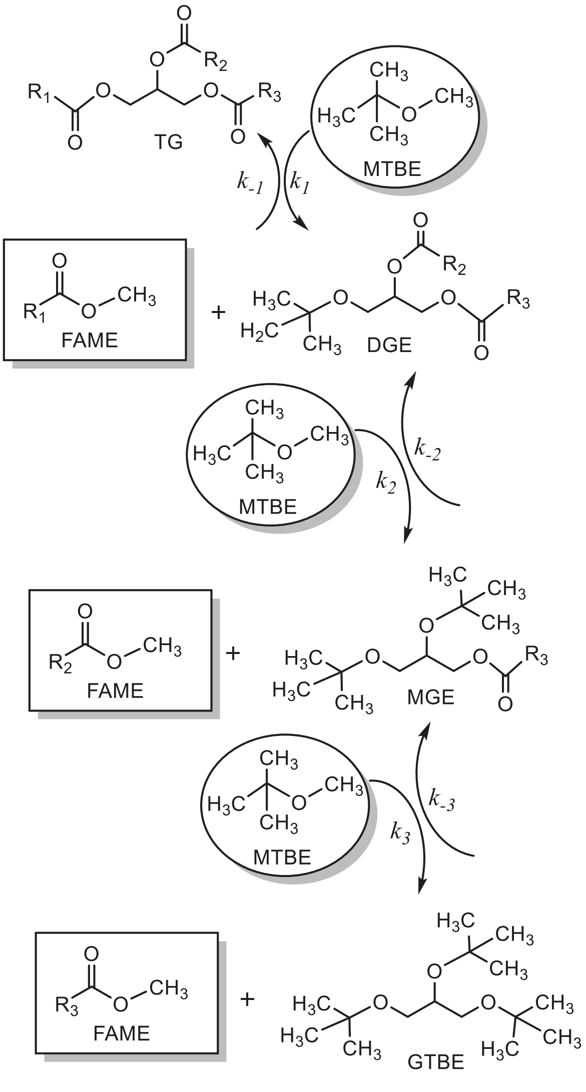


Fig. 8.7. Reaction mechanism of biodiesel production using MTBE.

The next step is to fit the experimental data with a kinetic model with the aim of elucidating its kinetic parameters. The rate equation for each reaction shown above is assumed to follow second-order kinetics; and the rate of change in concentration can thus be expressed by the differential rate equations shown in Eqs. 8.3–8.8.

$$\frac{d[TG]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] + k_{-1}\,[\mathrm{FAME}]\,[\mathrm{DGE}] \qquad (8.3)$$

$$\frac{d[DGE]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] - k_{-1}\,[\mathrm{FAME}]\,[\mathrm{DGE}] - k_2\,[\mathrm{DGE}]\,[\mathrm{MTBE}]$$
$$+ k_{-2}\,[\mathrm{FAME}]\,[\mathrm{MGE}] \qquad (8.4)$$

$$\frac{d[MGE]}{dt} = k_2\,[\mathrm{DGE}]\,[\mathrm{MTBE}] - k_{-2}\,[\mathrm{FAME}]\,[\mathrm{MGE}] - k_3\,[\mathrm{MGE}]\,[\mathrm{MTBE}]$$
$$+ k_{-3}\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \qquad (8.5)$$

$$\frac{d[FAME]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] - k_{-1}\,[\mathrm{FAME}]\,[\mathrm{DGE}] + k_2\,[\mathrm{DGE}]\,[\mathrm{MTBE}]$$
$$- k_{-2}\,[\mathrm{FAME}]\,[\mathrm{MGE}] + k_3\,[\mathrm{MGE}]\,[\mathrm{MTBE}]$$
$$- k_{-3}\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \qquad (8.6)$$

$$\frac{d[MTBE]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{MTBE}] + k_{-1}\,[\mathrm{FAME}]\,[\mathrm{DGE}] - k_2\,[\mathrm{DGE}]\,[\mathrm{MTBE}]$$
$$+ k_{-2}\,[\mathrm{FAME}]\,[\mathrm{MGE}] - k_3\,[\mathrm{MGE}]\,[\mathrm{MTBE}]$$
$$+ k_{-3}\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \qquad (8.7)$$

$$\frac{d[GTBE]}{dt} = k_3\,[\mathrm{MGE}]\,[\mathrm{MTBE}] - k_{-3}\,[\mathrm{FAME}]\,[\mathrm{GTBE}] \qquad (8.8)$$

where; [TG] is triglyceride concentration [mol dm^{-3}], [DGE] is diglyceride mono *tert*-butyl ether concentration [mol dm^{-3}], [MGE] is monoglyceride di *tert*-butyl ether concentration [mol dm^{-3}], [MTBE] is *tert*-butyl methyl ether concentration [mol dm^{-3}],

[FAME] is fatty acid methyl ester concentration [mol dm^{-3}], [GTBE] is *tert*-butyl glycerol ether concentration [mol dm^{-3}], k_i is reaction rate constants [dm^{3} mol^{-1} min^{-1}], and t is residence time [min].

The least square error (LSE) method giving the best fitting between experimental and calculated values was used for the determination of the rate constants. The kinetic parameters identified for the reaction pathways in the temperature range of 300–400 °C is shown in **Table 8.2**. It was observed that all of the reaction rate constants increased with temperature. However, the reaction rate constants were not affected by pressure so much.

Table 8.2. Kinetic parameters obtained for the reaction pathways in the pressure range of 10–30 MPa.

Kinetic parameters [dm^{3} mol^{-1} min^{-1}]	10 MPa			20 MPa			30 MPa		
	300 °C	350 °C	400 °C	300 °C	350 °C	400 °C	300 °C	350 °C	400 °C
k_1	0.0060	0.0201	0.1355	0.0076	0.0316	0.1650	0.0078	0.0336	0.1660
k_{-1}	0.0249	0.0375	0.0480	0.0211	0.0413	0.0600	0.0201	0.0400	0.0590
k_2	0.0997	0.2405	0.6255	0.0897	0.2019	0.4555	0.0907	0.2059	0.4575
k_{-2}	0.5470	0.8400	1.3400	0.4700	0.8400	1.3400	0.4650	0.8200	1.3200
k_3	0.0585	0.1247	0.4039	0.0625	0.1836	0.3388	0.0630	0.1846	0.3408
k_{-3}	0.0081	0.0160	0.0300	0.0154	0.0305	0.0600	0.0164	0.0296	0.0580

By employing Arrhenius equation, the activation energy and pre-exponential factor were determined. Arrhenius plots in this study was derived by taking average reaction rate constants of all pressures, assuming there is no pressure effect. **Fig. 8.8** shows the Arrhenius plots of the individual rate constants. Meanwhile, the activation energy (*Ea*) and pre-exponential factor (*A*) for the detailed kinetic anlaysis are presented in **Table 8.3**. Activation energies between 29.85 and 98.36 kJ mol^{-1} and pre-exponential factors between 11.85 and 5.97×10^{6} dm^{3} mol^{-1} min^{-1} were obtained. Concentration changes of TG, FAME, and GTBE shown in Figs. 8.4–8.6 were determined using these reaction parameters. As observed, the experimental results are in a good agreement with the calculation values. In addition, the effectiveness of the reaction rate parameters presented in Table 8.3 is clear.

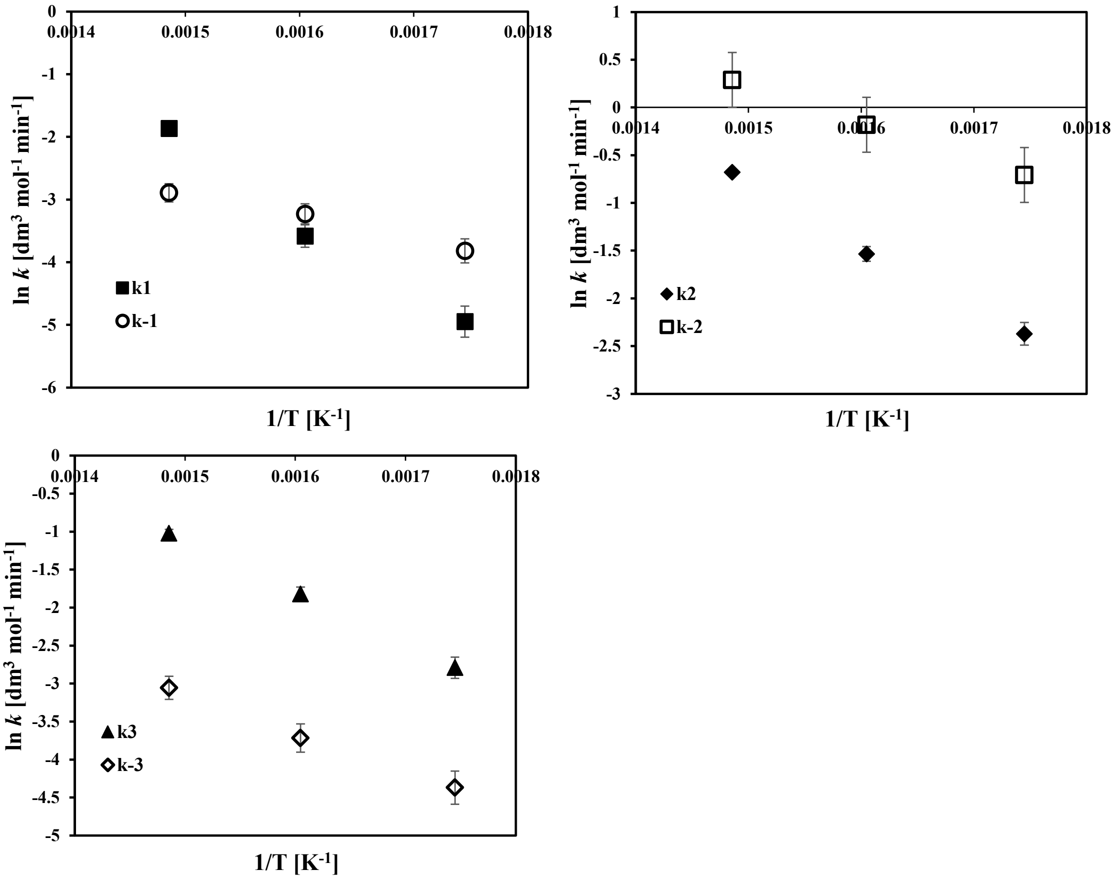


Fig. 8.8. Arrhenius plots of the individual reaction rate constants.

Table 8.3. Activation energy and pre-exponential factor.

Reaction direction	Reaction rate constant [$dm^3\ mol^{-1}\ min^{-1}$]	Activation energy, *Ea* [$kJ\ mol^{-1}$]	Pre-exponential factor, *A* [$dm^3\ mol^{-1}\ min^{-1}$]	*r2*
TG→DGE	k_1	98.36	5.97×10^6	0.99
DGE→TG	k_{-1}	29.85	11.85	0.99
DGE→MGE	k_2	54.16	7.87×10^3	0.99
MGE →DGE	k_{-2}	31.92	397.82	0.99
MGE →GTBE	k_3	56.80	9.24×10^3	0.99
GTBE→MGE	k_{-3}	42.07	84.88	0.99

8.5. Conclusion

The effect of pressure on biodiesel production in supercritical MTBE using spiral reactor was examined. The results showed the effect of pressure on final product composition as well as reaction rate was negligible for the conditions employed here. This negligible effect could be explained by the almost constant density of MTBE. The pre-exponential factors and activation energy for each reaction step as well as its reverse reaction have been determined.

CHAPTER 9

A comparative study of biodiesel production in supercritical methanol, ethanol, and MTBE

9.1. Introduction

Biodiesel production under supercritical conditions is one of the most promising methods since transesterification reaction can be proceeded within short reaction time and without any catalyst. In addition, transesterification of triglyceride and esterification of free fatty acid (FFA) occur simultaneously as well as easier separation and purification steps. This method was firstly invented by Japanese researchers, Saka and Dadan (2001), who employed methanol as a reaction medium following reaction as shown in **Fig. 9.1.**

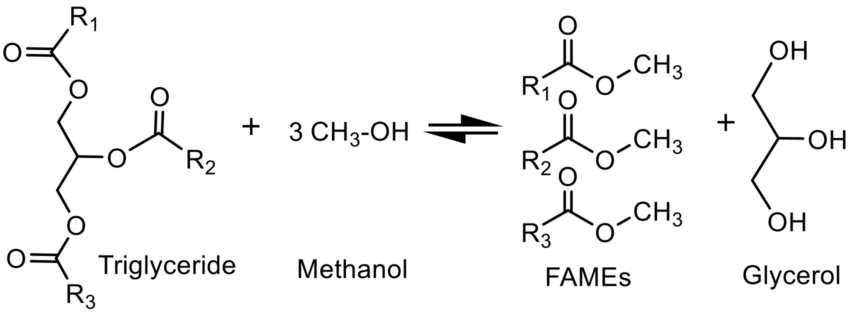


Fig. 9.1. Reaction between triglyceride and methanol to generate fatty acid methyl esters (FAMEs) and glycerol.

Since then, biodiesel production increases rapidly leading to abundance of glycerol. It has caused oversupply and depreciation of glycerol in the market. To circumvent this problem, a new approach of biodiesel production using supercritical MTBE method has been developed in our laboratory (Farobie et al., 2014), obtaining glycerol-*tert* butyl ether (GTBE) as a by-product following reaction as presented in **Fig. 9.2**.

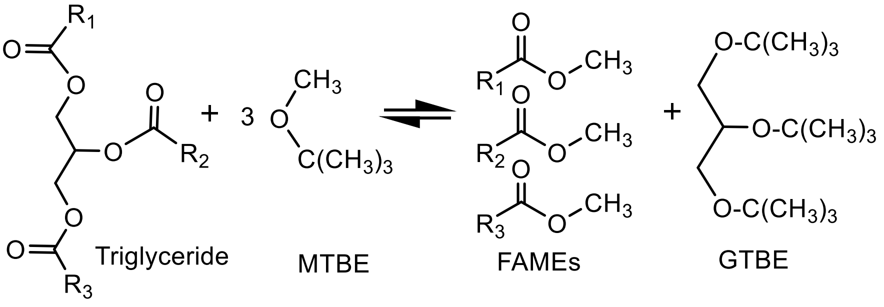


Fig. 9.2. Reaction between triglyceride and MTBE to generate FAMEs and GTBE.

However, the difference in reaction behavior among MTBE, methanol, and ethanol with triglyceride under supercritical conditions has not been studied previously. A comparative study on biodiesel production using supercritical alcohol and MTBE is a vital in order to know their reaction behavior. Thus, the purpose of this study is to elucidate the difference of their reaction behavior to produce biodiesel under supercritical conditions by examining temperature and residence time effects on biodiesel yields as well as reaction kinetics.

9.2. Experimental procedures

Transesterification of canola oil under supercritical methanol, ethanol, and MTBE conditions was carried out in spiral reactor that is schematically illustrated in **Fig. 4.2** (chapter 4). A comparative study was carried out in the temperature range of 270–400 °C under a pressure of 20 MPa. Transesterification was performed over 3 min to 30 min using a fixed oil-to-reactant molar ratio of 1:40. Samples were collected after achieving a steady state and after passing through the filter and back-pressure regulator. The liquid samples were analyzed by gas chromatography (GC-390B; GL Sciences) equipped with a MET-Biodiesel column (14 m × 0.53 mm × 0.16 μm film thickness) with an integrated 2 m guard column (Sigma Aldrich, 28668-U) and flame-ionization detector (FID). Experimental biodiesel yields were calculated by dividing the moles of biodiesel product by the moles of fatty acid groups in the initial triglyceride (TG), as shown in Eq. 9.1.

$$\text{(Product yield)} = \frac{\text{(Molar amount of product biodiesel)}}{\text{(Molar amount of fatty acid group in initial TG)}} \qquad (9.1)$$

9.3. Experimental conditions

The experimental conditions for this study are presented in **Table 9.1**.

Table 9.1. Experimental conditions for this corresponding study

Types of condition	Experimental range
Feedstock	Canola oil
Reaction time	3-30 min
Molar ratio of oil to MTBE	1:40
Reactor type	Spiral reactor
Temperature	270-400 °C
Pressure	20 MPa

9.4. Results and Discussion

9.4.1. Comparison of temperature effect

Effect of temperature on biodiesel yields in SCM, SCE, and SCMTBE at the same residence time of 15 min is presented in **Fig. 9.3**. For all cases, biodiesel yield increased with temperature. Biodiesel production in supercritical methanol method was superior to supercritical ethanol and MTBE methods. It could be attributed to the fact that methanol is the smallest molecule among others, so that oxygen atom from methanol can easily attack carbon atom of carbonyl functional group from triglycerides as illustrated in **Fig. 9.4**.

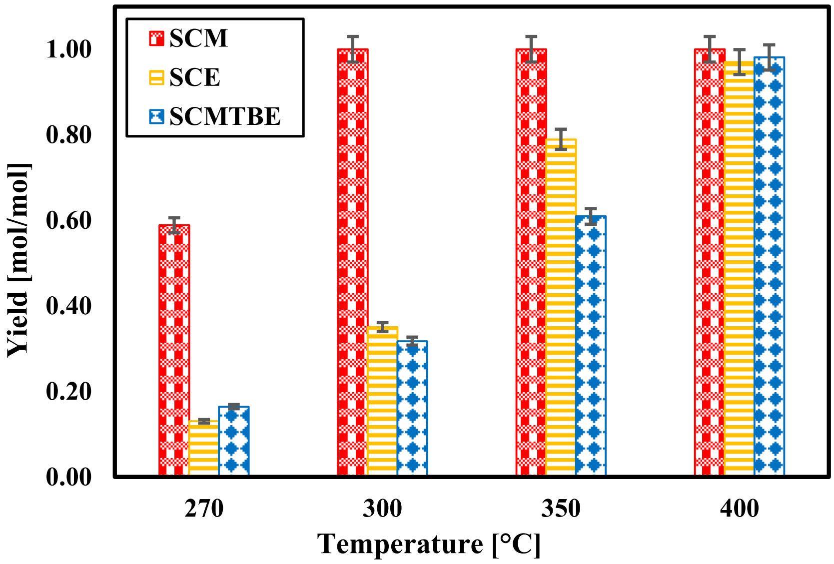


Fig. 9.3. Effect of temperature on biodiesel yield.

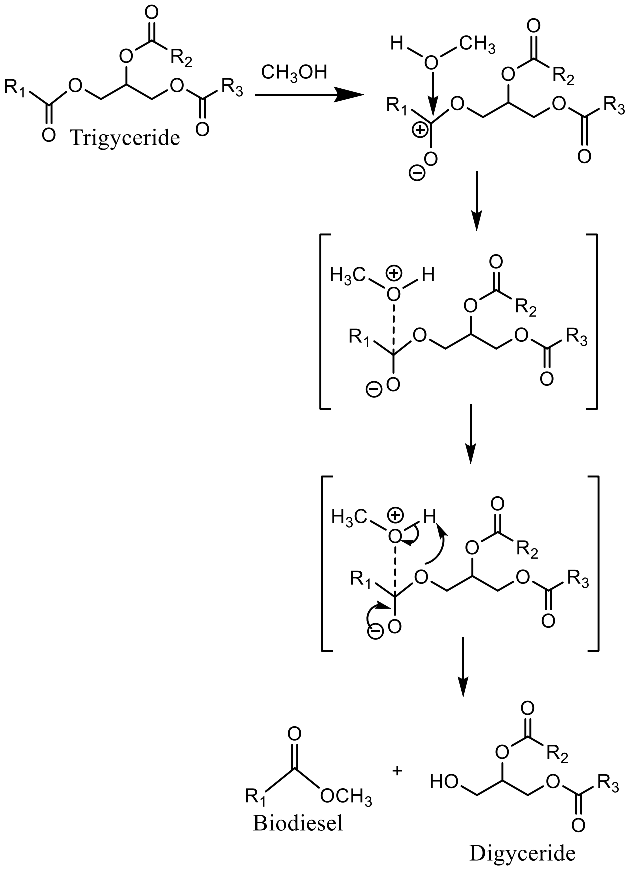


Fig. 9.4. The reaction of methanol molecule with triglyceride under supercritical conditions.

It is interesting to note that at low temperature of 270 °C, biodiesel yield in supercritical MTBE was higher than that in supercritical ethanol. It presumed that at low temperature, the effect of solubility gave more impact than steric effect. In fact, the polarity of MTBE is lower than that of ethanol, leading to more able to miscible with oil than ethanol. However, at 300 °C and thereafter, biodiesel yield in supercritical ethanol was higher than that in supercritical MTBE due to the bulkier structure of MTBE.

9.4.2. Comparison of reaction time effect

A comparison of reaction behavior on biodiesel production in supercritical methanol, ethanol, and MTBE was further studied by examining effect of time. **Figs. 9.5, 9.6, 9.7,** and **9.8** show the changes in feedstock TG, final product of biodiesel, and by-product yields at 270, 300, 350, and 400 °C, respectively. For all cases, a longer reaction time allowed the transesterification to proceed to completion and results in a higher yield of biodiesel, as expected.

Initially, at the temperature just above the critical temperature of methanol, ethanol, and MTBE, 270 °C, the yields of biodiesel were relatively low for both SCE and SCMTBE even within 30 min reaction, whereas a significant yield of biodiesel in SCM could be achieved after 25 min. In this experimental conditions, the yields of biodiesel of 72.6 wt%, 18.8 wt%, and 19.9 wt% were obtained within 20 min for SCM, SCE, and SCMTBE, respectively.

The conversion to biodiesel at 300 °C was higher than that at 270 °C for all cases. A considerable conversion of oil to biodiesel could be achieved within 15 min in SCM, obtaining a biodiesel yield of 96.5 wt%. This result is in a good agreement with the previous work of Warabi et al. (2004) who reported that almost a complete conversion of biodiesel was obtained in SCM at 300 °C by 15 min. Meanwhile, biodiesel yields of merely 37.2 wt% and 28.9 wt% were obtained within 15 min reaction time in SCE and SCMTBE, respectively.

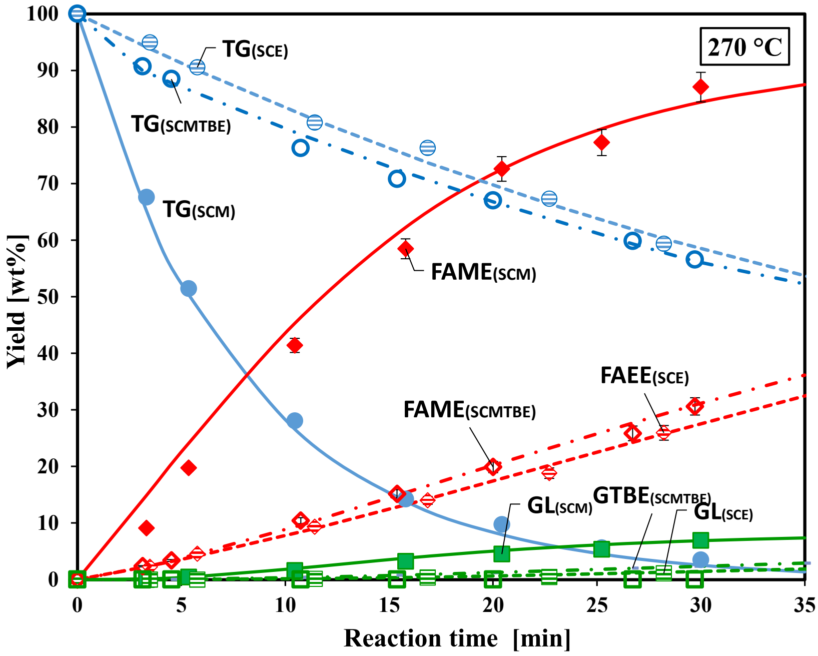


Fig. 9.5. Effect of reaction time on TG consumption and biodiesel yield in SCM, SCE, and SCMTBE at 270°C.

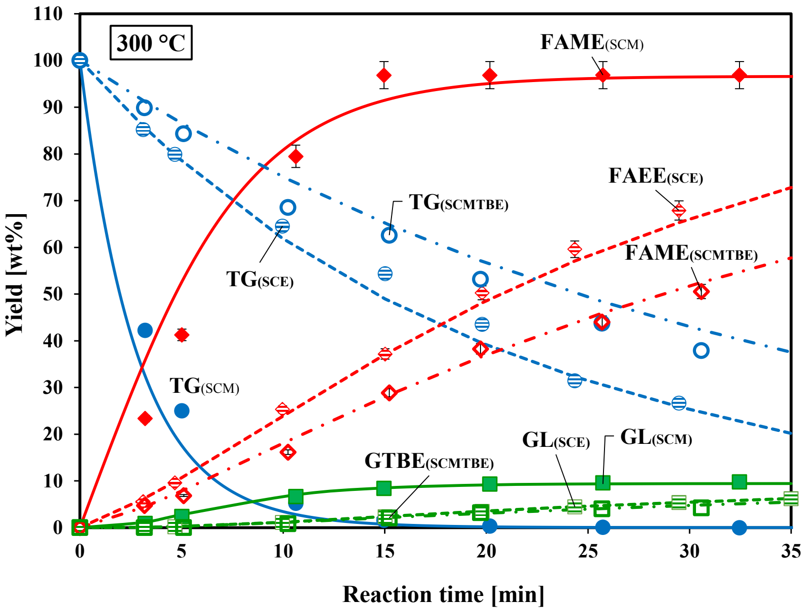


Fig. 9.6. Effect of reaction time on TG consumption and biodiesel yield in SCM, SCE, and SCMTBE at 300°C.

At 350 °C, a complete conversion of canola oil to biodiesel was noted to be achieved within 10 min, 30 min, and 30 min for SCM, SCE, and SCMTBE. In SCM, FAME yields of about 68.3 wt% and 97.7 wt% were obtained after 3 and 5 min, respectively. Particularly, transesterification was almost complete within 10 min, converting almost all canola oil to FAME. Meanwhile, biodiesel yields of about 59.6 wt% and 22.9 wt% were obtained after 5 min for SCE and SCMTBE, respectively and a significant change of oil to biodiesel was observed after 20 min. A complete conversion of oil to biodiesel for both SCE and SCMTBE was found after 30 min reaction time. It is noted that 350 °C was the best temperature to carry out transesterification under supercritical conditions, giving a good agreement with the previous works (Kusdiana and Saka, 2001; Silva et al., 2007; Madras et al., 2004).

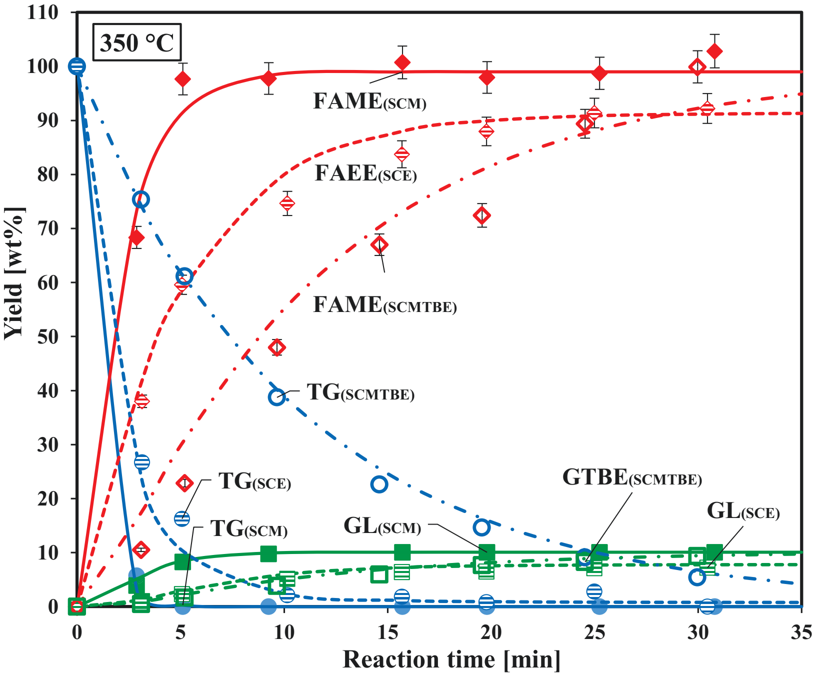


Fig. 9.7. Effect of reaction time on TG consumption and biodiesel yield in SCM, SCE, and SCMTBE at 350 °C.

At 400 °C, in SCM, the complete conversion of canola oil to FAME was observed in the initial time of 3 min. Meanwhile, in SCE and SCMTBE, the transesterification of canola oil was complete after 10 min, obtaining 100 wt% of biodiesel.

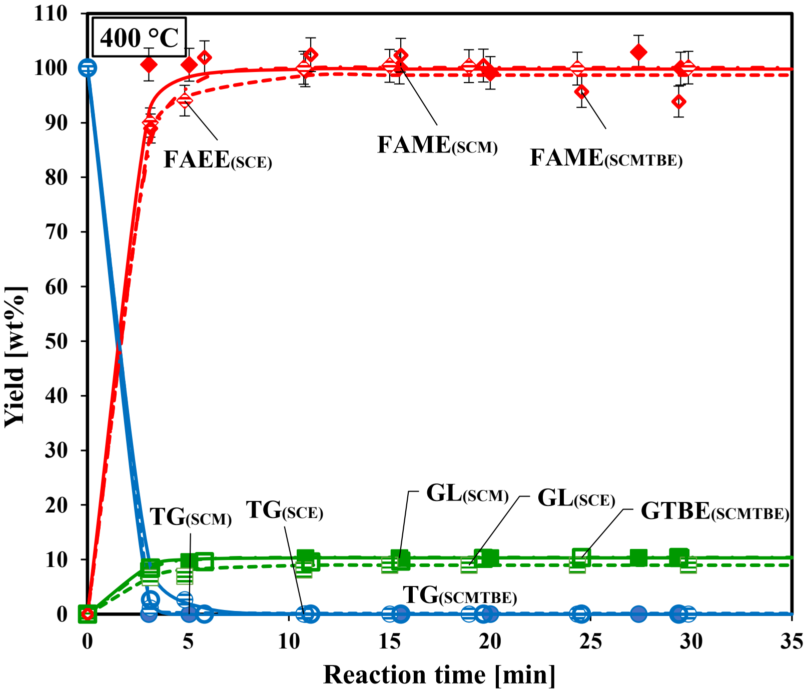


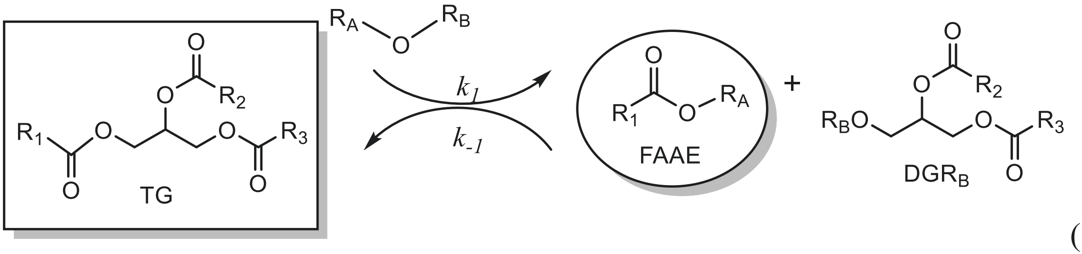
Fig. 9.8. Effect of reaction time on TG consumption and biodiesel yield in SCM, SCE, and SCMTBE at 400 °C.

Overall, consumption of TG was favored with increasing reaction temperature and time. In addition, at 270–350 °C, SCM gave the highest by-product glycerol (GL), whereas at 400 °C, the by-product yields were relatively the same for all SCM, SCE, and SCMTBE cases.

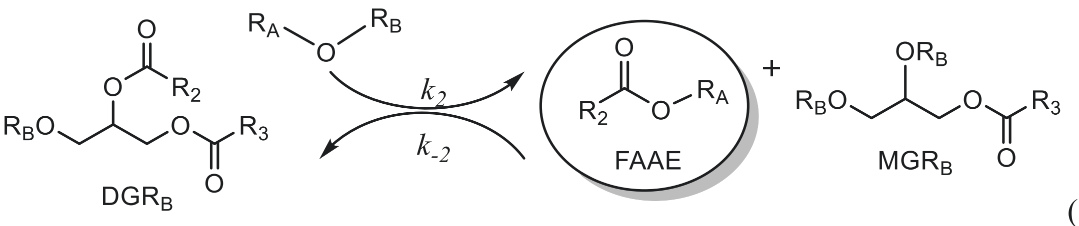
9.4.3. Comparison of reaction kinetics

Finally, reaction kinetics of transesterification reaction of oil in SCM, SCE, and SCMTBE was compared. The transesterification reaction of oil with MTBE as well as the differential rate equations in SCMTBE have been reported in the previous report (Farobie et al., 2014). However, the rate equation for FAME decomposition should be eliminated since the temperature condition employed here was until 400 °C and no decomposition products observed.

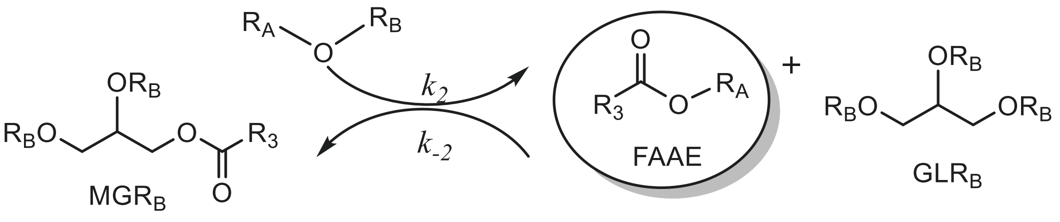
The transesterification reaction of triglyceride with methanol, ethanol, or MTBE was assumed to occur in three reversible reaction steps as presented in Eqs. 3–5. Reaction rate constants were determined using the non-linear regression with the least squares of error (LSE) method (i.e., the difference between experimental and calculated values) as a criterion to fit the model with the experimental data.



(9.2)



(9.3)



(9.4)

where, R_1, R_2, R_3 is hydrocarbon residues, R_A is CH_3 residue for methanol and MTBE moieties and C_2H_5 is residue for ethanol moiety, R_B is H residue for methanol and ethanol moieties and $C(CH_3)_3$ residue for MTBE moiety

Each reaction shown above is assumed to follow the second-order kinetics; and the rate of change in concentration, hence, can be expressed by the differential rate equations shown in Eqs. 9.5–9.10.

$$\frac{d[\mathrm{TG}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{R_AOR_B}] + k_{-1}\,[\mathrm{FAAE}]\,[\mathrm{DGR_B}] \tag{9.5}$$

$$\frac{d[\mathrm{DGR_B}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{R_AOR_B}] - k_{-1}\,[\mathrm{FAAE}]\,[\mathrm{DGR_B}] - k_2\,[\mathrm{DGR_B}]\,[\mathrm{R_AOR_B}] + k_{-2}\,[\mathrm{FAAE}]\,[\mathrm{MGR_B}] \tag{9.6}$$

$$\frac{d[\mathrm{MGR_B}]}{dt} = k_2\,[\mathrm{DGR_B}]\,[\mathrm{R_AOR_B}] - k_{-2}\,[\mathrm{FAAE}]\,[\mathrm{MGR_B}] - k_3\,[\mathrm{MGR_B}]\,[\mathrm{R_AOR_B}] + k_{-3}\,[\mathrm{FAAE}]\,[\mathrm{GLR_B}] \tag{9.7}$$

$$\frac{d[\mathrm{FAAE}]}{dt} = k_1\,[\mathrm{TG}]\,[\mathrm{R_AOR_B}] - k_{-1}\,[\mathrm{FAAE}]\,[\mathrm{DGR_B}] + k_2\,[\mathrm{DGR_B}]\,[\mathrm{R_AOR_B}] - k_{-2}\,[\mathrm{FAAE}]\,[\mathrm{MGR_B}] + k_3\,[\mathrm{MGR_B}]\,[\mathrm{R_AOR_B}] - k_{-3}\,[\mathrm{FAAE}]\,[\mathrm{GLR_B}] \tag{9.8}$$

$$\frac{d[\mathrm{R_AOR_B}]}{dt} = -k_1\,[\mathrm{TG}]\,[\mathrm{R_AOR_B}] + k_{-1}\,[\mathrm{FAAE}]\,[\mathrm{DGR_B}] - k_2\,[\mathrm{DGR_B}]\,[\mathrm{R_AOR_B}] + k_{-2}\,[\mathrm{FAAE}]\,[\mathrm{MGR_B}] - k_3\,[\mathrm{MGR_B}]\,[\mathrm{R_AOR_B}] + k_{-3}\,[\mathrm{FAAE}]\,[\mathrm{GLR_B}] \tag{9.9}$$

$$\frac{d[\mathrm{GLR_B}]}{dt} = k_3\,[\mathrm{MGR_B}]\,[\mathrm{R_AOR_B}] - k_{-3}\,[\mathrm{FAAE}]\,[\mathrm{GLR_B}] \tag{9.10}$$

where, [TG] is triglyceride concentration [mol dm^{-3}], [DGR_B] is diglyceride concentration for SCM and SCE or diglyceride mono *tert*-butyl ether concentration for SCMTBE [mol dm^{-3}], [MGR_B] is monoglyceride concentration for SCM and SCE or monoglyceride di *tert*-butyl ether concentration for SCMTBE [mol dm^{-3}], [R_AOR_B] is reactant concentration, in this case methanol, ethanol, or MTBE [mol dm^{-3}], [FAAE] is fatty acid alkyl ester or biodiesel concentration [mol dm^{-3}], [GLR_B] is glycerol concentration for SCM and SCE or glycerol *tert*-butyl ether concentration for SCMTBE [mol dm^{-3}], k_i is reaction rate constants [dm^3 mol^{-1} min^{-1}], and t is residence time [min].

Table 9.2 shows the values of corresponding reaction rate constants. As observed, the reaction rate constants for forward reaction in SCM were the highest, followed by SCMTBE and SCE. **Fig. 9.9** shows the comparison of the Arrhenius plots of the individual rate constants for SCM, SCE, and SCMTBE. The logarithm of the overall reaction rate constants were linear with the inverse temperatures, demonstrating that the transesterification reaction of oil to biodiesel obeyed the Arrhenius behavior for all cases.

Activation energy (*Ea*) and pre-exponential factor (*A*) for the detailed kinetic analysis of biodiesel production in SCM, SCE, and SCMTBE are comparatively shown in **Table 9.3**. Activation energies of oil conversion to biodiesel were determined between 44.98 and 100.99 kJ/mol, 43.05 and 141.28 kJ/mol, and 44.16 and 103.68 kJ/mol for SCM, SCE, and SCMTBE, respectively. Activation energies for forward reaction in SCM was the lowest followed by SCMTBE and SCE, meaning that the energy needs to achieve the complete transesterification reaction in SCM was the lowest. It is interesting to note that the activation energies of SCMTBE calculated here were close to those of SCM.

Table 9.2. Reaction rate constants obtained from the second order model (Experimental conditions: 270–400 °C, 20 MPa, reactant-to-oil molar ratio of 40:1)

Rate constants [$dm^3\ mol^{-1}\ min^{-1}$]	Supercritical methanol (SCM)				Supercritical ethanol (SCE)				Supercritical MTBE (SCMTBE)			
	270 °C	300 °C	350 °C	400 °C	270 °C	300 °C	350 °C	400 °C	270 °C	300 °C	350 °C	400 °C
k_1	0.0133	0.0428	0.2338	0.9985	0.0024	0.0068	0.0883	0.9085	0.0052	0.0095	0.0390	0.4760
k_{-1}	0.0015	0.0035	0.0165	0.0590	0.0080	0.0208	0.0738	0.2690	0.0022	0.0086	0.0300	0.0800
k_2	0.0180	0.0428	0.1505	0.3810	0.0080	0.0210	0.0580	0.2810	0.0157	0.0374	0.1341	0.3546
k_{-2}	0.0300	0.0900	0.2800	0.9242	0.0680	0.1737	0.7363	1.6242	0.0350	0.1015	0.3200	1.0150
k_3	0.0165	0.0661	0.1857	0.5094	0.0085	0.0372	0.0880	0.3439	0.0148	0.0520	0.1255	0.5388
k_{-3}	0.0280	0.0420	0.1050	0.1800	0.0488	0.0840	0.1876	0.3000	0.0283	0.0458	0.1070	0.1800

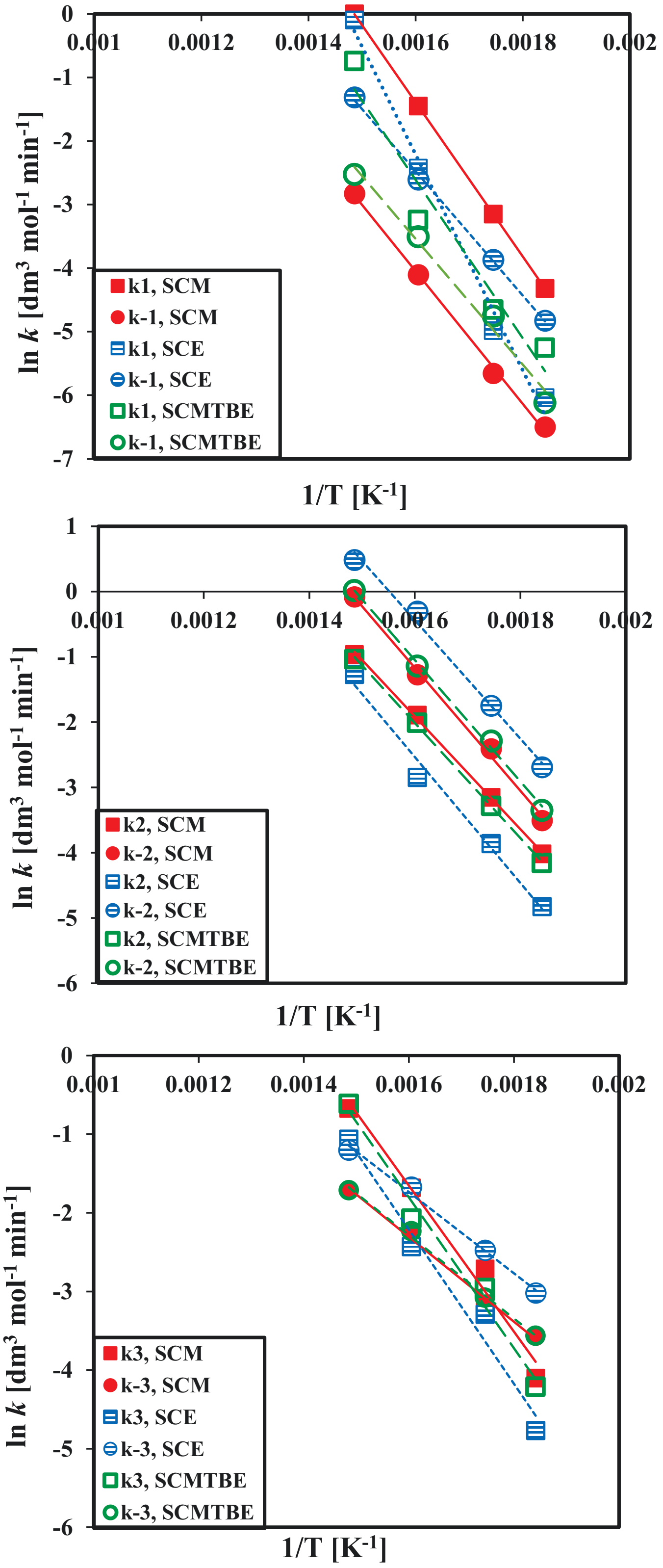


Fig. 9.9. Arrhenius plots for SCM, SCE, and SCMTBE (experimental conditions: 20 MPa, oil-to-reactant molar ratio of 1:40

Table 9.3. Activation energies and pre-exponential factors (Experimental conditions: 270–400 °C, 20 MPa, oil-to-reactant molar ratio of 1:40)

Rate constants	SCM		SCE		SCMTBE	
[dm^3 mol^{-1} min^{-1}]	Activation energy, *Ea* [kJ mol^{-1}]	Pre-exponential factor, *A* [dm^3 mol^{-1} min^{-1}]	Activation energy, *Ea* [kJ mol^{-1}]	Pre-exponential factor, *A* [dm^3 mol^{-1} min^{-1}]	Activation energy, *Ea* [kJ mol^{-1}]	Pre-exponential factor, *A* [dm^3 mol^{-1} min^{-1}]
k_1	100.99	6.85×10^7	141.28	7.03×10^{10}	103.68	3.39×10^7
k_{-1}	86.81	3.13×10^5	81.32	5.25×10^5	82.32	2.19×10^5
k_2	71.77	1.47×10^5	80.31	4.09×10^5	73.28	1.78×10^5
k_{-2}	78.36	1.10×10^6	75.52	1.32×10^6	77.24	3.43×10^6
k_3	77.28	5.50×10^5	81.64	7.29×10^5	79.84	7.76×10^5
k_{-3}	44.98	5.73×10^2	43.05	6.98×10^2	44.16	5.00×10^2

9.5. Conclusion

Reaction behaviours of biodiesel production in supercritical methanol, ethanol, and MTBE were compared by investigating the effects of temperature, time, and reaction kinetics. The results showed that biodiesel yield increased with reaction time and temperature for all cases. At the same reaction conditions, supercritical methanol method gave the highest yields of biodiesel. At 270 °C, biodiesel yield in supercritical MTBE was higher than that in supercritical ethanol owing to the solubility effect, whereas above 270 °C, biodiesel yield in supercritical ethanol was higher than that in supercritical MTBE due to the bulkier structure of MTBE. At 350 °C and 20 MPa, a complete conversion to biodiesel was achieved after 10, 30, and 30 min for biodiesel production in supercritical methanol, ethanol, and MTBE, respectively. Reaction parameters for oil conversion to biodiesel in supercritical methanol, ethanol, and MTBE were also determined.

CHAPTER 10

Conclusion and Recommendations for Future Work

10.1. Introduction

The last chapter of this thesis is remarked with the conclusion and the recommendations for future works. The conclusion of the current study are presented in section 10.2. Meanwhile, the recommendations for future work are proposed in section 10.3.

10.2. Conclusion

New approach of non-catalytic biodiesel production using supercritical MTBE method was proposed. Interestingly, MTBE could react with triglyceride under supercritical conditions, generating fatty acid methyl ester (FAME) and glycerol *tert*-butyl ether (GTBE). This GTBE is a higher added-value than glycerol since it has a good blending property with diesel fuel and can enhance cetane number. No glycerol was observed under these reaction conditions. The results of temperature effect on FAME yield showed that the FAME yields and TG consumption were favored by increasing temperature from 200 to 400 °C. However, thermal decomposition was identified at temperature above 400 °C. The optimum yield of FAME was achieved in short reaction time of 12 min at 400 °C under a pressure of 10 MPa and an oil-to-MTBE molar ratio of 1:40. The activation energies for transesterification of canola oil conversion to FAME under supercritical conditions were determined, obtaining 14.63–53.19 kJ mol^{-1} which was close to the value for transesterification of canola oil in supercritical methanol.

Since supercritical conditions require elevated temperature and high pressure, a novel spiral reactor comprised heat exchanger and reactor at once was proposed for biodiesel production in supercritical ethanol. The results showed that the spiral reactor is a good reactor candidate for biodiesel production under supercritical condition that was proven by the successful recovery of the heat. In addition, the quantitative analysis revealed that spiral reactor for biodiesel production in supercritical ethanol improves the biodiesel production process by reducing energy requirement from 0.4544 MJ/d to 0.066 MJ/d owing to the heat recovery.

Effectiveness of spiral reactor on biodiesel production in supercritical MTBE was also examined. There are at least two important results that can be concluded from this study. The first is that the spiral reactor was superior to a conventional flow reactor in terms of leading to a higher FAME yields as a consequence of the portion of the reaction that takes place in the heat exchanger. The second important result is that the spiral reactor was effective for biodiesel production using MTBE under high temperature and high pressure conditions due to successful recoverery of heat.

The effect of pressure on biodiesel production in supercritical MTBE was also investigated. It can be confirmed from this study that effect of pressure on both final product composition and reaction kinetics was negligible.

Finally, reaction behaviours of biodiesel production in supercritical methanol, ethanol, and MTBE were compared by investigating the effects of temperature, time, and reaction kinetics. Supercritical methanol method gave the highest biodiesel yield under the same reaction conditions. At 270 °C, biodiesel yield in supercritical MTBE was higher than that in supercritical ethanol owing to the solubility effect, whereas above 270 °C, biodiesel yield in supercritical ethanol was higher than that in supercritical MTBE due to the bulkier structure of MTBE. At 350 °C and 20 MPa, a complete conversion of canola oil to biodiesel was obtained after 10, 30, and 30 min for biodiesel production in supercritical methanol, ethanol, and MTBE, respectively.

10.3. Recommendations for future work

In spite of the successful study on biodiesel production under supercritical MTBE and alcohol conditions using spiral reactor, there are still a number of interesting topics that can be explored. The recommendations for future work are described as follows:

1) As mentioned in the chapter 5, thermal decomposition of biodiesel occurred above 400 °C. It would be a possibility of interesting topic for the next study to determine detailed reaction pathways, kinetics and mechanism of thermal decomposition of biodiesel production in supercritical MTBE.

2) A new approach of biodiesel production has been proposed by employing MTBE. However, high temperature and high pressure are required to achieve complete conversion of oil to biodiesel. In order to reduce the severity of conditions, there are two possibilities of methods that can be conducted:

    a) Two-steps supercritical MTBE method for biodiesel production. Oil is firstly hydrolyzed under subcritical conditions of water to generate free fatty acid (FFA) and glycerol. Subsequently, the products are furthered esterified under supercritical MTBE conditions, following the reaction as shown in **Fig. 10.1**. Since FFA is much more reactive than triglyceride, the optimum conditions of biodiesel probably can be achieved under a milder reaction condition.

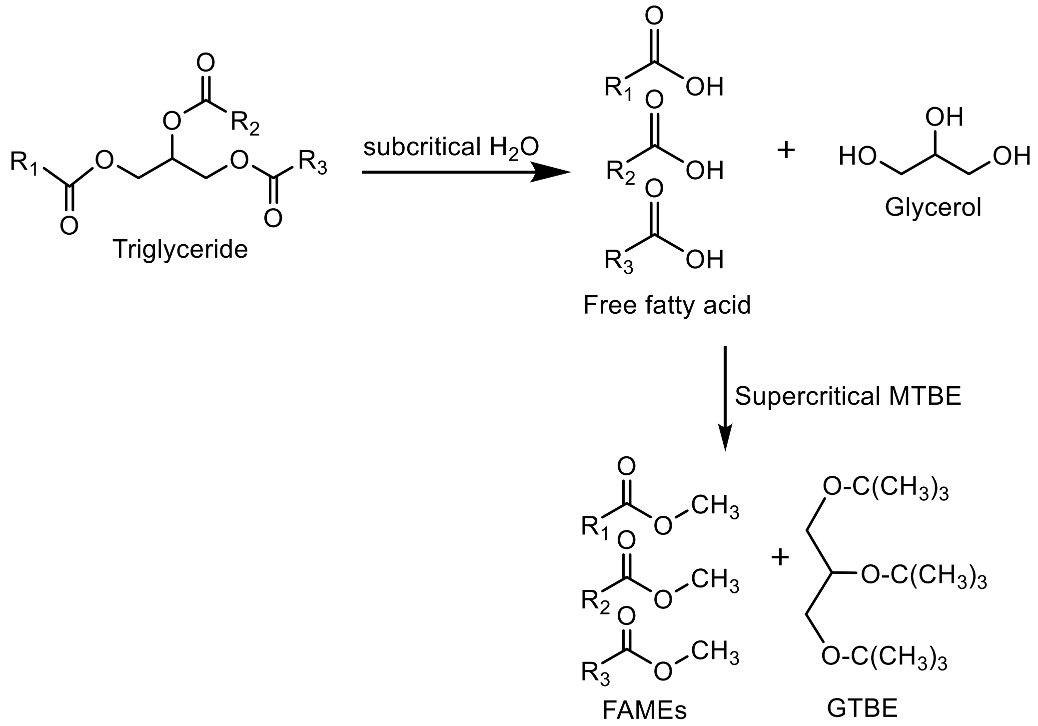


Fig. 10.1. The proposed reaction design for two-steps supercritical MTBE method for biodiesel production.

b) The addition of co-solvent such as n-hexane. Since the critical properties of n-hexane is much lower than that of MTBE, the addition of co-solvent probably would help the highest biodiesel yield can be achieved under milder conditions. Besides, the addition of co-solvent can reduce the amount of MTBE required to achieve optimum biodiesel yield.

3) The study on a new route of biodiesel production using spiral reactor by employing dimethyl carbonate and or methyl acetate is another interesting part that should be discovered further. Since to the best of my knowledge, there has been no previous report determined reaction kinetics of biodiesel production in supercritical dimethyl carbonate. This might be because the reaction mechanism of this process is little bit complicated. Thus, the study on biodiesel production in supercritical dimethyl

carbonate is challenging. Besides, the reaction behavior obtained from this study can be compared with the previous studies of supercritical MTBE, methanol, and ethanol.

4) It has been reported in the previous studies that GTBE is a useful compound for diesel fuel since it has a good blending properties and can reduce particulate matter and carbon monoxide as well as can enhance the cetane number of diesel fuel. Therefore, further study of physico-chemical properties of biodiesel obtained in this study as well as the characteristics of diesel engine performance would be an interesting topic for the next study.

5) As described in chapter 9, the reactivity of biodiesel production in supercritical methanol is better than that of supercritical MTBE. On the other hand, biodiesel production using supercritical MTBE results in a higher added-value of by-product (GTBE) over supercritical methanol (glycerol). Thus, in order to know the feasibility for industrial application, economic analysis of those methods would be another interesting topic for future study.

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