

**ALTERNATIVE DIESELS FROM PLANT OILS
AND THEIR EVALUATION OF FUEL PROPERTIES**

YUITSU SUGAMI

Contents

Chapter 1

Introduction

1.1	World Energy Problems and Transportation Fuel	1
1.2	Alternative Diesel Fuels from Plant Oils.....	2
1.3	Biodiesel as Alternative Diesel Fuel.....	4
1.3.1	Biodiesel production from plant oils	5
1.3.2	Current situation of biodiesel	6
1.4	Hydrocarbon as Alternative Diesel Fuel.....	9
1.4.1	Hydrocarbon production from triglycerides	10
1.4.1.1	Thermal and catalytic cracking.....	10
1.4.1.2	Hydrotreating.....	12
1.4.2	Hydrocarbon production from fatty acids	16
1.5	Summative Descriptions of this Dissertation	20

Chapter 2

The Prediction of Low-Temperature Properties for Biodiesel Model Fuel by Solid-Liquid Equilibrium Equation

2.1	Introduction	21
2.2	Materials and Methods	22
2.2.1	Materials.....	22
2.2.2	Experimental methods and definitions	23
2.2.3	Thermodynamic model.....	25
2.3	Results and Discussion	28
2.3.1	Properties of pure component.....	28
2.3.2	Binary mixture.....	30
2.3.3	Multi-component mixture.....	36
2.4	Conclusions	38

Chapter 3

The Effect of Biodiesel Fuel on Its Low-Temperature Properties by Monoglyceride Polymorphism

3.1	Introduction	39
3.2	Materials and Methods	40
3.2.1	Materials	40
3.2.2	Experimental and analytical methods	40
3.2.3	Thermodynamic model	41
3.3	Results and Discussion	42
3.4	Concluding Remarks	50

Chapter 4

Renewable Diesel Production from Rapeseed Oil and Its Evaluation of Fuel Properties

4.1	Introduction	51
4.2	Materials and Methods	53
4.2.1	Experimental procedures	53
4.2.1.1	Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)	54
4.2.1.2	Decarboxylation	54
4.2.2	Analytical methods	55
4.3	Results and Discussion	55
4.3.1	Hydrolysis/hydrogenation	56
4.3.2	Decarboxylation	58
4.3.3	Fuel properties of renewable diesel from rapeseed oil	61
4.4	Concluding Remarks	62

Chapter 5

Renewable Diesel Production from Coconut Oil and Its Evaluation of Fuel Properties

5.1	Introduction	64
5.2	Materials and Methods	66
5.2.1	Experimental procedures	66

5.2.1.1	Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)	66
5.2.1.2	Decarboxylation.....	66
5.2.2	Analytical methods	67
5.3	Results and Discussion	68
5.3.1	Hydrolysis/hydrogenation	70
5.3.2	Decarboxylation.....	72
5.3.3	Fuel properties of renewable diesel from coconut oil	75
5.4	Concluding Remarks	76

Chapter 6

Concluding Remarks

6.1	Conclusions	78
6.2	Prospects for Future Research	80

References	82
-------------------------	-----------

Acknowledgements.....	96
------------------------------	-----------

List of Publications.....	98
----------------------------------	-----------

List of Figures

Fig. 1-1 Global demand of petroleum products for 2014, 2020 and 2040	2
Fig. 1-2 Transesterification of triglyceride with methanol to fatty acid methyl esters.....	4
Fig. 1-3 Pathways for methanolysis reaction of triglyceride.....	5
Fig. 1-4 Thermal decomposition pathways of triglyceride.....	11
Fig. 1-5 Reaction pathways of triglyceride (triolein) by hydrotreating.....	13
Fig. 1-6 Decarboxylation mechanism of carboxylic acid on surface of Pd catalyst	18
Fig. 1-7 Proposed reaction routes of stearic acid with heterogeneous catalyst at 300 °C under inert atmosphere	19
Fig. 1-8 Schematic reaction pathway of linoleic acid by decarboxylation condition.....	19
Fig. 2-1 Schematic diagram of the visual observation equipment used to estimate the solid–liquid equilibrium	24
Fig. 2-2 DSC curves for the mixture of 30 wt% 1-monopalmitin and 70 wt% methyl oleate.....	31
Fig. 2-3 Changes in the solid–liquid equilibrium temperature (T_{SLE}) of 1-monopalmitin in methyl oleate for each crystal type.....	32
Fig. 2-4 Changes in the solid–liquid equilibrium temperature (T_{SLE}) of 1-monolaurin in methyl laurate for each crystal type.....	33
Fig. 2-5 Solidification temperatures on cooling (T_S) and melting temperatures on heating (T_M) measured by visual observation for mixtures of (a) 1-monopalmitin/methyl oleate and (b) 1-monolaurin/methyl laurate, compared with the calculated T_{SLE} for β' and β structures	35
Fig. 3-1 Cloud points of the binary mixtures of 1-monopalmitin in methyl oleate measured without agitation (CP) and measured under ultrasonic treatment (CP_{US}) with the calculated solid–liquid equilibrium temperatures (T_{SLE}) for α , β' and β forms of 1-monopalmitin	43
Fig. 3-2 Precipitation times for the mixtures of (a) 1.0 wt%, (b) 0.5 wt% and (c) 0.1 wt% 1-monopalmitin in methyl oleate at constant temperatures from 0 to 30 °C in comparison with the T_{SLE} of the α , β' and β forms	44

Fig. 3-3 Changes in the visual appearance and XRD pattern measured in transmission mode of the 1 wt% monopalmitin and methyl oleate mixture as soaked at 20 °C for 14 days	46
Fig. 3-4 Microscopic observations viewed through crossed polars of the precipitates in the liquid fraction obtained by (a) the ordinary CP measurement, (b) the CP measurement under ultrasonic treatment and (c) standing at 20 °C for the mixture of 1 wt% 1-monopalmitin in methyl oleate.....	48
Fig. 3-5 XRD patterns of the precipitates obtained by (a) the ordinary CP measurement, (b) the CP measurement under ultrasonic treatment and (c) standing at 20 °C for the mixture of 1 wt% 1-monopalmitin in methyl oleate. Standard samples of α + sub- α , β' and β crystals of 1-monopalmitin shown for comparison	49
Fig. 4-1 Schematic diagram of the saturated hydrocarbon production process via saturated fatty acids from rapeseed oil	53
Fig. 4-2 (a) GPC and (b) HPLC chromatograms of the obtained saturated fatty acids by hydrolysis/hydrogenation from rapeseed oil at 270 °C/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C	58
Fig. 4-3 HPLC chromatograms of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation (270 °C/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C for 60 min) and the saturated hydrocarbons by decarboxylation (300 °C/ 1 MPa (H_2) with 0.45 g Pd/C for 120 min)	59
Fig. 5-1 Yields of saturated fatty acids from coconut oils by hydrolysis/hydrogenation at 270 °C/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C catalyst. Just for comparison, the data for rapeseed oil are shown.....	71
Fig. 5-2 Yields of saturated hydrocarbons from coconut oil-derived fatty acids by decarboxylation at 300 °C/ 1 MPa (H_2) with 0.45 g of Pd/C catalyst. Just for comparison, the data for rapeseed oil are shown.....	72

List of Tables

Table 1-1 Fatty acid compositions of various plant oils.....	3
Table 1-2 Biodiesel standards in EU, US and Kyoto	8
Table 1-3 Boiling ranges of petroleum products and linear alkane carbon numbers for gasoline, kerosene, diesel and heavy oil	9
Table 1-4 Fuel properties of methyl stearate and <i>n</i> -heptadecane	10
Table 1-5 Hydrocarbon production from fatty acids at various conditions.....	17
Table 2-1 Properties of each pure component used to calculate solid–liquid equilibria.....	29
Table 2-2 Activity coefficients γ_i^L calculated by the modified UNIFAC (Dortmund) model in binary mixtures of FAME and MG at the eutectic point	34
Table 2-3 Chemical compositions of the multi-component mixtures and the measured T_S and T_M by visual observation compared with the calculated T_{SLE} for β' and β structures of MG.....	37
Table 4-1 Fatty acid composition of rapeseed oil, obtained saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation. 55	
Table 4-2 Fuel properties of renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204).....	62
Table 5-1 Fatty acid composition of coconut oil, and obtained yields of saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation	69
Table 5-2 Recovery of hydrocarbons as treated under the same decarboxylation conditions (300 °C/ 1 MPa (H ₂) with Pd/C catalyst for 360 min)	74
Table 5-3 Fuel properties of obtained saturated hydrocarbons as renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204).....	76

Chapter 1

Introduction

1.1 World Energy Problems and Transportation Fuel

Our development and lives are inseparably related to the use of fossil resources. Fossil fuel is essential for energy use in the world, which accounts for 81.1 % of total primary energy supply in 2014 (International Energy Agency 2016). Additionally, about half of oil is consumed as transportation fuel. The global demand of the petroleum products are shown in Fig. 1-1. It shows that diesel demand is high and it is expected to increase steadily in the future (Organization of the Petroleum Exporting Countries 2015).

The mass consumption of fossil fuel has been causing various problems such as depletion of resources, environmental pollution and energy security due to its exhaustibility, exhaust emission and unevenly distribution. Especially, emissions produced from the combustion of fossil fuel are also causing environmental issues such as air pollution, environmental destruction and global warming.

Under these circumstances, remedies for dealing with the problems caused by the use of independent fossil resource are desired. To solve this problem, renewable energies have been introduced around the world. Among renewable energies, biomass energy is expected to play a significant role as a substitute because it can be used with the transportation fuel for existing infrastructure. However, most of the other renewable energies can be replaced in the coming electricity generation. The followings are the other characteristics of biomass. Firstly, biomass resources are produced by photosynthesis. Therefore, they can be sustainably developed in the future. Secondly, biomass resources are carbon-neutral, thus biomass does not contribute to the increase in CO₂ concentration in the atmosphere. Thirdly, biomass has very low sulfur content. Additionally, biomass fuel can be put into existing infrastructure, while other renewable energies such as hydrogen or electronic need reconstruction of infrastructure.

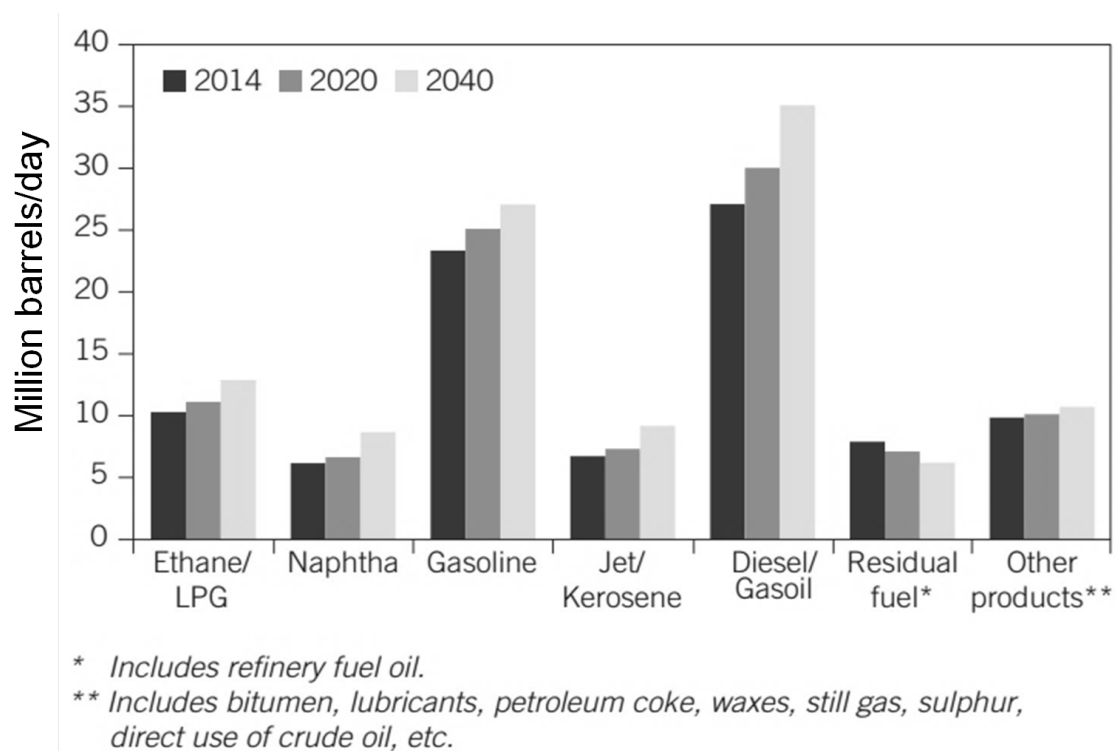


Fig. 1-1 Global demand of petroleum products for 2014, 2020 and 2040 based on Organization of the Petroleum Exporting Countries (2015)

1.2 Alternative Diesel Fuels from Plant Oils

At the Exposition Universelle of 1900 in Paris, a diesel engine was demonstrated using peanut oil as fuel by Rudolf Diesel (Diesel 1912; Knothe 2001)(Knothe 2001; Diesel 1912). Plant oil has been considered as alternative or emergency heat fuels for diesel engines as they have heat contents approximately 90 % of that of No.2 diesel fuel (Schwab et al. 1987). Plant oil is composed of triglycerides which contain one glycerol with three fatty acid chains. The fatty acid composition of plant oils is shown in Table 1-1. The fatty acids in triglyceride mainly contain 16 and 18 carbon atoms such as palmitic (C16:0) and oleic (C18:1) acids; the first and second numbers in parentheses mean the number of carbon atoms and double bonds, respectively. Some plant oils such as palm kernel and coconut oils include shorter chain fatty acid such as lauric (C12:0) and myristic (C14:0) acids. These differences of the composition affect its properties.

Production of plant oil depends on the countries and the climate where they are planted. For example, rapeseed oil is mainly produced in Europe. Soybean oil is largely

produced in United States (IEA 2009). These oils mainly contain oleic acid which is monounsaturated fatty acid. Most Asian countries with tropical climate produce coconut and palm oil. These oils contain many saturated fatty acids such as lauric (C12:0) and palmitic (C16:0) acids.

Table 1-1 Fatty acid compositions of various plant oils (Zambiasi et al. 2007)

Plant oil	Fatty acid							
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	Others
Rapeseed	-	-	3.8	1.9	62.4	20.1	8.4	3.4
Soybean	-	-	9.6	4.4	23.4	52.9	7.6	2.1
Corn	-	-	10.3	2.0	25.5	59.3	1.1	1.8
Cottonseed	-	-	21.9	2.3	16.6	56.4	0.3	2.5
Sunflower	-	-	5.7	4.8	15.3	71.2	0.5	2.5
Olive	-	-	10.8	3.6	75.6	7.0	0.7	2.3
Peanut	-	-	9.4	2.7	48.7	31.1	0.2	7.9
Palm	-	-	42.7	4.6	39.4	10.6	0.2	2.5
Palm kernel	46.1	16.2	8.7	2.3	16.5	2.8	-	7.4
Coconut	45.5	18.8	10.1	4.3	7.5	1.8	-	12.0

Using plant oil as alternative petroleum diesel is a promising way for solving the above-mentioned problems. However, it is difficult to use plant oil directly in a direct-injection type diesel engine due to its high viscosity and poor volatility of triglyceride which causes to carbon deposits in a diesel engine.

To improve its viscosity and volatility, several conversion technologies have been studied. A dilution and microemulsion with fossil diesel are simple ways for reducing its viscosity. Additionally, the way of using plant oil as alternative diesel fuel can be classified as biodiesel and hydrocarbon from plant oil through a conversion. Biodiesel production is the most widespread method to convert plant oil by transesterification. On the other hand, hydrocarbon production as an alternative way to produce diesel fuel from plant oils has been studied, which should remove oxygen atoms in triglyceride. The following sections explain each technology.

1.3 Biodiesel as Alternative Diesel Fuel

Biodiesel is defined as the mono-alkyl esters of long-chain fatty acids derived from renewable biomass feedstocks, such as plant oils and animal fats for use in diesel compression-ignition engines (Krawczyk 1996). In general, biodiesel from plant oil is produced by transesterification with methanol as shown in Fig. 1-2. Biodiesel is a safe fuel with non-toxic, low aromatic content, higher flash point and biodegradability. It also contributes to relieving the issue of exhaust gas for its improved combustibility (Krawczyk 1996; Chandra 1998; Demirbas 2007).

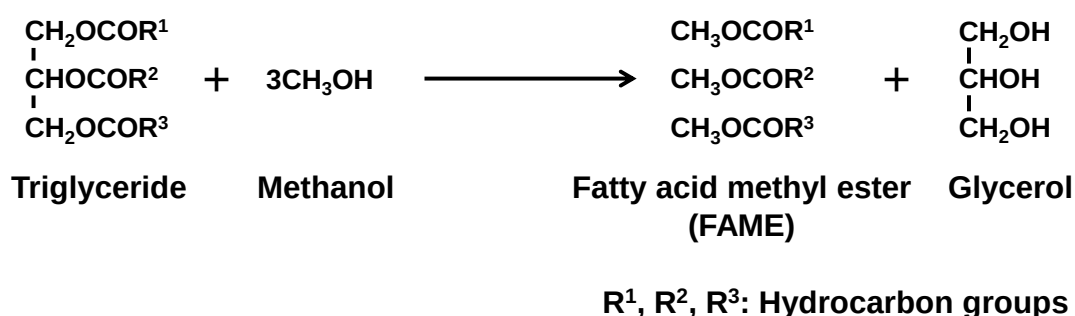


Fig. 1-2 Transesterification of triglyceride with methanol to fatty acid methyl esters

Transesterification of triglyceride proceed through some intermediates such as diglyceride and monoglyceride. Fig. 1-3 shows the proposed pathways for methanolysis of triglyceride (Jin et al. 2007). The paper showed that the intermediate products of triglyceride by transesterification contain 1,3-diglyceride but no 2-monoglycerie. The results indicate that 2-position ester bond in triglycerides and diglycerides can be transesterified easily. Therefore, main intermediate would be 1,3-diglyceride and 1-monoglyceride. Activation energies by Gaussian software also showed that the center ester band in triglycerides is transesterified more easily than the outside ones (Asakuma et al. 2011). Additionally, transesterification of monoglycerides and diglycerides is more difficult than that of triglycerides.

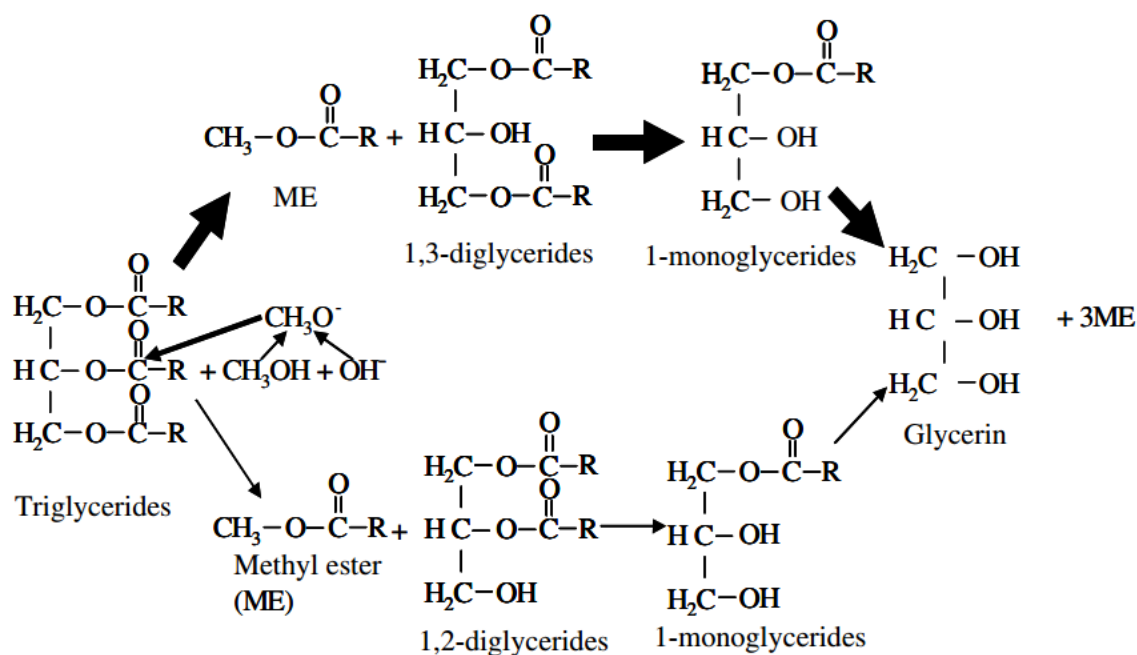


Fig. 1-3 Pathways for methanolysis reaction of triglyceride (Jin et al. 2007)

Though biodiesel production has significantly increased, there are still problems remaining to be solved when it comes to practical use. For example, if high concentration biodiesel is used with existing infrastructures directly, engine troubles such as carbon deposits, swelling of natural rubber and metal collusion tend to occur (MLIT 2009). Additionally, biodiesel has poor oxidation stability and cold-flow properties compared with diesel fuel derived from petroleum fuel (Krawczyk 1996; GCSI 1998; Demirbas 2007; Moser 2009; Yoshimoto & Kinoshita 2009; Bezergianni & Dimitriadis 2013). These defects are in the relationship of trade-off. For example, high concentration of unsaturated fatty acid methyl ester leads to poor oxidation stability, while it shows better cold-flow properties. If the ratio of saturated fatty acid methyl esters is high, cold-flow properties become worse and oxidation stability gets better.

1.3.1 Biodiesel production from plant oils

Biodiesel from plant oil with transesterification can be produced by the following methods: alkali-catalyzed, acid-catalyzed, enzymatic and supercritical methods. The details of each method are described as the followings:

Alkali-catalyzed method is the most major one for biodiesel production. NaOH or KOH is mainly used as a catalyst (Ma & Hanna 1999). Heterogeneous alkali catalysts

such as CaO and MgO are also used to convert plant oil into fatty acid methyl ester (Kouzu et al. 2008). Merits of this method are relatively mild reaction condition and high yield. To obtain maximum yield by transesterification, the feedstock should be free of moisture with a free fatty acid content of less than 0.5 % (Freedman et al. 1984). If raw material includes some free fatty acids, saponification reaction occurs with alkali catalyst. Additionally, a large amount of waste is produced by purification process to remove alkali catalyst.

For acid-catalyzed method, H_2SO_4 is mainly used as a catalyst (Lotero et al. 2005). The free fatty acid contained in the raw material can be converted into esters by esterification. However, the yield of ester can be lowered if the raw material contains water. Moreover, with this method, it takes longer time to achieve high conversion compared with the alkali-catalyzed method.

Enzymatic method uses a resin with the enzyme fixed. This method is conducted under mild conditions without neutralization. Additionally, a small amount of free fatty acids and water does not affect the reaction and high grade glycerol can be obtained as a byproduct (Fukuda et al. 2001). Disadvantages of this method are the relatively higher cost of catalyst and slower reaction rate (Robles-Medina et al. 2009).

Supercritical method is conducted at high temperature and high pressure in supercritical methanol without a catalyst (Saka & Kusdiana 2001). If raw material contains free fatty acid and/or water, the reaction proceeds effectively (Kusdiana & Saka 2001). Additionally, it takes very short time to complete the reaction. However, this method requires equipment that can endure severe condition.

Biodiesel production has been researched and introduced worldwide. However, biodiesel has different chemical structure from that of fossil diesel, which leads to some problems for the existing infrastructures as mentioned above. These problems need to be solved to spread the use of biodiesel.

1.3.2 Current situation of biodiesel

The use of biodiesel has been adopted by many countries such as European Union (EU), United States (US) and Southeast Asia. In Japan, Kyoto City has been producing biodiesel from waste cooking oil as a raw material from 1997. In 2015, 183,000 liters of wasted oil was collected and converted into biodiesel. As of 2016,

100 % biodiesel (B100) was used for 136 garbage trucks, and petroleum diesel mixed with 5 % biodiesel (B5) was used for 103 municipal buses (Kyoto City 2016). In 2015, 30.1 billion liters of biodiesel were produced in the world (Renewable Energy Policy Network for the 21st Century 2016). Biodiesel productions of EU, US and Southeast Asia are 11.5, 4.8 and 4.6 billion liters in 2015, respectively.

These countries have established a biodiesel standard to ensure its quality. Table 1-2 shows the biodiesel standards in EU, US and Japan. Among these properties, kinematic viscosity can be an indicator for reaction rate of methyl ester. High kinematic viscosity shows that transesterification reaction probably does not proceed enough. Water and methanol contents are important factors because they can cause a metal corrosion. Glycerides contents, triglycerides, diglycerides, monoglycerides and free glycerol, are also important. These impurities can form deposits easily. Other fuel properties should be satisfied to prevent various problems such as damages on parts of fuel system, engine trouble and poor exhaust gas.

Table 1-2 Biodiesel standards in EU, US and Kyoto

Fuel property	EU EN 14214	US ASTM D6751	Japan JIS K2390
Density (15 °C, g/ml)	0.86 – 0.90	0.88	0.86 – 0.90
Kinematic viscosity (40 °C, mm ² /s)	3.5 – 5.0	1.9 – 6.0	3.5 – 5.0
Pour point (°C)	-	-	≤ -7.5
Cold filter plugging point(°C)	-20 – 5 ^{*1}	-	≤ -5
10% carbon residue (%)	≤ 0.30	≤ 0.50 ^{*2}	≤ 0.30
Cetane number	≥ 51	≥ 47	≥ 51
Sulfur content (ppm)	≤ 10	≤ 500	≤ 10
Flash point (°C)	≥ 101	≥ 130	≥ 100
Water content (ppm)	≤ 500	≥ 500	≤ 500
Monoglyceride (%)	≤ 0.8	-	≤ 0.8
Diglyceride (%)	≤ 0.2	-	≤ 0.2
Triglyceride (%)	≤ 0.2	-	≤ 0.2
Free glycerol (%)	≤ 0.02	≤ 0.02	≤ 0.02
Total glycerol (%)	≤ 0.25	≤ 0.24	≤ 0.25
Methanol (%)	≤ 0.2	-	≤ 0.2
Alkali metals (Na + K) (mg/kg)	≤ 5	-	≤ 5
Acid value	≤ 0.5	-	≤ 0.5
Iodine value	≤ 120	-	≤ 120

*1: depends on climate

*2: 100% biodiesel

The properties of the produced biodiesel depend on feedstock. Fatty acid methyl esters have more similar properties to fossil diesel than pure plant oil does. When biodiesel contains high amount of unsaturated fatty acids, cold-flow properties show good values but oxidation stability gets worse. Conversely, if it contains much saturated fatty acid, cold-flow properties become worse but oxidation stability is improved. Therefore, these properties are in a trade-off relation. Additionally, the properties have to deal with the production and purification of biodiesel.

Some problems still remain on the use of biodiesel: degradation of elastomers, oxidation production and poor cold-flow properties (Ma & Hanna 1999; Alves et al. 2013; Yaakob et al. 2014). The problem of the occurrence of precipitation is especially hard to deal with, although the cold-flow properties were determined.

1.4 Hydrocarbon as Alternative Diesel Fuel

In order to overcome the drawbacks of the conventional biodiesel, hydrocarbon production for an alternative diesel fuel from plant oil has been studied. Linear alkanes which have carbon numbers from 14 to 20 can be used as alternative diesel fuel as shown in Table 1-3. To convert plant oil into hydrocarbon, it is necessary to remove the oxygen atoms in triglyceride. Several technologies have been studied to remove oxygen atoms. The technologies can be classified into cracking and hydrotreating. These products are known as green diesel or renewable diesel. In this dissertation, the hydrocarbon as an alternative diesel fuel produced from plant oils is called as “renewable diesel”.

Table 1-3 Boiling ranges of petroleum products and linear alkane carbon numbers for gasoline, kerosene, diesel and heavy oil (International Energy Agency 2013)

	Gasoline	Kerosene	Diesel	Heavy oil
Boiling range (°C)	35-215	150-300	180-380	380-540
Linear alkane carbon numbers	5-11	9-16	11-21	22-

Similar to conventional biodiesel, hydrocarbon from plant oil has the same advantages: sustainability, carbon-neutrality and no sulfur content. Moreover, its properties are close to petroleum fuel because both constituent atoms are hydrocarbon. Table 1-4 shows the difference in properties between methyl stearate and *n*-heptadecane, which are typical products as biodiesel and hydrocarbon respectively from stearic acid. Firstly, calorific value of methyl stearate is lower than that of *n*-heptadecane in which oxygen atoms are present in its molecule. Secondly, *n*-heptadecane has a lower melting point than that of methyl stearate. A lower melting point means better cold-flow properties. Moreover, a value of kinetic viscosity of *n*-heptadecane is close to that of

No.2 diesel (1.9-4.1 mm²/s (38 °C) (Maher & Bressler 2007)). Thus, *n*-heptadecane is more favorable as an alternative diesel fuel than methyl stearate.

Table 1-4 Fuel properties of methyl stearate and *n*-heptadecane

	Methyl stearate	<i>n</i> -Heptadecane
Molecular formula	C ₁₉ H ₃₈ O ₂	C ₁₇ H ₃₆
Lower calorific value (kJ/g)	37.80	44.02
Melting point (°C)	39.1	22.0
Boiling point (1atm) (°C)	352	302
Kinetic viscosity (40°C) (mm ² /s)	5.82	3.98

1.4.1 Hydrocarbon production from triglycerides

1.4.1.1 Thermal and catalytic cracking

In the 20th century, pyrolysis of plant oils to produce a fuel has been studied. Pyrolysis can be divided into direct thermal cracking and catalytic cracking (Maher & Bressler 2007). Generally, thermal cracking of plant oils is carried out at 500-800 °C, while catalytic cracking is carried out at 300-500 °C with catalysts. In general, an increase in temperature leads to an increase in selectivity towards light hydrocarbons. This proceeds through the scission of carbon-carbon bonds. Typical pressure of cracking is from atmospheric pressure to several bars

The thermal decomposition of triglyceride generates diverse products because the reaction pathways are estimated to be multiple and complex (Chang & Wan 1947). Therefore, the obtained products include not only hydrocarbon, but also oxygenated compounds such as carboxylic acid and ketone (Lappi & Alén 2011). When soybean oil was thermally decomposed and distilled in air or in nitrogen spurge with standard ASTM distillation apparatus, it was converted into various hydrocarbons with carbon numbers ranging from 4 to more than 20, such as alkanes, alkenes, aromatics and carboxylic acids as shown in Fig. 1-4 (Schwab et al. 1988).

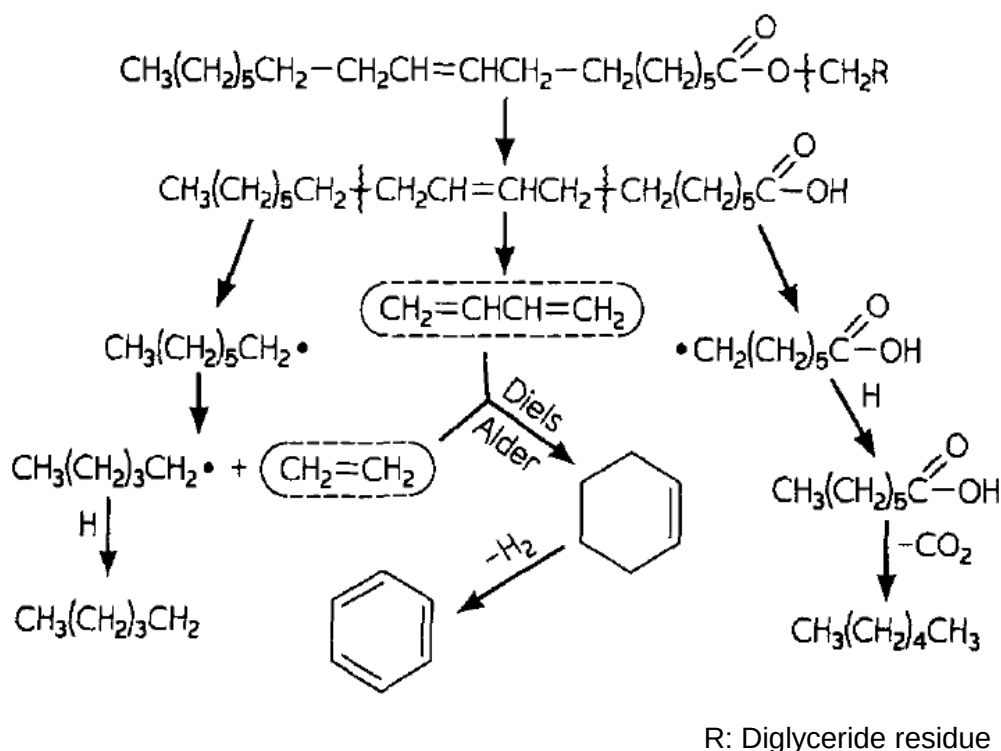


Fig. 1-4 Thermal decomposition pathways of triglyceride (Schwab et al. 1988)

Also, catalytic decomposition mechanism from rapeseed oil to fatty acids using a catalyst for fluid catalytic cracking (FCC) by radical reaction was proposed (Dupain et al. 2007). Even in this case, relatively high amounts of coke and large amounts of aromatics in the gasoline fraction are formed. The rate of aromatization highly depends on the olefins of the fatty acid and the reaction temperature. Lower aromaticity leads to the serial cracking reactions to the lower olefins. The free fatty acids are predominately responsible for the formation of radicals and the oxygen from the fatty acids is evolved predominantly as water (Dupain et al. 2007). The radicals from fatty acids would produce hydrocarbons as mentioned above, but it would also convert them into lighter hydrocarbons or coke on the catalyst surface. Although it has been studied that various catalyst and feedstock were used (Chang & Wan 1947; Rao 1978; Twaiq et al. 1999), catalytic cracking reactions produce more gasoline-type products containing significant amount of aromatic compounds and gaseous products (Satyarthi et al. 2013). Additionally, obtained products still contain a high amount of carboxylic acids (Chang & Wan 1947) and a mass of olefins, which can cause poor oxidation stability (Satyarthi et

al. 2013).

In cracking process, the degree of unsaturation of the triglyceride has a significant effect on the cracking behavior. Decarboxylation and decarbonylation can occur before or after the cleavage of carbon-carbon bond. When the triglyceride is unsaturated, the cleavage occurs probably before the decarboxylation and decarbonylation. With an increase in double bonds of triglyceride molecules, aromatics can be obtained by cyclization reaction.

1.4.1.2 Hydrotreating

Hydrotreating is an established petroleum refining process to remove contaminants such as sulfur, nitrogen, oxygen and metal compounds. Besides, hydrotreating of plant oils was proposed almost two decades ago, using processes and catalysts similar to those used for petroleum refining process (Monnier et al. 1998). To compare with the conventional biodiesel, the product obtained by hydrotreating are generally called as “Renewable Diesel” in Europe, “Hydrogenation Derived Renewable Diesel” in U.S., and “Hydro-generated Biodiesel” in Far East (Neste Corporation 2015).

Compared with catalytic cracking, hydrotreating process requires hydrogen gas to selectively eliminate the oxygen and saturate the double bonds present in plant oils. The final products are mainly linear saturated paraffin (mainly C15 to C18) which can be used as an alternative diesel and kerosene. Propane obtained as byproduct also can be used as fuel. To remove oxygen atoms in plant oil, conventional catalysts in petroleum refining process such as CoMo and NiMo have been used. CoMo and NiMo are supported on solid acid such as SiO₂, Al₂O₃, ZrO₂, TiO₂ and various zeolite, and sulfide bifunctional catalysts are mainly used (Gong et al. 2012; Kubička et al. 2010; Madsen et al. 2011; Krár et al. 2010).

It is generally acknowledged that the triglycerides of hydrotreating are saturated on their side chain first, followed by scission of the C–O bond, leading to the formation of diglycerides, monoglycerides, carboxylic acids and waxes (Satyarthi et al. 2013; Gong et al. 2012). Then, these are transformed into hydrocarbons by hydrotreating. The removal of oxygen is accomplished through hydrodeoxygenation, decarboxylation and decarbonylation (Kubička et al. 2010) as shown in Fig. 1-4. Priority of these pathways is reaction conditions such as temperature, pressure, atmosphere and catalyst. When CO

and H_2O are formed by decarbonylation, they are probably transformed into CO_2 and hydrogen by means of the water gas shift reaction. Catalytic cracking of these compounds into lighter hydrocarbons is favored as pressure increases (Sotelo-Boyás et al. 2010).

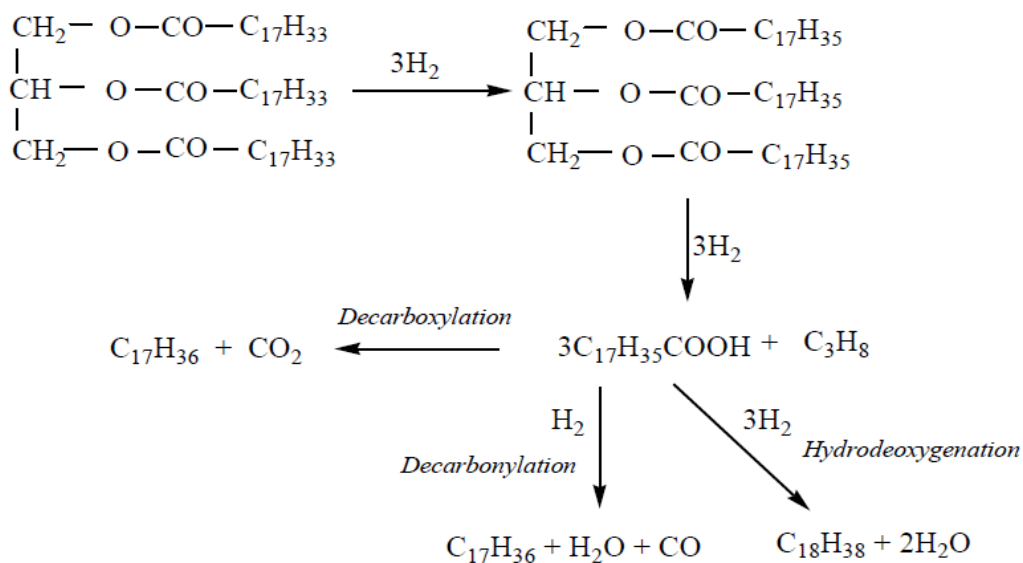


Fig. 1-5 Reaction pathways of triglyceride (triolein) by hydrotreating (Sotelo-Boyás et al. 2012)

Plant oils are mainly converted into saturated or unsaturated linear hydrocarbons with carbon ranging from 15 to 18 such as *n*-heptadecane and *n*-octadecane by hydrotreating (Mikulec et al. 2010). CO , CO_2 , H_2O and propane are obtained as byproducts. Saturated compounds have good cetane value compared with corresponding esters, but cold properties is poor (Monnier et al. 1998; Casanave et al. 2007). Yields of the product and its composition depend on various factors such as temperature, pressure, catalyst and feedstock.

Both temperature and pressure play important roles in the transformation of triglyceride. In general, hydrotreating is carried out at 350-450 °C under 4-15MPa hydrogen atmosphere (Monnier et al. 1998). Reaction temperature of hydrotreating is the most dominant effects on the product yields. The oxygen removal from feedstocks is less at low temperatures, and more at higher temperatures. With the increase in

temperature, a decrease in diesel range product is observed, which is expected that increasing temperature can promote the undesirable hydrocracking reactions competing with the desirable hydrotreating reactions (Satyarthi et al. 2013). An increase in alkanes with an odd number of carbon atoms was also observed as the reaction temperature was raised. As the temperature increases, diesel selectivity gradually drops and gasoline-like products are obtained (Bezergianni et al. 2010). For the purpose of obtaining hydrocarbon appropriate for diesel, high temperature may not be suitable. The low-temperature properties, such as cloud point and pour point, were found to improve with increasing temperature, as expected from the increase in isoalkanes and shorter chain hydrocarbon content. To increase the conversion into hydrocarbons, it was necessary to increase the severity of reaction conditions. However, with an increase in temperature, a high degree of cracking was observed (Sotelo-Boyás et al. 2010).

Hydrogen pressure is also an important factor for hydrotreating reaction. In the case of insufficient hydrogen, side reactions such as cracking, cyclization and aromatization may occur. Stoichiometric hydrogen is needed to saturate the olefins formed by cracking or decarbonylation. Another role of hydrogen is keeping the catalyst activity by inhibiting coke formation. Additionally it helps remove H₂O on the catalyst and prevent deactivation of the catalyst. For example, the yields of hydrocarbons decreased when the amount of water was increased during hydrodeoxygenation of aliphatic esters on sulphided NiMo/ γ -Al₂O₃ (Şenol et al. 2005). Additionally, a higher H₂/oil ratio also favors the hydrodeoxygenation over decarboxylation and decarbonylation because hydrodeoxygenation requires more hydrogen (Donnis et al. 2009).

In hydrotreating of plant oil, sulfide catalysts and noble metal catalysts are mainly used. Sulfide catalysts such as sulfide NiMo and CoMo are widely used for hydrotreating of plant oil for its high activity and scission of ester bonds. However, the sulfur from the sulfide catalyst is removed by hydrogen. Therefore, to keep the catalytic activity in sulfide form, up to 1–2% sulfiding agent is added to the feed (Satyarthi et al. 2013). On the other hand, noble metal catalysts are expensive compared with sulfide catalyst. Despite their high cost, noble metal catalysts possess several advantages. Firstly, they have high reactivity at moderate temperature. Secondly, noble metal does not require sulfur stripping. Finally, it can be flexible catalyst design by tailoring the

active phase and support (Murata et al. 2010; Do et al. 2009). Zeolite type catalysts have also been used for the hydrotreating of plant oil. But microporous molecular sieves and strong acid sites decompose feedstock and tend to obtain gasoline-type fuel (Sotelo-Boyás et al. 2010). Due to the acid function of the catalyst, isomerization and cyclization of the olefin intermediates can occur, leading to the formation of isoparaffins, naphthenes and aromatics. Dehydrogenation is favored at high temperature and low pressure (Kubička & Kaluža 2010). Alumina catalyst promotes hydrodeoxygenation effectively due to its medium acidity, and isoparaffin production is suppressed (Sotelo-Boyás et al. 2010). In contrast to zeolites and alumina supports, mesoporous supports such as mesoporous molecular sieves (MCM-41, SBA-15) or organized mesoporous alumina (OMA) have very high specific surface areas that can be used to achieve very high dispersions of the supported active phase and high loadings of the active phase. These properties such as larger pore diameters as compared with zeolites make mesoporous supports great candidates for applications where large organic molecules like triglycerides have access to the well dispersed active sites located inside the pores.

The research of hydrotreating has shown that the products of alkanes contain same or one fewer number of carbons than the parent fatty acids. Accordingly, the composition of the product from hydrotreating can be roughly estimated based on the fatty acid composition of the feedstock. However, depending on the chain length and the degree of saturation of the feedstock, some differences have been observed in the products. With a decrease in chain length and degree of unsaturation of plant oils, yield of gaseous products increased. Some researchers have reported production of some amount of cycloalkane and aromatics (Gong et al. 2012). Cycloalkane production is also observed with a higher degree of unsaturation and alkane selectivity increases with an increase in the degree of saturation (Knothe 2010). But these products are not generally found in hydrotreating because most of the unsaturated bonds become saturated and do not lead to cyclization or aromatization at process conditions of temperature and pressure. Thus, this process may convert plant oil into high grade diesel. In 2015, 2.5 billion liters of renewable diesel was produced in the world (Renewable Energy Policy Network for the 21st Century 2016).

1.4.2 Hydrocarbon production from fatty acids

Hydrocarbon production from fatty acids has been studied to understand deoxygenation mechanism because triglyceride is converted into hydrocarbon through fatty acid.

Table 1-5 shows the research of hydrocarbon production from fatty acids. For deoxygenation reaction, noble metal catalyst is generally used. The performance of various metals on equivalent supports was compared, and their relative deoxygenation activity was found to be in the order of Pd>Pt>Ni>Rh>Ir>Ru>Os (Snåre et al. 2006). Additionally, the gas phase analysis demonstrated that the decarboxylation reaction was more profound over the Pd/C catalyst, while the decarbonylation reaction was more evident over the Pt/C catalyst (Snåre et al. 2006). Catalysts with carbon supports were attributed to the ability of the support to promote the reaction through its amphoteric properties and surface functionalities and minimize the effect of deactivation induced by coke through its large surface area (Snåre et al. 2006).

Temperature and Pressure are important factors for deoxygenation, and most studies showed that deoxygenation was achieved at 300 °C and approximately 1 MPa. With respect to an atmosphere, when inert gas such as He or Ar is used, main product is decarboxylated hydrocarbon from fatty acid because the decarboxylation reaction does not require additional hydrogen stoichiometrically. However, most studies for decarboxylation have used H₂ gas for keeping a catalyst activity. Figure 1-6 shows decarboxylation mechanism of carboxylic acid (Maier et al. 1982). It describes the cleavage of carbon-carbon bond on catalyst.

Table 1-5 Hydrocarbon production from fatty acids at various conditions

Fatty acid	Catalyst		Reaction condition	Main product	Ref.
	Type	Amount (wt%)			
Oleic acid	5wt% Pd/C	4.3	300°C/1.5MPa(5%H ₂ in Ar)/6h	Stearic acid	Lestari et al. 2009
Linoleic acid	5wt% Pd/C	4.3	300°C/1.5MPa(5%H ₂ in Ar)/6h	Stearic acid	Lestari et al. 2009
Palmitic acid	4wt% Pd/C	39	300°C/1.7MPa(5%H ₂ in Ar)/3h	<i>n</i> -C15	Berenblyum et al. 2011
Stearic acid	4wt% Pd/C	35	300°C/1.7MPa(5%H ₂ in Ar)/3h	<i>n</i> -C17	Berenblyum et al. 2011
	5wt% Pd/Al ₂ O ₃	25	350°C/1.4MPa(H ₂)/3h	<i>n</i> -C17	Snåre et al. 2008
	5wt% Pd/C	22	300°C/1.5MPa(He)/5h	<i>n</i> -C17	Simakova et al. 2011
	Pd-SBA-15	38	300°C/1.7MPa(5%H ₂ in Ar)/5h	<i>n</i> -C17	Lestari et al. 2010
	5wt% Ru/MgO	22	300°C/0.6MPa(He)/6h	C35	Snåre et al. 2006
	5wt% Pd/C	22	300°C/0.6MPa(He)/6h	<i>n</i> -C17	Snåre et al. 2006
	5wt% Pt/C	22	300°C/0.6MPa(He)/6h	<i>n</i> -C17	Snåre et al. 2006
	4wt% Pd/C	38	330°C/1.7MPa(He)/20min	<i>n</i> -C17	Lestari et al. 2008

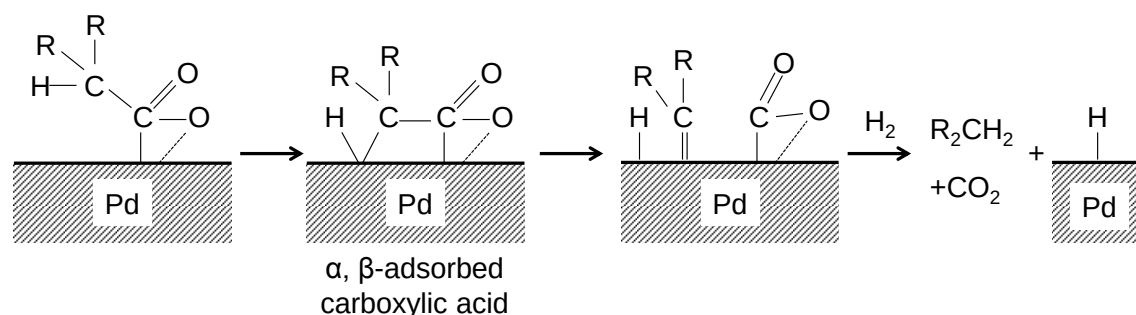
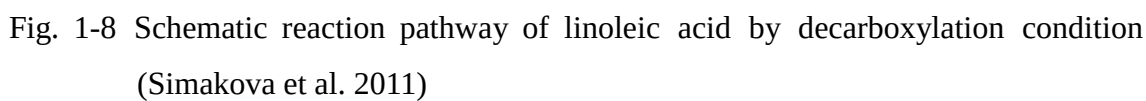
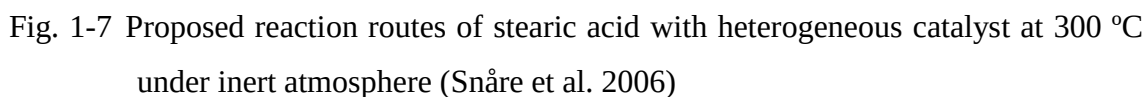


Fig. 1-6 Decarboxylation mechanism of carboxylic acid on surface of Pd catalyst based on Maier et al. (1982)

When stearic acid was used as feedstock under inert atmosphere condition, many reactions may occur, such as hydrogenation, dehydrogenation, cyclization, ketonization, dimerization and cracking as shown in Fig. 1-7 (Snåre et al. 2006). Moreover, when unsaturated fatty acids are used, dimers or trimers may be formed before saturation of double bonds as shown in Fig. 1-8 (Simakova et al. 2011). This high molecular compounds lead to the deactivation of catalyst and the decline of an aimed product yield. One the other hand, when saturated fatty acid was used as feedstock under H_2 condition, hydrocarbon with one fewer carbon number was generally produced. When unsaturated fatty acid was used as feedstock under H_2 condition, stearic acid was produced as shown in Table 1-5. After that, stearic acid would be converted into hydrocarbon by deoxygenation.



1.5 Summative Descriptions of this Dissertation

To use plant oil as alternative diesel fuel, some methods have been studied and applied. Biodiesel is widely used as a diesel substitute and its demand is expected to increase. As another approach, hydrocarbon production from plant oil has been studied as similar product of fossil diesel.

Biodiesel is one of the most applied energy for biomass fuel. However, some issues remain to exist on practical use. Especially, low-temperature properties would be the biggest problem when it comes to practical used. Monoglyceride in biodiesel affects its low-temperature properties. A prediction of the low-temperature properties is important to elucidate a behavior of biodiesel in under the condition of low temperature. Therefore, the prediction of low-temperature properties for biodiesel based on thermodynamic solid-liquid equilibrium equation was performed in Chapter 2.

Because monoglyceride has polymorphism, its low-temperature behavior is more complicated than pure FAME. In Chapter 3, the problem focused on the polymorphism of biodiesel was discussed.

Besides, hydrocarbon production as an alternative diesel fuel has been studied for more suitable fuel in an existing infrastructure. In Chapter 4, a new method for hydrocarbon production from rapeseed oil was proposed and discussed. Additionally, the fuel properties of the obtained product were discussed.

As to the composition of plant oils, fatty acids in typical plant oil, such as rapeseed oil, mainly consist of 16 and 18 carbon numbers. However, some plant oils such as palm kernel and coconut oils have fewer carbon atoms as mentioned above. This difference may affect the reaction condition and properties of final products. Therefore, hydrocarbon production from coconut oil as a feedstock was studied in Chapter 5.

Finally, the concluding remarks about an alternative diesel fuel were mentioned in Chapter 6.

Chapter 2

The Prediction of Low-Temperature Properties for Biodiesel Model Fuel by Solid-Liquid Equilibrium Equation

2.1 Introduction

Fatty acid methyl esters (FAMES) produced from plant oils are the main constituent of biodiesel, which is widely used as an alternative to petroleum diesel. FAMES are generally produced by transesterification of triglycerides, which are the main component of plant oils. Although biodiesel is attractive because it is a renewable energy source, it has some drawbacks owing to the differences in chemical structure from petroleum-derived diesel. Unsaturated double bonds in FAMES are prone to oxidation, leading to poor stability in oxidizing conditions. Moreover, saturated FAMES such as methyl palmitate and methyl stearate have relatively high melting points and often solidify at low temperatures.

The use of biodiesel in high-level blends has been promoted in recent years, especially in Southeast Asian countries (Chanthawong & Dhakal 2015). Indonesia started to use 20% biodiesel blended with petroleum diesel (B20) in 2016. The Indonesian government also plans to implement a B30 policy in 2020 (Kharina et al. 2016). However, there is a concern that the above-mentioned drawbacks may become problematic in such high-level blends. Dunn and Bagby (1995) have reported that a high concentration of biodiesel in blends causes deterioration of the cold-flow property of the fuel. This leads to clogging of fuel filters, and thus engine stalling may occur. Predicting the cold-flow property of a biodiesel blend is of great importance to minimize the risk of fuel clogging.

Cloud point (CP) is an indicator of the cold-flow property of a fluid, defined in ISO 3015 (International Organization for Standardization 1992) as the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under specified conditions. Simple linear regression analyses have been undertaken for the CP prediction of biodiesels and the models obtained had relatively good correlation with

experimental results (Sarin et al. 2009; Su et al. 2011; Dunn & Bagby 2015). However, these models are not applicable to all biodiesels because they were established using only a few feedstocks. The prediction of CPs based on the solid–liquid equilibrium of FAME mixtures was established in a previous study (Imahara et al. 2006). The theoretical and experimental values were consistently in a good agreement each other, even with the assumption of simple ideal solution. This finding has been supported by some other groups (Lopes et al. 2008; Coutinho et al. 2010), and this thermodynamic approach has proven to work well for CP prediction.

These predictions were only used for high-purity biodiesel composed of only FAMES. A small amount of monoglycerides (MGs) and diglycerides (DGs) are included as intermediate compounds as well as unreacted triglycerides in actual biodiesel. MG has a higher melting point than the corresponding methyl ester and solidifies easily at low temperatures. Tang et al. have reported that the insoluble precipitate from palm oil-based biodiesel consisted mainly of MGs (Tang et al. 2008) and Chupka et al. found that the amount of saturated MGs highly affected the CP of biodiesel blend (Chupka et al. 2014). MGs have several polymorphic crystalline forms referred to as α , β' and β , and each has different melting point ($\alpha < \beta' < \beta$) (Lutton & Jackson 1948). The potential for several MG polymorphs makes the cold-flow property of biodiesel complicated. Chupka et al. have applied the ideal solution model for the calculation of solid–liquid equilibrium to predict the CP of biodiesel containing MGs but found a large deviation between the experimental and predicted values (Chupka, McCormick, et al. 2011). This implies that a mixture of MGs and FAMES behaves as a non-ideal solution unlike a mixture of only FAMES.

This study attempts to elucidate the solid–liquid equilibrium for mixtures of MGs and FAMES, taking non-ideality into consideration.

2.2 Materials and Methods

2.2.1 Materials

In typical plant oils, palmitic (C16:0), oleic (C18:1) and linoleic (C18:2) acids are the major fatty acid moieties. The MGs of palmitic acid are probably an important cause of precipitation because they are saturated MGs and have higher melting points than unsaturated MGs, especially in the case of palm oil. We chose a binary mixture of

1-monopalmitin and methyl oleate as a model for biodiesel from typical plant oils. Coconut and palm kernel oils are different from most plant oil because they are composed of shorter fatty acids including lauric acid (C12:0). A binary mixture of 1-monolaurin and methyl laurate was also studied as a model for fuel from coconut and palm kernel oils. Finally, some multi-component mixtures of MGs and FAMEs were also evaluated.

1-Monolaurin (C12:0 MG, >98%) and 1-monopalmitin (C16:0 MG, >95%) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, while 1-monoolein (C18:1 MG, >99%), methyl laurate (C12:0 FAME, 99.5%), methyl palmitate (C16:0 FAME, >99%), methyl oleate (C18:1 FAME, >99%), and methyl linoleate (C18:2 FAME, >99%) were obtained from Sigma-Aldrich Japan Co., LLC., Tokyo, Japan. All chemicals were used without purification.

2.2.2 Experimental methods and definitions

Differential scanning calorimetry (DSC) was performed using a DSC-50 system (Shimadzu Corp.) to evaluate the solid–liquid equilibrium of samples in non-hermetic aluminum-based pans under dry nitrogen flow. Indium and zinc were used to calibrate temperature and heat capacity. Heating and cooling rates were set to 10 and -3 °C/min, respectively. Each sample was heated until fully melted for each measurement and then cooled until the first phase transition was observed from liquid to solid. The sample was then reheated until the solid phase melted and the temperature of the endothermic peak top was defined as the solid–liquid equilibrium temperature (T_{SLE}) (Matsuoka & Ozawa 1989). The reason that the T_{SLE} was measured on the heating cycle was to remove the effect of overcooling. Therefore, the measured T_{SLE} will be slightly higher than the CP, because CP occurs during the cooling cycle and often includes an overcooling effect. The melting point and enthalpy of fusion were also estimated for each pure component based on the onset temperature of the endothermic peak (Matsuoka & Ozawa 1989), and the values obtained were used to calculate the solid–liquid equilibrium.

Visual observation was conducted using a glass cell apparatus developed by Matsuda et al. (2011) as shown in Fig. 2-1 when the concentration of MG was less than 2 wt% because the endothermic peak was too small to detect at such low concentrations on DSC. Approximately 10 mL of the melted sample was placed in the sample cell

(inner diameter, 20 mm; height, 150 mm) for each observation and cooled with agitation until solid substance formed. The temperature at which solids formed was defined as the solidification temperature on cooling (T_S). The sample was then heated maintaining agitation, and the temperature at which the solid substance completely melted was defined as the melting temperature on heating (T_M). The heating and cooling rates were approximately 1 and -1 °C/min, respectively.

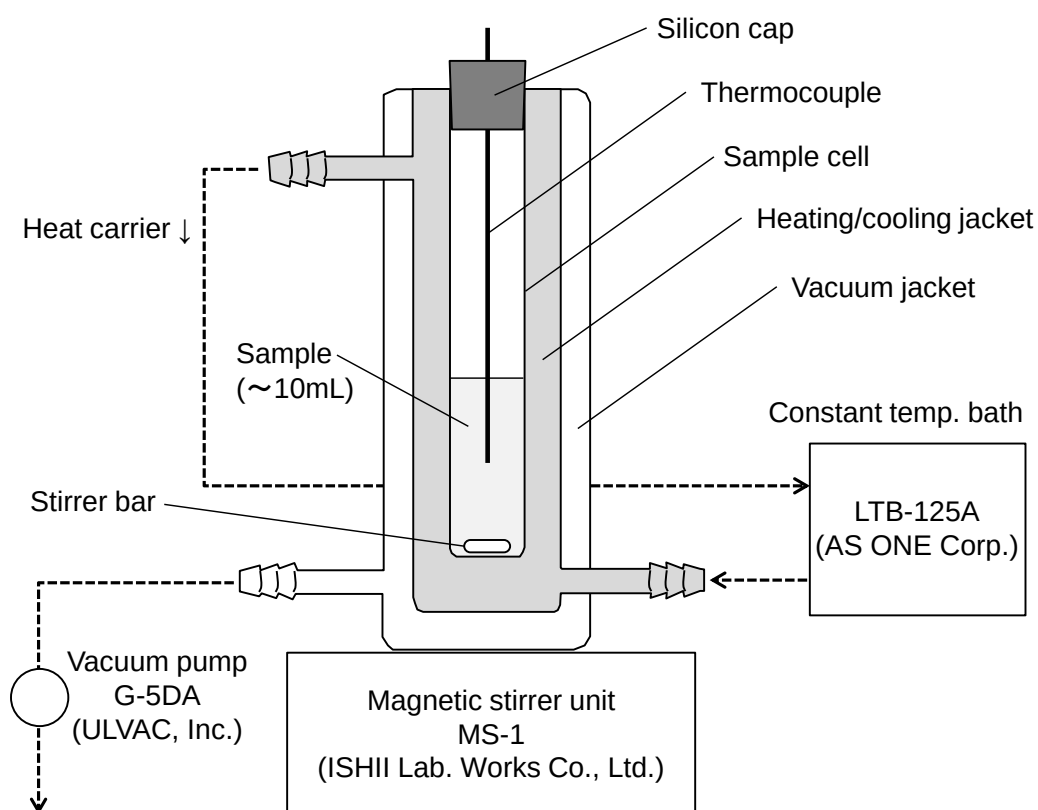


Fig. 2-1 Schematic diagram of the visual observation equipment used to estimate the solid–liquid equilibrium (Matsuda et al. 2011)

2.2.3 Thermodynamic model

The solid–liquid equilibrium can be thermodynamically expressed as the equality of fugacities in solid and liquid phases (f_i^{L*} and f_i^{S*} , respectively) for each component i by the following equation:

$$f_i^{L*} = f_i^{S*}, \text{ thus } \gamma_i^L x_i f_i^L = \gamma_i^S z_i f_i^S \quad (2-1)$$

where γ_i^L and γ_i^S are activity coefficients of component i , and f_i^L and f_i^S are fugacities of pure component i in liquid and solid phases, respectively. The x_i and z_i terms are mole fractions of component i in liquid and solid phases, respectively. Furthermore, the fugacity ratio of a pure component in solid and liquid phases can be described as the followings (Smith J.M. et al. 2005):

$$\frac{f_i^L}{f_i^S} = \exp \left[\left(\frac{T_{SLE} - T_{m,i}}{RT_{SLE}} \right) \left(\frac{\Delta H_{m,i}}{T_{m,i}} \right) \right] = \frac{\gamma_i^L x_i}{\gamma_i^S z_i} \quad (2-2)$$

where $\Delta H_{m,i}$ and $T_{m,i}$ are enthalpy of fusion and the melting point of each component i , respectively. It should be noted that the term of heat capacity can be omitted in this equation because it is usually small enough to be non-consequential (Smith J.M. et al. 2005).

It was assumed that the solid phase that formed at T_{SLE} is composed of only a single-component and both z_i and γ_i^S are equal to unity. This assumption is not always true but in the case of a binary mixture of MG and FAME, it is plausible because their chemical structures are clearly different and may not form a mixed crystal.

To estimate the γ_i^L , many methods have been established based on thermodynamics since Margules' equation was developed (Margules 1895). Solution of Groups model for activity coefficients was introduced (Wilson & Deal 1962). Further, non-random two liquid (NRTL) (Renon & Prausnitz 1968) and universal quasi-chemical (UNIQUAC) (Abrams & Prausnitz 1975) models were developed based on the concept of local composition. These models can estimate the γ_i^L of multicomponent mixtures by using parameters of the binary pure components. However,

it also means that more experimental data was required with the increase of numbers of components.

A group contribution method is widely used as a predictive technique for the estimation of γ_i^L . The method can calculate the γ_i^L based on chemical group of each component without experimental parameters. According to the group contribution method, the γ_i^L can be described as the following equation:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2-3)$$

where γ_i^C is a combinatorial component and γ_i^R is a residual component. The γ_i^C expresses molecular size and shape difference. The γ_i^R expresses a contribution of molecular interaction as the following equation:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (2-4)$$

where $v_k^{(i)}$ is the number of groups of k in molecule i , Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual coefficient of group k . By differences in expression of γ_i^C and Γ_k , some models were proposed such as the analytical solution of groups model (ASOG) (Derr & Deal 1969), universal quasi-chemical functional-group activity coefficients (UNIFAC) (Fredenslund et al. 1975) and modified UNIFAC (Larsen et al. 1987; Weidlich & Gmehling 1987; Gmehling et al. 1998) as group contribution method. Among these modified models, the modified UNIFAC model (Dortmund) has a modified combinatorial part from original UNIFAC (Weidlich & Gmehling 1987).

$$\ln \gamma_i^C = 1 - V'_i + \ln V'_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right) \quad (2-5)$$

where V_i is a volume per mole fraction ratio, V'_i is a modified volume per mole fraction ratio and F_i is a surface area per mole fraction ratio. In case of the original

UNIFAC, each V'_i is V_i . These parameters can be calculated by using the relative van der Waals volumes (r_i) and van der Waals surface areas (q_i) of the molecules as the following equations:

$$V_i = \frac{r_i}{\sum_j x_j r_j} \quad (2-6)$$

$$V'_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \quad (2-7)$$

$$F_i = \frac{q_i}{\sum_j x_j q_j} \quad (2-8)$$

$$r_i = \sum v_k^{(i)} R_k \quad (2-9)$$

$$q_i = \sum v_k^{(i)} Q_k \quad (2-10)$$

On the other hand, the Γ_k is described as UNIQUAC equation as the following equations:

$$\ln \Gamma_k = Q_k \left(1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right) \quad (2-11)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (2-12)$$

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \quad (2-13)$$

$$\Psi_{nm} = \exp \left(- \frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T} \right) \quad (2-14)$$

where θ_m is the surface area fractions, X_m is the mole fractions of group m and Ψ_{nm} is the group interaction parameters between the groups n and m .

In this study, modified UNIFAC (Dortmund) was adopted because it can be applied to a wide range of temperatures compared with other models. The calculation

for estimating γ_i^L was conducted using a program coded with Microsoft Visual Basic for Applications 7.0 in Excel 2010.

2.3 Results and Discussion

2.3.1 Properties of pure component

Table 2-1 shows the melting point and enthalpy of each pure component measured by DSC, along with the numbers of functional groups of each compound. The properties of the MGs were estimated considering their polymorphic behavior. Generally α type crystals form first when a pure MG is cooled until the phase transition occurs from liquid to solid. The α crystals convert irreversibly to the β' structure and then to the most stable β form after a certain transition time (Maruyama et al. 1973). The transition times tend to be faster for MGs with shorter chains and more degrees of unsaturation (Maruyama et al. 1971). High temperature and presence of the solvent also shorten the transition times (Maruyama et al. 1971). For these reasons, the melting point and enthalpy of α type MGs were measured by heating the sample immediately after the solid phase had formed. The properties of the β' and β type crystals were measured after a certain transition time has passed. The transition times were extremely fast for 1-monolaurin and 1-monoolein and the α type structures quickly converted into the β form. Therefore, it was difficult to measure the enthalpy of fusion for the β' type of these compounds.

Table 2-1 Properties of each pure component used to calculate solid–liquid equilibria

Component	Crystal type	Melting point (°C)	Enthalpy of fusion (J/mol)	Number of functional groups						
				CH ₃	CH ₂	CH	CH=CH	OH(p)	OH(s)	CH ₂ COO
FAME										
Methyl laurate (C12:0)		4.5	36,400	2	9	0	0	0	0	1
Methyl palmitate (C16:0)		29.8	60,400	2	13	0	0	0	0	1
Methyl oleate (C18:1)		-20.7	41,600	2	13	0	1	0	0	1
Methyl linoleate (C18:2)		-42.4	36,200	2	11	0	2	0	0	1
MG										
1-monolaurin (C12:0)	α	44.8	22,400	1	11	1	0	1	1	1
	β'	59.5	-							
	β	62.3	38,000							
1-monopalmitin (C16:0)	α	66.4	34,100	1	15	1	0	1	1	1
	β'	72.7	49,900							
	β	75.7	63,600							
1-monoolein (C18:1)	α	15.0*	11,000*	1	15	1	1	1	1	1
	β'	30.1	-							
	β	35.0	49,400							

* : From reference (Maruyama et al. 1979b)

- : Not measureable because of fast transition

There are many publications reporting the thermodynamic properties of various FAMES and MGs, such as melting point and enthalpy (Lutton 1971; Knothe & Dunn 2009; Dunn 2008; Maruyama et al. 1979). The values measured in this study were consistent with those previously reported, and the values obtained were applied for the calculation of solid–liquid equilibriums. However, the enthalpies of β' type monolaurin and monoolein have not been reported, probably because of the difficulty of measuring this transition.

2.3.2 Binary mixture

Fig. 2-2 shows the DSC curves for the binary mixture of 30 wt% 1-monopalmitin and 70 wt% methyl oleate. An exothermic peak was observed at 46.6 °C on cooling the liquid sample (a), which is related with the formation of α type monopalmitin. Immediately exposing the sample to heating after the α type crystals formed resulted in an endothermic peak at 51.5 °C (b), which can be assigned to the T_{SLE} of the α type monopalmitin. When the sample was heated 6 hours (c) or 11 days (d) after the α type crystals formed the endothermic peaks shift to higher temperatures at 59.5 °C and 66.4 °C, respectively, which are the T_{SLE} values of the β' and β type crystals, respectively.

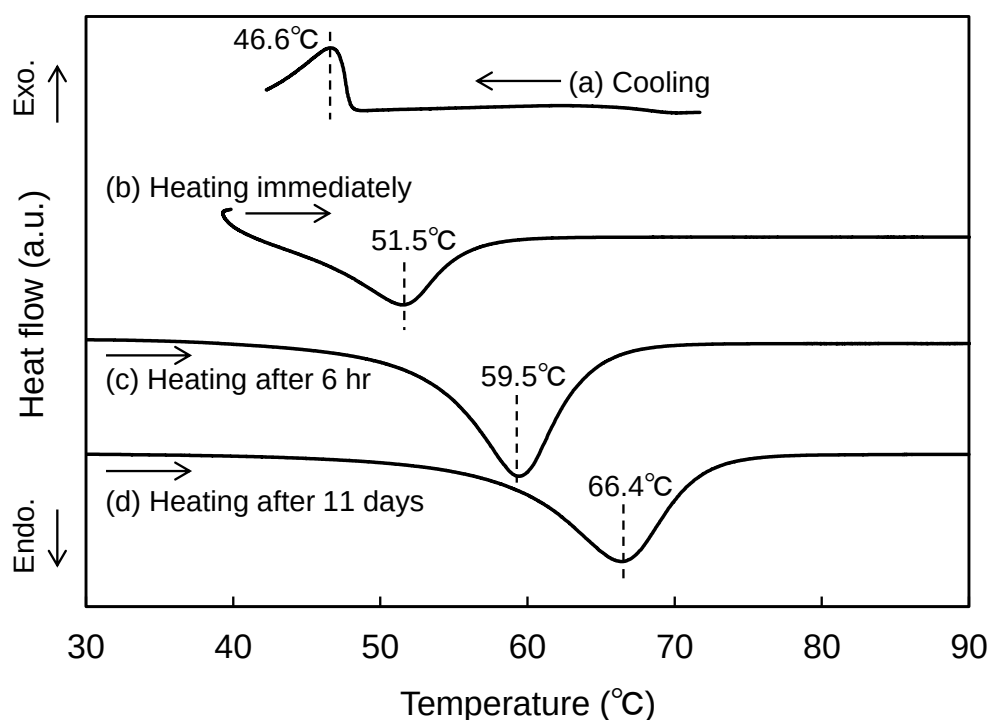


Fig. 2-2 DSC curves for the mixture of 30 wt% 1-monopalmitin and 70 wt% methyl oleate

The binary mixture of 1-monopalmitin and methyl oleate was studied in the same way at various concentrations and each T_{SLE} of the crystalline types are shown in Fig. 2-3. As already reported (Chupka, McCormick, et al. 2011), the ideal solution model ($\gamma_i^L = 1$) (shown as a dashed line) has a large deviation from the experimental results (shown as filled circles) for every crystalline form. However, the UNIFAC (Dortmund) model (shown as a solid line) provides excellent agreement with the experimental values. Similar analyses for a binary mixture of 1-monolaurin and methyl laurate are shown in Fig. 2-4. Although there is a small deviation for the α type structure, it is obvious that the UNIFAC (Dortmund) model fits well with the experimental results. The T_{SLE} of β' monolaurin was not measureable because of the aforementioned reason.

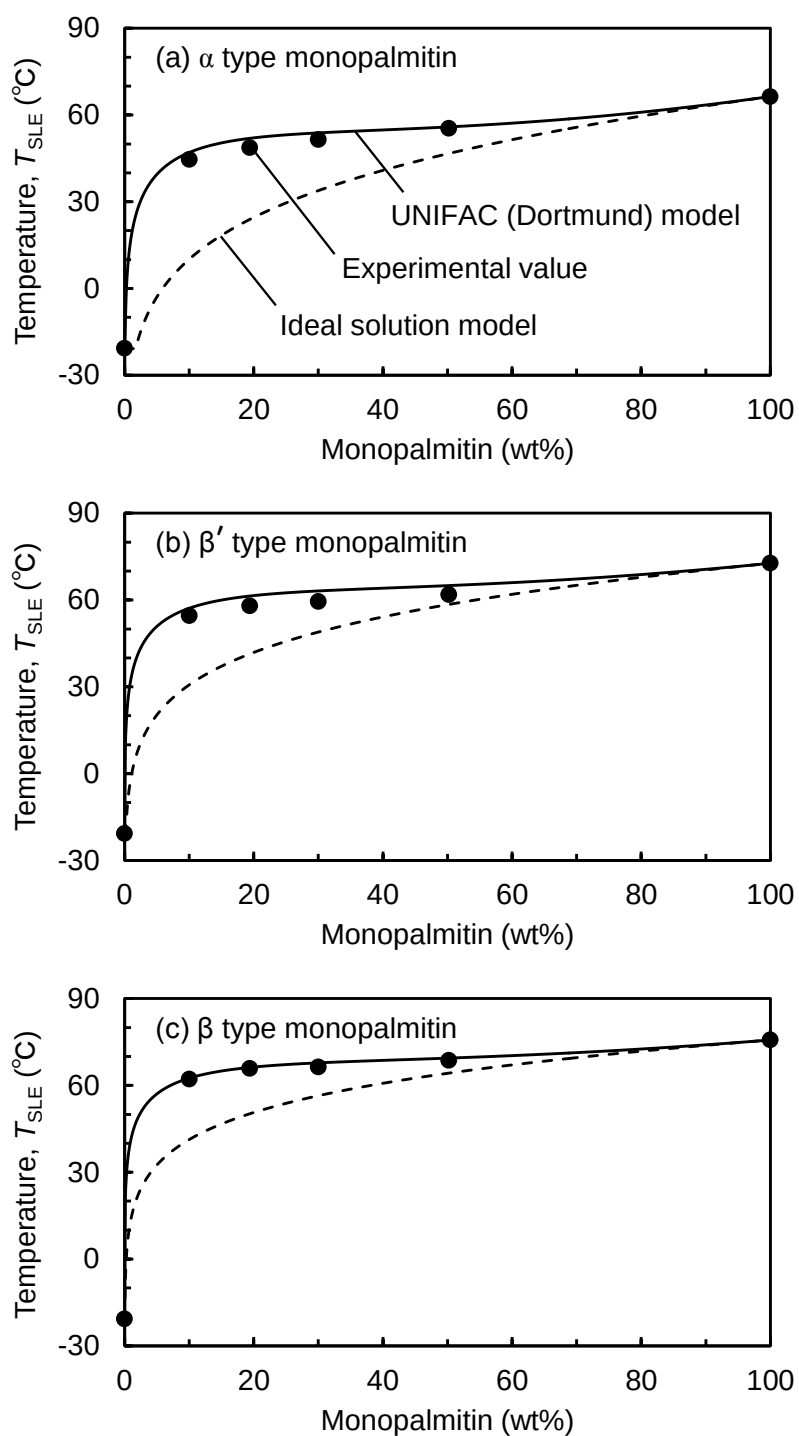


Fig. 2-3 Changes in the solid–liquid equilibrium temperature (T_{SLE}) of 1-monopalmitin in methyl oleate for each crystal type

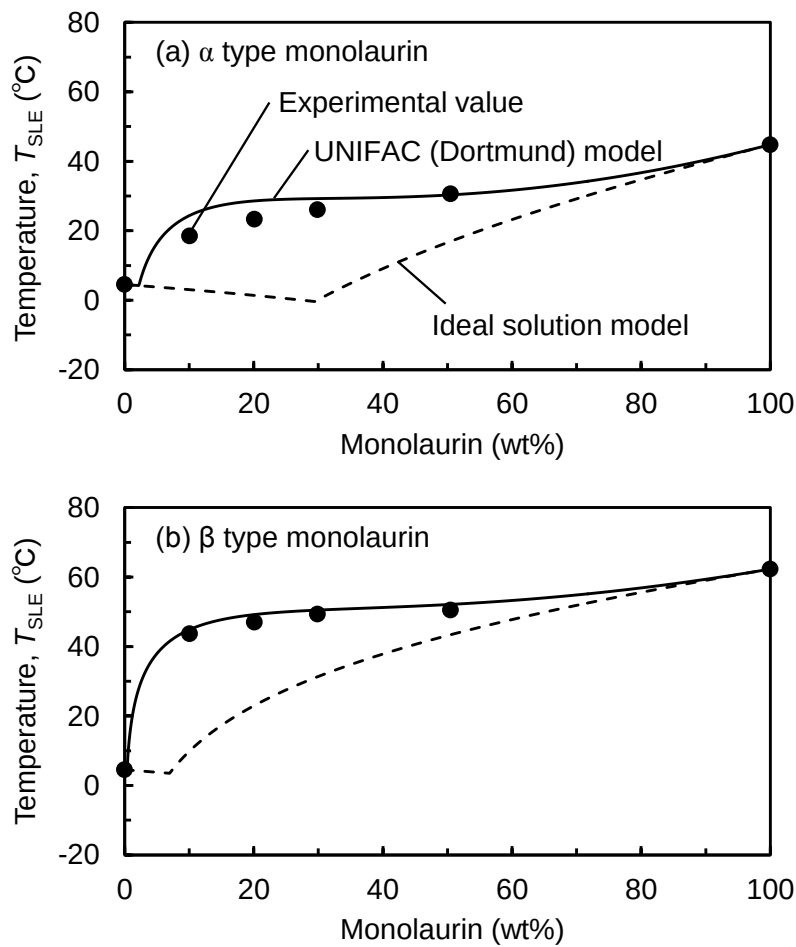


Fig. 2-4 Changes in the solid–liquid equilibrium temperature (T_{SLE}) of 1-monolaurin in methyl laurate for each crystal type

These results show that the modified UNIFAC (Dortmund) model accounts for the non-ideality in MG and FAME mixtures, and the solid–liquid equilibrium is well predicted for the different types of FAMES, MGs and their crystalline structures. The γ_i^L at the eutectic point for various binary mixtures were calculated to discuss the degree of non-ideality (Table 2-2). Activity coefficients were estimated to be almost unity by the UNIFAC (Dortmund) model for binary mixtures of only FAMES. This is why CPs were successfully predicted for mixtures of only FAMES in the previous study (Imahara et al. 2006), even assuming an ideal solution ($\gamma_i^L = 1$). MG in FAME has a large activity coefficient; for example, $\gamma_i^L=59$ for 1-monolaurin in methyl linoleate. This means that MG in FAME shows remarkable non-ideality, and solids form easily, even if the concentration is quite low.

Table 2-2 Activity coefficients γ_i^L calculated by the modified UNIFAC (Dortmund) model in binary mixtures of FAME and MG at the eutectic point

Solute	Solvent	Eutectic point		γ_i^L of solute
		Fraction (wt% of solute)	Temperature (°C)	
Methyl palmitate	Methyl laurate	11.65	2.8	1.009
	Methyl oleate	0.75	-20.7	1.001
	Methyl linoleate	0.06	-41.7	1.008
1-monolaurin (α)	Methyl laurate	2.22	4.3	16.679
	Methyl oleate	0.22	-20.7	46.870
	Methyl linoleate	0.07	-42.4	59.000
1-monopalmitin (α)	Methyl laurate	0.83	4.5	12.643
	Methyl oleate	0.06	-20.7	31.099
	Methyl linoleate	0.01	-42.4	39.235

Visual observation was conducted for the sample containing less than 2 wt% of MG (Fig. 2-5). For monopalmitin in methyl oleate (a), the sample was cooled with agitation and the solidification temperature (T_S) was measured (indicated by open circles). The sample was then heated and the melting temperature (T_M) of the solid phase was also estimated (filled circles). The measured T_S and T_M correspond completely with the T_{SLE} values calculated by the UNIFAC (Dortmund) model for the β' and β type structures, respectively. Similar behaviors were observed for monolaurin in methyl laurate (b). It should be noted that the T_{SLE} values of β' monolaurin (dashed line) was calculated assuming a tentative value of 27,000 J/mol as the enthalpy of fusion because it was not measurable by DSC.

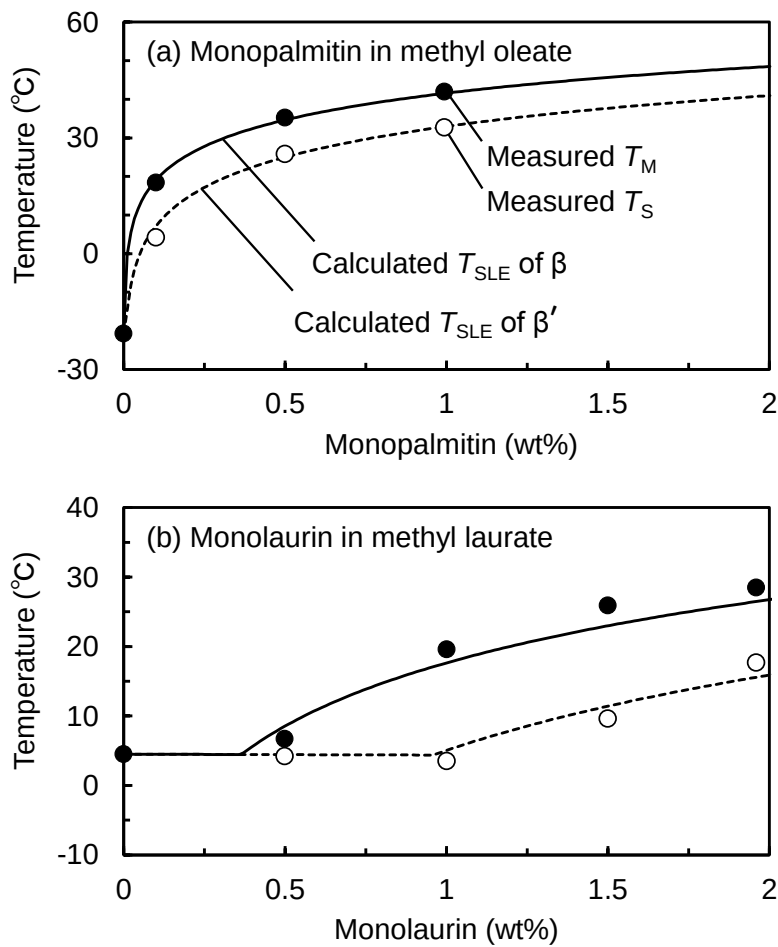


Fig. 2-5 Solidification temperatures on cooling (T_S , *open circles*) and melting temperatures on heating (T_M , *filled circles*) measured by visual observation for mixtures of (a) 1-monopalmitin/methyl oleate and (b) 1-monolaurin/methyl laurate, compared with the calculated T_{SLE} for β' (*dashed line*) and β (*solid line*) structures

The reason MG solidifies at the T_{SLE} of β' during the visual observation can probably be explained as follows: the MG is not overcooled under agitation with a slow cooling rate, so solidification occurs immediately when the temperature reaches the T_{SLE} of β' . Once the solid phase formed, it did not melt until the temperature exceeded the T_{SLE} of β , even if the sample was immediately exposed to a heating cycle. It seems like that the β' structure of MG was quickly converted into β under the given conditions. Although the reason for these behaviors remain unclear, it is possible that the β' form is partly dissolved in FAME on the heating cycle but immediately solidified as the β form,

and this process is repeated until the transition is finished. This mechanism is generally known as Ostwald's law for the transition of polymorphs in a solvent (Ostwald 1897). However, further study is needed to explore the behaviors of MG in FAME.

2.3.3 Multi-component mixture

This study was extended to multi-component mixtures prepared by blending various MGs and FAMEs. The T_S and T_M were measured by visual observation (Table 3). The measured T_S and T_M values are close to the calculated T_{SLE} values of the β' and β structures of the MGs, respectively. Hence, similar phenomena seem to occur in these multi-component mixtures as those in the binary mixtures (Fig. 2-5). Samples 1 to 5 — which contain two kinds of MGs — had slight deviations between the measured and calculated values, whereas samples 6 and 7 — which contain only one MG — were almost consistent with the calculated values.

Table 2-3 Chemical compositions of the multi-component mixtures and the measured T_S and T_M by visual observation compared with the calculated T_{SLE} for β' and β structures of MG

Sample No.	Composition of the mixture (wt%)							Measured (°C)		Calculated T_{SLE} (°C)	
	Fatty acid methyl esters				1-Monoglycerides			T_S	T_M	β'	β
	Laurate (C12:0)	Palmitate (C16:0)	Oleate (C18:1)	Linoleate (C18:2)	Laurin (C12:0)	Palmitin (C16:0)	Olein (C18:1)				
1	49.52	-	49.48	-	0.50	0.50	-	15.6	26.0	19.4	30.2
2	-	9.45	19.93	70.09	0.10	0.43	-	5.3	16.0	5.1	17.3
3	-	13.95	75.04	9.96	-	0.21	0.84	9.8	22.2	13.8	25.0
4	-	40.64	49.43	8.90	-	0.50	0.53	16.6	32.2	23.8	33.7
5	-	65.17	23.95	9.88	-	0.71	0.29	11.0	20.6	12.1	23.7
6	49.49	49.51	-	-	-	1.00	-	28.3	37.0	28.4	37.7
7	-	13.96	75.52	10.31	-	0.21	-	15.0	25.4	14.9	25.9

The solid phase was assumed to be formed as a single component (i.e., $z_i\gamma_i^S = 1$) for the calculation of the solid–liquid equilibrium. This assumption is probably appropriate when the mixture contains only one MG. However, in cases including two or more MGs, the MGs could cocrystallize (i.e., $z_i\gamma_i^S \neq 1$). Maruyama et al. have reported a mixed crystal (solid solution) composed of different MGs (Maruyama et al. 1979). Further studies on the effect of solid solutions of MGs are needed to allow precise prediction of the solid–liquid equilibrium of complex mixtures.

2.4 Conclusions

A series of model mixtures of MGs and FAMEs were studied to aid the prediction of cold-flow property of biodiesel. Although remarkable non-ideality was found between MG and FAME, it was determined that the modified UNIFAC (Dortmund) model can successfully predict the non-ideality. Binary mixture of MG and FAME showed good agreement between the theoretical values and measured equilibrium temperatures. This study was further extended to multi-component mixtures, and the theoretical and experimental values were also consistent. However, mixtures with two kinds of MGs deviated from the model to some extent, which might be caused by the effect of solid solution MGs.

Chapter 3

The Effect of Biodiesel Fuel on Its Low-Temperature Properties by Monoglyceride Polymorphism

3.1 Introduction

Fatty acid methyl esters (FAMES) are produced from plant oils and are the main component of biodiesel, which is widely used as an alternative to petroleum diesel with minor or no engine modification required. FAMES are a renewable and carbon neutral fuel that does not increase net CO₂ release to the atmosphere, and these advantages may mitigate environmental problems such as exhaustion of fossil resources and global warming.

Specification standards for biodiesel have been established in many countries with the spread of biodiesel use to ensure quality. Nevertheless, some problems occur in practical use of biodiesel owing to a corrosion of rubbers (Haseeb et al. 2011), poor oxidation stability (Moser 2009) and poor cold-flow properties (Dunn & Bagby 1995)(Lopes et al. 2008). Poor cold-flow properties especially restrict the use of biodiesel in cold climates and during the winter season.

There are three kinds of cold-flow properties for liquid fuels: cloud point (CP), cold filter plugging point (CFPP), and pour point (PP). The CP refers to the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled (International Organization for Standardization 1992). The crystals grow and clog fuel filters when the fuel is cooled further, and the temperature at which this occurs is defined as the CFPP. Finally, the fuel completely solidifies and loses fluidity at the PP. The CP is a useful indicator for the formation of precipitates generally because it has the highest value among these properties. However, precipitates are often found at a temperature higher than the CP, and the precipitates consist mainly of monoglycerides (MGs) (Tang et al. 2008), which are intermediate compounds from the transesterification reaction used to produce biodiesel that slightly contaminate the fuel.

MGs precipitate easily because they have higher melting points than the corresponding methyl esters. MGs have several polymorphic crystalline forms referred to as sub- α , α , β' and β . Each form has a different melting point ($\text{sub-}\alpha < \alpha < \beta' < \beta$) (Lutton & Jackson 1948; Lutton 1950; Chapman 1962), and the polymorphs of MGs make the cold-flow properties of biodiesel complicated. A pure liquid MG crystallizes first as the α or sub- α form when cooled, and these

forms can interconvert reversibly (Maruyama et al. 1973). The α and sub- α forms are metastable and irreversibly convert to the β' form. The β' form finally changes to the most stable β structure after a certain transition time. However, the behavior of MG polymorphs in FAMES remains unclear. Although some studies reported that the effects of MGs in biodiesel are significant on the cold-flow properties (Tang et al. 2008; Chupka, Yanowitz, et al. 2011; Chupka et al. 2014), the mechanism of precipitation has not been established.

In Chapter 2, a thermodynamic study for mixtures of MGs and FAMES to predict the solid–liquid equilibrium was conducted, and found that binary mixtures of MGs and FAMES behave as non-ideal solutions, but the temperature of solid–liquid equilibrium is well predicted by a modified UNIFAC model, referred to as “modified UNIFAC (Dortmund)” (Gmehling et al. 1993). In this Chapter, the precipitation behavior of MGs in FAMES is discussed based on this prediction model to reveal the reason for inconsistencies between the CP and practical precipitation temperature, focusing on the effect of MG polymorphism.

3.2 Materials and Methods

3.2.1 Materials

In typical plant oils, palmitic (C16:0), oleic (C18:1) and linoleic (C18:2) acids are the major fatty acid moieties. The MGs of palmitic acid are probably an important cause of precipitation because they have higher melting points than unsaturated MGs. Therefore, a binary mixture of 1-monopalmitin (C16:0 MG, >95%, Tokyo Chemical Industry Co., Ltd. Tokyo, Japan) and methyl oleate (C18:1 FAME, >99%, Sigma-Aldrich Japan Co., LLC., Tokyo, Japan) was used as a model for biodiesel. These chemicals were used without purification. Binary mixtures were prepared by adding 1-monopalmitin to methyl oleate in concentrations of 0.10, 0.50 and 1.0 wt%.

3.2.2 Experimental and analytical methods

CPs of the binary mixtures prepared were measured by an automated cloud point tester (APM-7, Tanaka Scientific Co. Ltd., Tokyo, Japan) in conformity to ISO 3015 (International Organization for Standardization 1992) with a cooling rate of $-1\text{ }^{\circ}\text{C}/\text{min}$. An approximately 4 mL sample was placed in a cylindrical glass cup and heated on a plate heater set at $80\text{ }^{\circ}\text{C}$ until fully melted prior to CP measurement. It should be noted that the effect of overcooling is often involved in CP measurement because the sample is cooled under an unruffled condition.

Therefore, the precipitation behavior was also observed under ultrasonic treatment to mitigate the effect of overcooling. Approximately 10 mL of the sample was placed in a 50-mL glass vial and fully melted on the plate heater. The sample was then cooled in an ultrasonic water bath (US-103, SND Co., Ltd., Nagano, Japan) shaking the vial by hand, and the temperature at which the solid phase first appeared was defined as the cloud point under the ultrasonic treatment (CP_{US}). The temperature of the sample was measured by a thermocouple and the cooling rate was around -10 to -20 °C/min. The precipitation behavior was observed under storage at constant temperatures. Approximately 10 mL samples were placed in 50-mL glass vials, fully melted, and then held in a thermostatic chamber (FLI-301NH, Tokyo Rikakikai Co., LTD., Tokyo, Japan) set at constant temperatures from 0 to 30 °C, and confirmed whether precipitates were formed once within 12 hours.

The precipitates formed during the above experiments were analyzed by X-ray diffraction (XRD, RINT2200V, Rigaku Corp., Tokyo, Japan). A portion of the precipitates were collected with a pipette, transferred into a capillary tube together with the liquid fraction and directly analyzed by XRD in transmission mode. The precipitates were also observed with the liquid fraction by a microscope (OPTIPHOT XF-21, Nikon Corp., Tokyo, Japan) through crossed polars.

Pure precipitates were isolated from the liquid fractions using centrifugation tubes with a 0.45 μ m membrane filter and the solid phases obtained were washed with a small amount of *n*-hexane. The pure precipitates obtained were analyzed by XRD in refraction mode to identify the crystalline structure.

3.2.3 Thermodynamic model

The temperature of solid–liquid equilibrium (T_{SLE}) of 1-monopalmitin in methyl oleate was thermodynamically calculated according to Chapter 2 using equation (2-1).

$$\exp \left[\left(\frac{T_{SLE} - T_{m,i}}{RT_{SLE}} \right) \left(\frac{\Delta H_{m,i}}{T_{m,i}} \right) \right] = \gamma_i^L x_i \quad (3-1)$$

where γ_i^L and x_i are an activity coefficient and a mole fraction of component *i* in the liquid phase, respectively. The $\Delta H_{m,i}$ and $T_{m,i}$ are an enthalpy of fusion and a melting point of pure

component i , respectively. In this Chapter, it was assumed that the solid phase that formed at T_{SLE} is composed of only a single-component. The modified UNIFAC (Dortmund) model was applied to calculate γ_i^L and the measured values used for $\Delta H_{m,i}$ and $T_{m,i}$ were those from Chapter 2.

3.3 Results and Discussion

Fig. 3-1 shows the CPs of binary mixtures of 1-monopalmitin in methyl oleate compared with the calculated solid–liquid equilibrium temperatures (T_{SLE}) of 1-monopalmitin. The measured CPs (CP, shown by open circles) are very close to the equilibrium curve for the α form of 1-monopalmitin. In spite of the very low concentrations of 1-monopalmitin, the CP is significantly affected by this MG because of its high melting point. The CPs measured under ultrasonic treatment (CP_{US}, shown by filled circles) are consistent with the equilibrium curve for the β' form. These results indicate that 1-monopalmitin is unlikely to crystallize as the β form in methyl oleate, even if the temperature drops below the equilibrium temperature of the β form. In the case under ultrasonic treatment, 1-monopalmitin seems to crystallize directly as the β' form immediately after the temperature reaches the equilibrium curve of the β' form without the effect of overcooling. Similar behaviors were also found in the case cooled with agitation by a magnetic stirrer in Chapter 2. However, 1-monopalmitin in methyl oleate may be overcooled under the unruffled condition of ordinary CP measurement. When the temperature was further decreased below the equilibrium temperature of the α form, 1-monopalmitin immediately crystallizes as the α form and this temperature is measured as the CP.

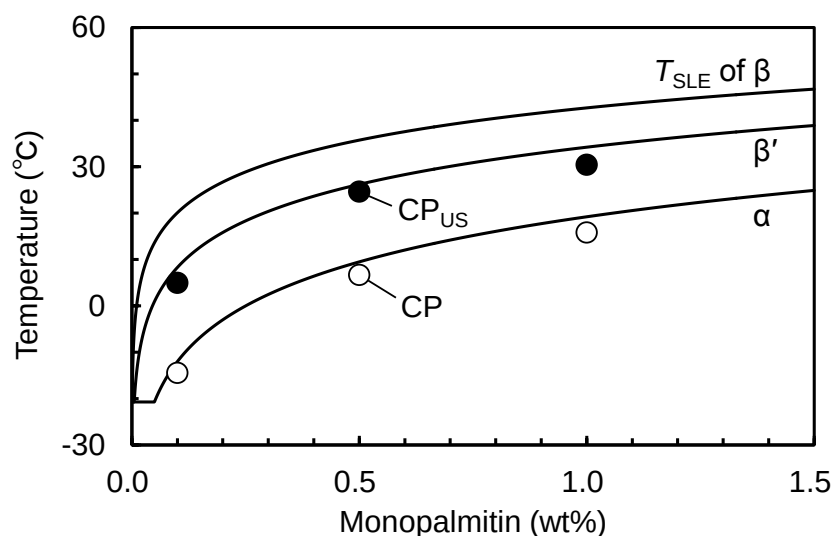


Fig. 3-1 Cloud points of the binary mixtures of 1-monopalmitin in methyl oleate measured without agitation (CP) and measured under ultrasonic treatment (CP_{US}) with the calculated solid–liquid equilibrium temperatures (T_{SLE}) for α , β' and β forms of 1-monopalmitin

Fig. 3-2 shows the times at which the formation of precipitates were first confirmed when the samples were stood at constant temperatures from 0 to 30 °C. In the case of 1.0 wt% 1-monopalmitin in methyl oleate, precipitates formed within 1 hour when the storage temperature was lower than the T_{SLE} of the α form, because the temperature was below the CP of the sample. When the storage temperature was higher than the T_{SLE} of the α form, the precipitated time was abruptly increased and seems to be asymptotically closed to the T_{SLE} of the β' form. Similar behaviors were also observed in cases of (b) 0.5 wt% and (c) 0.1 wt%. However, when the storage temperature was higher than the T_{SLE} of the β' form, precipitates did not formed in any case as shown by cross marks. This indicates that 1-monopalmitin cannot crystallize as the β form under storage at constant temperatures, similar to the results shown in Fig. 3-1. At temperatures lower than the T_{SLE} of the β' form, 1-monopalmitin can directly crystallize as the β' form after a certain period under the constant temperature in an unruffled condition.

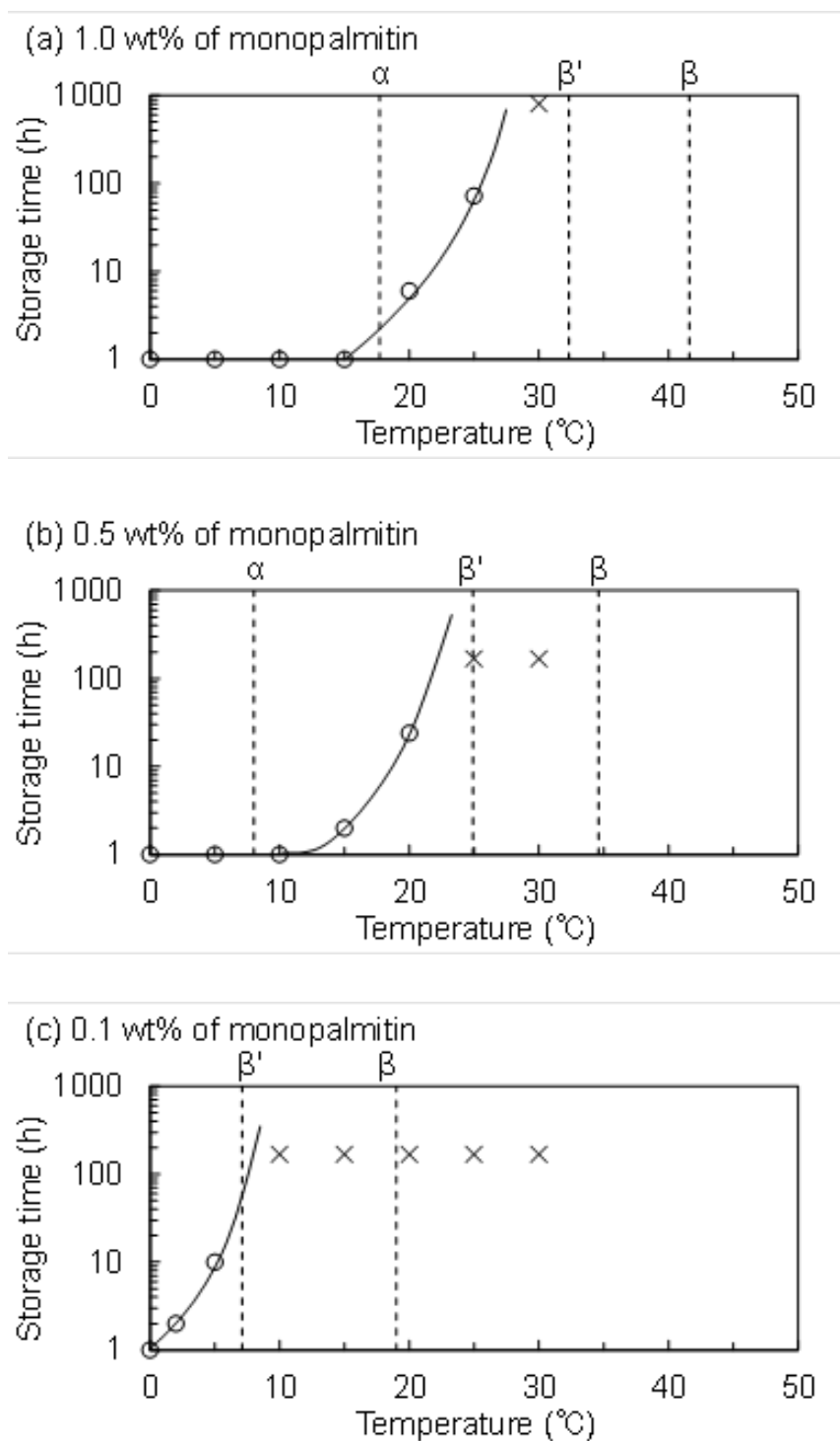


Fig. 3-2 Precipitation times for the mixtures of (a) 1.0 wt%, (b) 0.5 wt% and (c) 0.1 wt% 1-monopalmitin in methyl oleate at constant temperatures from 0 to 30 °C in comparison with the T_{SLE} of the α , β' and β forms (If precipitates were not observed, the finished times are shown by cross marks.)

Fig. 3-3 shows the changes in the visual appearance for the mixture of 1 wt% 1-monopalmitin in methyl oleate held at 20 °C, which is higher than the CP, for 14 days with their XRD patterns measured together with the liquid fraction in the transmission mode. The visual appearance of the precipitates did not appear to change much once solids had formed in the vial, even after 14 days. The intensity of the XRD pattern gradually increased with storage time, probably indicating that the crystallinity of 1-monopalmitin increased. However, the diffraction patterns observed were too broad to identify its crystalline structure, probably because of the presence of the liquid phase.

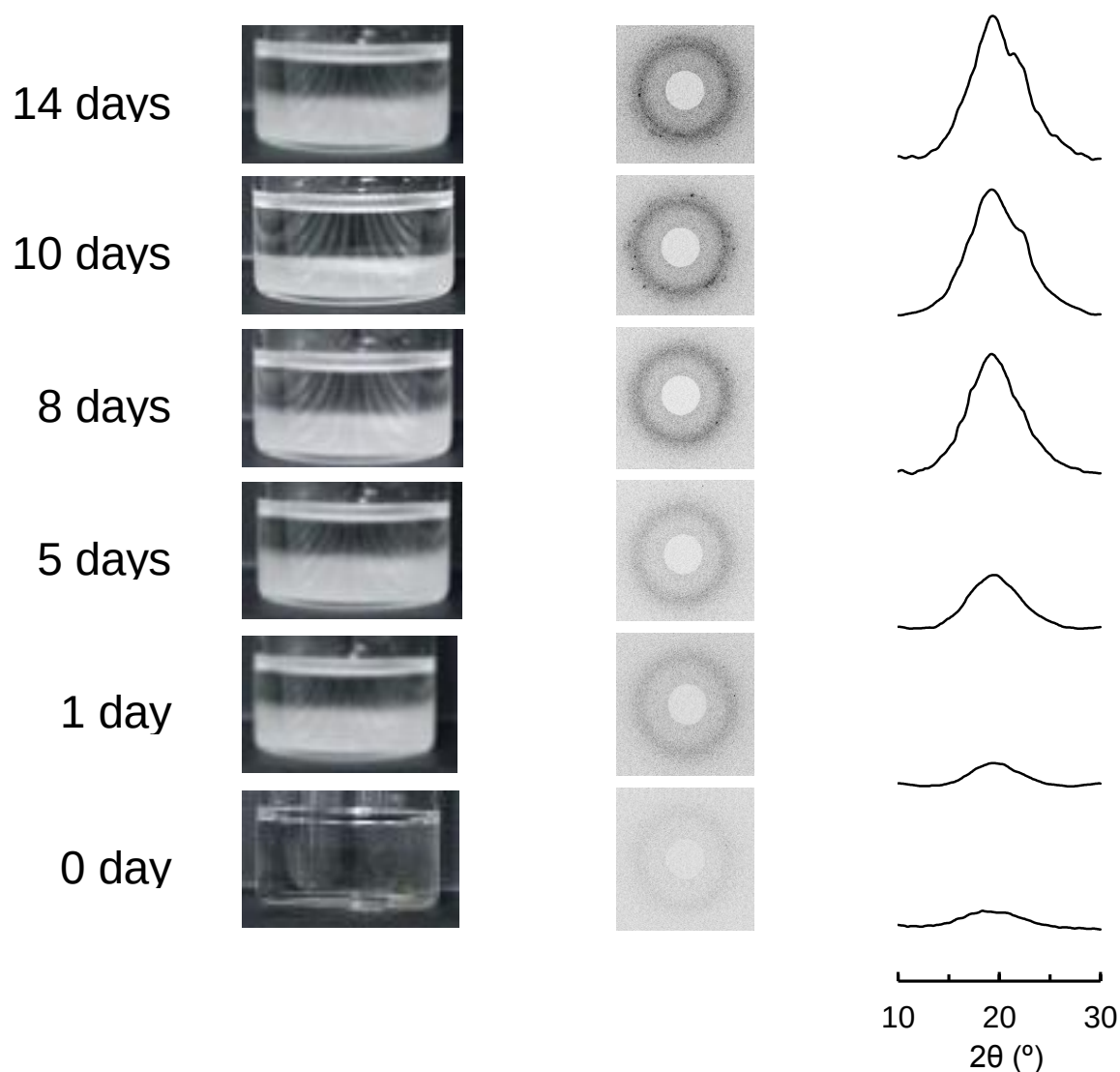


Fig. 3-3 Changes in the visual appearance and XRD pattern measured in transmission mode of the 1 wt% monopalmitin and methyl oleate mixture as soaked at 20 °C for 14 days

Microscopic observations of the precipitates in the liquid fraction were conducted through crossed polars (Fig. 3-4), in which the white areas indicate the presence of crystals and black sections are from the liquid phase. Crystals formed in every case but their morphologies are quite different depending on the conditions under which the crystals formed. Crystals obtained under (a) the conditions of ordinary CP measurement were relatively large and flaky. In case of the CP measurement under (b) ultrasonic treatment, agglomerated fine crystals

formed. The crystals obtained when the mixture was held (c) at 20 °C had an apparent columnar shape.

The crystallinity and form of the precipitates formed in the solutions were confirmed by XRD analyses conducted in reflection mode for the pure precipitates after the liquid fractions were completely removed. The XRD spectra of the precipitates are shown in Fig. 3-5, with standard samples of α (including sub- α), β' and β crystal forms of 1-monopalmitin for comparison. The XRD pattern of the precipitates obtained by (a) the ordinary CP measurement differs from that of the α form and is unexpectedly similar to that of the β' form. The precipitates obtained by (b) CP measurement under ultrasonic treatment and by (c) standing at 20 °C have XRD spectra that are consistent with the pattern of β' form. The precipitates of (b) and (c) crystallized as β' form in methyl oleate because precipitates formed at temperatures that were higher than the T_{SLE} of the α form and the β' crystal have not converted to the β form.

It is unclear why the precipitates obtained by (a) the ordinary CP measurement were the β' form when CP showed good agreement with the T_{SLE} of the α form (Fig. 3-1). One possibility is that the CP matching the T_{SLE} of the α form is coincidental and the crystals are the β' form. In this case the deviation between the CP and T_{SLE} of the β' form could be rationalized by the effect of overcooling. However, the experimental CP values were reproducible and the deviation between the CP and the T_{SLE} of β' seems too large to be explained by the overcooling effect. We postulate that the CP is related with the formation of the α crystal form. Some possible explanations for the β' form in the XRD spectra are that the α type crystals form and are converted to the β' form during the experimental procedure; or that α type crystals form first and act as nuclei for β' crystal growth. However, further studies are required to elucidate the mechanism of precipitation at the CP.

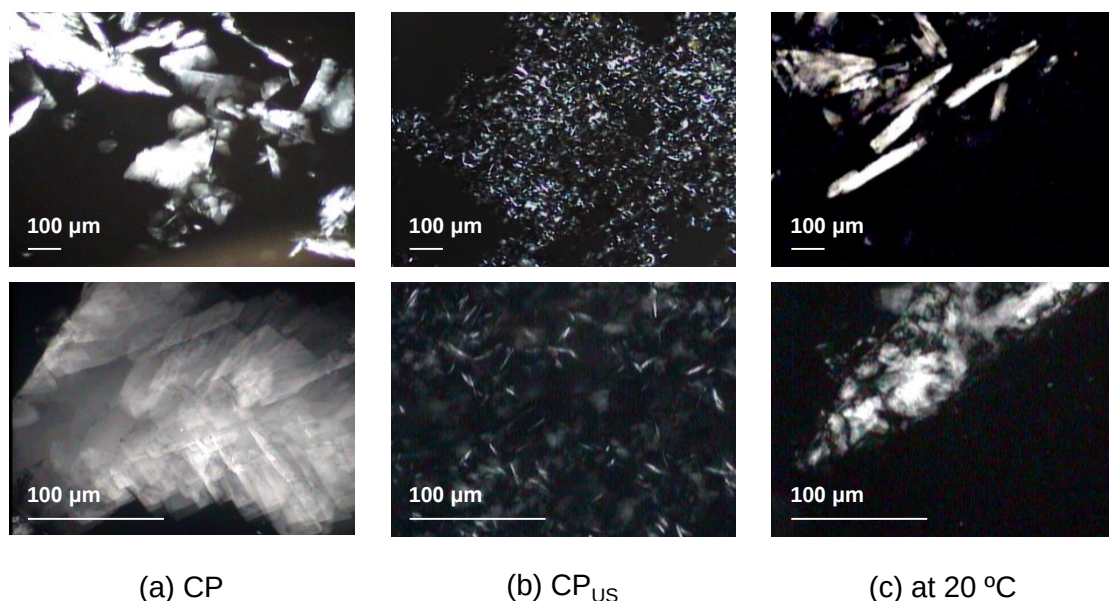


Fig. 3-4 Microscopic observations viewed through crossed polars of the precipitates in the liquid fraction obtained by (a) the ordinary CP measurement, (b) the CP measurement under ultrasonic treatment and (c) standing at 20 °C for the mixture of 1 wt% 1-monopalmitin in methyl oleate

The precipitates formed in the solution were thus proved to be crystalline form. Therefore, XRD analysis was conducted in reflection mode for the pure precipitates after the liquid fraction was completely removed to identify the crystalline form. The XRD charts of the precipitates were shown in Fig. 3-5 in comparison with the standard samples of α (including sub- α), β' and β crystals of monopalmitin. Regarding the precipitates obtained by (a) the ordinary CP measurement, the XRD pattern is different from the α form's one but seems like similar as the β' form against an expectation. The precipitates obtained by (b) the CP measurement under ultrasonic and by (c) soaking at 20 °C are consistent with the pattern of β' . Hence, the precipitates (b) and (c) are considered to be crystallized as β' form in methyl oleate because the temperature was higher than the T_{SLE} of α form and the β crystal cannot convert back to β' .

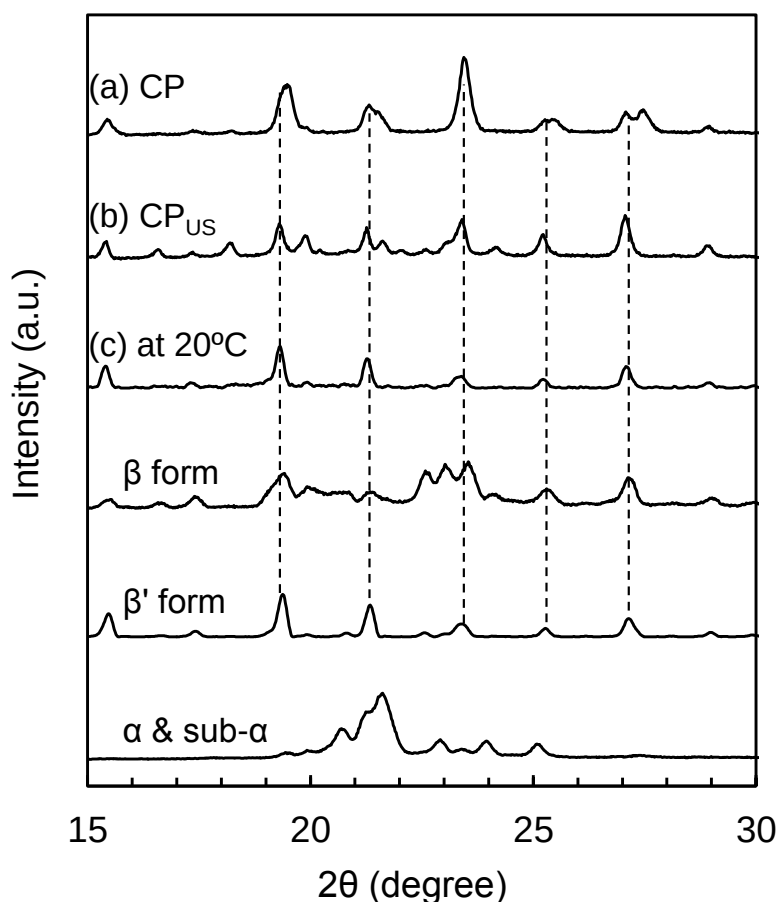


Fig. 3-5 XRD patterns of the precipitates obtained by (a) the ordinary CP measurement, (b) the CP measurement under ultrasonic treatment and (c) standing at 20 °C for the mixture of 1 wt% 1-monopalmitin in methyl oleate. Standard samples of α + sub- α , β' and β crystals of 1-monopalmitin shown for comparison

The reason is not clear yet that the precipitates by the ordinary CP measurement (a) were β' form even though the CP showed a good agreement with the calculated T_{SLE} of α form as shown in Fig. 3-1. One possibility is that the consistency is just a coincidence and the β' formation is true. In this case the deviation between the CP and T_{SLE} of β' form can be explained by the effect of overcooling. However, the experimental values of CP were well reproducible and the deviation between CP and T_{SLE} of β' seems too large for the overcooling. Therefore we think that the CP is related with the formation of α crystal. There are some possibilities: the one is that the α type crystal formed was converted to β' during the experimental procedure. The other is that the α type crystals are formed first and act as nuclei for the crystal growth of β' . However, further studies are required to elucidate the mechanism

of precipitation at the CP. The observation of precipitation by standing at constant temperature requires a great deal of time. Accordingly, an acceleration test for precipitation was performed with ultrasonic in water bath. Besides, when the temperature set between $\beta' < T < \beta$ for 1 hour, no precipitation was observed.

3.4 Concluding Remarks

CP measurements and the observation of precipitation at constant temperatures were conducted using mixtures of 1-monopalmitin and methyl oleate to understand the effect of MG polymorphism on the cold-flow properties of biodiesel. Precipitates formed in the mixtures at temperatures higher than the CPs when the mixtures were held at constant temperatures below the calculated T_{SLE} of the β' form of 1-monopalmitin. The precipitates obtained were identified as the β' form of 1-monopalmitin by XRD analyses, proving that 1-monopalmitin can crystallize directly as the β' form in methyl oleate. The CPs of the mixtures were close to the T_{SLE} of the α form of 1-monopalmitin, implying that the precipitation at the CP relates to the crystallization of the α form. However, the precipitates obtained at the CP had β' structure, and the mechanism of precipitation at the CP remains unclear.

The effect of MG polymorphism on precipitation was determined in this study, and the generally accepted concept of using the CP as an indicator of cold-flow fuel properties is not appropriate for biodiesel. The possibility of crystallization of MGs in the β' form needs to be considered.

Chapter 4

Renewable Diesel Production from Rapeseed Oil and Its Evaluation of Fuel Properties

4.1 Introduction

The fossil fuels are finite resources and their mass consumption has significant impacts on our environment and society. For these reasons, fatty acid methyl ester (FAME) is being used as an alternative diesel fuel produced by transesterification of triglyceride, a main component of plant oil, with methanol. Because FAME is renewable fuel containing no aromatics and sulfur, it can reduce exhaust emissions (Krawczyk 1996; Knothe et al. 2006). However, FAME has some drawbacks caused by the difference in chemical structure from petroleum diesel, for example, corrosiveness against certain types of rubber and metal (Haseeb et al. 2011) and poor oxidation stability due to unsaturated double bonds (Krawczyk 1996; Knothe et al. 2006; Haseeb et al. 2011; Moser 2009). To overcome such drawbacks, hydrocarbon productions from plant oils with the hydrotreating and catalytic cracking are being researched worldwide as mentioned in Chapter 1.

The hydrotreatment of plant oils was usually studied in the temperature range between 350 and 450 °C under the pressure between 4 and 15 MPa with H₂ and a catalyst (Monnier et al. 1998; Satyarthi et al. 2013; Gong et al. 2012; Kubička & Kaluža 2010; Madsen et al. 2011; Krár et al. 2010; Huber et al. 2007; Watanabe et al. 2006; Mikulec et al. 2010). As a catalyst, for example, sulfided CoMo and NiMo supported on SiO₂, Al₂O₃, ZrO₂, TiO₂ and zeolites were used (Monnier et al. 1998; Satyarthi et al. 2013a; Gong et al. 2012; Kubička & Kaluža 2010; Madsen et al. 2011; Krár et al. 2010; Huber et al. 2007). As mentioned in Chapter 1, under the hydrotreating reaction, first, double bonds in fatty acid moieties of triglyceride are hydrogenated into saturated C-C bonds, followed by the cleavage of ester linkages to produce one molecule of propane and three molecules of saturated fatty acids (Satyarthi et al. 2013; Watanabe et al. 2006). The obtained saturated fatty acids are then deoxidized into hydrocarbons having carbon numbers mainly between 15 and 18 through hydrodeoxygenation, decarbonylation and decarboxylation (Kubička et al. 2010; Mikulec et al. 2010). This reaction may also produce various hydrocarbons such as iso-paraffin and naphthene through

isomerization and cyclization of olefin intermediates, which contributes to improving the low-temperature properties although there are undesirable products. In addition, CO, CO₂, H₂O and propane are produced as byproducts (Satyarthi et al. 2013).

On the other hand, the catalytic cracking of plant oils was usually carried out in the temperature range between 300 and 500 °C under atmospheric pressure with a solid catalyst such as zeolites, Al₂O₃ and MgO (Tani, Shimouchi, et al. 2011; Maher & Bressler 2007; Rao 1978; Twaiq et al. 1999), under which the thermal decomposition is predominant. First, triglycerides are decomposed to fatty acids, ketones, aldehydes and esters (Taufiqurrahmi & Bhatia 2011). These products undergo secondary cracking to form short and long chain paraffins and olefins with CO, CO₂, H₂O and alcohols by breaking C-O and C-C bonds via decarboxylation and decarbonylation. Finally, this process makes various hydrocarbons with wide range of carbon numbers including olefins and aromatics.

After all, the selectivity of the products is not so high with the conventional hydrotreating and catalytic cracking mentioned above. It should be caused by the presence of unsaturated fatty acid moieties, which leads to various side reactions. Actually, the study of the catalytic cracking of prehydrogenated soybean oil and crude one reported that the prehydrogenated oil yielded essentially pure hydrocarbon products, while the crude oil yielded a mixture of oxygen-containing products and the lower molecular weight hydrocarbons (Dos Anjos et al. 1983).

In this Chapter, therefore, hydrocarbon production from plant oil was studied through a two-step reaction with hydrolysis and subsequent decarboxylation. During the hydrolysis step, hydrogenation was simultaneously conducted to produce stable saturated fatty acids, which may suppress undesirable side reactions during subsequent decarboxylation (Snåre et al. 2008; Dos Anjos et al. 1983). In the literature (Monnier et al. 1998; Satyarthi et al. 2013; Gong et al. 2012; Kubička & Kaluža 2010; Madsen et al. 2011; Krár et al. 2010; Huber et al. 2007; Watanabe et al. 2006; Mikulec et al. 2010; Tani et al. 2011; K. D. D. Maher & Bressler 2007; Rao 1978; Twaiq et al. 1999; Taufiqurrahmi & Bhatia 2011; Snåre et al. 2008; Dos Anjos et al. 1983; Wang et al. 2012), furthermore, an organic solvent such as *n*-dodecane was usually added to enhance the fluidity of the reactants and to avoid the deactivation of catalyst. However, the use of such organic solvent requires additional separation and purification steps after the reaction, and it makes the whole process complicated. Therefore, the reactions of this study were conducted without any organic solvent so as to simplify the process for production

of hydrocarbons as renewable diesel.

4.2 Materials and Methods

4.2.1 Experimental procedures

Fig. 4-1 shows the schematic diagram of the saturated hydrocarbon (renewable diesel) production process in this study via saturated fatty acids from rapeseed oil. Prior to the experiment, a Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 °C and reduced in H₂ flow (15 ml/min) at 200 °C for 60 min. Rapeseed oil (reagent grade, Nacalai Tesque, Inc.) was, then, treated in hot-compressed water with H₂ gas and Pd/C catalyst for hydrolysis and hydrogenation to obtain saturated fatty acids. The obtained saturated fatty acids were then decarboxylated with H₂ gas and Pd/C catalyst to produce saturated hydrocarbons by decarboxylation.

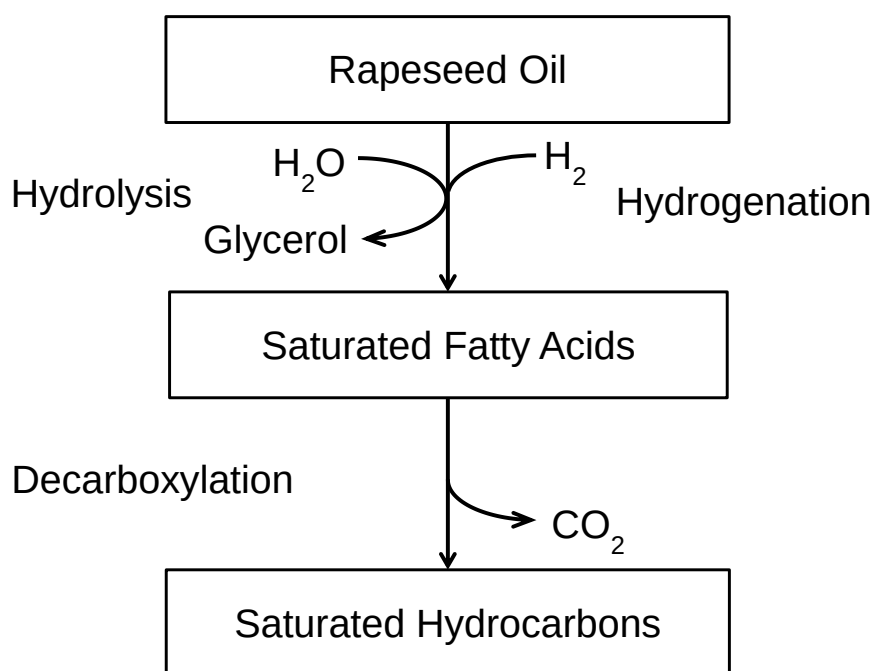


Fig. 4-1 Schematic diagram of the saturated hydrocarbon production process via saturated fatty acids from rapeseed oil

4.2.1.1 Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)

A batch-type reaction vessel (inner volume: 5.0 ml) made of Inconel-625 (Saka & Kusdiana 2001) was used for the reaction. One gram of rapeseed oil and 1.0 - 3.0 g of ion-exchanged water were placed into the reaction vessel with 0.05 g of Pd/C. Hastelloy balls (total volume: 0.2 ml) were also placed into the vessel to agitate the mixture efficiently. After the vessel was sealed, the inside of the vessel was purged and pressurized to 5 MPa with H₂ gas using a gas-supplying system. The hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation) reaction was then conducted by immersing the vessel into a molten salt bath preheated at 270 °C, which is the optimum temperature for hydrolysis of triglycerides found in previous works (Kusdiana & Saka 2004; Minami & Saka 2006). The reaction vessel was swung from side to side to agitate the mixture during the reaction. After a designated treatment time, the vessel was moved into a water bath to quench the reaction. The obtained reaction mixture was taken out from the vessel with tetrahydrofuran (THF, specially prepared reagent grade, Nacalai Tesque, Inc.), and then, sonicated for 30 min. The catalyst was removed with a filter paper in a micropore of 0.45 µm (Merck Millipore Co.). The products were, then, warmed up in a water bath at 70 °C for 30 min and separated into THF and water phases. The product of the hydrolysis/hydrogenation reaction was collected by removing THF from the THF phase with a rotary vacuum evaporator, and its yield was determined.

4.2.1.2 Decarboxylation

For subsequent decarboxylation, approximately 0.9 g of the obtained product from the hydrolysis/hydrogenation reaction and 0.05 - 0.45 g of Pd/C were placed into the 5 ml reaction vessel with Hastelloy balls. The inside of the reaction vessel was then purged and pressurized with H₂ gas to be 1 MPa which is a favorable pressure for decarboxylation reaction (Marker et al. 2011). The decarboxylation was, then, conducted with the molten salt bath at 300 °C for 120 min, which is an appropriate condition reported by Lestari et al. (Lestari et al. 2008), and quenched into the water bath. After the reaction, the obtained product dissolved in THF was taken out from the vessel, sonicated for 30 min, and the catalyst was removed with the filter paper. After removing THF by the evaporator, the decarboxylated product was obtained to determine its yield. To clarify the decarboxylation reaction of the saturated fatty acid, palmitic acid, stearic acid and arachidic acid (all being guaranteed reagent grade from Nacalai Tesque, Inc.) were also studied.

4.2.2 Analytical methods

The fatty acid composition of rapeseed oil used in this work was determined in accordance with the Japan Oil Chemists' Society standard method (Japan Oil Chemists' Society 2013). The products, obtained from hydrolysis/hydrogenation and subsequent decarboxylation, were analyzed by gel permeation chromatography (GPC, Shimadzu Co. LC-10VP system, column: GF-310 HQ (Showa Denko K.K.), oven temperature: 40 °C, mobile phase: THF, flow-rate: 1.0 ml/min, detector: refractive index detector RID-10A) and high performance liquid chromatography (HPLC, column: Cadenza CD-C18 (Imtakt Co.), oven temperature: 40 °C, mobile phase: methanol, flow-rate: 1.0 ml/min, detector: RID-10A).

The fuel properties of the renewable diesel were evaluated for flash point, pour point, cold filter plugging point, kinematic viscosity and density as in Table 4-2. In addition, the renewable diesel was blended in various ratios with fossil diesel (#1 diesel of the Japanese Industrial Standard (JIS), purchased from Showa Shell Sekiyu K.K.), and their fuel properties were also evaluated. The density was determined in accordance with the ASTM International's standard ASTM D1298 (ASTM International & ASTM 2012), while the flash point, pour point, cold filter plugging point and kinematic viscosity were measured by the automated Pensky-Martens closed cup flash point tester (APM-7), the mini pour point tester (MPC-102), the automated cold filter plugging point tester (AFP-102) and the automatic kinematic viscosity measuring system (AKV-201), respectively. All of these measuring systems were made by Tanaka Scientific Co. Ltd. The acid and iodine values were determined in accordance with ASTM D974 (ASTM 2006).

4.3 Results and Discussion

Table 4-1 shows the fatty acid composition of rapeseed oil and yields of the products obtained after hydrolysis/hydrogenation and subsequent decarboxylation. Rapeseed oil used in this study is composed of saturated and unsaturated fatty acids with 16, 18 and 20 carbon atoms. Through this study, appropriate reaction conditions for hydrolysis/hydrogenation and decarboxylation were evaluated as described in the following subsections.

Table 4-1 Fatty acid composition of rapeseed oil, obtained saturated fatty acids by

hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation

Fatty acid composition of rapeseed oil (mol%)		Yield (mol%) ^{*1}		
		Saturated fatty acids by hydrolysis/hydrogenation ^{*2}	Saturated hydrocarbons by decarboxylation ^{*3}	
C16:0	4.3	4.5 (4.6)	4.1 (4.5)	C ₁₅ H ₃₂
C16:1	0.2	0.0	-	
C18:0	0.7	89.7 (91.2)	85.7 (93.6)	C ₁₇ H ₃₆
C18:1	66.4	0.0	-	
C18:2	19.4	0.0	-	
C18:3	7.5	0.0	-	
C20:0	0.5	1.9 (1.9)	1.7 (1.9)	C ₁₉ H ₄₀
C20:1	1.0	0.0	-	
Glycerides	-	2.3 (2.3)	0.0	
Total	100	98.4 (100)	91.5 (100)	

^{*1}: The values in parenthesis indicate the mol% on the total yield basis of rapeseed oil

^{*2}: 270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C for 60 min

^{*3}: 300 °C/ 1 MPa (H₂) with 0.45 g Pd/C for 120 min

4.3.1 Hydrolysis/hydrogenation

Fig. 4-2 shows respectively GPC and HPLC chromatograms of the obtained products through hydrolysis/hydrogenation reaction from 0.9 g of rapeseed oil as treated at 270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C. In Fig. 4-2 (a), triglycerides (TG) in rapeseed oil are decreasing as reaction time is prolonged. For 20 and 40 min treatments, diglycerides (DG) and monoglycerides (MG) are being observed as intermediate compounds, but almost all of them also disappear after 60 min. Meanwhile, fatty acids (FA) are increasing with reaction time until 60 min treatment. Incidentally, the retention time of triglycerides in the GPC chart shifts slightly to the shorter retention time after 20 min treatment. It would imply that the

double bonds in fatty acid moieties are converted into saturated ones through hydrogenation, because saturated fatty acids have a slightly shorter retention time than unsaturated ones on the GPC column used in this study. Actually, only saturated fatty acids such as palmitic (C16:0), stearic (C18:0) and arachidic (C20:0) acids can be found after 20 min treatment by HPLC analysis as shown in Fig. 4-2 (b). It indicates that hydrogenation is faster than hydrolysis and completed within 20 min.

From the above, an appropriate reaction time for hydrolysis/hydrogenation was found to be 60 min at the given conditions. Based on the HPLC and GPC analyses, the yield of the products from rapeseed oil was determined as shown in Table 4-1. Triglycerides in rapeseed oil were converted into saturated fatty acids and their yield was summed up to be 96.1 (= 4.5 + 89.7 + 1.9) mol%. In addition, 2.3 mol % of glycerides still remained as intermediate compounds. Finally, the total yield of fatty acids and glycerides was 98.4 mol% and no other product was visible on the HPLC chart. In addition, no gaseous products were produced and saturated fatty acids are stable under the given condition. Thus, no product decomposition would be occurred. Therefore, the rest of 1.6 mol% would probably be lost through the purification steps. By excluding the lost portion, the molar ratio upon the obtained products basis was shown in parenthesis in Table 1. As a result, the molar ratio of the obtained saturated fatty acids (C16:0 : C18:0 : C20:0 = 4.6 : 91.2 : 1.9) is close to the fatty acid composition of rapeseed oil (C16:0 + C16:1 : C18:0 + C18:1 + C18:2 + C18:3 : C20:0 + C20:1 = 4.5 : 94.0 : 1.5). It means that the selective reaction to be saturated fatty acids has occurred during the hydrolysis/hydrogenation step.

With regard to the amount of water, on the other hand, 1.0 g of rapeseed oil was hydrolyzed with 3.0 g of water. Thus, the weight ratio of water/rapeseed oil was 3.0/1.0 for Table 4-1 and Fig. 4-2. However, when its ratio decreased from 3.0/1.0 to 1.0/1.0, the yield of saturated fatty acids decreased from 97.7 mol% to 77.2 mol% due to the insufficient hydrolysis of glycerides and fatty acids under the same reaction condition. From these results, it was concluded that an appropriate hydrolysis/hydrogenation condition is 270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C for 1.0 g of rapeseed oil.

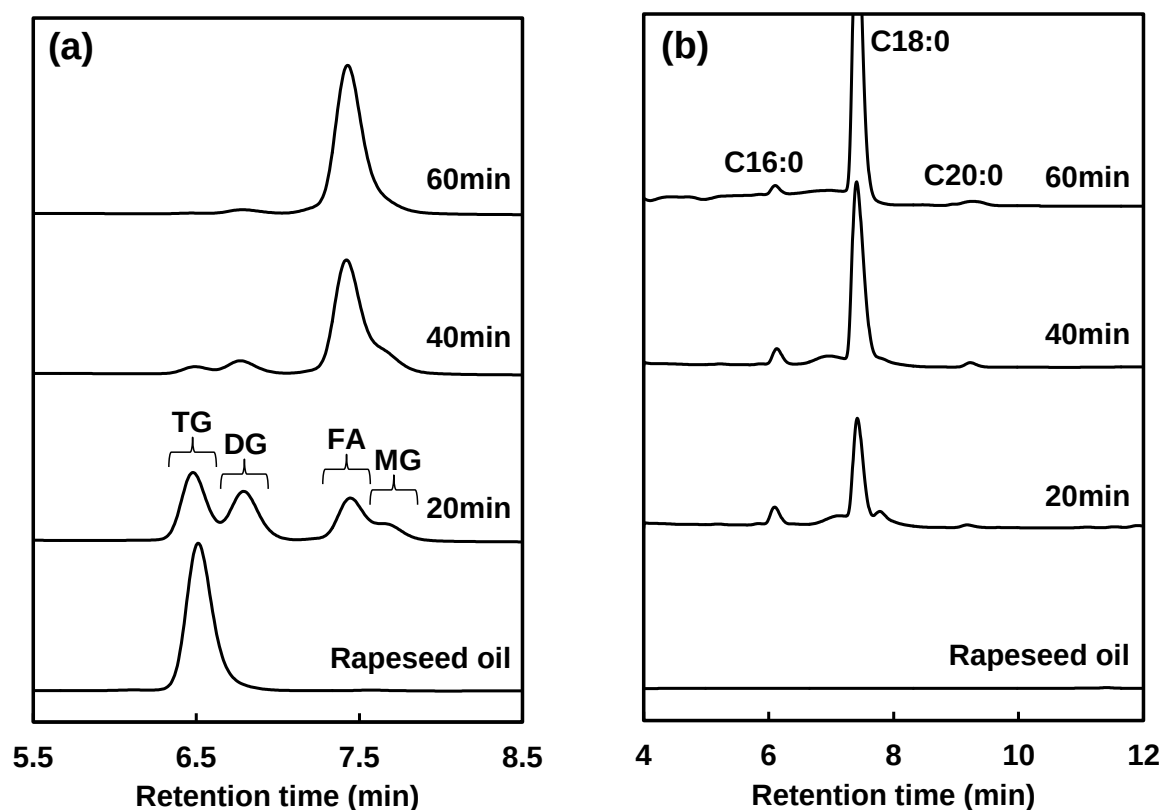


Fig. 4-2 (a) GPC and (b) HPLC chromatograms of the obtained saturated fatty acids by hydrolysis/hydrogenation from rapeseed oil at 270 °C/ 5 MPa (H_2) with 3.0 g of water and 0.05 g of Pd/C

4.3.2 Decarboxylation

As a preliminary experiment, decarboxylation reactions were individually carried out for 0.9 g of palmitic, stearic and arachidic acids as model compounds to determine an appropriate amount of the catalyst at the conditions of 300 °C/ 1 MPa (H_2) for 120 min. When the two different amounts of Pd/C were studied to be 0.05 and 0.25 g, incomplete conversions were found respectively to be 16.3 and 26.1 mol% from stearic acid into *n*-heptadecane. On the other hand, 90.3 mol% of *n*-heptadecane was achieved with 0.45 g of Pd/C. Similarly, 0.9 grams of palmitic and arachidic acids were respectively converted into *n*-pentadecane and *n*-nonadecane hydrocarbons with 0.45 g of Pd/C. Therefore, it was concluded that 0.45 g of Pd/C is required for the efficient decarboxylation of 0.9 g of fatty acids at the given conditions. In general, decarboxylation of fatty acids proceeds in three phases, gaseous H_2 , liquid fatty acids and a solid catalyst, in which the mutual accessibility is an important factor. Although an organic solvent is usually added to improve its accessibility in the literature (Wang et al. 2012),

decarboxylation was conducted without any organic solvent in this study to simplify the reaction process. That might be the reason why such a large amount of Pd/C catalyst was needed. Therefore, an effective agitation would be required to reduce the amount of the catalyst.

On the other hand, Fig. 4-3 shows HPLC chromatograms of rapeseed oil, the obtained fatty acids by hydrolysis/hydrogenation and hydrocarbons after decarboxylation. Triglycerides in rapeseed oil are composed of various fatty acids, thus many peaks are found in Fig. 4-3. However, these peaks are converted mainly into three peaks of saturated fatty acids, palmitic (C16:0), stearic (C18:0) and arachidic (C20:0) acids, by hydrolysis/hydrogenation of triglycerides. These saturated fatty acids are then converted into *n*-pentadecane (C₁₅H₃₂), *n*-heptadecane (C₁₇H₃₆) and *n*-nonadecane (C₁₉H₄₀), respectively, by subsequent decarboxylation. Therefore, the obtained renewable diesel from rapeseed oil consists of these three kinds of saturated hydrocarbons.

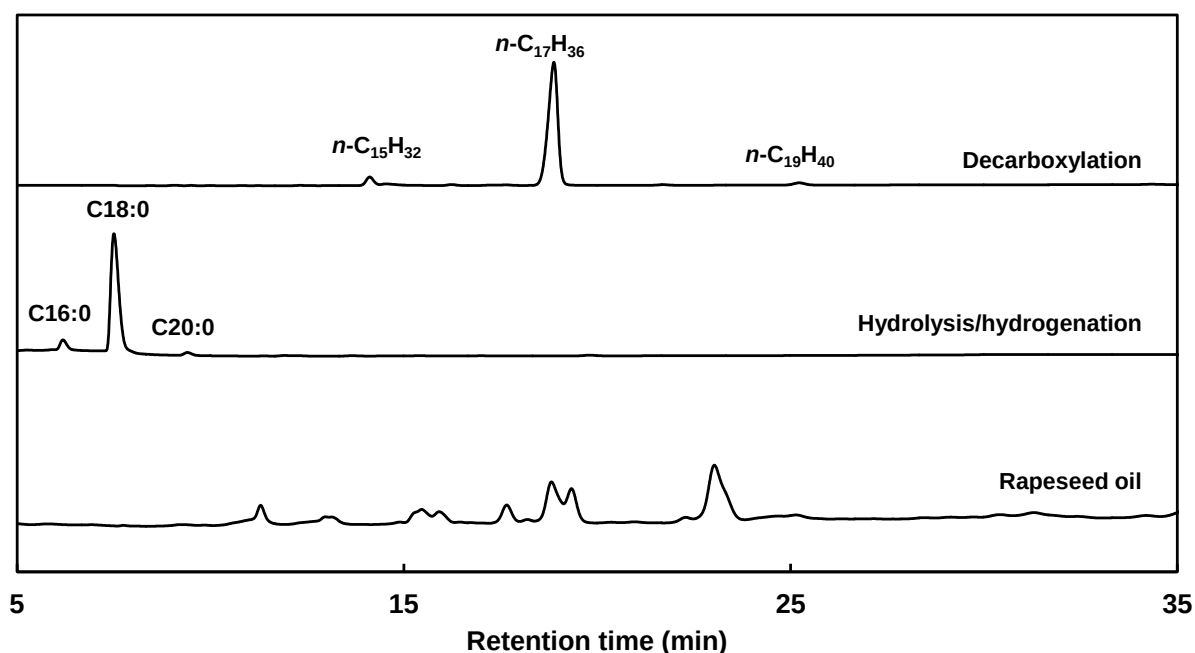


Fig. 4-3 HPLC chromatograms of rapeseed oil, the obtained saturated fatty acids by hydrolysis/hydrogenation (270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C for 60 min) and the saturated hydrocarbons by decarboxylation (300 °C/ 1 MPa (H₂) with 0.45 g Pd/C for 120 min)

Based on the HPLC and GPC analyses, the yields of hydrocarbons were determined as shown in Table 4-1. The total yield of hydrocarbons was 91.5 mol% and any other products were not observed. Since hydrocarbons are stable enough under the given condition, no decomposition of the products can be occurred. Therefore, the rest of 8.5 mol% would probably be lost through the purification steps. The loss of the products would be caused by using a large amount of catalyst, on which the products were adsorbed. The molar ratio upon the obtained hydrocarbon basis was shown in parenthesis in Table 4-1. As a result, the molar ratio of obtained *n*-pentadecane, *n*-heptadecane and *n*-nonadecane was found out to be 4.5 : 93.6 : 1.9. This molar ratio is nearly close to the one of saturated fatty acids (C16:0 : C18:0 : C20:0 = 4.6 : 91.2 : 1.9 in Table 4-1) obtained after hydrolysis/hydrogenation. Therefore, these saturated fatty acids seem to be selectively converted without any side reaction into the corresponding hydrocarbons through decarboxylation. In case of unsaturated fatty acids, however, various side reactions such as hydrogenation, dehydrogenation, cyclization, ketonization, dimerization and cracking have been reported to occur concurrently due to the unstable double bonds present (Simakova et al. 2011; Snåre et al. 2006), which lead to decrease the degree of the specific production of hydrocarbons. Therefore, unsaturated fatty acids should be converted into saturated ones before decarboxylation to maintain its high selectivity. For this specificity, the process shown in Fig. 4-1 is appropriate and promising.

After hydrolysis/hydrogenation, 2.3 mol% of glycerides such as monoglycerides and diglycerides still remain as shown in Table 4-1. However, these intermediate compounds are disappeared after decarboxylation, and converted into hydrocarbons. Actually, when 1-monostearin was treated at the same condition, it was converted into *n*-heptadecane by decarboxylation treatment with H₂ gas and Pd/C catalyst even though the reactivity was slightly low, compared with saturated fatty acids. Therefore, the remaining glycerides must be converted to saturated fatty acids during decarboxylation treatment.

The iodine and acid values of the obtained hydrocarbons from rapeseed oil were evaluated and found out to be zero. This means that the obtained products have neither double bonds nor fatty acids. It is, therefore, evident that hydrogenation and decarboxylation reactions are successfully completed during the process.

4.3.3 Fuel properties of renewable diesel from rapeseed oil

It is very important to evaluate the fuel properties of the renewable diesel. However, the prepared renewable diesel is not sufficient in amount to test the fuel properties. As in Table 4-1, it consists of the saturated linear hydrocarbons of *n*-pentadecane, *n*-heptadecane and *n*-nonadecane in a molar ratio of 4.5 : 93.6 : 1.9. In addition, it was confirmed that such a mixture does not contain any contaminants. Therefore, a mixture of these three kinds of hydrocarbons was prepared from their chemicals purchased as the renewable diesel and evaluated for the fuel properties.

Table 4-2 shows the evaluated fuel properties of the mixtures of renewable diesel with #1 fossil diesel in various ratios. In case of 100 vol% renewable diesel, it has a higher flash point than that of the fossil diesel (0 vol% renewable diesel in Table 4-2), and satisfies the specification standard of the fossil diesel in Japan (JIS K2204) (Japanese industrial standards Committee. 2007). Such a property should be originated from *n*-heptadecane, a main component of the fuel, which has a relatively high boiling point among the hydrocarbons in petroleum diesel. In addition, the values of kinematic viscosity and density also satisfy the requirements for the Japanese diesel standard. These values are also close to the ones of *n*-heptadecane. On the other hand, the cold-flow properties such as pour point and cold filter plugging point are poor due to the presence of saturated linear hydrocarbons, because these have relatively high melting points, especially in case of *n*-heptadecane. Therefore, the cold-flow properties should be improved to meet the fossil diesel standard. Blending the renewable diesel with fossil one is a simple way for this purpose. In case of 20 vol% renewable diesel, as shown in Table 4-2, the pour point and cold filter plugging point are improved, and thus, it can satisfy the requirements for the fuel standard. However, when the ratio of renewable diesel is increased to be 30 vol%, the pour point exceeds the limit of the standard. From such a reason, the blending ratio would be limited up to around 20 vol% to meet all requirements of the specification standard in Table 4-2. This further indicates that the obtained hydrocarbons through this process can be used as renewable diesel by blending with fossil diesel.

Table 4-2 Fuel properties of renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204) (Japanese industrial standards Committee. 2007)

Property	Ratio of renewable diesel ^{*1} to #1 fossil diesel (vol%)					#1 diesel standard
	100	30	20	5	0 ^{*2}	
Flash point (°C)	153	75.0	69.5	64.5	63.5	≥ 50
Pour point (°C)	20	3.0	-2.5	-7.0	-8.0	≤ -2.5
Cold filter plugging point (°C)	22	-2.0	-6.0	-3.0	-5.0	≤ -1
Kinematic viscosity at 30 °C (mm ² /s)	4.5	3.7	3.6	3.6	3.5	≥ 2.7
Density at 15 °C (g/cm ³)	0.77	0.82	0.83	0.83	0.83	≤ 0.86

^{*1}: Renewable diesel was prepared by mixing pure hydrocarbons with the same molar ratio as in Table 4-1

^{*2}: Renewable diesel 0 vol% corresponds to fossil diesel 100 vol%

4.4 Concluding Remarks

To produce hydrocarbons from plant oil as renewable diesel fuel, the conventional hydrotreating and catalytic cracking processes are not really specific for the products selectivity due to unsaturated double bonds. In this study, therefore, the process composed of hydrolysis/hydrogenation and subsequent decarboxylation was proposed. In the first treatment, triglycerides in rapeseed oil were converted into saturated fatty acids through hydrolysis in hot-compressed water and simultaneous hydrogenation under the presence of Pd/C catalyst and H₂ gas. In the second treatment, the obtained saturated fatty acids were decarboxylated into the corresponding hydrocarbons under the presence of Pd/C. In this process, unsaturated double bonds in fatty acid moieties, which lead to various side reactions, were hydrogenated into saturated ones prior to the second treatment. Therefore, the selective conversion was achieved by this two-step treatment without any side reaction. As a result, the composition of the obtained hydrocarbons corresponded to the fatty acid composition of rapeseed oil.

However, the obtained renewable diesel fuel should be improved in cold-flow properties because saturated linear hydrocarbons have relatively high melting points, whereas

other properties such as flash point, kinematic viscosity and density satisfied the requirements of the fossil diesel. To satisfy the requirements, a blend of renewable diesel with fossil diesel was found out to weaken the inferior fuel properties of pour point and cold filter plugging point. Consequently, 20 vol% blend of the renewable diesel was found out to satisfy the requirements for the Japanese specification standard of the fossil fuel.

Hydrocarbon (renewable diesel) production from rapeseed oil was studied with hydrothermal hydrogenation and subsequent decarboxylation in a batch-type reaction vessel. An appropriate reaction condition for hydrothermal hydrogenation was found to be 270 °C/ 5 MPa (H₂ pressure) with water and Pd/C catalyst for 60 min, under which triglycerides were simultaneously hydrolyzed and hydrogenated into saturated fatty acids in a yield of 98.4 mol%. The obtained saturated fatty acids were then decarboxylated to hydrocarbons under the condition of 300 °C/ 1 MPa (H₂ pressure) with Pd/C for 120 min in a yield of 91.5 mol% on rapeseed oil. In addition, the composition of the obtained hydrocarbons corresponded nearly to that of the fatty acid in rapeseed oil. Such a result indicates that the composition of hydrocarbons produced in this proposed process can be foreseen from fatty acid composition of the feedstock triglycerides. By blending the obtained hydrocarbons from rapeseed oil with an adequate amount of fossil diesel, the blended fuel could satisfy the specification standard of fossil diesel in Japan.

Chapter 5

Renewable Diesel Production from Coconut Oil and Its Evaluation of Fuel Properties

5.1 Introduction

Fatty acid methyl ester (FAME) is used as an alternative fossil diesel with no or minor engine modification. In general, FAME is produced by transesterification of triglyceride, which is the main component of plant oil, with methanol. Because plant oil includes no aromatics and sulfur, the use of FAME can reduce exhaust emissions (Bajpai & Tyagi 2006; Demirbas 2007). However, as mentioned in Chapter 1, FAME has some drawbacks caused by differences in chemical structure from fossil diesel, such as a corrosiveness against certain types of rubbers and metals, a poor oxidation stability due to its unsaturated double bonds and poor cold-flow properties because saturated compounds have a high melting point (Bajpai & Tyagi 2006; Singh et al. 2012; Knothe 2005).

In recent years, hydrocarbon production, which is often termed green diesel or renewable diesel, has been researched worldwide by hydrotreatment or catalytic cracking of plant oils in order to fundamentally solve the above disadvantages. The hydrotreatment has been studied typically in the temperature range between 300 and 450 °C under a H₂ pressure between 4 and 15 MPa with sulfide or noble metal catalysts (Mikulec et al. 2010; Satyarthi et al. 2013; Kubička & Kaluža 2010; Santillan-Jimenez & Crocker 2012; Krár et al. 2010; Šimáček et al. 2009). This process concurrently involves hydrogenation of unsaturated double bonds, cleavage of ester linkages in triglycerides, followed by deoxidization such as hydrodeoxygenation, decarboxylation and decarbonylation, to produce hydrocarbons mainly between C15 and C18 (Šimáček et al. 2009). On the other hand, the catalytic cracking is usually carried out between 350 and 500 °C under atmospheric pressure with a catalyst such as zeolite, Al₂O₃ and MgO (Tani et al. 2011; K. D. Maher & Bressler 2007; Katikaneni et al. 1995; Twaiq et al. 1999). In this case, thermal decomposition dominates and produces various hydrocarbons with a wide range of carbon numbers. However, the product yield and selectivity on these conventional processes may be low. The first reason is the presence of unstable double bonds in fatty acid moieties, which leads to various side reactions (Snåre et al. 2008). The

second reason is the relatively severe reaction condition for converting triglyceride into hydrocarbons (Santillan-Jimenez et al. 2013). In particular, a high temperature may lead to low selectivity due to undesirable reactions (Satyarthi et al. 2013).

To improve the product yield and selectivity, the hydrocarbon production process from plant oils by a two-step reaction was proposed in Chapter 4 (Sugami et al. 2016). In the first step, plant oil is treated in subcritical water with H₂ gas and a Pd/C catalyst to produce saturated fatty acids. In subcritical water, the cleavage of ester linkages easily proceeds through hydrolysis around at 270 °C (Minami & Saka 2006), which is lower than the above-mentioned conventional processes. Concurrently, unsaturated double bonds are hydrogenated into saturated bonds because of the presence of Pd/C and H₂. Thus, saturated fatty acids are produced selectively from triglycerides. In the second step, the obtained saturated fatty acids are decarboxylated into saturated hydrocarbons with a Pd/C catalyst at 300°C. The temperature is relatively low compared with the conventional processes, because fatty acids is more easily decarboxylated than triglycerides (Santillan-Jimenez et al. 2013), resulting in a high yield and selectivity.

In Chapter 4, the proposed two-step process achieved an excellent conversion of rapeseed oil into hydrocarbons with a high selectivity (Sugami et al. 2016). With this process, all of C16 fatty acid (palmitic acid) and C18 fatty acids (stearic, oleic, linoleic and linolenic acids) moieties in the triglyceride were completely converted into corresponding saturated hydrocarbons, *n*-pentadecane (C15) and *n*-heptadecane (C17), respectively, without any side reaction. This result further indicates that the composition of hydrocarbons produced in the proposed process can be predicted from the fatty acid composition of the feedstock triglycerides.

As a feedstock for renewable diesel, various plant oils such as rapeseed, soybean, sunflower and olive oils are available. These plant oils are composed mainly of C16 and C18 fatty acids. However, several plant oils, for example coconut and palm kernel oils, have unique fatty acid compositions with shorter carbon chain, such as C10 (capric acid), C12 (lauric acid) and C14 (myristic acid) fatty acids. The difference in carbon chain length may affect the reaction conditions of the proposed two-step process. The fuel properties of hydrocarbons produced from coconut and palm kernel oils may also differ from those produced from typical plant oils.

In this Chapter, therefore, hydrocarbon production as a renewable diesel from coconut

oil by the two-step process was investigated, and is compared with that from rapeseed oil. In addition, the fuel properties of the obtained renewable diesel from coconut oil were evaluated.

5.2 Materials and Methods

5.2.1 Experimental procedures

Renewable diesel production from coconut oil was conducted based on the previous study (Sugami et al. 2016). Prior to the experiment, a Pd/C catalyst (Pd/C = 5/95 (w/w), Nacalai Tesque, Inc.) was dried overnight at 105 °C, and then reduced in H₂ flow (15 ml/min) at 200 °C for 60 min.

5.2.1.1 Hydrolysis coupled with hydrogenation (hydrolysis/hydrogenation)

For the hydrolysis/hydrogenation reaction, 1.0 g of coconut oil (reagent grade, Nacalai Tesque, Inc.), 3.0 g of ion-exchanged water and 0.05g of Pd/C were placed in a 5 mL batch-type reaction vessel made of Inconel-625 (Saka & Kusdiana 2001) with Hastelloy balls (total volume: 0.2 ml) to agitate the mixture efficiently. The vessel was sealed, purged and pressurized to 5 MPa with H₂ gas using a gas-supplying system. Subsequently, the vessel was immersed into a molten salt bath preheated at 270 °C and agitated. After a designated treatment time, the vessel was moved into a water bath to quench the reaction.

The reaction mixture was removed from the vessel by its dissolution in tetrahydrofuran (THF, specially prepared reagent grade, Nacalai Tesque, Inc.) and sonicated for 30 min to detach products that had adsorbed on the catalyst surface. The catalyst was then removed by using a 0.45 µm micropore filter paper (Merck Millipore Co.). The obtained mixture was separated into THF and water phases, and the water phase, including glycerol, was removed. By removing THF from the THF phase with a rotary vacuum evaporator, a hydrolysis/hydrogenation product was obtained and weighed by using an electronic balance. The chemical composition of the product was determined by gas chromatography with a flame ionization detector (GC-FID), and the yield of fatty acids was estimated based on the weight of the product and its chemical composition.

5.2.1.2 Decarboxylation

The subsequent decarboxylation was conducted as the same manner as the hydrolysis/hydrogenation step. Approximately 0.8 g of the obtained products by hydrolysis/hydrogenation

was treated at 300 °C with 0.40 g of Pd/C, H₂ gas (1 MPa) and Hastelloy balls. Although H₂ is not essentially required for the decarboxylation reaction, sometimes it maintains the catalyst activity (Satyarthi et al. 2013). Therefore, H₂ was used in this study as in Chapter 4 (Sugami et al. 2016). After a designated reaction time, the obtained reaction mixture, which is expected to contain volatile hydrocarbons such as *n*-pentane (C₅), was taken out from the vessel by its dissolution in 50 ml of 2-propanol (extra pure prepared reagent grade, Nacalai Tesque, Inc.). To analyze the chemical composition of the product, the 2-propanol solution was centrifuged at 5,000 rpm for 10 min, and then 1.0 µl of the clear supernatant was immediately applied to the GC-FID analysis to prevent volatilization of short chain hydrocarbons. After that, the 2-propanol solution (approximately 50 ml) with the catalyst was sonicated for 30 min to detach a part of the products remained on the catalyst surface. The catalyst and 2-propanol were then removed by using the filter paper and a rotary vacuum evaporator, respectively. The product of decarboxylation was, thus, obtained and weighed by the electronic balance. During these purification steps, however, short chain hydrocarbons such as *n*-pentane were partially lost. Therefore, the absolute yield was estimated by adding the lost part, which was calculated from the chemical compositions and the weights before and after the purification

5.2.2 Analytical methods

The fatty acid composition of coconut oil was determined according to the Japan Oil Chemists' Society standard method (Japan Oil Chemists' Society 2013a). The products after the hydrolysis/hydrogenation and decarboxylation were analyzed by GC-FID (GC-2014, Shimadzu Co.). For the glycerides and hydrocarbons, CP-TAP CB for triglycerides (Agilent Technology; length, 25 m; diameter, 0.25 mm; thickness, 0.10 µm) was used as a column under the following conditions: injector temperature, 350 °C; detector temperature, 370 °C; column temperature, 30 °C (7 min), 30 °C → 80 °C (5 °C/min), 80 °C → 120 °C (10 °C/min), 120 °C → 230 °C (5 °C/min), 230 °C → 350 °C (27 °C/min), 350 °C (40 min); carrier gas, He; flow rate, 27.7 ml/min. For fatty acids and short chain hydrocarbons, CP-FFAP CB (Agilent Technology; length, 25 m; diameter, 0.32 mm; thickness, 0.30 µm) was used under the following conditions: injector temperature, 270 °C; detector temperature, 280 °C; column temperature, 50 °C (0.2 min), 50 °C → 150 °C (22 °C/min), 150 °C → 240 °C (6 °C/min), 240 °C (20 min); carrier gas, He; flow rate, 65.7 ml/min.

The fuel properties of the obtained renewable diesel were evaluated by using the

automated Pensky-Martens closed cup flash point tester (APM-7), the mini pour point tester (MPC-102), the automated cold filter plugging point tester (AFP-102) and the automatic kinematic viscosity measuring system (AKV-201). These measuring systems were made by Tanaka Scientific Co. Ltd. The density was determined according to the ASTM International's standard D1298 (ASTM International & ASTM 2012). In addition, the renewable diesel was blended with fossil diesel (#1 diesel of the Japanese Industrial Standard (JIS), Showa Shell Sekiyu K.K.) in various ratios, and their fuel properties were also evaluated.

5.3 Results and Discussion

Table 5-1 shows the fatty acid composition of coconut oil and the yields of the products that were obtained after hydrolysis/hydrogenation and subsequent decarboxylation. Coconut oil used in this study is composed of 94.7 mol% saturated fatty acids (C6 ~ C18) and 5.3 mol% unsaturated fatty acids (C18). Through this study, appropriate reaction conditions were evaluated for this coconut oil in the hydrolysis/hydrogenation and decarboxylation reactions as described in the following subsections.

Table 5-1 Fatty acid composition of coconut oil, and obtained yields of saturated fatty acids by hydrolysis/hydrogenation and saturated hydrocarbons by decarboxylation

Fatty acid composition of coconut oil (mol%)		Yield (mol%) ^{*1}					
		Saturated fatty acids			Saturated hydrocarbons		
		by hydrolysis/hydrogenation ^{*2}			by decarboxylation ^{*3}		
C6:0	0.8	0.6	(0.7)		C ₅ H ₁₂	0.3	(0.6)
C8:0	10.0	12.0	(13.1)		C ₇ H ₁₆	2.2	(4.2)
C10:0	6.6	7.6	(8.4)		C ₉ H ₂₀	2.8	(5.2)
C12:0	52.3	51.1	(56.0)		C ₁₁ H ₂₄	31.6	(59.2)
C14:0	16.7	10.7	(11.7)		C ₁₃ H ₂₈	9.9	(18.5)
C16:0	6.7	4.0	(4.4)		C ₁₅ H ₃₂	3.5	(6.5)
C18:0	1.6	4.3	(4.7)		C ₁₇ H ₃₆	3.1	(5.8)
C18:1	4.3	0.0				-	
C18:2	1.0	0.0				-	
Glycerides	0.0	0.9	(1.0)			0.0	
Total	100.0	91.2	(100.0)			53.3	(100)

^{*1}: Values in parentheses indicate mol% on total yield basis

^{*2}: 270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C for 60 min

^{*3}: 300 °C/ 1 MPa (H₂) with 0.40 g of Pd/C for 360 min

5.3.1 Hydrolysis/hydrogenation

Fig. 5-1 shows the saturated yield of fatty acids through the hydrolysis/hydrogenation of coconut oil in subcritical water at 270 °C/ 5 MPa under the presence of H₂ and Pd/C. Just for comparison, the data from rapeseed oil in previous study (Sugami et al. 2016) are shown in Fig. 5-1. The yield of saturated fatty acids increases slowly in coconut oil followed by a rapid increase, and then reached equilibrium after around 40 to 60 min. Such a time-dependence is considered due to the auto-catalytic effect of fatty acids revealed in a previous work (Minami & Saka 2006).

Under subcritical water conditions, triglycerides are hydrolyzed into fatty acids without any catalyst due to the high ionic product of water. In addition, once fatty acids are produced, they can also act as an acid catalyst and accelerate the hydrolysis reaction. Therefore, the reaction rate becomes faster with increase in fatty acid content. Regarding hydrogenation reaction, on the other hand, unsaturated fatty acids were not observed in the GC-FID chart, even after 20 min treatment. It indicates that the hydrogenation of unsaturated double bonds is faster than the hydrolysis and was completed within 20 min. Thus, an appropriate reaction time for the hydrolysis/hydrogenation was found to be 40 ~ 60 min under the given conditions. These trends are the same as rapeseed oil in Chapter 4 (Sugami et al. 2016), as shown in Fig. 5-1. Therefore, the difference in carbon chain length of fatty acid moieties does not affect the reaction conditions for the hydrolysis/hydrogenation step.

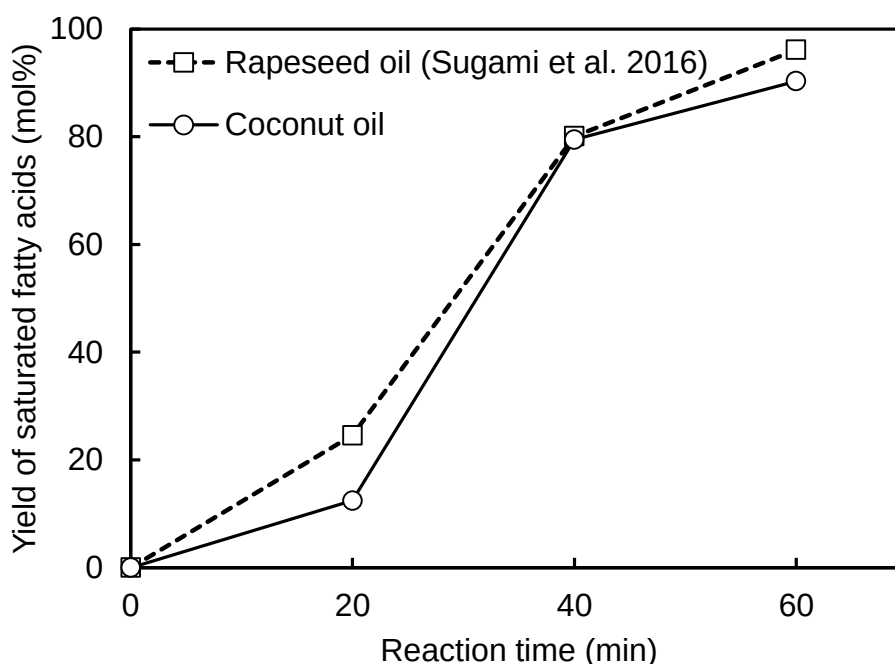


Fig. 5-1 Yields of saturated fatty acids from coconut oils by hydrolysis/hydrogenation at 270 °C/ 5 MPa (H₂) with 3.0 g of water and 0.05 g of Pd/C catalyst. Just for comparison, the data for rapeseed oil are shown

The yield of each saturated fatty acid product after 60 min treatment is shown in Table 1. Although 1.0 mol% of glycerides still remained as intermediate compounds, almost triglycerides were converted into saturated fatty acids with carbon numbers from C6 to C18. The total yield of fatty acids and glycerides are 91.2 mol%, and the remaining 8.8 mol% would probably be lost through the purification steps because no other product was visible on the GC-FID chart. The molar ratio upon the obtained product basis except the lost portion is shown in parentheses in Table 5-1. From this result, the molar ratio of the obtained saturated fatty acids seems to be close to the fatty acid composition of the coconut oil. For example, the sum of the C18 fatty acid moieties in coconut oil (18:0, 18:1 and 18:2) is 6.9 mol% (= 1.6 + 4.3 + 1.0), all of which is expected to convert into stearic acid (18:0) after the reaction. Actually, the yield of stearic acid is 4.7 mol%. It indicates that the reaction into saturated fatty acid has occurred selectively during the hydrolysis/hydrogenation step.

5.3.2 Decarboxylation

Fig. 5-2 shows the yields of saturated hydrocarbons after decarboxylation reaction at 300 °C/ 1 MPa (H₂) from the coconut oil-derived saturated fatty acids. The yield of hydrocarbons increases as the reaction time prolonged. It seems to be a typical first-order reaction, unlike the hydrolysis/hydrogenation reactions. Under the given conditions, 360 min was required for the complete conversion of fatty acids into hydrocarbons. It is approximately 3 times longer than in the case of rapeseed oil in the previous study (Sugami et al. 2016). This would be due perhaps to the difference in carbon chain length of the fatty acids. Actually, Ford *et al.* studied the decarboxylation of saturated fatty acids from C10 to C18 with Pd/C and showed that the shorter chain fatty acids require a longer reaction time because less shorter chain fatty acid adsorption occurs on the activated carbon compared with the longer chain fatty acids (Ford et al. 2012). This difference may be the reason why decarboxylation of fatty acids from coconut oil requires a longer time than that from rapeseed oil.

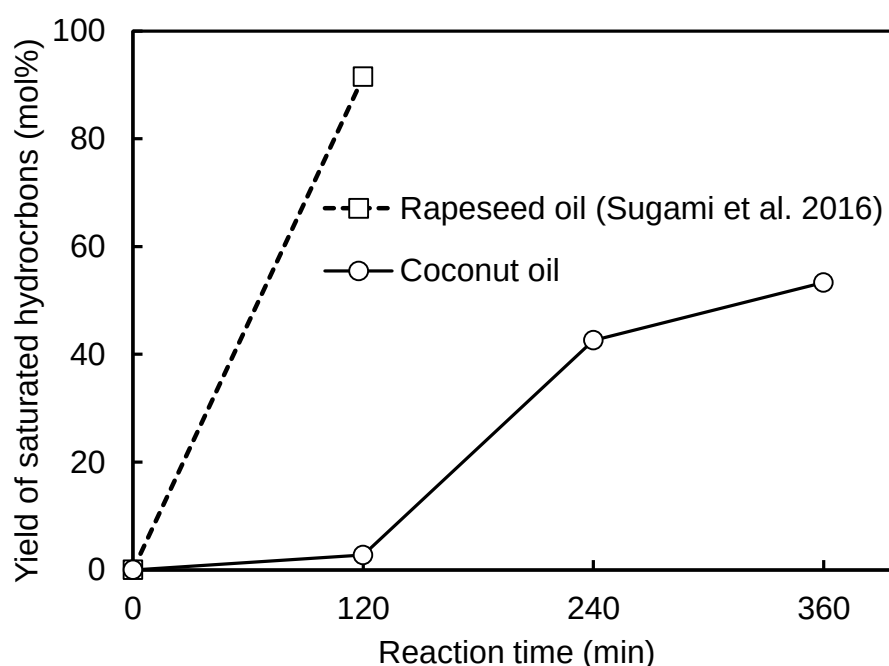


Fig. 5-2 Yields of saturated hydrocarbons from coconut oil-derived fatty acids by decarboxylation at 300 °C/ 1 MPa (H₂) with 0.45 g of Pd/C catalyst. Just comparison, the data for rapeseed oil are shown

The yield of each hydrocarbon after 360 min is shown in Table 5-1. The total yield of hydrocarbons is 53.3 mol% based on coconut oil, and no other product was visible in the GC-FID chart. The yields of long chain hydrocarbons with 13 or more carbons are nearly equal to those of the obtained fatty acids. On the other hand, the yields of short chain hydrocarbons with 11 or less carbons decrease. It is assumed that a recovery of short chain hydrocarbons is difficult due to their high volatility and decomposability.

To confirm the stability of the hydrocarbons as a product under the given conditions, 1.0 g of hydrocarbons (from Nacalai Tesque, Inc.) with 0.5 g of Pd/C was treated under the same decarboxylation condition (300 °C/ 1 MPa (H₂) for 360 min). The results are shown in Table 5-2. The recovery of *n*-undecane (C₁₁H₂₄) was 39.0 mol% although each recovery of C13 or more hydrocarbons reached over 80 mol% without any visible peaks in the GC-FID charts. Shorter chain hydrocarbons such as *n*-pentane (C₅H₁₂), *n*-heptane (C₇H₁₆) and *n*-nonane (C₉H₂₀) were undetectable under the same decarboxylation condition due to their high volatility. This indicates that shorter chain hydrocarbons may be easier to decompose into gaseous products. Therefore, the lost portion of 37.9 mol% (= 91.2 – 53.3) probably results from the purification and the decomposition of the products. In the case of rapeseed oil as feedstock, it has taken 120 min for completing the reaction, and the hydrocarbon yield has reached 91.5 mol% as shown in Fig. 5-2 for comparison (Sugami et al. 2016). The products from rapeseed oil were *n*-pentadecane (C₁₅H₃₂), *n*-heptadecane (C₁₇H₃₆) and *n*-nonadecane (C₁₉H₄₀), which are sufficiently stable under these reaction conditions. Hence, the high yield from rapeseed oil was maintained unlike that from coconut oil.

Table 5-2 Recovery of hydrocarbons as treated under the same decarboxylation conditions (300 °C/ 1 MPa (H₂) with Pd/C catalyst for 360 min)

Hydrocarbon	Recovery (mol%)
<i>n</i> -Heptadecane (C ₁₇ H ₃₆)	85.0
<i>n</i> -Pentadecane (C ₁₅ H ₃₂)	81.1
<i>n</i> -Tridecane (C ₁₃ H ₂₈)	86.1
<i>n</i> -Undecane (C ₁₁ H ₂₄)	39.0
<i>n</i> -Nonane (C ₉ H ₂₀)	-
<i>n</i> -Heptane (C ₇ H ₁₆)	-
<i>n</i> -Pentane (C ₅ H ₁₂)	-

-: undetectable under the same decarboxylation conditions due to volatile products

In Table 5-1, the values in parentheses indicate the molar ratio achieved with the obtained hydrocarbon basis by excluding the lost portion. Due to the loss of the short chain hydrocarbons, the molar ratio of hydrocarbons under C11 relatively decreases and is not constant in comparison with that of saturated fatty acids. In contrast with short chain hydrocarbons, the molar ratio of hydrocarbons over C9 increases and is as much as that of saturated fatty acids. Therefore, unlike rapeseed oil, the composition of hydrocarbon produced from coconut oil in this process could not be predicted from fatty acid composition of the feedstock triglycerides.

Besides, 0.9 mol% of glycerides that remains after hydrolysis/hydrogenation also decreases during the decarboxylation reaction and disappears after 360 min treatment as shown in Table 5-1. These intermediates must be converted into corresponding hydrocarbons through decarboxylation. In Chapter 4, it was confirmed that 1-monostearin was converted into *n*-heptadecane under the same conditions, and that even the reactivity was slightly low compared with stearic acid (Sugami et al. 2016). Therefore, the glycerides as a result of an incomplete reaction on the hydrolysis/hydrogenation are acceptable to some extent for the decarboxylation.

Consequently, coconut oil seems to be converted selectively into corresponding

hydrocarbons by the proposed two-step process; however, the yield was lower due to difficulties in recovering the shorter chain hydrocarbons.

5.3.3 Fuel properties of renewable diesel from coconut oil

In order to evaluate the fuel properties of the obtained hydrocarbons as renewable diesel, a model fuel was prepared by mixing purchased pure hydrocarbons (from Nacalai Tesque, Inc.) in the same hydrocarbon composition as in Table 5-1, because a large amount of the fuel is required for the testing of fuel properties. In this subsection, the prepared model fuel is referred simply to as “renewable diesel”.

Table 5-3 shows the evaluated fuel properties of the mixtures of renewable diesel and #1 fossil diesel in various volumetric ratios. The 100 vol% renewable diesel has a lower pour point and cold filter plugging point than those of 100 vol% fossil diesel, and satisfies the specification standard of the #1 fossil diesel in Japan (JIS K2204) (Japanese industrial standards committee 2007). Since the renewable diesel from coconut oil has many shorter chain hydrocarbons compared with the fossil diesel, such favorable cold-flow properties were achieved due to their low melting points. The melting point of *n*-undecane (-26 °C), which is the main component of the renewable diesel that was obtained from this study, affects these cold-flow properties significantly. In the case of renewable diesel from rapeseed oil, the cold-flow properties were poor because it was composed of long chain hydrocarbons, which have a high melting point (Sugami et al. 2016). Besides, the density also satisfies the specification. However, the values of flash point and kinematic viscosity of 100 vol% renewable diesel are outside of the standard specification because of the relatively low boiling points and viscosities of the shorter chain hydrocarbons compared with those from rapeseed oil, and the renewable diesel does not meet the standards. Therefore, these properties should be improved for its practical use.

Table 5-3 Fuel properties of obtained saturated hydrocarbons as renewable diesel blended with fossil diesel in various ratios compared with Japanese #1 diesel standard (JIS K2204)(Japanese industrial standards Committee. 2007)

Property	Ratio of renewable diesel ^{*1} to #1 fossil diesel (vol%)				#1 diesel standard
	100	40	30	0 ^{*2}	
Flash point (°C)	42	52	55	64	≥ 50
Pour point (°C)	-23	-16	-13	-8.0	≤ -2.5
Cold filter plugging point (°C)	-22	-10	-7	-5.0	≤ -1
Kinematic viscosity at 30 °C (mm ² /s)	1.6	2.5	2.7	3.5	≥ 2.7
Density at 15 °C (g/cm ³)	0.75	0.81	0.81	0.83	≤ 0.86

^{*1}: Renewable diesel was prepared by mixing pure hydrocarbons with the same molar ratio as in Table 5-1

^{*2}: Renewable diesel 0 vol% corresponds to fossil diesel 100 vol%

One solution is to blend the renewable diesel with fossil one for this purpose. As shown in Table 5-3, although 40 vol% renewable diesel still exceeds the limits of kinematic viscosity, 30 vol% one satisfies all these specifications. Therefore, the renewable diesel from coconut oil can meet all of the standard requirements when it is blended with fossil one in concentration 30 vol% or below.

5.4 Concluding Remarks

For hydrocarbon production from plant oils, conventional hydrotreatment and catalytic cracking are not really specific for product selectivity due to the relatively severe condition. In Chapter 4, a two-step process was developed, and an excellent yield and selectivity from rapeseed oil was achieved. However, the potential of some plant oils with short chain fatty acid moieties remained unclear. Therefore, the current study aimed to elucidate the effect of carbon chain length on the reaction conditions and fuel properties by using coconut oil as a feedstock.

As a result, triglycerides in coconut oil were successfully converted into saturated hydrocarbons as observed in rapeseed oil. However, the yield of shorter chain hydrocarbons decreased because of its decomposition. Compared with rapeseed oil, although the reaction time of the hydrolysis/hydrogenation step was the same, that of the decarboxylation took approximately three times longer to achieve a complete reaction under the same conditions. It can be concluded that plant oils with short chain fatty acid moieties, such as coconut and palm kernel oils, require a prolonged reaction time for decarboxylation to obtain hydrocarbons as renewable diesel even though a low recovery is achieved due to a loss of short chain hydrocarbons.

With regard to the fuel properties, the obtained renewable diesel exhibited good cold-flow properties, but the flash point and kinematic viscosity were out of the Japanese specification standard for fossil diesel. Such properties result from the presence of short chain hydrocarbons from coconut oil. To satisfy the specification standard, a blending of renewable diesel with fossil one was the simplest way. Consequently, the blended fuel in a concentration of 30 vol% or below satisfied all requirements in the specification standard. The potential for use of coconut oil as a feedstock for renewable diesel was proven by the proposed two-step process.

Chapter 6

Concluding Remarks

6.1 Conclusions

Biomass has been attracting attention as environment-friendly resource amid concerns of the depletion of fossil resources and global warming. To use biomass as energy, a conversion into an alternative diesel fuel from oil and fats is one of the widely applied methods.

Biodiesel generally means fatty acid methyl ester (FAME) produced by transesterification of triglycerides, which are main component of plant oils. Biodiesel has been mainly used in EU, US, and Southeast Asia. However, FAME is easily oxidized if it includes unsaturated double bonds (i.e. methyl linolate), which causes fuel degeneration. Additionally, a small amount of monoglyceride (MG) as intermediate through transesterification often remains in biodiesel. MG easily forms a precipitate due to its high melting point, which leads to clogging of fuel filters in districts with a cold climate. Moreover, MG has polymorphic crystalline forms such as α , β' and β , and each has different melting point ($\alpha < \beta' < \beta$). This fact might make the low-temperature properties of biodiesel more complicated. It is important to elucidate unclear points about the formation behavior of the precipitates.

On the other hand, the problems such as oxidation stability and low-temperature property of biodiesel is caused by the difference of chemical structure between FAME and fossil diesel, which is composed mainly of hydrocarbons. Therefore, hydrocarbon productions from plant oils with the hydrotreating and catalytic cracking are being researched. This hydrocarbon fuel is called as “renewable diesel” in order to distinguish it from biodiesel. However, there still remain some problems in these methods: it requires high temperature condition, and the selectivity of the products is not so high because the products include not only hydrocarbon, but also carboxylic acid and ketone. In addition, a carbon number distribution of the products varies.

Given things mentioned above, the elucidation of precipitate behavior and the prediction of biodiesel under the condition of low temperature were first investigated.

Besides, to solve the drawbacks of conventional biodiesel such as low-temperature properties, renewable diesel production process was proposed, which produces hydrocarbon from plant oils with hydrothermal hydrogenation and subsequent decarboxylation. An appropriate reaction condition was also discussed. Additionally, the fuel properties of the obtained renewable diesel were evaluated.

Generally, biodiesel contains a small number of monoglycerides as intermediate compounds, which have high melting points and often solidify and clog fuel filters. The prediction of the cold-flow property of biodiesel is of great importance for practical application. In Chapter 2, a thermodynamic study was conducted for mixtures of monoglycerides and fatty acid methyl esters. Temperatures of the solid–liquid equilibrium for the mixtures were measured by differential scanning calorimetry and visual observation, while the theoretical values were calculated using the modified UNIFAC model (Dortmund). The theoretical and experimental results were in good agreement, especially for binary mixtures of monoglycerides and methyl esters. The importance of monoglycerides on the cold-flow properties of biodiesel was determined, and the effects could be well described by the modified UNIFAC model (Dortmund).

The cloud point (CP) of biodiesel refers to the temperature at which precipitates begin to form and the fuel becomes cloudy when it is cooled. However, precipitates are often observed even at temperature higher than CP and they are known to consist largely of monoglycerides which has polymorphisms such as α , β' and β forms with different melting points ($\alpha < \beta' < \beta$). In Chapter 3, the monoglyceride polymorphism on low-temperature properties of biodiesel was studied. A series of model fuels were prepared by adding small amount of 1-monopalmitin to methyl oleate in various concentrations. As the result, the CPs of these samples were close to the temperature at which α form monopalmitin begins to crystallize. On the other hand, the precipitation obtained by standing at a constant temperature showed β' form monopalmitin. It implies that the concept of the generally accepted CP is not appropriate as an index of low-temperature property of biodiesel.

In Chapter 4, hydrocarbon (renewable diesel) production from rapeseed oil was studied with hydrothermal hydrogenation and subsequent decarboxylation in a batch-type reaction vessel. An appropriate reaction condition for hydrothermal hydrogenation was found to be 270 °C/ 5 MPa (H_2 pressure) with water and Pd/C

catalyst for 60 min, under which triglycerides were simultaneously hydrolyzed and hydrogenated into saturated fatty acids with a yield of 98.4 mol%. The obtained saturated fatty acids were then decarboxylated to hydrocarbons under the condition of 300 °C/ 1 MPa (H₂ pressure) with Pd/C for 120 min with a yield of 91.5 mol% on rapeseed oil. In addition, the composition of the obtained hydrocarbons almost corresponded to that of the fatty acid in rapeseed oil. Such a result indicates that the composition of hydrocarbons produced in this proposed process can be predicted from fatty acid composition of the feedstock triglycerides. By blending the obtained hydrocarbons from rapeseed oil with an adequate amount of fossil diesel, the blended fuel could satisfy the specification standard of fossil diesel in Japan.

In Chapter 5, hydrocarbon production from coconut oil for the use as a renewable diesel was studied by the two-step process, which was hydrolysis coupled with hydrogenation and subsequent decarboxylation. In the first step, coconut oil was treated in subcritical water at 270 °C/5 MPa (H₂) with a Pd/C catalyst for 60 min, in which triglycerides were hydrolyzed and hydrogenated into saturated fatty acids with a yield of 91.2 mol%. In the second step, the obtained saturated fatty acids were decarboxylated into hydrocarbons as renewable diesel at 300 °C/1 MPa (H₂) with Pd/C for 360 min. However, its yield was only 53.3 mol% based on coconut oil. Although the reaction time for the hydrolysis/hydrogenation of coconut oil was the same as that of rapeseed oil that was studied in Chapter 4, the complete decarboxylation conversion took three times longer. Such differences in reaction time and final hydrocarbon yield are related to the shorter coconut oil chains. The obtained renewable diesel was evaluated and their cold-flow properties were satisfactory, but the flash point and kinematic viscosity were out of the fossil diesel specification standard range, unlike those from rapeseed oil. The renewable diesel properties could be improved by blending an adequate amount of fossil diesel to satisfy the specification.

6.2 Prospects for Future Research

This dissertation covers the prediction and the behavior of biodiesel including monoglyceride under the condition of low temperature, and the hydrocarbon production method from plant oils. In terms of low-temperature properties of biodiesel, model biodiesel was used in this dissertation so that the low-temperature properties of an

actual biodiesel should be considered. Additionally, fossil diesel was blended with biodiesel for practical use. Therefore, the further step of this research is considering mixture of biodiesel and fossil diesel. Because these fuels include various components, it is necessary that the experiment use the corresponding materials with the same methods. Moreover, there still unclear points about the behavior of biodiesel under low-temperature condition, so that this field should be explored further.

Regarding to the hydrocarbon production as renewable diesel, the reaction conditions of the proposed process should be optimized. The process showed that the hydrocarbon was produced from rapeseed oil with high reactivity and yield. However, the obtained renewable diesel had poor low-temperature properties, which should be improved. A simple solution is blending the renewable diesel with petroleum diesel as mentioned in Chapter 4. Another way for improving properties is a reforming or isomerizing of the saturated *n*-hydrocarbon using acidity catalyst. Through this method, the linear hydrocarbon would be converted into a branched one. One of the features of the branched hydrocarbon is its higher melting point compared to the linear one. Additionally, petroleum diesel contains various types of hydrocarbons such as *n*-alkane, iso-alkane and cyclic hydrocarbon. Accordingly, if selective reaction is conducted for alternative diesel, more “drop-in” diesel will be obtained.

References

- Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE Journal*, 21(1), pp.116–128. Available at: <http://doi.wiley.com/10.1002/aic.690210115> [Accessed February 17, 2017].
- Alves, S.M., Mello, V.S., Medeiros, J.S., 2013. Palm and soybean biodiesel compatibility with fuel system elastomers. *Tribology International*, 65, pp.74–80.
- Dos Anjos, J.S., De Araujo Gonzalez, W., Lam, Y.L., Frety, R., 1983. Catalytic decomposition of vegetable oil. *Applied Catalysis*, 5(3), pp.299–308.
- Asakuma, Y., Kawanami, O., Maeda, K., Kuramochi, H., Fukui, K., 2011. Theoretical study of the transesterification of triglycerides to biodiesel fuel under various conditions. In *International Journal of Thermodynamics*. pp. 193–196.
- ASTM, 2006. ASTM D974 - 06 Standard Test Method for Acid and Base Number by Color-Indicator Titration.
- ASTM International, ASTM, 2012. *ASTM D1298-12b, Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*.
- Bajpai, D., Tyagi, V.K., 2006. Biodiesel: Source, Production, Composition, Properties and Its Benefits. *Journal of Oleo Science*, 55(10), pp.487–502.
- Bezergianni, S., Dimitriadis, A., 2013. Comparison between different types of renewable diesel. *Renewable and Sustainable Energy Reviews*, 21, pp.110–116. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1364032112007472> [Accessed March 5, 2014].
- Bezergianni, S., Dimitriadis, A., Kalogianni, A., Pilavachi, P. a, 2010. Hydrotreating of waste cooking oil for biodiesel production. Part I: Effect of temperature on product yields and heteroatom removal. *Bioresource technology*, 101(17), pp.6651–6. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/20395136> [Accessed March 6, 2014].
- Casanave, D., Duplan, J.-L., Freund, E., 2007. Diesel fuels from biomass. *Pure and Applied Chemistry*, 79(11), pp.2071–2081. Available at: <http://www.scopus.com/inward/record.url?eid=2-s2.0-36048985774&partnerID=tZ>

Otx3y1.

- Chandra, B.P., 1998. A critical review of biodiesel as a transportation fuel in Canada. *Air Pollution Prevention Directorate*.
- Chang, C.-C., Wan, S.-W., 1947. China's Motor Fuels from Tung Oil. *Industrial & Engineering Chemistry*, 39(12), pp.1543–1548. Available at:
<http://pubs.acs.org/doi/abs/10.1021/ie50456a011>.
- Chanthawong, A., Dhakal, S., 2015. Liquid Biofuels Development in Southeast Asian Countries: An Analysis of Market, Policies and Challenges. *Waste and Biomass Valorization*, 7(1), pp.157–173. Available at:
<http://link.springer.com/10.1007/s12649-015-9433-9>.
- Chapman, D., 1962. The Polymorphism of Glycerides. *Chemical Reviews*, 62(5), pp.433–456. Available at:
<http://pubs.acs.org/cgi-bin/doilookup/?10.1021/cr60219a003> [Accessed December 15, 2016].
- Chupka, G.M., Fouts, L., Lennon, J.A., Alleman, T.L., Daniels, D.A., McCormick, R.L., 2014. Saturated monoglyceride effects on low-temperature performance of biodiesel blends. *Fuel Processing Technology*, 118, pp.302–309. Available at:
<http://dx.doi.org/10.1016/j.fuproc.2013.10.002> [Accessed December 15, 2016].
- Chupka, G.M., McCormick, R.L., Chiu, G., 2011. Effect of saturated monoglyceride polymorphism on low-temperature performance of biodiesel. *Energy & Fuels*, 25, pp.398–405.
- Chupka, G.M., Yanowitz, J., Chiu, G., Alleman, T.L., McCormick, R.L., 2011. Effect of Saturated Monoglyceride Polymorphism on Low-Temperature Performance of Biodiesel. *Energy Fuels*, 25(4), p.398.
- Coutinho, J.A.P., Gonçalves, M., Pratas, M.J., Batista, M.L.S., Fernandes, V.F.S., Pauly, J., Daridon, J.L., 2010. Measurement and modeling of biodiesel cold-flow properties. In *Energy and Fuels*. pp. 2667–2674.
- Demirbas, A., 2007. Importance of biodiesel as transportation fuel. *Energy Policy*, 35(9), pp.4661–4670. Available at:
<http://linkinghub.elsevier.com/retrieve/pii/S0301421507001516> [Accessed January 20, 2014].
- Derr, E.L., Deal, C.H., 1969. Analytical Solutions of Groups: Correlation of Activity

- Coefficients Through Structural Group Parameters. *Inst. Chem. Eng. Symp. Ser.*, 32, p.44.
- Diesel, R., 1912. The Diesel Oil Engine, and Its Industrial Importance, Particularly for Great Britain. *Proc. Inst. Mech. Eng.*, pp.179–280. Available at: <http://doi.wiley.com/10.1111/j.1559-3584.1912.tb04624.x> [Accessed October 24, 2016].
- Do, P.T., Chiappero, M., Lobban, L.L., Resasco, D.E., 2009. Catalytic Deoxygenation of Methyl-Octanoate and Methyl-Stearate on Pt/Al₂O₃. *Catalysis Letters*, 130(1–2), pp.9–18. Available at: <http://link.springer.com/10.1007/s10562-009-9900-7> [Accessed March 6, 2014].
- Donnis, B., Egeberg, R.G., Blom, P., Knudsen, K.G., 2009. Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes. *Topics in Catalysis*, 52(3), pp.229–240. Available at: <http://link.springer.com/10.1007/s11244-008-9159-z> [Accessed February 10, 2014].
- Dunn, R.O., 2008. Crystallization Behavior of Fatty Acid Methyl Esters. *Journal of the American Oil Chemists' Society*, 85(10), pp.961–972. Available at: <http://link.springer.com/10.1007/s11746-008-1279-x> [Accessed January 9, 2017].
- Dunn, R.O., Bagby, M.O., 2015. Cold weather properties and performance of biodiesel. In G. Knothe, J. Kahl, & J. Van Gerpen, eds. *The biodiesel handbook*. 2nd ed. Illinois: AOCS Press, pp. 147–204.
- Dunn, R.O., Bagby, M.O., 1995. Low-temperature properties of triglyceride-based diesel fuels: Transesterified methyl esters and petroleum middle distillate/ester blends. *Journal of the American Oil Chemists' Society*, 72(8), pp.895–904.
- Dupain, X., Costa, D.J., Schaverien, C.J., Makkee, M., Moulijn, J. a., 2007. Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysis B: Environmental*, 72(1–2), pp.44–61. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S092633730600419X> [Accessed March 6, 2014].
- Ford, J.P., Immer, J.G., Lamb, H.H., 2012. Palladium Catalysts for Fatty Acid Deoxygenation: Influence of the Support and Fatty Acid Chain Length on Decarboxylation Kinetics. *Topics in Catalysis*, 55(3–4), pp.175–184. Available at:

- <http://link.springer.com/10.1007/s11244-012-9786-2> [Accessed January 31, 2014].
- Fredenslund, A., Jones, R.L., Prausnitz, J.M., 1975. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE Journal*, 21(6), pp.1086–1099. Available at: <http://doi.wiley.com/10.1002/aic.690210607> [Accessed January 9, 2017].
- Freedman, B., Pryde, E., Mounts, T., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists ...*, 61(10), pp.1638–1643. Available at: <http://link.springer.com/article/10.1007/BF02541649> [Accessed March 7, 2014].
- Fukuda, H., Kondo, A., Noda, H., 2001. Biodiesel fuel production by transesterification of oils. *Journal of bioscience and bioengineering*, 92(5), pp.405–16. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/23837337>.
- Gmehling, J., Li, J., Schiller, M.A.R.T.I.N., 1993. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res*, 32, pp.178–193.
- Gmehling, J., Lohmann, J., Jakob, A., Li, J., Joh, R., 1998. A Modified UNIFAC (Dortmund) Model. 3. Revision and Extension. *Industrial & Engineering Chemistry Research*, 37, pp.4876–4882. Available at: <http://dx.doi.org/10.1021/ie0108043%5Cnhttp://pubs.acs.org/doi/full/10.1021/ie0108043%5Cnhttp://pubs.acs.org/doi/pdfplus/10.1021/ie0108043> [Accessed February 17, 2017].
- Gong, S., Shinozaki, A., Shi, M., Qian, E.W., 2012. Hydrotreating of jatropha oil over alumina based catalysts. *Energy & Fuels*, (26), pp.2394–2399.
- Haseeb, A.S.M.A., Fazal, M.A., Jahirul, M.I., Masjuki, H.H., 2011. Compatibility of automotive materials in biodiesel: A review. *Fuel*, 90(3), pp.922–931.
- Huber, G.W., O'Connor, P., Corma, A., 2007. Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Applied Catalysis A: General*, 329, pp.120–129.
- Imahara, H., Minami, E., Saka, S., 2006. Thermodynamic study on cloud point of biodiesel with its fatty acid composition. *Fuel*, 85(12–13), pp.1666–1670. Available at: <http://www.sciencedirect.com/science/article/pii/S001623610600086X> [Accessed

March 7, 2014].

International Energy Agency, 2016. Energy Statistics. *Statistics*. Available at:

<http://www.iea.org/statistics/statisticssearch/>.

International Energy Agency, 2013. *Oil Information 2013*,

International Organization for Standardization, 1992. *Petroleum products --*

Determination of cloud point. ISO 3015:1992,

Japan Oil Chemists' Society, 2013a. *Fatty acids composition (FID temperature programmed gas chromatography)*,

Japan Oil Chemists' Society, 2013b. Standard Methods for the Analysis of Fats , Oils and Related Materials, 2.4.2.2-2013, Fatty acids composition (FID temperature programmed gas chromatography).

Japanese industrial standards committee, 2007. *JIS K2204, Diesel fuel*,

Japanese industrial standards Committee., 2007. *JIS K2204, Diesel fuel*.

Jin, F., Kawasaki, K., Kishida, H., Tohji, K., Moriya, T., Enomoto, H., 2007. NMR spectroscopic study on methanolysis reaction of vegetable oil. *Fuel*, 86(7–8), pp.1201–1207.

Katikaneni, S.P.R., Adjaye, J.D., Bakhshi, N.N., 1995. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *The Canadian Journal of Chemical Engineering*, 73(4), pp.484–497. Available at:

<http://onlinelibrary.wiley.com/doi/10.1002/cjce.5450730408/abstract%5Cnhttp://onlinelibrary.wiley.com/store/10.1002/cjce.5450730408/asset/5450730408 ftp.pdf?v=1&t=i673ouq5&s=ce16bbf2b148590f45dd8ce8bdb3e329de7b44f1> [Accessed September 25, 2016].

Kharina, A., Malins, C., Searle, S., 2016. *Biofuels Policy in Indonesia : Overview and Status Report*, Available at:

[http://www.theicct.org/sites/default/files/publications/Indonesia Biofuels Policy_ICCT_08082016.pdf](http://www.theicct.org/sites/default/files/publications/Indonesia%20Biofuels%20Policy_ICCT_08082016.pdf) [Accessed January 9, 2017].

Knothe, G., 2010. Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3), pp.364–373. Available at:

<http://linkinghub.elsevier.com/retrieve/pii/S0360128509000677> [Accessed January 26, 2014].

Knothe, G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid

- alkyl esters. *Fuel Processing Technology*, 86, pp.1059–1070. Available at: www.elsevier.com/locate/fuproc [Accessed December 2, 2016].
- Knothe, G., 2001. Historical Perspectives on Vegetable Oil-Based Diesel Fuels. *Inform*, 12(March 1912), pp.103–107.
- Knothe, G., Dunn, R.O., 2009. A Comprehensive Evaluation of the Melting Points of Fatty Acids and Esters Determined by Differential Scanning Calorimetry. *Journal of the American Oil Chemists' Society*, 86(9), pp.843–856. Available at: <http://link.springer.com/10.1007/s11746-009-1423-2> [Accessed January 9, 2017].
- Knothe, G., Sharp, C.A., Ryan, T.W., 2006. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. *Energy and Fuels*, 20(1), pp.403–408.
- Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S., Hidaka, J., 2008. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel*, 87(12), pp.2798–2806. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0016236107004589> [Accessed January 25, 2014].
- Krár, M., Kovács, S., Kalló, D., Hancsók, J., 2010. Fuel purpose hydrotreating of sunflower oil on CoMo/Al₂O₃ catalyst. *Bioresource technology*, 101(23), pp.9287–93. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/20655744> [Accessed March 6, 2014].
- Krawczyk, T., 1996. Biodiesel - Alternative Fuel Makes Inroads but Hurdles Remain. *Inform*, 7(8), pp.801–829.
- Kubička, D., Bejblová, M., Vlk, J., 2010. Conversion of vegetable oils into hydrocarbons over CoMo/MCM-41 catalysts. *Topics in Catalysis*, 53(3–4), pp.168–178.
- Kubička, D., Kaluža, L., 2010. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts. *Applied Catalysis A: General*, 372(2), pp.199–208. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0926860X09007431> [Accessed January 23, 2014].
- Kusdiana, D., Saka, S., 2001. Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol. *Journal of chemical engineering of Japan*, 34(3), pp.383–387. Available at: <http://cat.inist.fr/?aModele=afficheN&cpsidt=971019>

[Accessed March 6, 2014].

- Kusdiana, D., Saka, S., 2004. Two-Step Preparation for Catalyst-Free Biodiesel Fuel Production: Hydrolysis and Methyl Esterification. *Applied Biochemistry and Biotechnology*, 115(1–3), pp.0781–0792. Available at: <http://link.springer.com/10.1385/ABAB:115:1-3:0781> [Accessed January 9, 2017].
- Lappi, H., Alén, R., 2011. Pyrolysis of vegetable oil soaps - Palm, olive, rapeseed and castor oils. *Journal of Analytical and Applied Pyrolysis*, 91(1), pp.154–158. Available at: <http://dx.doi.org/10.1016/j.jaap.2011.02.003>.
- Larsen, B.L., Rasmussen, P., Fredenslund, A., 1987. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Industrial & Engineering Chemistry Research*, 26(3), pp.2274–2286.
- Lestari, S., Simakova, I., Tokarev, A., Mäki-Arvela, P., Eränen, K., Murzin, D.Y., 2008. Synthesis of Biodiesel via Deoxygenation of Stearic Acid over Supported Pd/C Catalyst. *Catalysis Letters*, 122(3–4), pp.247–251. Available at: <http://link.springer.com/10.1007/s10562-008-9457-x> [Accessed January 21, 2014].
- Lopes, J.C.A., Boros, L., Krähenbühl, M.A., Meirelles, A.J.A., Daridon, J.L., Pauly, J., Marrucho, I.M., Coutinho, J.A.P., Krähenbühl, M.A., Meirelles, A.J.A., Daridon, J.L., Pauly, J., Marrucho, I.M., Coutinho, J.A.P., 2008. Prediction of cloud points of biodiesel. *Energy and Fuels*, 22(2), pp.747–752.
- Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, Jr., J.G., 2005. Synthesis of Biodiesel via Acid Catalysis. *Industrial & Engineering Chemistry Research*, 44(14), pp.5353–5363. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie049157g>.
- Lutton, E.S., 1950. Review of the Polymorphism of Saturated Even Glycerides. *Journal of the American Oil Chemists Society*, 27(7), pp.276–281. Available at: <http://link.springer.com/10.1007/BF02634906> [Accessed January 9, 2017].
- Lutton, E.S., 1971. The phases of saturated 1-monoglycerides C14-C22. *Journal of the American Oil Chemists Society*, 48(12), pp.778–781.
- Lutton, E.S., Jackson, F.L., 1948. The Polymorphism of 1-Monostearin and 1-Monopalmitin. *Journal of the American Oil Chemists Society*, 70(7), pp.2245–2249.
- Ma, F., Hanna, M., 1999. Biodiesel production: a review. *Bioresource technology*, 70,

- pp.1–15. Available at:
<http://www.sciencedirect.com/science/article/pii/S0960852499000255> Viitattu
 17.8.2012 [Accessed March 7, 2014].
- Madsen, A.T., Ahmed, E.H., Christensen, C.H., Fehrmann, R., Riisager, A., 2011. Hydrodeoxygenation of waste fat for diesel production: Study on model feed with Pt/alumina catalyst. *Fuel*, 90(11), pp.3433–3438. Available at:
<http://linkinghub.elsevier.com/retrieve/pii/S0016236111003103> [Accessed
 February 10, 2014].
- Maher, K.D.D., Bressler, D.C.C., 2007. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*, 98(12), pp.2351–2368.
- Maier, W.F., Roth, W., Thies, I., Ragukschleyer, P., Maier, W.F., Roth, W., Thies, I., Schleyer, R., 1982. Gas Phase Decarboxylation of Carboxylic Acids. *Chem. Ber.*, 115, pp.808–812.
- Margules, M., 1895. Über die Zusammensetzung der gesättigten Dämpfe von Mischungen. *Sitzungsberichte der Kaiserliche Akademie der Wissenschaften Mathematisch-Naturwissenschaftliche Classe*, 104, pp.1243–1278.
- Marker, T.L., Kokayeff, P., Abdo, S.F., Baldiraghi, F., Sabantino, L.M.F., 2011. Production of Diesel Fuel From Biorenewable Feedstocks with Lower Hydrogen Consumption.
- Maruyama, T., Isao, N., Imamura, M., Okada, M., Matsumoto, T., Horisawa, M., Matsumoto, T., 1971. Study on Polymorphism of Monoglyceride. I. Transition of Crystal Modification of 1-Monolaurin, 1-monomyristin, 1-monopalmitin and 1-monostearin. *Journal of Japan Oil Chemists' Society*, 20, pp.395–402.
- Maruyama, T., Niiya, I., Imamura, M., Okada, M., Matsumoto, T., 1973. Study on Polymorphism of Monoglyceride . II. Thermodynamic Considerations on Transition. *Journal of Japan Oil Chemists' Society*, 22(2), pp.85–88.
- Maruyama, T., Niiya, I., Okada, M., Matsumoto, T., 1979a. Studies on Polymorphism of Monoglycerides. VIII. Phase Behaviour of Binary Monoglycerides Systems. *Journal of Japan Oil Chemists' Society*, 28(2), pp.100–105. Available at:
<http://joi.jlc.jst.go.jp/JST.Journalarchive/jos1956/28.100?from=CrossRef>
 [Accessed January 9, 2017].

- Maruyama, T., Niiya, I., Okada, M., Matsumoto, T., 1979b. Studies on Polymorphism of Monoglycerides. X. Transition of Crystal Modification of cis-Monounsaturated Monoglycerides. *Journal of Japan Oil Chemists' Society*, 28(7), pp.486–490. Available at: <http://joi.jlc.jst.go.jp/JST.Journalarchive/jos1956/28.486?from=CrossRef> [Accessed January 9, 2017].
- Matsuda, H., Kimura, H., Nagano, Y., Kurihara, K., Tochigi, K., Ochi, K., 2011. Solid-liquid equilibria in three binary mixtures containing diphenyl carbonate. *Journal of Chemical and Engineering Data*, 56(4), pp.1500–1505.
- Matsuoka, M., Ozawa, R., 1989. Determination of solid-liquid phase equilibria of binary organic systems by differential scanning calorimetry. *Journal of Crystal Growth*, 96(3), pp.596–604.
- Mikulec, J., Cvengroš, J., Joríková, L., Banič, M., Kleinová, A., 2010. Second generation diesel fuel from renewable sources. *Journal of Cleaner Production*, 18(9), pp.917–926. Available at: <http://www.sciencedirect.com/science/article/pii/S0959652610000296> [Accessed March 11, 2014].
- Minami, E., Saka, S., 2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel*, 85(17–18), pp.2479–2483. Available at: <http://www.sciencedirect.com/science/article/pii/S0016236106001475> [Accessed March 10, 2014].
- Monnier, J., Tourigny, G., Soveran, W.D., Wong, A., Hogan, N.E., Stumborg, M., Soveran, D.W., Wong, A., Hogan, E.N., Stumborg, M., 1998. Conversion of Biomass Feedstock To Diesel Fuel Additive. *United States Patent*, pp.1–10.
- Moser, B.R., 2009. Biodiesel production, properties, and feedstocks. *In Vitro Cellular & Developmental Biology - Plant*, 45(3), pp.229–266. Available at: <http://link.springer.com/10.1007/s11627-009-9204-z> [Accessed February 23, 2014].
- Murata, K., Liu, Y., Inaba, M., Takahara, I., 2010. Production of Synthetic Diesel by Hydrotreatment of Jatropha Oils Using Pt–Re/H-ZSM-5 Catalyst. *Energy & Fuels*, 24(4), pp.2404–2409. Available at: <http://pubs.acs.org/doi/abs/10.1021/ef901607t>

- [Accessed February 10, 2014].
- Neste Corporation, 2015. *Neste Renewable Diesel*,
 Organization of the Petroleum Exporting Countries, 2015. *World Oil Outlook*, Available
 at: <http://library.seg.org/doi/10.1190/1.1439163>.
- Ostwald, W., 1897. Studies on formation and transformation of solid materials. *Z. Phys. Chem.*, 22, pp.289–330. Available at:
http://www.hathitrust.org/access_use#pd-us-google [Accessed January 9, 2017].
- Rao, K., 1978. Production of hydrocarbons by thermolysis of vegetable oils. *US Patent 4,102,938*. Available at: <http://www.google.com/patents/US4102938> [Accessed March 11, 2014].
- Renewable Energy Policy Network for the 21st Century, 2016. *Renewables 2016 Global Status Report*, Paris.
- Renon, H., Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE Journal*, 14(1), pp.135–144. Available at: <http://doi.wiley.com/10.1002/aic.690140124> [Accessed February 17, 2017].
- Robles-Medina, A., González-Moreno, P. a, Esteban-Cerdán, L., Molina-Grima, E., 2009. Biocatalysis: towards ever greener biodiesel production. *Biotechnology advances*, 27(4), pp.398–408. Available at:
<http://www.ncbi.nlm.nih.gov/pubmed/19268517> [Accessed February 23, 2014].
- Saka, S., Kusdiana, D., 2001. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel*, 80(2), pp.225–231. Available at:
<http://www.sciencedirect.com/science/article/pii/S0016236100000831> [Accessed March 10, 2014].
- Santillan-Jimenez, E., Crocker, M., 2012. Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. *Journal of Chemical Technology & Biotechnology*, 87(8), pp.1041–1050. Available at: <http://doi.wiley.com/10.1002/jctb.3775> [Accessed February 16, 2014].
- Santillan-Jimenez, E., Morgan, T., Lacny, J., Mohapatra, S., Crocker, M., 2013. Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel. *Fuel*, 103, pp.1010–1017. Available at:
<http://linkinghub.elsevier.com/retrieve/pii/S0016236112006722> [Accessed March

- 6, 2014].
- Sarin, A., Arora, R., Singh, N.P., Sarin, R., Malhotra, R.K., Kundu, K., 2009. Effect of blends of Palm-Jatropha-Pongamia biodiesels on cloud point and pour point. *Energy*, 34(11), pp.2016–2021.
- Satyarthi, J.K., Chiranjeevi, T., Gokak, D.T., Viswanathan, P.S., 2013. An overview of catalytic conversion of vegetable oils/fats into middle distillates. *Catal. Sci. Technol.*, 3(1), pp.70–80. Available at: <http://xlink.rsc.org/?DOI=C2CY20415K> [Accessed February 10, 2014].
- Schwab, A.W., Bagby, M.O., Freedman, B., 1987. Preparation and properties of diesel fuels from vegetable oils. *Fuel*, 66(10), pp.1372–1378. Available at: <http://linkinghub.elsevier.com/retrieve/pii/0016236187901840>.
- Schwab, A.W., Dykstra, G.J., Selke, E., Sorenson, S.C., Pryde, E.H., 1988. Diesel Fuel from Thermal Decomposition of Soybean Oil. *Journal of the American Oil Chemists' Society*, 65(November), pp.1781–1786.
- Şenol, O.I., Viljava, T.R., Krause, A.O.I., 2005. Hydrodeoxygenation of aliphatic esters on sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalyst: The effect of water. *Catalysis Today*, 106(1–4), pp.186–189.
- Šimáček, P., Kubička, D., Šebor, G., Pospíšil, M., 2009. Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel. *Fuel*, 88(3), pp.456–460. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S001623610800416X> [Accessed February 19, 2014].
- Simakova, I., Rozmysłowicz, B., Simakova, O., Mäki-Arvela, P., Simakov, A., Murzin, D.Y., 2011. Catalytic Deoxygenation of C18 Fatty Acids Over Mesoporous Pd/C Catalyst for Synthesis of Biofuels. *Topics in Catalysis*, 54(8–9), pp.460–466. Available at: <http://link.springer.com/10.1007/s11244-011-9608-y> [Accessed March 6, 2014].
- Singh, B., Korstad, J., Sharma, Y.C., 2012. A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition. *Renewable and Sustainable Energy Reviews*, 16(5), pp.3401–3408. Available at: <http://dx.doi.org/10.1016/j.rser.2012.02.042>.
- Smith J.M., Van Ness, H.C., Abbott, M.M., 2005. *Introduction to chemical engineering thermodynamics* 7th ed., New York: McGraw-Hill. Available at:

- <http://highereducation.mheducation.com/sites/0073104450/index.html> [Accessed January 9, 2017].
- Snåre, M., Kubičková, I., Mäki-Arvela, P., Chichova, D., Eränen, K., Murzin, D.Y., 2008. Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. *Fuel*, 87(6), pp.933–945. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0016236107002840> [Accessed January 21, 2014].
- Snåre, M., Kubičková, I., Mäki-Arvela, P., Eränen, K., Murzin, D.Y., 2006. Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel. *Industrial & Engineering Chemistry Research*, 45(16), pp.5708–5715. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie060334i> [Accessed March 10, 2014].
- Sotelo-Boyás, R., Liu, Y., Minowa, T., 2010. Renewable diesel production from the hydrotreating of rapeseed oil with Pt/Zeolite and NiMo/Al₂O₃ catalysts. *Industrial & Engineering Chemistry Research*, pp.2791–2799. Available at: <http://pubs.acs.org/doi/abs/10.1021/ie100824d> [Accessed March 10, 2014].
- Sotelo-Boyás, R., Trejo-Zárraga, F., Jesus Hernandez-Loyo, F. de, 2012. Hydroconversion of Triglycerides into Green Liquid Fuels. In I. Karamé, ed. *Hydrogenation*. INTECH, pp. 187–216. Available at: <http://dx.doi.org/10.5772/48710%5Cnhttp://www.intechopen.com/books/hydrogenation/hydroconversion-of-triglycerides-into-green-liquid-fuels> [Accessed March 10, 2014].
- Su, Y.C., Liu, Y.A., Diaz Tovar, C.A., Gani, R., 2011. Selection of prediction methods for thermophysical properties for process modeling and product design of biodiesel manufacturing. *Industrial and Engineering Chemistry Research*, 50(11), pp.6809–6836.
- Sugami, Y., Minami, E., Saka, S., 2016. Renewable diesel production from rapeseed oil with hydrothermal hydrogenation and subsequent decarboxylation. *Fuel*, 166, pp.376–381.
- Tang, H., De Guzman, R.C., Salley, S.O., Ng, K.Y.S., 2008. Formation of insolubles in palm oil-, yellow grease-, and soybean oil-based biodiesel blends after cold soaking at 4 °C. *JAOCs, Journal of the American Oil Chemists' Society*, 85(12), pp.1173–1182.

- Tani, H., Makoto, S., Haga, H., Fujimoto, K., 2011. Development of Direct Production Process of Diesel Fuel from Vegetable Oils. *Journal of the Japan Institute of Energy*, 90, pp.466–470. Available at:
<http://doi.wiley.com/10.1046/j.1365-2559.2002.14891.x>.
- Tani, H., Shimouchi, M., Haga, H., Fujimoto, K., 2011. Development of Direct Production Process of Diesel Fuel from Vegetable Oils. *Journal of the Japan Institute of Energy*, 90(5), pp.466–470. Available at:
<http://joi.jlc.jst.go.jp/JST.JSTAGE/jie/90.466?from=CrossRef> [Accessed January 9, 2017].
- Taufiqurrahmi, N., Bhatia, S., 2011. Catalytic cracking of edible and non-edible oils for the production of biofuels. *Energy & Environmental Science*, 4(4), p.1087. Available at: <http://xlink.rsc.org/?DOI=c0ee00460j> [Accessed January 9, 2017].
- Twaiq, F.A., Zabidi, N.A.M., Bhatia, S., 1999. Catalytic Conversion of Palm Oil to Hydrocarbons: Performance of Various Zeolite Catalysts. *Industrial & Engineering Chemistry Research*, 38(9), pp.3230–3237. Available at:
<http://pubs.acs.org/doi/abs/10.1021/ie980758f> [Accessed January 9, 2017].
- Wang, W.C., Thapaliya, N., Campos, A., Stikeleather, L.F., Roberts, W.L., 2012. Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. *Fuel*, 95, pp.622–629.
- Watanabe, M., Iida, T., Inomata, H., 2006. Decomposition of a long chain saturated fatty acid with some additives in hot compressed water. *Energy Conversion and Management*, 47(18–19), pp.3344–3350.
- Weidlich, U., Gmehling, J., 1987. A modified UNIFAC Model. 1. Prediction of VLE, hE, and y^∞ . *Industrial & Engineering Chemistry Research*, 26(8), pp.1372–1381.
- Wilson, G.M., Deal, C.H., 1962. Activity Coefficients and Molecular Structure. Activity Coefficients in Changing Environments-Solutions of Groups. *Ind. Eng. Chem. Fundamen*, 1(1), pp.20–23.
- Yaakob, Z., Narayanan, B.N., Padikkaparambil, S., Unni K., S., Akbar P., M., 2014. A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews*, 35, pp.136–153. Available at:
<http://linkinghub.elsevier.com/retrieve/pii/S1364032114002275> [Accessed March 4, 2017].

- Yoshimoto, Y., Kinoshita, E., 2009. Applied technology of vegetable oils for diesel engines — Use of biodiesel fuel —. *Journal of the combustion society of japan*, 51(156), pp.121–128.
- Zambiasi, R.U.I.C., Przybylski, R., Zambiasi, M.W., Mendonça, C.B., 2007. FATTY ACID COMPOSITION OF VEGETABLE OILS AND FATS. *Boletim do Centro de Pesquisa de Processamento de Alimentos*, 25(1), pp.111–120.

Acknowledgements

First of all, I would like to express my deepest and sincerest gratitude to Prof. Shiro Saka, Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University for his excellent guidance and perpetual encouragement throughout my research. His generous and patient instruction and his unwavering support and belief allowed me to overcome difficulties of my research and encourage my willingness to accomplish it.

I would like to express my high appreciations to Prof. Masahiro Shioji, Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University and Associate Prof. Haruo Kawamoto, Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University for their valuable evaluations, suggestions and comments to the betterment of my study.

I would like to gratefully thank Assistant Professor Eiji Minami, Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University for his essential and patient advices and helps. Without his guidance and patient help, this dissertation would not have been possible.

I also convey my appreciation to Mr. Shinichiro Yoshidomi, a Master course graduate student in Saka laboratory. His collaborative work with him has been a great contribution to Chapter 2 of this dissertation.

I would like to thank Mr. Hitoshi Hayashi and Ms. Noriko Shisa, Material Enginnering Division, Toyota Motor Corporation for their collaborative work and financial support. Their supports and comments always inspired me.

I warmly thank the Saka laboratory's secretary, Ms. Rie Nakanishi for all the assistances.

My research has been started with tutorship of previous seniors of the biodiesel group, Dr. Zul Ilham and Dr. Fadjar Goembira. I am deeply grateful them. I would like to thank Ms. Zan Win Moh Moh Phoo, Mr. Sakditat Chaimusig, Mr. Asif Aunillah and Ms. Kiky Corneliasari Sembiring.

I also thank all the members of the Saka's laboratory for their wonderful support. Especially, I would like to thank Dr. Nattanon Phaiboonsilpa, Dr. Mohd Asmadi, Dr.

Harifara Rabemanolontsoa, Dr. Pramila Tamunaidu, Dr. Rosnah Abdullah, Ms. Asuka Fukutome, Mr. Yu Nakahara, Mr, Nguyen Van Dung, Mr. Masatsugu Takada and Mr. Rui Niu.

To my family, for always being kind to me and finally, to friends and all who have contributed directly or indirectly to the production in this dissertation which names are not specifically mentioned, thank you very much.

Yuitsu Sugami

March 4, 2017

List of Publications

Applied Patent

1. Inventor: Noriko Shisa, Hitoshi Hayashi, Shiro Saka, Eiji Minami, Yuitsu Sugami, Shinichiro Yoshidomi (2016) Applicant: Toyota Motor Corporation, Kyoto University, Patent application 2016-151206, August 1, 2016.

Original Papers

2. Yuitsu Sugami, Eiji Minami, Shiro Saka (2016) Renewable diesel production from rapeseed oil with hydrothermal hydrogenation and subsequent decarboxylation, *Fuel* **166**: 376-381 (DOI:10.1016/j.fuel.2015.10.117)
3. Yuitsu Sugami, Eiji Minami, Shiro Saka (2017) Hydrocarbon production from coconut oil by hydrolysis coupled with hydrogenation and subsequent decarboxylation, *Fuel* **197**: 272-276 (DOI: 10.1016/j.fuel.2017.02.038)
4. Shinichiro Yoshidomi, Yuitsu Sugami, Eiji Minami, Noriko Shisa, Hitoshi Hayashi, Shiro Saka (2016) Predicting solid–liquid equilibrium of fatty acid methyl ester and monoglyceride mixtures as biodiesel model fuels, *Journal of the American Oil Chemists' Society* (under review)
5. Yuitsu Sugami, Shinichiro Yoshidomi, Eiji Minami, Noriko Shisa, Hitoshi Hayashi, Shiro Saka (2016) The effect of monoglyceride polymorphism on low-temperature properties of biodiesel model fuel, *Journal of the American Oil Chemists' Society* (under review)

Abstracts and Proceedings of International Conferences

6. Yuitsu Sugami, Eiji Minami, Shiro Saka (2015) Renewable diesel production from rapeseed oil by hydrolysis/hydrogenation in subcritical water and decarboxylation, *11th International Symposium on Supercritical Fluids (ISSF 2015)*, P-115 (Poster), October 12, 2015, Seoul, Korea
7. Yuitsu Sugami, Eiji Minami, Shiro Saka (2015) Renewable diesel production

- from plant oils by hydrothermal hydrogenation and decarboxylation, *The 2015 International Chemical Congress of Pacific Basin Societies (Pacifichem 2015)*, ENRG-574 (Poster), December 17, 2015, Honolulu, USA
8. Shinichiro Yoshidomi, Yuitsu Sugami, Eiji Minami, Noriko Shisa, Hitoshi Hayashi, Shiro Saka (2017) Prediction of the solidification temperature of biodiesel model fuel studied with the solid-liquid equilibrium, *6th International Conference on Biorefinery (ICB2017)*, OB4 (Oral), January 19, 2017, Christchurch, New Zealand
 9. Yuitsu Sugami, Shinichiro Yoshidomi, Eiji Minami, Noriko Shisa, Hitoshi Hayashi, Shiro Saka (2017) The effect of monoglyceride polymorphism on low-temperature properties of biodiesel fuel, *6th International Conference on Biorefinery (ICB2017)*, OA11 (Oral), January 19, 2017, Christchurch, New Zealand

Abstracts and Proceedings of Domestic Conferences

10. Yuitsu Sugami, Eiji Minami, Shiro Saka (2014) Drop-in Diesel Production from Papeseed Oil by Hydrothermal Hydrogenation and Decarboxylation, Proceedings of the 23th Annual Meeting of the Japan Institute of Energy, 3-11-2 (Oral), July 20, 2014, Fukuoka, Japan, 146-147.
11. Yuitsu Sugami, Eiji Minami, Shiro Saka (2015) Hydrocarbon Production from Plant Oils with Hydrothermal Hydrogenation and Decarboxylation, Proceedings of the 24th Annual Meeting of the Japan Institute of Energy, 3-7-1 (Oral), August 4, 2015, Sapporo, Japan, 110-111.
12. Yuitsu Sugami, Shinichiro Yoshidomi, Eiji Minami, Shiro Saka, Noriko Shisa, Hitoshi Hayashi (2016) The effect of monoglyceride polymorphism on low-temperature fuel properties of biodiesel, Proceedings of the 25th Annual Meeting of the Japan Institute of Energy, 3-8-3 (Oral), August 10, 2016, Tokyo, Japan, 112-113.
13. Shinichiro Yoshidomi, Yuitsu Sugami, Eiji Minami, Shiro Saka, Noriko Shisa, Hitoshi Hayashi (2016) Prediction of the solidification temperature of biodiesel

based on the solid-liquid equilibrium, Proceedings of the 25th Annual Meeting of the Japan Institute of Energy, 3-8-4 (Oral), August 10, 2016, Tokyo, Japan, 114-115.