

**PRODUCTION OF HYDROCARBONS FROM PLANT OIL
FOR RENEWABLE GASOLINE AND DIESEL FUELS**

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Chapter 1 Introduction

1.1 Global energy overview

Global energy consumption in 2015 was 13.6 Mtoe (Million tonnes of oil equivalent) and the transport sector accounted for 29 % [1]. About 96 % of the transport sector's energy came from fossil fuels (coal, oil and natural gas), while renewable energy accounted for only 3.1 % [1]. The breakdown of renewable energy was 1.6 % from bioethanol, 0.8 % from biodiesel, 0.4 % from other liquid biofuels and 0.3 % from renewable electricity. Additionally, the current global demand and future projection for petroleum products are shown in Figure 1-1 [2]. Gasoline and diesel fuels occupy the most abundant part of transportation fuels.

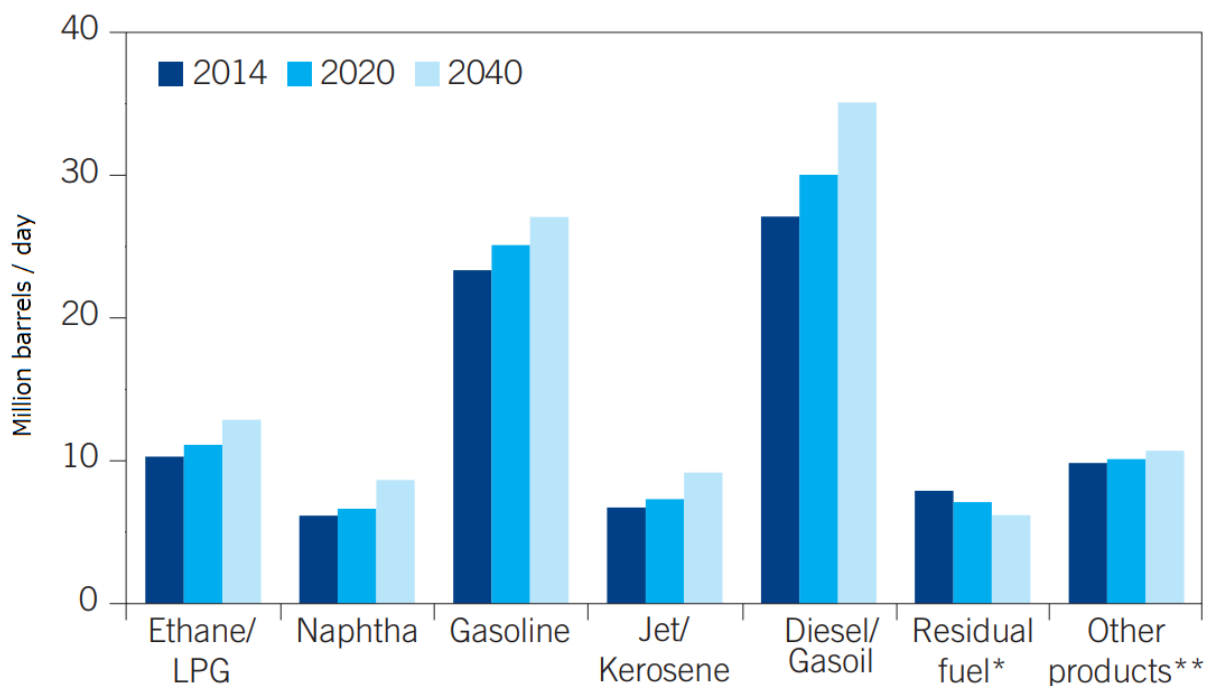


Figure 1-1 Global demand for petroleum products in 2014, 2020, and 2040 based on Organization of the Petroleum Exporting Countries [2].

At the end of 2015, the world reserves of fossil resources were estimated about 1700 billion barrels of oil, 187 trillion cubic meters (tcm) of natural gas and 892 billion tons of coal. Their reserves-to-production (R/P) ratios were estimated to be 50.7, 52.8 and 114 years, respectively [3]. Due to this energy security problem, the development of renewable energy gets more attention.

Several factors boost the prospect of renewable energy, such as the fluctuation of oil prices, the environmental issues related to fossil fuel, energy security and strong government incentives. Fossil fuel is not distributed evenly around the world; that is why the fluctuation in oil prices demonstrates the impact of political, social and military issues to many countries, especially the world source suppliers for oil. Besides, environmental concerns are mostly related to air pollution and global warming. The use of fossil fuels harms the environment by releasing CO₂, which is the most abundant greenhouse gas (GHG). The continuous GHG emissions will cause further warming and irreversible climate change. In term of energy security, renewable energy can enhance energy availability by reducing the dependence on energy imports. Renewable energy is more widely distributed and its use for energy source can be located close to end-users. In order for renewable energy to grow more rapidly, some countries established energy policies to give incentives for renewable energy production, such as low-interest loans, tax exemption and price incentives [4].

1.2 Plant oils for biofuel

The most popular biomass-based liquid fuels to replace petroleum-based fuels are biofuels, such as bioethanol and biodiesel. Biodiesel mainly refers to fatty acid methyl esters (FAME). Among the biomass, plant oils attract high interest for renewable energy sources

because they are naturally renewable and environmentally friendly. The major component in plant oils is triglycerides, a triester of one glycerol and three fatty acids (

Figure 1-2), which have similar carbon chains to petroleum-based fuels. There are more than 1000 possible structures for fatty acids due to the differences in carbon chain length, the number of unsaturated double bonds, and their positions. However, over 80 % of fatty acids in nature are in the form of palmitic, stearic, oleic and linoleic acids [5]. Many kinds of plant oils are available for food and biofuel industries. However, there are not many types of plant oils that meet the requirements for industrial use, such as high oil content and well-structured supply chains. Plant oils for food sources, such as rapeseed, sunflower, soybean, oil palm and coconut, have been used for biofuel production [6]. However, the rapid population growth worldwide and the extensive human consumption of edible oils have caused numerous problems, such as the global imbalance in the food supply and market demand [7]. In addition, the large-scale expansion of oil crop plantations has caused deforestation and destruction of the ecosystem. Furthermore, the significantly high demand for edible oils as food competes with its high demand for biofuels production, which have led to increases in the global price for plant oils. Therefore, non-edible oils have potential as feedstocks for biofuel production.

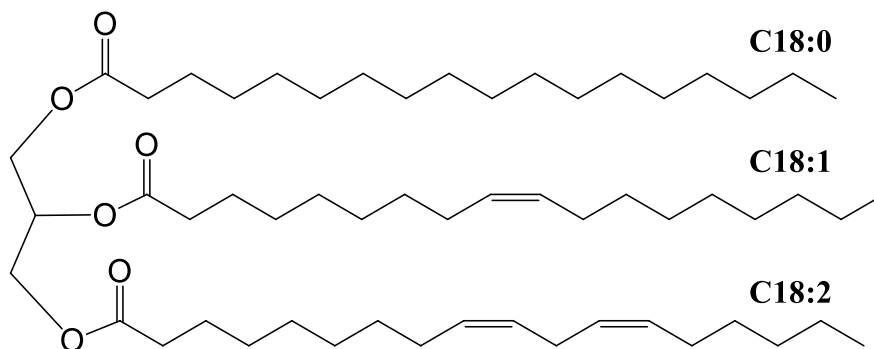


Figure 1-2 Triglyceride composed of stearic (C18:0), oleic (C18:1) and linoleic (C18:2)

acids.

Non-edible plant oils for biofuel production overcomes many problems, such as food-versus-fuel, environmental, and economic issues [8]. The presence of some toxic components in non-edible plant oils makes them unsuitable for human consumption. Moreover, non-edible plant oils are expected to be cultivated in unproductive lands and degraded forests [9].

1.2.1 Plant oil yield

The feedstock for biofuel production depends on the availability of an ample amount of oil in a particular region. Therefore, different countries can use different plant oils as raw materials to produce biofuels. The critical factor in determining the suitability of a feedstock for biofuel production is its oil yield; therefore, plant oils with higher yields are preferable.

Table 1-1 shows the oil yield and content in various edible and non-edible plant oils. In terms of edible plant oils, the oil yields range between 147 and 5,000 kg oil per hectare (kg/ha). The oil palm (*Elaeis guineensis*) [10] gave the highest oil yield with 5,000 kg/ha, followed by coconut (*Cocos nucifera*) [10] and walnut (*Juglans regia*) [11], which can produce 2,260 and 2,160 kg/ha oil yields, respectively. Table 1-1 includes other edible plant oils that can be considered for biofuels feedstock. Plant oils are found in large amounts in seeds and occasionally in the kernel part for almost all edible plant oils. Among them, palm oil is highly contained in both seed and kernel parts with oil contents of 30–60 and 44–65 wt%, respectively [8, 12]. These palm oils are mainly available in Malaysia and Indonesia, while coconut oil is available in the Philippines, soybean (*Glycine max*) oil is commonly available in the United States, and rapeseed (*Brassica napus*) and sunflower (*Helianthus annuus*) oils are widely available in many European countries [13].

Table 1-1 Oil yield and content in various edible and non-edible plant oils.

Plant	Oil yield (kg/ha)	Oil content (wt%)		References
		Seed	Kernel	
<u>Edible oils</u>				
Almond (<i>Prunus dulcis</i>)	1,500	55	-	[14, 15]
Canola (<i>Brassica campestris</i>)	1,190	38–45	-	[12, 16]
Cashew (<i>Anacardium occidentale</i>)	148	43–50	11.8	[10, 17]
Coconut (<i>Cocos nucifera</i>)	2,260	-	65–75	[10, 16]
Corn (<i>Zea mays</i>)	147	40–55	-	[10, 14, 16, 18]
Cotton (<i>Gossypium hirsutum</i>)	273	15–25	-	[10, 16]
Hazelnut (<i>Corylus avellana</i>)	405	-	51.4–75.1	[10, 19]
Hemp (<i>Cannabis sativa</i>)	305	30–35	-	[10, 20]
Jojoba (<i>Simmondsia chinensis</i>)	1,528	43–49	-	[10, 12, 21]
Oil palm (<i>Elaeis guineensis</i>)	5,000	30–60	44–65	[8, 10, 12]
Peanut (<i>Arachis hypogaea</i>)	890	36–56	-	[10, 14]
Pumpkin (<i>Cucurbita pepo</i>)	449	31.6	-	[22]
Rapeseed (<i>Brassica napus</i>)	1,000	38–46	-	[8, 10, 12]
Safflower (<i>Carthamus tinctorius</i>)	665	17.5–32	-	[10, 14, 23]
Sesame (<i>Sesamum indicum</i>)	585	48.5–60	-	[10, 24, 25]
Soybean (<i>Glycine max</i>)	375	16–22	-	[10, 14, 16]
Sunflower (<i>Helianthus annuus</i>)	800	25–50	-	[10, 12, 14]
Walnut (<i>Juglans regia</i>)	2,160	54.2–72.2	-	[11, 14]
<u>Non-edible oil</u>				
Castor (<i>Ricinus communis</i>)	1,188	45–53	-	[8, 10, 12, 14]
Country almond (<i>Terminalia catappa</i>)	-	49–57.5	-	[26]
Croton (<i>Croton tiglium</i>)	900	30–45	50–60	[14]

Table 1-1 Oil yield and content in various edible and non-edible plant oils. (continued)

Plant	Oil yield (kg/ha)	Oil content (wt%)		References
		Seed	Kernel	
Cuphea (<i>Cuphea painter</i>)	144–446	10–39.5	-	[27, 28]
Desert date (<i>Balanites aegyptiaca</i>)	1,816	36–47	-	[14]
Ethiopian mustard (<i>Brassica carinata</i>)	481	42	2.2–10.8	[14, 29]
Green algae (<i>Botryococcus braunii</i>)	>15,000	25–75*	-	[30]
Jatropha (<i>Jatropha curcas</i>)	1,590	30–50	45–60	[10, 14, 16, 31, 32]
Kapok (<i>Ceiba pentandra</i>)	1,167	28.7	-	[33]
Karanja (<i>Pongamia pinnata</i>)	225–2,250	25–50	30–50	[12, 14, 34]
Kokum (<i>Garcinia indica</i>)	570	45–45.5	-	[28, 35]
Kusum (<i>Schleichera triguga</i>)	500–800	-	55–70	[14, 28]
Linseed (<i>Linum usitatissimum</i>)	402	28–44	-	[10, 16, 28]
Mahua (<i>Madhuca indica</i>)	3,621	35–50	50	[12, 14]
Milkweed (<i>Asclepias syriaca</i>)	1,100	20–25	-	[12, 14]
Moringa (<i>Moringa oleifera</i>)	1,230	33–41	2.9	[36]
Nahor (<i>Mesua ferrea</i>)	-	58–75	-	[14]
Neem (<i>Azadirachta indica</i>)	2,670	20–30	25–45	[36]
Oleander (<i>Thevetia peruviana</i>)	1,575	8.41	60–67	[36, 37]
Rubber (<i>Hevea brasiliensis</i>)	80–120	40–60	40–50	[8, 36]
Sea mango (<i>Cerbera odollam</i>)	-	54	-	[38]
Soapnut (<i>Sapindus mukorossi</i>)	-	51.8	-	[31]
Sugar apple (<i>Annona squamosa</i>)	314	15–23	-	[14, 39]
Syringa (<i>Melia azedarach</i>)	-	10	-	[36]
Tobacco (<i>Nicotiana tabacum</i>)	100	30–43	-	[12]
Tung (<i>Aleurites fordii</i>)	790	16–40	-	[10, 12, 14]

* In the cell.

Regarding the non-edible plant oils in Table 1-1, except for green algae (*Botryococcus braunii*), the oil yields range between 80 and 3,621 kg/ha. Mahua (*Madhuca indica*) [12, 14] has the highest oil yield of 3,621 kg/ha, followed by neem (*Azadirachta indica*) [36], karanja (*Pongamia pinnata*) [34], jatropha (*Jatropha curcas*) [10, 32], which can produce 2,670; 2,250; and 1,590 kg/ha, respectively. Among these non-edible plant oils, jatropha is the most studied feedstock for producing biofuels. It is a fast-growing tree capable of producing high amounts of oil from its seed (30–50 wt%) and kernel (45–60 wt%) in tropical and semitropical regions, and even on marginal land [40–44]. Jatropha is originally from South America, but it has long spread throughout Africa and Asia. Mahua and karanja grow in India and have been successfully introduced to humid, tropical regions of Australia, New Zealand, China, and the USA [28]. Neem is native to India, Pakistan, and Sri Lanka, and it can grow in almost all kinds of soils including clay, saline, alkaline, and even dry soils [40, 45]. Many non-edible plant oils are extracted from both seed and kernel parts.

The latest research on biofuel production from plant oils and microalgae have attracted considerable interest worldwide. As a non-edible plant oil, microalgae are superior to other plant oils in its high growth rates, short maturity, high lipid productivity, and ability to cultivate on marginal and nonarable land areas [30, 46, 47]. The lipid content of several microalgae species may exceed 70% of dry weight [48]. For example, *Botryococcus braunii*, one of the green algae, has high oil productivity, which is more than 15,000 kg/ha and the oil content of its cells can range from 25 to 75 dry wt% (Table 1-1). However, oil extraction from microalgae is tedious and expensive, involving high energy consumption [40, 45], which is a crucial reason why the production of biofuels from microalgae has not yet entered the commercial stage [49].

1.2.2 Plant oil composition

Feedstock characteristics, such as fatty acid composition, are other important criteria to determine the suitability of plant oils for producing biofuels. The oil composition will determine the type of production process and the properties of resultant biofuels.

Fatty acid moieties in plant oils are categorized into saturated and unsaturated fatty acids. Unsaturated fatty acids have one or more double bonds between their carbon atoms. The fatty acid composition of various types of edible and non-edible plant oils are shown in Table 1-2. Fatty acids are often abbreviated by using the number of carbon atoms, followed by a colon and the number of double bonds as shown in parentheses in Table 1-2.

The type of fatty acids and their composition depend on the plant species and their growth conditions. The major fatty acids in both edible and non-edible plant oils are mostly similar, except for coconut [50], castor (*Ricinus communis*) [12], and tung (*Aleurites fordii*) [16] oils, whose major fatty acids are palmitic, stearic, oleic, and linoleic acids. Coconut oil has the highest composition of lauric acid (47.5–52.0 wt%) [50], while castor oil has a special fatty acid of an unsaturated ricinoleic acid (86–90 wt%) [12] and tung oil has a high content of trienoic α -eleostearic acid (84 wt%) [16].

Table 1-2 Fatty acid compositions for various edible and non-edible plant oils.

Plant	Decanoic (C10:0)	Lauric (C12:0)	Tetradecanoic (C14:0)	Palmitic (C16:0)	Palmitoleic (C16:1)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)	Arachidic (C20:0)	Eicosenoic (C20:1)	Behenic (C22:0)	Special	Reference
<u>Edible oil</u>														
Almond	-	-	-	4.5–6.0	-	1.7–2.0	61.3–72.1	17.5–19.8	0.5	-	-	-	-	[51]
Canola	-	-	-	4.3	0.2	1.9	61.5	20.6	8.3	0.5	1.1	0.2	-	[16]
Cashew	-	-	-	14.1	0.4	10.2	57.3	17.2	0.2	-	-	0.5	-	[17]
Coconut	5.5	47.7–52.0	19.9	-	-	2.7	6.2	1.6	-	-	-	-	-	[50]
Corn	-	-	-	11.3	0.1	1.9	32.2	52.5	1.0	0.4	0.3	0.1	-	[16]
Cotton	-	-	0.6	19.6	0.6	2.5	22.1	52.3	0.6	-	-	0.6	-	[52]
Hazelnut	-	-	-	10.6–21.6	0.6–1.9	2.5–6.1	38.7–73.2	11.3–27.5	0.6–2.1	-	0.3–0.8	0.3–0.7	-	[19]
Hemp	-	-	-	5.0–7.0	-	1.0–2.0	8–13	52.0–62.0	15.0–26.0	-	0.5	0.4–0.8	-	[20]
Jojoba	-	-	0.2	6.21–9.1	-	-	13.5–24.3	0.3–0.5	0.7–1.1	-	-	53.1–71.8	-	[21]
Oil palm	-	-	0.5–2.0	32.0–45.0	-	2.0–7.0	38.0–52.0	5.0–11.0	-	-	-	-	-	[12]
Oil palm kernel	3.0–7.0	40.0–52.0	14.0–18.0	7.0–9.0	-	1.0–3.0	11.0–19.0	0.5–2.0	-	-	-	-	-	[12]
Peanut	-	-	0.1–1.0	6.0–9.0	0.1–1.7	2.1–6.0	52.0–71.1	13.0–27.0	-	1.0–4.0	-	1.0–3.0	-	[31, 50]
Pumpkin	-	-	-	15.6–16.4	-	4.1–5.2	43.5–44.8	33.8–35.8	-	0.1–0.8	-	-	-	[22]
Rapeseed	-	-	-	3.1–4.9	0.2	1.0–1.7	15.3–63.3	13.1–20.4	1.2–8.4	0.7	0.6	0.7	-	[12, 50]
Safflower	-	-	0.1	6.4	-	2.2	13.9	76.0	0.2	0.4	0.2	0.2	-	[16]
Sesame	-	-	0.1	8.0–11.0	0.3	4.0–6.0	37.0–42.0	39.0–47.0	0.6	-	0.4	1.0	-	[25]
Soybean	-	-	0.5	7.0–11.0	-	2.0–6.0	19.0–34.0	43.0–56.0	5.0–11.0	-	-	1.0	-	[12]
Sunflower	-	-	-	6.1	-	4.2	24.0	63.5	0.4	0.3	0.1	0.8	-	[16]
Walnut	-	-	0.19	5.82	-	1.9	22.7	51.6	17.8	-	-	-	-	[53]
<u>Non-edible oil</u>														
Castor	-	-	-	2.0	-	1.0	7.0	5.0	-	-	-	-	Ricinoleic 86–90	[12]
Country almond	-	-	-	32.3–33.9	-	5.7–6.3	22.7–26.7	30.0–32.0	-	0.8	-	-	-	[26]

Table 1-2 Fatty acid compositions for various edible and non-edible plant oils. (continued)

Plant	Decanoic	Lauric	Tetradecanoic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Linolenic	Arachidic	Eicosenoic	Behenic	Special	Reference
	(C10:0)	(C12:0)	(C14:0)	(C16:0)	(C16:1)	(C18:0)	(C18:1)	(C18:2)	(C18:3)	(C20:0)	(C20:1)	(C22:0)		
Croton	-	1.1	1.5	30.7	2.9	4.9	34.1	18.5	2.9	0.5	-	1.4	-	[54]
Cuphea	28.1	64.7	2.9	0.2	-	-	0.9	1.9	-	-	-	-	-	[27]
Desert date	-	-	-	15.4–16.1	-	18.6–19.3	25.6–27.0	38.5–40.8	-	-	-	-	-	[41]
Ethiopian mustard	-	-	-	4.3	-	0.5	7.4	18.2	24.9	4.7	-	-	Ricinoleic 35–40	[29]
Green algae	-	0.7	0.8	21.0	2.0	2.9	3.2	13.6	33.0	0.2	-	0.2	Hexadecatrienoic 15	[48]
Jatropha	-	-	0.5–1.4	12.0–17.0	-	5.0-9.5	37–63	19–41	-	0.3	-	-	-	[33]
Kapok	-	-	0.1	22.6	-	5.2	30.1	37.5	-	1.7	-	0.3	-	[33]
Karanja	-	-	-	3.7–7.9	-	2.4-8.9	44.5–71.3	10.8–18.3	-	2.2–4.7	4.2–5.3	-	-	[12]
Kokum	-	-	-	8.0	-	5.5	50.2	26.0	-	-	-	-	-	[35]
Kusum	-	-	-	5.0–8.0	-	2.0–6.0	57.0–62.0	-	-	20.0–25.0	-	-	-	[55]
Linseed	-	-	-	6.7	-	3.7	21.7	15.8	52.1	-	-	-	-	[16]
Mahua	-	-	-	20.0–25.0	-	20.0–25.0	41.0–51.0	10.0–14.0	-	0.1–3.3	-	-	-	[12]
Milkweed	-	-	-	15.1	5.7	2.6	27.1	49.6	1.0	0.3	-	-	-	[56]
Moringa	-	-	0.2–0.3	5.4–6.4	1.1–1.4	3.8–5.8	67.9–79.5	0.1–0.8	0.2–2.2	2.2–3.7	-	5.1–6.7	-	[57]
Nahor	-	-	-	15.3	-	12.0	53.2	17.0	-	2.0	-	0.5	-	[58]
Neem	-	-	0.2–2.6	13.6–16.2	-	14.4–24.0	49.0–62.0	2.3–15.8	-	0.8–3.4	-	-	-	[12]
Oleander	-	-	0.2	20.2	0.3	7.7	46.1	15.9	0.4	-	-	-	-	[37]
Rubber	-	-	-	8.8	0.2	6.2	39.0	42.1	2.4	0.7	-	-	-	[59]
Sea mango	-	-	-	30.3	-	3.8	48.1	17.8	-	-	-	-	-	[38]
Soapnut	-	-	-	4.7	0.4	1.5	52.6	4.7	2.0	7.6	-	23.9	-	[31]
Sugar apple	-	-	-	12.1	-	13.6	47.4	22.9	-	0.9	-	-	-	[39]
Syringa	-	-	-	10.1	-	3.5	21.8	64.1	-	-	-	-	-	[60]
Tobacco	-	-	-	9.6	-	6.3	21.7	55.6	-	-	-	-	-	[12]
Tung	-	-	-	3.0	-	2.0	4.0	9.0	-	-	-	-	α -eleostearic 82	[16]

1.2.3 Plant oils extraction

Extraction of plant oils from seeds and kernels first requires drying to the appropriate moisture level. There are three oil extraction methods; mechanical, chemical, and enzymatic methods [28], but mechanical and chemical methods are the most commonly used for commercial oil processes. The mechanical extraction with expellers can extract oils directly from seeds, kernels, or both, whereas the chemical extraction requires pretreatment of the materials [61, 62].

(1) Mechanical extraction

Mechanical pressing is the most conventional method for oil extraction. This method can use a manual ram press or an engine-driven screw press to squeeze the oil out of the seeds and kernels physically. The screw press expeller is a machine that presses oil using friction and continuous pressure. The pressure and friction in the process will increase the heat of the system up to 60 °C, but this process is still considered as cold pressing because supplemental heat is not necessary to the process. This method was reported to extract 60–86% of the available oil [28, 63] and can process many oilseeds, including soybean, sunflower, sesame (*Sesamum indicum*), Ethiopian mustard (*Brassica carinata*), and jatropha seeds [64, 65]. A hydraulic press expeller was reported to extract the oil from jatropha seeds, successfully recovering about 86 wt% of oil [63, 66], while the screw press expeller recovered around 70 wt% oil from soybean seeds [67] and successfully recovered oil from sunflower seeds [68].

The advantages of the mechanical extraction method are simple and available for processing small capacities. Because the mechanical extraction is a solvent-free process, it can produce high-quality, clean and pure plant oils, which have good color and flavor. However, the machine design is not always suitable for any seed types, which may affect the level of

residual oil in the press cake, resulting in relatively low oil yield. Nevertheless, most of the oil left in the press cake can be recovered by the solvent extraction.

(2) Chemical extraction

Chemical extraction is a method for processing oil from seeds and kernels using a liquid solvent. This method overcomes the problem with the mechanical extraction process, which leaves residual oil in the press cake, and can achieve oil yields of over 95 wt% [28]. Chemical extraction can be used to extract jatropha, neem, soybean, and safflower (*Carthamus tinctorius*) oils, among others [43, 44].

The rate of solvent extraction depends on many factors, such as the water content of the seed, particle size and shape, type and amount of the solvent, extraction temperature, level of agitation during the extraction process, and extraction time [42, 64]. The water content of the seed is important because the presence of water could wet the seed surface, which will interfere with the penetration of the solvent into the seeds. However, a certain degree of moisture is necessary to maintain the elasticity of the seed flakes and prevent disintegration. Furthermore, the particle size and shape must allow the optimum extraction from each particle by minimizing diffusion pathways. Selection of the solvent is also essential; the viscosity of the solvent should be sufficiently low to allow free circulation. The most commonly used solvent is hexane because of its specific characteristics. The high volatility of hexane facilitates the separation of solvent and plant oil with low energy input. Furthermore, hexane dissolves well with plant oils, so that the desired oils can be easily extracted from the seeds and kernels.

The oldest type of chemical extraction method is the Soxhlet equipment. Many recent studies have explored the application of ultrasonication to improve the extraction rate and product quality, and to reduce the extraction time [69]. Furthermore, various studies have conducted to develop stable and nontoxic alternative solvents with low flammability. In

particular, supercritical CO₂ has attracted great interest. Soybean oil yield was increased from 20.37 wt% by soxhlet extraction to 23.59 wt% by supercritical CO₂ extraction (at 30 MPa, 50 °C, and 1.63 L/min of CO₂ flow rate within 4 h) [70]. Moreover, the supercritical CO₂ extraction (at 35 MPa, 50 °C, and 0.4 L/min of CO₂ flow rate within 2 h) obtained almond oil yield around 53 wt%, which is higher than about 45 wt% by the hydraulic cold pressing [71]. Therefore, evaluation of other solvents for extracting plant oils could achieve important advances.

(3) Enzymatic extraction

Plant oil is contained in vacuoles inside seed cells, so that the walls of both vacuoles and cells must be disrupted to release and extract the oil. Specific enzymes can partially hydrolyze the polysaccharides in seed cells to increase membrane permeability, which results in higher extraction yield [72]. Oil extraction with aqueous enzymes usually uses a mixture of cell wall-degrading enzymes, such as pectinase, cellulase, and hemicellulase with water as a solvent, which has many advantages compared to chemical solvents. However, the high cost of enzyme production, downstream processing, and long incubation time have hampered the application of this technology [73]. Consequently, a combination of enzymatic extraction with other methods may solve the problems of environmental safety. For example, ultrasonic and aqueous enzymatic oil extraction (using protease) obtained 74 wt% yield of jatropha seed oil, higher than the only 17–20 wt% yield from chemical extraction [74]. The high yield of oil extraction is one of the main advantages of enzymatic oil extraction in addition to the environmentally friendly process and absence of by-production of volatile organic compounds.

Enzymatic extraction is affected by several factors. Pretreatment by grinding or flaking is important to reduce the size of the seeds to increase enzyme accessibility [73]. Furthermore,

the parameters of temperature and pH are important. The optimum incubation temperature varies for different oil seeds and enzymes. High temperatures will cause a gradual loss of enzyme activity due to denaturation of proteins and darken the oil [75], whereas low temperatures lead to slow enzymatic hydrolysis and low oil extraction. For example, the optimum temperature for olive oil extraction was reported to be 40 °C and that for linseed was 35 °C, and the maximum yield of peanut oil was obtained at 40 °C [76]. Therefore, the temperature range must depend on the desired quality of the oil and the nature of the seed. The optimum temperature range for enzymatic hydrolysis is between 45 and 55 °C [77].

Preparation of plant oil for biofuel production is more straightforward compared to that for food-grade oil. Crude oil will undergo the processes of refining, degumming, bleaching, and finally deodorizing for food use [78]. The refining and degumming steps are designed to remove the phospholipids, proteins, carbohydrates and free fatty acids from crude plant oil. The bleaching and deodorizing processes are required to remove the excess of carotenoid pigments, oxidation products and unwanted flavors. All such processes are omitted for biofuel production, because phospholipids and free fatty acids can also be converted into hydrocarbons [79].

1.3 Biofuels as fossil fuel substitutes

Fossil fuels mainly consist of various hydrocarbons produced from crude petroleum by fractional distillation based on the difference in boiling range. The boiling ranges of petroleum products and linear alkane carbon numbers for gasoline, jet fuel, diesel and heavy oil are summarized in Table 1-3 [80, 81].

Table 1-3 Boiling ranges of petroleum products and linear alkene carbon numbers for gasoline, jet fuel, diesel, and heavy oil [80, 81].

	Gasoline	Jet fuel	Diesel	Heavy oil
Boiling range (°C)	20-210	175-288	180-380	380-540
Linear alkane carbon numbers	4-10	8-15	11-21	22~

The most common biofuels are biodiesel and bioethanol, which are used as diesel and gasoline substitutes, respectively, due to the similar properties with petroleum fuels. These fuels can be used for automotive in pure forms (100% biodiesel, B100 or 100% bioethanol, E100). However, they usually used by blending with petroleum fuels. For commercial use, the ratio of biodiesel in fossil diesel ranges from B2 to B20 [82], while the ratio of bioethanol in gasoline is between E5 to E85 [83].

1.3.1 Biodiesel

Biodiesel is defined as monoalkyl esters of long-chain fatty acids for use in compression-ignition (diesel) engines. In general, biodiesel is produced through transesterification of plant oil with methanol in the presence of a catalyst as shown in Figure 1-3.

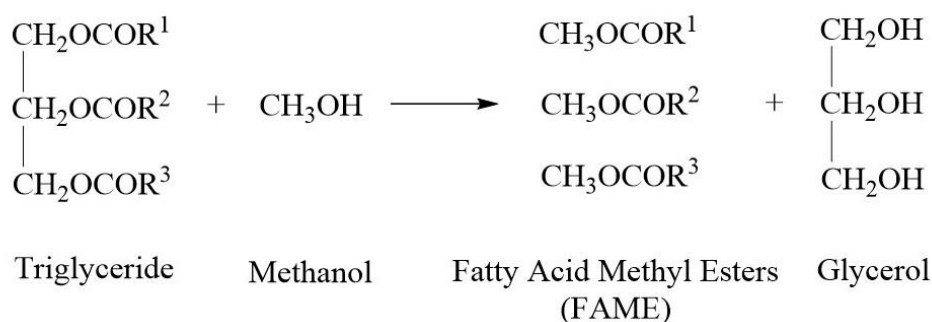


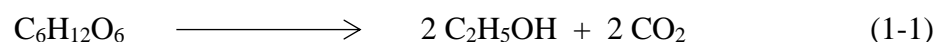
Figure 1-3 Transesterification of triglyceride with methanol into fatty acid methyl esters.

In addition, the enzymatic method is also used for biodiesel production. The enzyme was immobilized in support, and the reaction can be conducted under mild condition. A small amount of free fatty acids and water does not affect the reaction system and high-grade glycerol can be obtained as by-product [84]. Another method is supercritical transesterification under high temperature and pressure without catalyst [85, 86]. The reaction can perform very well even though free fatty acids and water present in the reaction system. This method takes a very short time to complete the reaction.

Many countries encourage the use of biodiesel, such as European countries, the United States, and Asian countries. The global biodiesel production in 2016 was about 34 million tonnes, 37% of which was accounted for by EU countries [87]. In Japan, annual biodiesel production is about 5,000 kilo liters and Kyoto city shares about 30% [88]. Biodiesel is produced from waste cooking oil in Kyoto and has become popular to run municipal buses with B5 and garbage-collecting trucks with B100. Among Asian countries, Indonesia in 2016 shared about 3.2 million tonnes of global biodiesel production [87].

1.3.2 Bioethanol

Bioethanol is used as a gasoline substitute in spark-ignition engines. Bioethanol has chemical and physical properties that are favorable for the spark-ignition engine; the octane number of bioethanol is higher than that of fossil gasoline to give better anti-knocking property. Bioethanol is commercially produced by alcohol fermentation with *Saccharomyces cerevisiae* as the following reaction:



Bioethanol from edible crops, such as sugar plants (sugarcane, sugar beet) and starchy plants (wheat, corn, cassava), is referred to as the first-generation bioethanol. The edible

resources compete with the food market; meanwhile, bioethanol from lignocellulosic biomass, such as wood, grass, cacao shell and other agricultural wastes, are hence promising [89], which is referred to as the second-generation bioethanol. Despite this, the production technology of the second-generation bioethanol has not been commercialized yet due to the presence of lignin and difficulty in the conversion of crystalline cellulose into monosaccharides.

More than 119 million m³ of bioethanol were produced globally in 2016 [87]. The US shared about 58.5 million m³. The large volume of bioethanol production in the US is because the government promotes the use of bioethanol by setting the target for renewable transport fuels. The second-largest bioethanol producer is Brazil in 2016, sharing about 24.8 million m³. In Asia, China shared about 3.2 million m³ in 2016 [87].

1.4 Hydrocarbon production from plant oils

The main difference between biofuels and petroleum-based fuels is in their oxygen content in molecules. The oxygen content in petroleum-based fuels is almost zero, whereas in biofuels is about 10–45% [90]; therefore, some fuel properties are different between them. The high oxygen content of bioethanol causes low energy density and corrodes common metals [91]. Thus, the need for renewable hydrocarbon as a gasoline substitute, which is hereinafter referred to as renewable gasoline, attracts high interest. The main component of plant oils is triglycerides, which have similar carbon chains to petroleum-based fuels. Therefore, the triglycerides in plant oils can be converted into hydrocarbons through the removal of oxygen atoms to produce renewable hydrocarbon fuels. Hydrocarbons with carbon numbers from C₄ to C₁₀ can be used as alternative gasoline, even though not only the carbon number but also other properties, such as octane number, are important. The properties of renewable gasoline

are close to petroleum-based gasoline because constituent molecules in both fuels are hydrocarbons.

1.4.1 Catalytic cracking

Catalytic cracking involves thermal and catalytic reactions, but the catalytic reaction becomes more important for smaller molecules. The catalyst can be acidic or basic catalysts. The conventional basic catalyst in a continuous reactor is Na_2CO_3 or K_2CO_3 [92]. Xu et al. [92] found that those catalysts could produce hydrocarbons from soybean oil in a yield over 80 wt% of diesel and gasoline fractions.

Catalytic cracking in plant oils is typically conducted in the temperature ranges between 360 and 525 °C. The reaction will always produce a solid fraction (coke), a liquid bio-oil product, and biogas [93, 94], which are highly affected by both temperature and residence time in the reactor. Reactions at lower temperatures and longer residence times will yield higher quality coke product, while higher temperatures and longer residence times will yield higher quality gas products, and moderate temperatures with shorter residence times will yield higher quality liquid products.

Several reaction conditions in the catalytic cracking of plant oils to obtain hydrocarbon biofuels are summarized in Table 1-4. A fixed-bed reactor is the most common for catalytic cracking of plant oil. The configuration of the fixed-bed reactor has an excellent mass and heat transfer distribution of the oil feed to avoid clogging, entrainment, and channeling, which are the major issues in catalytic cracking [95]. Zeolite-based catalysts are extensively used due to their acid properties and large specific surface areas [96, 97]. Ramya et al. [98] studied hydrocarbon production through catalytic cracking from jatropha oil with AlMCM-41/ZSM5 and obtained hydrocarbons shorter than 18 carbon chain length. The catalyst yielded 70 wt%

of liquid fuel from jatropha oil, in which 61 wt% renewable gasoline included. Ramya et al. [99] also reported catalytic cracking of castor, coconut, and neem oils with HZSM-5 catalyst at 400 °C produced not only renewable gasoline, but also volatile compounds in high concentration in the gas phase. Besides, Shimada et al. reported catalytic cracking of oil from *Euglena* (*Euglena gracilis*) to produce about 40 wt% of hydrocarbons in the composition of gasoline range with a large amount of paraffins and olefins. Edible sunflower and canola oils, and non-edible jatropha oil have the potential to produce biofuel with this method to obtain more than 60% of hydrocarbons [99–101].

Table 1-4 Several reaction conditions in catalytic cracking of plant oils to yield renewable hydrocarbon fuels.

Plant oil	Catalyst	Operation condition	Reactor	Main product	Yield (wt%)	Coke (wt%)	Reference
Canola	NiMo/ γ -Al ₂ O ₃ ; Pt/H-Y zeolite; Pt/HZSM-5	300–400 °C, 5–11 MPa	Batch	Diesel-like hydrocarbons	35–80	-	[101]
Castor	HZSM-5	400 °C	Fixed-bed	Bioliqum	38	1.5	[99]
Coconut	HZSM-5	400 °C	Fixed-bed	Bioliqum	27.6	2.2	[99]
Euglena	Zeolite Y	470 °C, 0.7 MPa	Fixed-bed	Gasoline	40	5	[91]
Jatropha	AlMCM-41/ZSM-5	400 °C	Fixed-bed	Bioliqum	70	-	[98]
Jatropha	Ni–W/SiO ₂ –Al ₂ O ₃	450 °C, 6 MPa	Fixed-bed	Biokerosene	25-30	-	[102]
Neem	HZSM-5	400 °C	Fixed-bed	Bioliqum	16.7	1.4	[99]
Oil palm	Microporous HZSM-5; mesoporous MCM-41; micromesoporous zeolite	450 °C	Fixed-bed	Gasoline	48	1.7	[103]
Rapeseed	Ni-Ecat-H; Pt-Ecat-H	525 °C, 0.1 MPa	Microriser	Gasoline	29–41	5–8.2	[104]
Soybean	NiMo/ZSM-5	360–450 °C, 4.5 MPa	Fixed-bed	Hydrocarbon biofuel	50	-	[105]
Sunflower	ZSM-5	450–550 °C, 0.1 MPa	Fixed-bed	Bio-jet fuel (C ₇ –C ₁₂)	77.3	-	[100]
Sunflower	Pt/HZSM-22/Al ₂ O ₃	280-370 °C, 3.5-8 MPa	Flow reactor	Bioliqum	>90	-	[106]

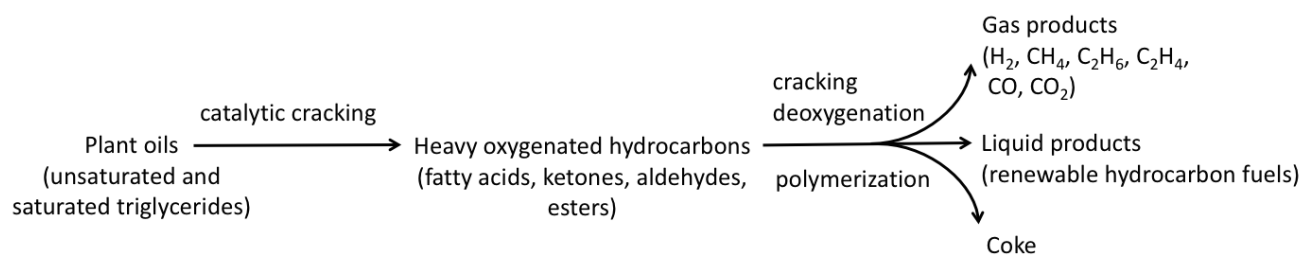


Figure 1-4 Catalytic cracking of plant oils to produce renewable hydrocarbon fuels [107–109].

The reactions in the catalytic cracking of plant oils to produce renewable hydrocarbons are shown in Figure 1-4 [107–109]. The cracking of triglycerides might be initiated with thermal cracking, which usually produces free radicals of ester carbonyl groups. These free radicals would then interact with the active site of the catalysts (e.g., a Lewis acid in the case of zeolite-based catalysts) to form heavy oxygenated hydrocarbons, such as fatty acids, ketones, aldehydes, and esters [107]. Further cracking of C–C bonds of oxygenated hydrocarbon molecules takes place followed by deoxygenation reactions, resulting in the liquid products, i.e., renewable hydrocarbon fuels. The composition of renewable hydrocarbon fuel depends on the reactions triggered by acid catalysts in the system, such as β -scission, hydrogen transfer, isomerization, cyclization, or aromatization. However, this process is highly unselective because a broad range of oxygenates and hydrocarbons could be formed. Gaseous products, such as CO, CO₂, and H₂O, were derived from this oxygen-removal reaction. As side reactions, the cracking associated with deoxygenation reactions of the heavy oxygenated hydrocarbons ended up to produce light hydrocarbons (i.e., CH₄, C₂H₆, C₂H₄). Furthermore, coke is formed from the polymerization reaction of oxygenated hydrocarbon molecules [110]. The coke formation usually creates the problem of catalyst deactivation, which tends to physically cover the active surface on catalysts or block catalyst pores. However, loading metals to zeolites to

increase selectivity and optimizing the catalytic cracking condition would be helpful to reduce coke formation [100].

1.4.2 Hydrotreating

The greatest concern during the catalytic cracking process is the water and oxygen content in biofuels; this concern can be reduced through catalytic hydrotreating using a heterogeneous catalyst, i.e., deoxygenation [111]. The resulting (oxygen-free) hydrocarbons are compatible with fossil fuels. This hydrotreating process involves oxygen removal through hydrodeoxygenation to form hydrocarbons and H_2O , and simultaneous saturation of double bonds or aromatic rings by hydrogenation. The hydrotreating process includes various reactions, such as hydrodeoxygenation, decarboxylation, and decarbonylation, depending on the reaction conditions and the type of catalyst [112–119].

The main reaction pathway in the conversion of plant oils into hydrocarbon biofuels via hydrotreating is shown in Figure 1-5 [100, 115, 118]. Hydrodeoxygenation yields hydrocarbons with the same chain length as the reactant, while decarboxylation and decarbonylation produce hydrocarbons with one less chain length than the starting compounds. Table 1-5 summarizes the deoxygenation process for fatty acids to yield renewable hydrocarbon fuels.

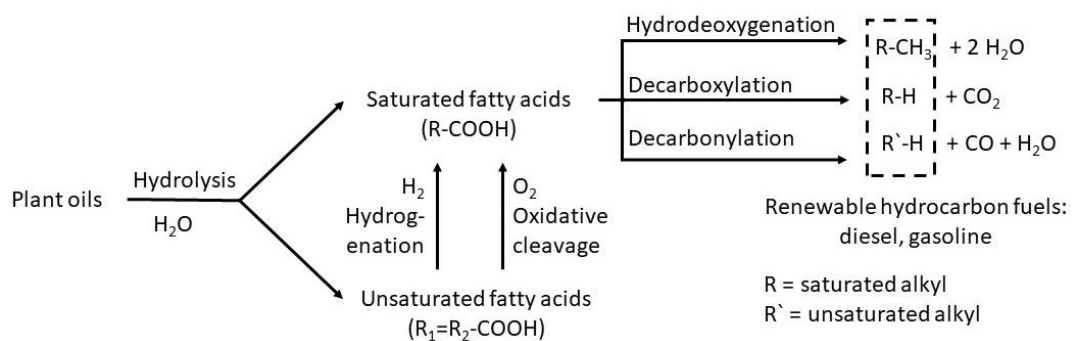


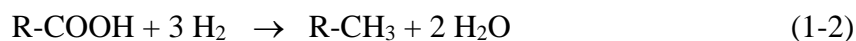
Figure 1-5 Hydrotreating of plant oils to hydrocarbon biofuels [100, 115, 118].

Table 1-5 Deoxygenation of fatty acids to yield renewable hydrocarbon fuels.

Process	Fatty acid	Catalyst	Operation condition	Reactor	Main product	Yield (wt%)	Ref.
Hydrodeoxygenation	Capric	Pt/Nb ₂ O ₅	180–250 °C, 0.8 MPa (H ₂)	Batch	Decane	88	[120]
	Lauric	Pt/Nb ₂ O ₅	180–250 °C, 0.8 MPa (H ₂)	Batch	Dodecane	99	[120]
	Myristic	Pt/Nb ₂ O ₅	180–250 °C, 0.8 MPa (H ₂)	Batch	Tetradecane	89	[120]
	Oleic acid	MoO ₂ C/graphene oxide	350 °C, 5 MPa (H ₂)	Continuous flow	Octadecane	60	[121]
	Palmitic	MoO ₂ /CNTs	190–260 °C, 4 MPa	Batch	Hexadecane	4.1–92	[122]
	Stearic	Pt/Nb ₂ O ₅	180–250 °C, 0.8 MPa (H ₂)	Batch	Octadecane	96	[120]
	Stearic	PdOx/zeolite	360 °C, 2 MPa (H ₂)	Batch	Octadecane	89	[123]
Decarboxylation	Stearic	Pd/C	300 °C, 1.7 MPa (He)	Semibatch	Heptadecane	82	[117]
	Stearic	Pd/C	300 °C, 0.6 MPa (He-H ₂)	Semibatch	Heptadecane	98	[124]
	Stearic	Pd/C	300 °C, 1 MPa (H ₂)	Batch	Heptadecane	90	[115]
	Palmitic	Pd/C	300 °C, 1 MPa (H ₂)	Batch	Pentadecane	53	[116]
	Stearic	Ni/C	370 °C	Batch	Heptadecane	81	[125]
	Pelargonic	Pd/C	300 °C, 10 MPa (N ₂)	Batch	Octane	98	[118]
	Azelaic	Pd/C	300 °C, 5 MPa (N ₂)	Batch	Heptane	73	[118]
Decarbonylation	Stearic	[(C ₆ H ₅) ₃ P] ₂ Rh(CO)Cl	280 °C	Batch	Heptadecene	81	[126]
	Stearic	Pd/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	90.1	[127]
	Stearic	Cu/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	77.6	[127]
	Stearic	Pt/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	45	[127]
	Stearic	Ni/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	36	[127]

(1) Hydrodeoxygenation

During the hydrodeoxygenation, carboxylic groups in fatty acids are reduced by using H₂ to form hydrocarbons with the same carbon chain length as the parent reactants, and H₂O molecules are released as the following reaction:



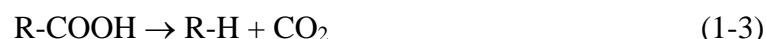
This reaction only occurs in the presence of H₂. Peng et al. [128], Murata et al. [129], Gosselink et al. [130], and Hollak et al. [131] reported selective hydrodeoxygenation reactions using Ni-loaded zeolites, Pt-Re/ZSM-5, and tungsten and molybdenum carbide catalysts at 260–350 °C under 1–5 MPa of H₂. Furthermore, Nino Rinaldi et al. [132] successfully investigated the oxygen removal in hydrodeoxygenation of bio-oil from pyrolyzed palm shell over NiMo catalyst. However, higher catalyst loading requires higher pressures and temperatures, but the low-product yields are still the main problem [131].

Several different catalysts have obtained high product yields for hydrodeoxygenation of fatty acids (Table 4). Kon et al. [120] reported the hydrodeoxygenation of capric, lauric, myristic, and stearic acids using Pt/Nb₂O₅ at 180–250 °C under 0.8 MPa, and resulted in 88–99 wt% of hydrocarbons corresponding to the reactants. The partial blocking of Pt by Nb₂O₅ increases the Lewis acidity of the suboxide and the cooperation of metal (Pt)-Lewis acid significantly enhances the selectivity in C–O and C=O bond reduction by the hydrodeoxygenation reaction [120]. Kim et al. [121] and Ding et al. [122] developed a low-cost Mo-based catalyst, which has the potential for hydrodeoxygenation due to its high activity of C–O bond scission because it could convert oleic and palmitic acids into hydrocarbons up to 92 wt% at 190–350 °C under 4–5 MPa. Ayodele et al. [123] developed functionalized PdOx/zeolite to convert oleic acid into 89 wt% of octadecane at 360 °C under 2 MPa.

The hydrodeoxygenation method is relatively carbon-efficient because it generates hydrocarbons with the same carbon number as that of fatty acid feedstocks. However, at least 2 mol of hydrogen are required to complete hydrodeoxygenation of 1 mol fatty acid and the formation of water during the reaction affects the stability of the catalyst, which is the weakness of this method [133].

(2) Decarboxylation and decarbonylation

Decarboxylation removes the oxygen atoms in fatty acids as CO₂ to form hydrocarbons with one less carbon length than the starting fatty acids. In principle, this process does not involve a reaction with hydrogen (Reaction 1-3) [118, 134]. However, the presence of hydrogen in low partial pressure was found to be beneficial for catalyst stability in some cases [117].



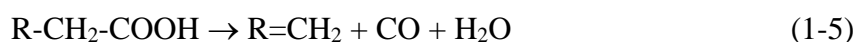
The decarboxylation reaction of fatty acids was first successfully demonstrated by Bertram [135] to obtain heptadecane from stearic acid through a homogeneous selenium catalytic reaction. The needs for green processing and recovery of the catalyst led to the investigation of various supported metal catalysts to develop promising heterogeneous catalysts with high activity for decarboxylation.

Murzin et al. [124] studied decarboxylation of stearic acid using dodecane as a solvent over different metal catalysts (Pd, Pt, Ni, Rh, Ir, Ru, and Os) supported on carbon and metal oxides. They found that Pd supported on carbon demonstrated high activity and selectivity to the desired product of heptadecane. Therefore, most decarboxylation studies have used Pd catalyst, and some examples are presented in Table 1-5. In addition, Murzin et al. [117, 124, 136] studied the effect of hydrogen concentrations in decarboxylation reactions and showed

that the hydrogen in the reaction atmosphere could reduce the undesired aromatization and increase the product yield from 82 to 98 wt% in stearic acid decarboxylation. Furthermore, Sugami et al. [115, 116] proposed a solvent-free decarboxylation of stearic acid and palmitic acid under hydrogen with Pd/C catalyst, and obtained the corresponding saturated hydrocarbons with 90 and 53 wt% yields, respectively, without by-product. In contrast, decarboxylation over inert atmosphere could also achieve outstanding results. Wu et al. [125] demonstrated a low cost and abundantly available supported Ni-based catalyst for decarboxylation of stearic acid, and obtained 81% heptadecane without hydrogen. The positive effect of hydrogen can generally be attributed to the preservation of the catalyst activity during the reaction, but this effect depends on the reactants and catalysts.

Decarboxylation has several advantages over hydrodeoxygenation. For example, decarboxylation under hydrogen is favored at lower pressures, so that the operational cost can be reduced. In addition, the catalytic stability is higher because water is not formed during the reaction. A high-selectivity decarboxylation can release relatively pure CO₂.

Decarbonylation is known to occur with the decarboxylation reaction under certain conditions, which eliminates the oxygen atoms in fatty acids as carbon monoxide (CO) and water, yielding hydrocarbons with one less carbon atoms as the following reactions:



An early study of the decarbonylation reaction was performed by Foglia and Barr [126], who converted stearic acid into 81 wt% heptadecene (Reaction 1-5) using a homogeneous transition metal complex rhodium with triphenylphosphine ligand [(C₆H₅)₃P]₂Rh(CO)Cl (Table 1-5). The presence of excessive ligand preserves catalyst activity by preventing metal reduction. Furthermore, Berenblyum et al. [127] studied the quantum chemical behavior of

stearic acid decarbonylation using Pd, Cu, Pt, and Ni supported on γ - Al_2O_3 . They found that the free energy of activation decreased in the following order, $\text{Ni} > \text{Pt} > \text{Cu} > \text{Pd}$, which improved the yields of desired hydrocarbons. Several deoxygenation reactions can occur through these two parallel pathways of decarboxylation and decarbonylation. However, decarboxylation is thermodynamically more favorable [137]. The mechanism of C-C bond cleavage in decarboxylation of carboxylic acid can be seen in Figure 1-6 [138].

Apart from the deoxygenation reactions, Snare et al. [124] described that several reactions occurred along with deoxygenation of stearic acid, such as hydrogenation, dehydrogenation, cyclization, ketonization, dimerization (Figure 1-7) depending on the kind of heterogeneous catalyst. However, metal-supported carbon catalysts were very selective toward deoxygenation products. All palladium and platinum on carbon catalysts achieved >90% selectivity toward deoxygenation products.



Figure 1-6 The mechanism of C-C bond cleavage in decarboxylation of carboxylic acid [138].

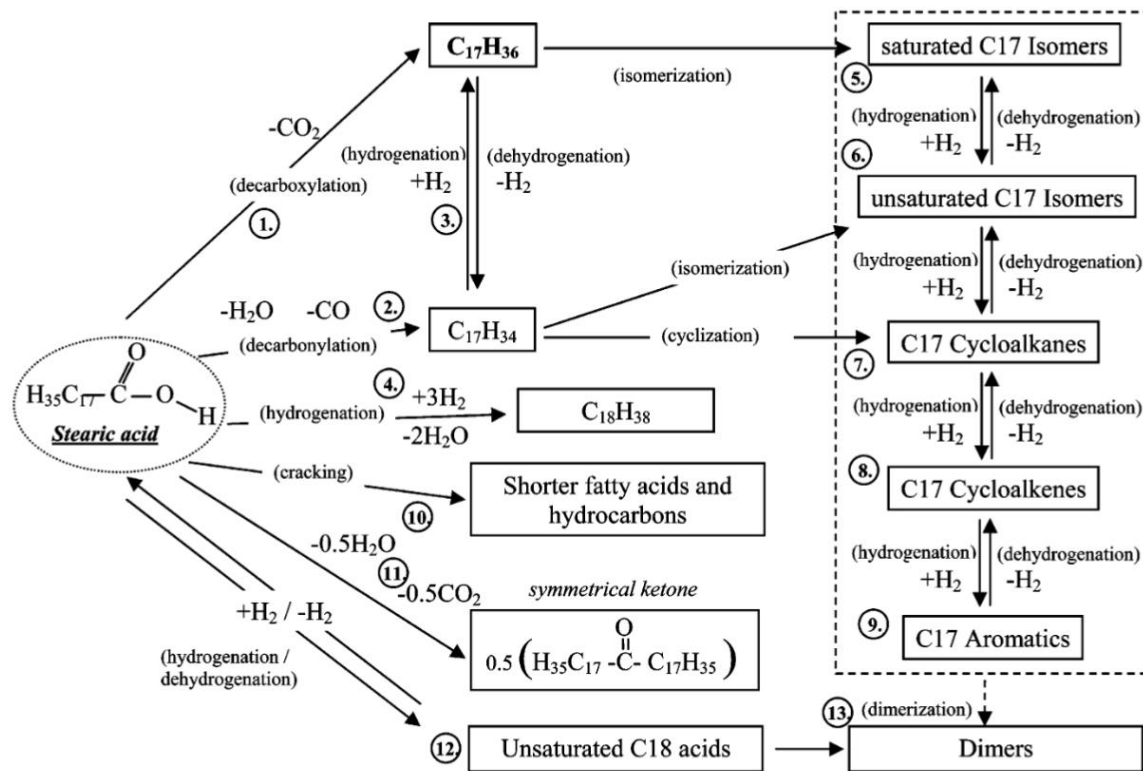


Figure 1-7 Reaction routes of stearic acid over heterogeneous catalyst at 300 °C under inert atmosphere [124].

1.5 Utilization of renewable hydrocarbon fuels

The chemical composition of petroleum fuels and renewable hydrocarbon fuels are both hydrocarbons. In theory, renewable hydrocarbon fuels can be used in high concentration to current motor engines if they achieve acceptable characteristics for engine fuel applications. Unsuitable properties of the fuel will result in carbon deposits inside the engine, higher coking index, and reduced engine life span. Renewable hydrocarbon fuels must meet the specification of international standard, such as ASTM D4814 or EN 228 for renewable gasoline (Table 1-6); ASTM D1655 for jet fuel (Table 1-7) ; and ASTM D975 or EN 590 for renewable diesel (Table 1-8).

Table 1-6 International standard properties of renewable hydrocarbon gasoline

Property	ASTM D 4814	EN 228
Flash point (°C)	-30	-
Octane number (min)	87.0	85
Density at 15 °C (kg/cm ³)	750–850	720-750
Kinematic viscosity, 20 °C (mm ² /s, min)	1	-
Initial boiling point (°C)	35	-
Final boiling point (°C)	210	210
Sulfur content (wt.%, max)	0.005	0.003
Reid vapor pressure (kPa) at 38 °C	60	60
Aromatics (vol.%, max)	42	35
Olefins (vol.%, max)	21	18

Table 1-7 International standard properties of jet fuel

Property	ASTM D 1655
Freezing point (°C, max)	-47
Flash point (°C, min)	38
Density at 15 °C (kg/cm ³)	775–840
Kinematic viscosity, -20 °C (mm ² /s, max)	8
Smoke point (mm, min)	25
Specific Energy (MJ/kg, min)	42.8
Copper Strip Corrosion (2Hr @ 100°C (max)	1
Electrical Conductivity (pS/m)	50-600

Table 1-8 International standard properties of renewable hydrocarbon diesel

Property	ASTM 975	EN 590
Flash point (°C, min)	52	55
Cetane number (min)	40	51
Density (kg/m ³)	-	820–845
Kinematic viscosity, 40 °C (mm ² /s)	1.9–4.1	2.0–4.5
Initial boiling point (°C)	190	85
Final boiling point (°C)	400	360
Sulfur content (wt.%, max)	0.05	0.01
Water and sediment (v%, max)	0.05	0.02
Cold filter plugging point (°C, max)	-	-15

The critical fuel property of gasoline for internal combustion engine is the resistance to engine knock which expressed as the octane number. The octane number of gasoline is measured in the test engine by comparing it with the mixture of 2,2,4-trimethylpentane (isooctane) and *n*-heptane [139]. Isooctane assigned a perfect anti-knocking property with octane number of 100, while *n*-heptane has very bad knocking intensity with octane number 0. Straight chain of *n*-alkanes usually give low octane numbers, but highly branched alkanes possess high octane numbers because they can be burned smoothly [140].

In jet fuel, a performance specification is more important than a chemical compound. A low freezing point is required because jet aircrafts are usually exposed to low operating temperatures. When it close to the freezing point, a waxy particle begins to form which can clog the filters and caused malfunction of fuel control system components [141].

In diesel engines, the ignition delay time is a fundamental parameter to control the combustion, which is associated with cetane number (CN) [142]. Fuels with high CN have a very short ignition delay, allowing for high thermal efficiency because of faster ignition and complete combustion. The CN is influenced by several physicochemical properties of the fuel,

such as molecular structure, volatility, viscosity, and surface tension [142]. Chemical of *n*-hexadecane is assigned to have a cetane number of 100 because it easily ignites under compression, while aromatic compounds usually perform lower cetane number.

Frequently, the produced renewable fuels cannot meet the standard requirements. In that case, blending the renewable fuels with petroleum-based fuels is one strategy. The main purposes of the blending are to optimize commercial value, to upgrade the renewable fuels to meet the specifications and to maintain the fuel phase stability. Another approach to improve the quality of renewable fuels is by rearrangement the structure of chemical compounds in fuels such as by isomerization.

1.6 Purpose of the dissertation

The properties of renewable gasoline and renewable diesel are close to petroleum fuels because all the constituent atoms are hydrocarbon. Both renewable gasoline and diesel have the potential for conventional petroleum-based fuel substitutes in the future. However, the present knowledge of renewable gasoline is still limited. Plant oils are potential for renewable fuels feedstock because of their high availability. Plant oils largely consist of triglycerides, which are triester of one glycerol and three fatty acids. Because fatty acids molecules have alkyl chains similar to petroleum fuels, plant oils hold the potential to be converted into hydrocarbons by removing oxygen atoms. Up to present, the progress in direct upgrading of triglycerides into hydrocarbons has applied catalytic cracking and hydrotreating. However, high temperatures of more than 300 °C are necessary to conduct catalytic cracking and hydrotreating because of low reaction rate of triglycerides. The high reaction temperatures can promote various side reactions, such as cyclization, and aromatization, so that these conventional methods are low-selectively process for hydrocarbon production.

Hence, this study proposed to hydrolyze plant oil triglycerides into fatty acids before hydrocarbons production because fatty acids are more reactive for hydrotreating than triglycerides, it allows lower reaction temperatures and high product selectivity. Furthermore, the conventional catalytic cracking and hydrotreating process did not consider the presence of saturated and unsaturated fatty acids content. Since C=C double bonds in unsaturated fatty acids, such as oleic, linoleic, and linolenic acids, are very reactive, many side reactions can occur during the high-temperature process, which results in poor product selectivity, yielding a broad range of hydrocarbons. Therefore, this study proposed an oxidative cleavage reaction for unsaturated fatty acids to produce short-chain fatty acids under very low reaction temperatures. Subsequently, the obtained short-chain fatty acids are subjected to decarboxylation reaction at mild temperature (300 °C) to remove oxygen atoms. The proposed process, which consist of hydrolysis, oxidative cleavage, and decarboxylation, will realize a high-selectivity hydrocarbons production in the composition range of gasoline (C4-C10). If the high-selectivity process is established, we can predict the composition of the hydrocarbons from fatty acid composition of feedstock plant oil. The main difference of this study compared to other published researches dealing with renewable energy issues is this study focused on oxidative cleavage of unsaturated fatty acids from plant oils. Furthermore, the obtained product is subjected for decarboxylation to get hydrocarbon in the range of gasoline fraction.

To obtain renewable gasoline (carbon numbers between C4 and C10) from plant oils, unsaturated fatty acid is the key compound because its C=C double bonds can be cleaved to get short saturated fatty acids, which are suitable to produce hydrocarbons in the gasoline fraction. The most common monosaturated fatty acid (MUFA) in plant oils is oleic acid, which has 18 carbon atoms and one double bond at the ninth carbon (C18:1). In chapter 2, a new reaction pathway for hydrocarbon production from oleic acid was proposed and discussed.

Besides, polyunsaturated fatty acids (PUFA) are usually found together with MUFA in plant oils. The two most common PUFA are linoleic acid and linolenic acid. Linoleic acid has two double bonds at carbon numbers 9 and 12 (C18:2), while linolenic acid has three double bonds at carbon numbers 9, 12, and 15 (C18:3). The difference in unsaturated fatty acid component may affect the reaction conditions of the proposed process. Therefore, linoleic acid and linolenic acid were investigated for renewable gasoline production in Chapter 3.

Furthermore, palm oil was selected as the feedstock to apply the proposed method for real plant oils. Palm oil contains saturated and unsaturated fatty acids with carbon number between C14 and C20; therefore, hydrocarbons in gasoline and diesel fractions are possible to produce. The studies were more complex because palm oil need to be hydrolyzed to get fatty acids before hydrocarbon production. The effect of separation process after hydrolysis was also investigated. This comprehensive study was discussed in Chapter 4.

Finally, the above-mentioned studies on renewable hydrocarbon fuels were summarized and concluded in Chapter 5 as concluding remarks.

Chapter 2 Renewable Gasoline Production from Monounsaturated Fatty Acid

2.1 Introduction

In the future, the importance of renewable energy sources is expected to increase significantly. Biomass, wind, and geothermal energy sources are already commercially competitive and development is making rapid progress. However, only 3% of energy consumption in industrialized countries is currently derived from biomass [90] and its utilization is increasing recently. This could be the fundamental strategy to reduce global CO₂ emissions.

As described in Chapter 1, plant oils are potential to substitute fossil fuels. More than 1000 different fatty acids structures are possible in terms of carbon chain length, number and position of unsaturated double bonds, and the present of substituents groups. However, over 80% of fatty acids in triglycerides are palmitic, stearic, oleic and linoleic acids in nature [5].

Various biomass-based gasoline and diesel fuels have been developed and used as alternatives to fossil-based transportation fuels [143, 144]. Bioethanol and ethyl *tert*-butyl ether (ETBE) are well-known gasoline substitutes. However, the oxygen contents of bioethanol and ETBE are a problem particularly in the case of bioethanol, leading to low calorific values, corrosion of engine components, and high affinities with water. To overcome these disadvantages, oxygen atoms in the triglyceride structure need to be removed to produce hydrocarbons, which is called renewable gasoline.

Renewable gasoline is generally produced from triglyceride by catalytic cracking at 300–500 °C under atmospheric pressure [110, 145–147]. Catalytic cracking of triglycerides with various catalysts such as NiMo/ γ -Al₂O₃, Ni/SiO₂, Al₂O₃, MgO, and zeolites are known to

produce 30–50% hydrocarbons in gasoline chain length [110, 146, 147]. Another technique is catalytic hydrotreating at 350–450 °C under 4–15 MPa of H₂. Commonly used catalysts are sulfided Ni–Mo and Co–Mo, which are usually supported on Al₂O₃, SiO₂, ZrO₂, TiO₂, or zeolites [111, 148–151]. However, this technique has low selectivity and undesirable products are produced such as carboxylic acids, ketones, and esters [146]. Decarboxylation is another approach to hydrocarbon production from fatty acids. However, although the decarboxylation reaction can give high selectivity for saturated fatty acids [89, 152], it cannot be easily applied to unsaturated fatty acids [153–157].

Renewable fuel production from plant oils has been investigated in our laboratory. Fatty acids, including saturated and unsaturated ones, are used as feedstocks for renewable diesel and renewable gasoline production. Sugami et al. reported renewable diesel production by hydrothermal hydrogenation of plant oils, followed by Pd/C-catalyzed decarboxylation to yield 91.5 mol% of hydrocarbons from rapeseed oil [115, 116]. The Pd/C catalyst was selected because of its superior decarboxylation activity among various types of supported metal catalysts (Pd, Pt, Ru, Mo, Ni, Rh, Ir, and Os on carbon or metal oxides) that was studied by Snare et al [124, 158].

In this study, unsaturated fatty acids were explored for renewable gasoline production. Unsaturated fatty acids are categorized into monounsaturated fatty acids (MUFA), such as oleic acid, and polyunsaturated fatty acids (PUFA), such as linoleic and linolenic acids.

In this Chapter, oleic acid was used as a model compound of MUFA in plant oils to investigate its conversion to hydrocarbons. This study proposed two-step reactions, which involves oxidative cleavage of oleic acid into short-chain fatty acids, followed by decarboxylation to obtain hydrocarbons with carbon chain lengths in the range C₄–C₁₀ as renewable gasoline. Oxidative cleavage of oleic acid was performed in a stirred reaction vessel with various reaction temperatures, concentrations of emulsifier and oxidizing agent.

Meanwhile, decarboxylation was conducted in a 5 mL batch-type reaction vessel made of Inconel-625 with Pd/C catalyst at 300 °C under various H₂ or N₂ pressures.

2.2 Materials and Methods

2.2.1 Materials

Reagent-grade chemicals of oleic acid, potassium permanganate (KMnO₄), polyoxyethylene lauryl ether (PLE), sulfuric acid (H₂SO₄), sodium hydrogen sulfite (NaHSO₃), sodium sulfate (Na₂SO₄), diethyl ether, tetrahydrofuran (THF), and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Extra-pure pelargonic acid and azelaic acid were obtained from Tokyo Chemical Industry Ltd. (Tokyo, Japan). Pd/C (5%) was purchased from Nacalai Tesque Inc. (Kyoto, Japan).

2.2.2 Experimental procedures

Figure 2-1 shows the schematic diagram of hydrocarbons production in this study via oxidative cleavage of oleic acid followed by decarboxylation. Oxidative cleavage was conducted to convert oleic acid into two short-chain fatty acids by the cleavage of C=C double bond. The obtained short-chain fatty acids will be then decarboxylated to produce short-chain hydrocarbons in the composition range of gasoline by removing oxygen atoms.

(1) Oxidative cleavage of oleic acid [159]

An emulsion was prepared by adding oleic acid (0.10 g) to water (2 mL) containing PLE (0.02 g) as an emulsifier and then ultrasonically agitated at room temperature for 30 min to form an emulsion. The emulsion was then mixed with KMnO₄ solution (designated

concentration, 4.5 mL) in aqueous H_2SO_4 (0.0225 N) for oxidative cleavage. At the end of the reaction, NaHSO_3 solution was added and the pH was adjusted to 1–2 using 9 N H_2SO_4 . The mixture was heated at 70 °C for 30 min to break the emulsion. It was, then, cooled and the products were extracted using diethyl ether and then dried using anhydrous Na_2SO_4 . The oxidative cleavage product was obtained by removal of diethyl ether using the rotary vacuum evaporator.

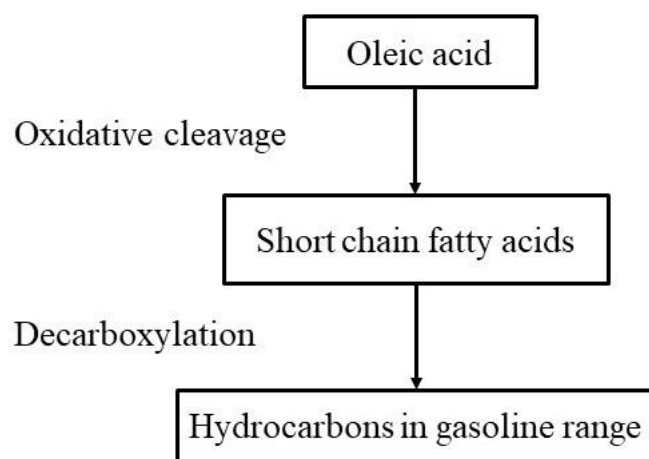


Figure 2-1 Schematic diagram of hydrocarbons in the gasoline range production via oxidative cleavage of oleic acid followed by decarboxylation.

(2) Decarboxylation of fatty acids to hydrocarbons

Prior to the experiments, the Pd/C catalyst was dried overnight at 105 °C and reduced by flowing H_2 (15 mL/min) at 200 °C for 2 h. Decarboxylation reaction was conducted using an equipment shown in Figure 2-2 [160]. The fatty acid, pelargonic acid (0.31 g) or azelaic acid (0.15 g), was placed in a 5 mL batch-type reaction vessel made of Inconel-625 together with the Pd/C catalyst (0.21 g). Actually the ratio of carboxylic groups in pelargonic acid or azelaic acid with catalyst should be similar. However, here I made a mistake in calculating the amount

of pelargonic as reactant. However, it should not give big different effect on the optimum condition of decarboxylation. The molar ratio of carboxylic group in the reactant to Pd catalyst was about 1.5:1. The vessel was sealed and pressurized with either H₂ or N₂. The reaction was conducted by immersing the vessel in a molten salt bath at a designated temperature, with shaking to agitate the mixture. The reaction was terminated by immersing the vessel into a water batch. THF was then added to the reaction mixture, sonicated for 20 min to detach the products adsorbed in the catalyst. Decarboxylation product was obtained by filtrating the catalyst.

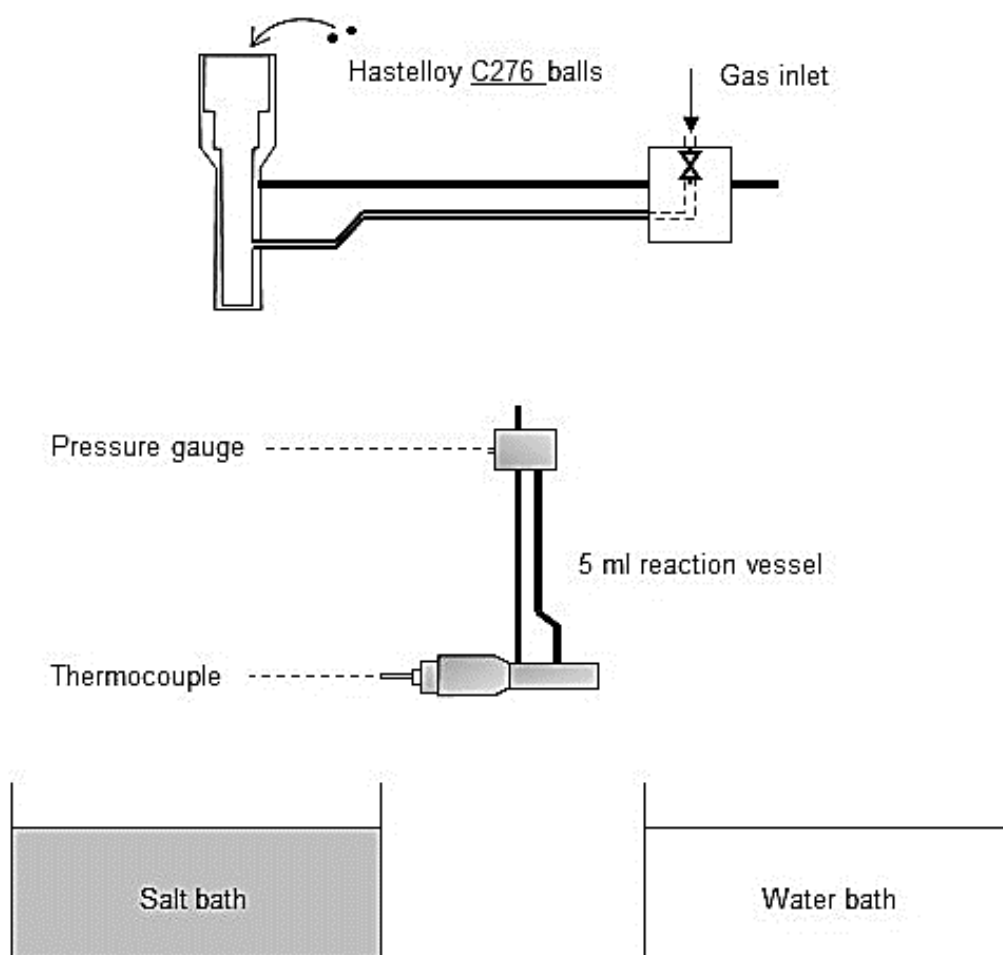


Figure 2-2 Batch reaction system for decarboxylation process [160].

(3) Analytical methods

The oxidative cleavage products were a mixture of monocarboxylic and dicarboxylic acids, and the decarboxylation products were hydrocarbons. The carboxylic acids were silylated using BSTFA at 45 °C for 20 min and then analyzed by gas chromatography-mass spectrometry (GC-MS) using a GCMS-QP2010 spectrometer (Shimadzu) equipped with a CP-Sil 8 CB column (30 m × 0.25 mm i.d., 0.25 μm thick, Agilent, Wilmington, US). The column temperature was increased linearly from 45 to 250 °C at a rate of 3.5 °C/min and then held at 250 °C for 1 min. The injector and detector temperatures were set at 230 °C. The sample was injected with a split ratio of 10/1.

The hydrocarbon products were analyzed using the same GC-MS system. The column was held at an initial temperature of 30 °C for 10 min, proportionally increased to 250 °C at a rate of 5 °C/min, and held at 250 °C for 6 min. The injector and detector temperatures were set at 230 °C. The samples were injected at a split ratio of 20/1.

The fresh or used catalysts were scanned by FTIR IRAffinity-1 spectrophotometer (Shimadzu, Kyoto, Japan). The sample was ground and dispersed in KBr pellet with a ratio of 1:100. Self-supported pressed wafers were prepared with 200 mg of the sample and pressure of 8 kg·cm⁻². The FTIR spectra were obtained from 45 scans taken at a resolution of 4 cm⁻¹, recorded from 4000–400 cm⁻¹.

The volatile products were determined using a Micro GC CP-4900 chromatograph (Varian, Middelburg, the Netherlands) fitted with two-channel columns. Channel 1 used an MS5A column (10 m x 0.32 mm i.d., 0.12 μm thick, Agilent), argon at 100 °C as the carrier gas and a thermal conductivity detector (TCD). Channel 2 used a PoraPLOT Q column (10 m x 0.32 mm i.d., 0.10 μm thick, Agilent), helium at 80 °C as the carrier gas, and a TCD. The analyses were performed under isothermal conditions.

2.3 Results and discussion

2.3.1 Oxidative cleavage of oleic acid

Double-bond in oleic acid can be expected to be oxidized and cleaved by KMnO_4 solution in acidic condition to give mono-carboxylic and di-carboxylic fatty acids. The optimum condition for oxidative cleavage of oleic acid was evaluated by performing experiments under various concentrations of emulsifier, molar ratios of oxidizing agent (KMnO_4) to oleic acid, and reaction temperatures. The results obtained are summarized in Table 2-1, showing that fatty acid products were monocarboxylic acids and dicarboxylic acids; they are denoted by two numbers in parentheses, separated by a colon. The first number represents the number of carbon atoms, while the second one the total number of double bonds present.

It can be seen in Table 2-1 that non-emulsified system (concentration of emulsifier = 0) gave low yields of acid products, which are pelargonic acid [monocarboxylic acid (C9:0)] and azelaic acid [dicarboxylic acid (C9:0)] being 33.0 and 9.4 mol%, respectively. Product of 9,10-dihydroxystearic acid and 9,10-diketostearic acid were also observed, which are intermediate product to be further oxidized into pelargonic and azelaic acids. The major pathway of oleic acid oxidative cleavage is shown in

Figure 2-3 [161].

Table 2-1 Product yield from oxidative cleavage of oleic acid with KMnO₄ in water emulsion.

Entry	Concentration	Molar ratio	Reaction	Conversion	Product yield (mol%)					
	of emulsifier	of KMnO ₄	temperature	of oleic acid	Monocarboxylic acid			Dicarboxylic acid		
	(wt%)	to oleic acid	(°C)	(mol%)	(C7:0)	(C8:0)	(C9:0)	(C7:0)	(C8:0)	(C9:0)
1	0			47.6	0.0	0.0	33.0	0.0	0.0	9.4
2	0.1	3:1	40	82.2	1.5	2.5	59.1	1.7	4.1	58.7
3	1.0			96.9	0.4	1.4	77.3	0.2	2.0	72.9
4	5.0			55.8	2.5	3.1	39.3	1.4	4.1	39.9
5		1:1		49.7	0.0	1.1	47.1	0.0	0.6	49.3
6	1.0	2:1	40	92.0	0.2	0.6	63.1	0.1	1.3	61.6
7		3:1		96.9	0.4	1.4	77.3	0.2	2.0	72.9
8		4:1		99.5	0.9	2.2	85.8	0.5	2.7	71.1
9					25	96.2	0.8	1.3	61.3	0.7
10	1.0	4:1	40	99.5	0.9	2.2	85.8	0.5	2.7	71.1
11			55	98.4	1.8	2.0	81.6	0.9	3.3	70.5

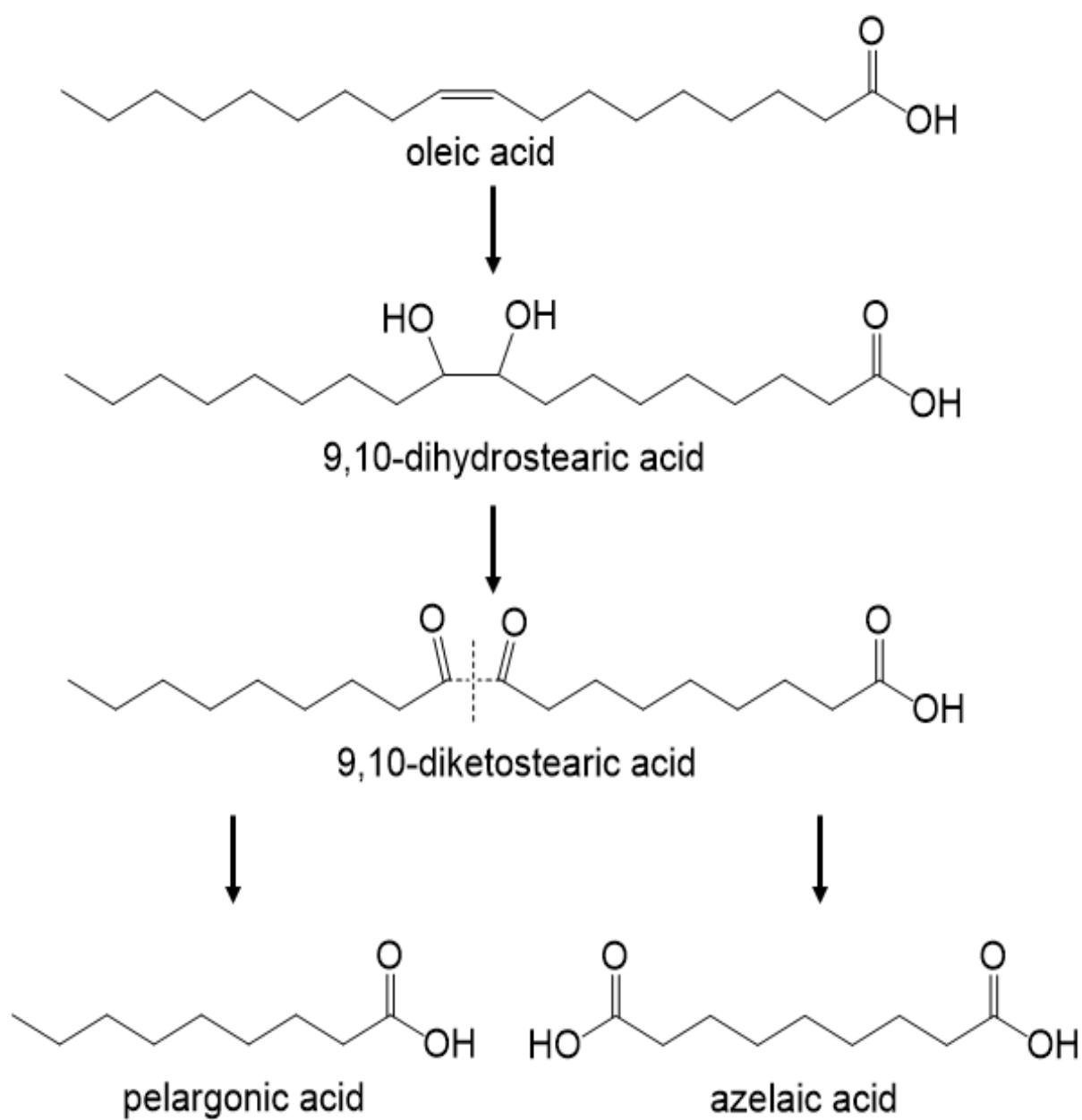
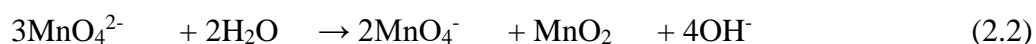


Figure 2-3 Major pathway of the oxidative cleavage of oleic acid in acidic condition [161].

The reaction was then conducted in the emulsion system by adding PLE as an emulsifier. Emulsifier reduced the surface tension of oleic acid and KMnO_4 in the water system, therefore, allowing the oleic acid and KMnO_4 as oxidizing agent to react. In an emulsion system condition, the conversion of oleic acid and reaction selectivity increased sharply. The optimum amount of emulsifier was 1.0 wt%, yielding 96.9 mol% conversion of oleic acid with 77.3 mol% of pelargonic acid and 72.9 mol% of azelaic acid. When the amount of emulsifier was further increased to 5.0 wt%, the conversion decreased to 55.8 mol%. This might be caused by a stable emulsion which would be unfavorable for the reaction.

In addition, the minor products of heptanoic [monocarboxylic acid (C7:0)], octanoic [monocarboxylic acid (C8:0)], heptanedioic [dicarboxylic acid (C7:0)], and octanedioic [dicarboxylic acid (C8:0)] acids were observed. Octanoic and octanedioic acids are usually produced in oxidative cleavage under basic condition [161]. The reaction mechanism during oxidative cleavage of unsaturated fatty acid is proposed in Figure 2-4 and reaction equations (2.1) and (2.2).



It involves the formation of manganese (III) as the dione forms (MnO_2^-). The dione will react with MnO_4^- in the reaction system to produce manganese dioxide (MnO_2) and dianion of manganate (VI) (MnO_4^{2-}). The dark brown colour of the system after the reaction was caused by this presence of MnO_2 . Furthermore, dianion of MnO_4^{2-} reacts with water to produce permanganate ion (MnO_4^-), precipitate of MnO_2 , and OH^- [162].

In these reactions, the solvent was acidified (with 0.0225 N H_2SO_4) as described in the oxidative cleavage procedure in Section 2.3.3 to neutralize the hydroxide ions formed. However, the presence of K^+ ion from KMnO_4 made it possible to also release KOH in some

occasion. Although the reaction mixture was conducted under acidic condition, the released KOH would change the pH into basic condition within local regions for a temporary period, and thus generates octanoic and octanedioic acids as shown in Figure 2-5 [161]. Such minor products are also expected to be decarboxylated into corresponding hydrocarbons in gasoline range. However, the reason of the production of heptanoic and heptanedioic acids remains unclear.

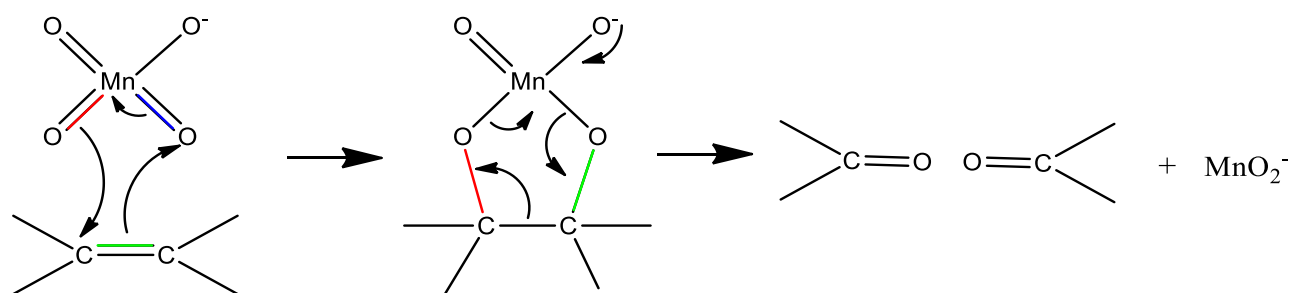


Figure 2-4 Proposed mechanism reaction in oxidative cleavage of unsaturated fatty acid.

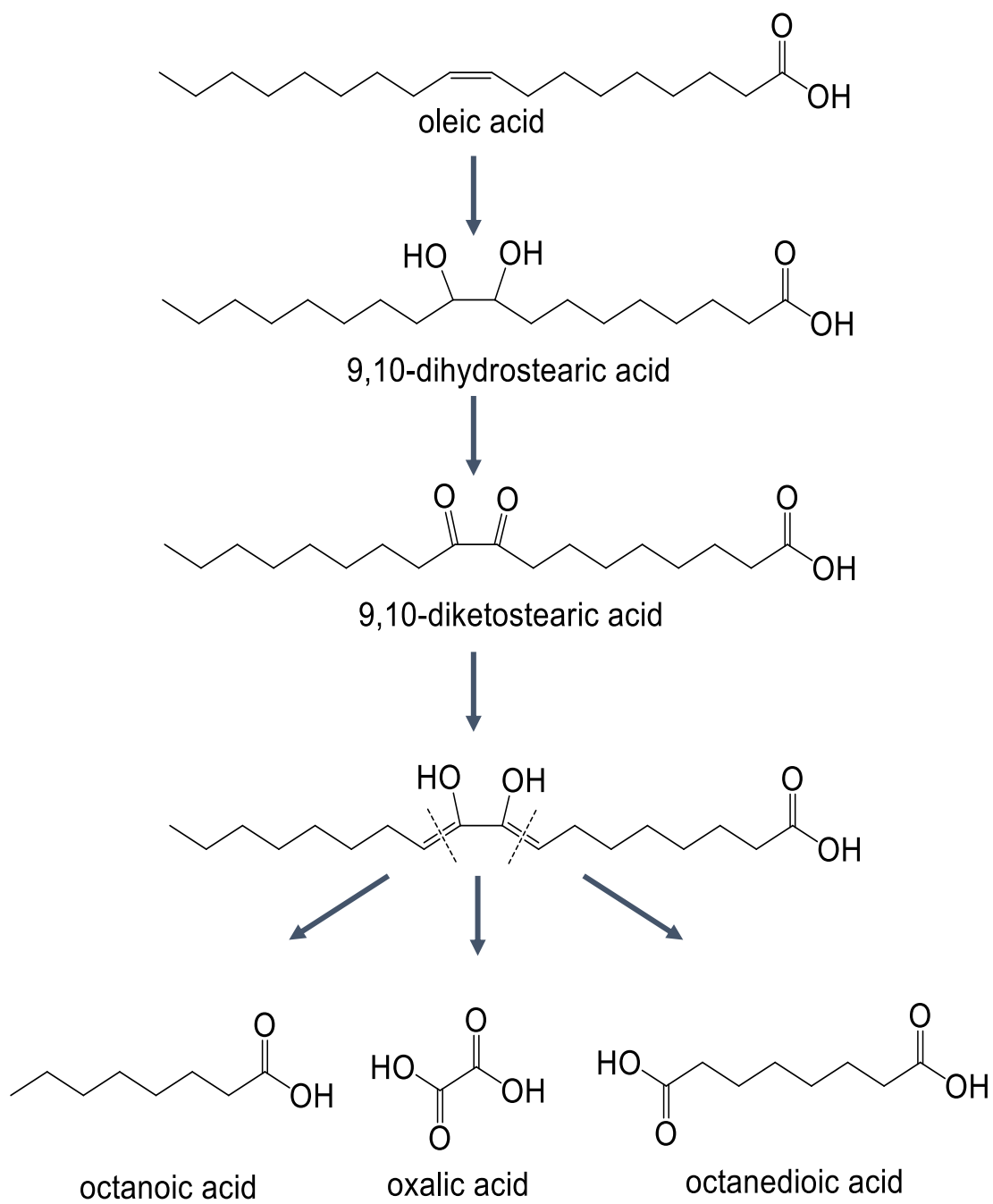


Figure 2-5 Major pathway of the oxidative cleavage of oleic acid in alkaline condition [161].

The effect of oxidizing agent (KMnO_4) on the obtained products was also investigated. In a stoichiometric reaction, 8 mol of KMnO_4 will react with 3 mol of oleic acid ($8:3 = 2.7:1$). The data in Table 2-1 show that when the amount of oxidizing agent was less than stoichiometric, the conversion of oleic acid was low, and by-product formation was high. When the molar ratio of KMnO_4 to oleic acid was increased to 4:1, interactions between the KMnO_4 oxidizing agent and oleic acid were enhanced and 99.5 mol% conversion was achieved, with 85.8 and 71.1 mol% of pelargonic and azelaic acids, respectively. In this way, an appropriate KMnO_4 to be 4:1 based on oleic acid.

The effects of reaction temperature on oxidative cleavage were also investigated. In Table 2-1, the data show that oleic acid conversion increased slightly with increasing temperature from 25 to 40 °C, but the yields of desired products increase sharply at 40 °C, similar to those at 55 °C. When the reaction temperature exceeded 55 °C, the emulsion was found to become unstable. If the emulsion breaks, contact between KMnO_4 and oleic acid would become low. These results suggest that the optimum reaction temperature would be around 40 °C.

The effects of the reaction time on oxidative cleavage were also studied as illustrated in Figure 2-6; the conditions were KMnO_4 solution with 1.0 wt% emulsifier at 40 °C (molar ratio of KMnO_4 to oleic acid was 4:1). The figure clearly shows that the yields of desired products increased sharply at the early stage of the reaction and about 10 ~ 30 min was enough to get the best for oxidative cleavage. The yields of pelargonic and azelaic acids for 30 min reaction time reached about 93 and 86 mol%, respectively.

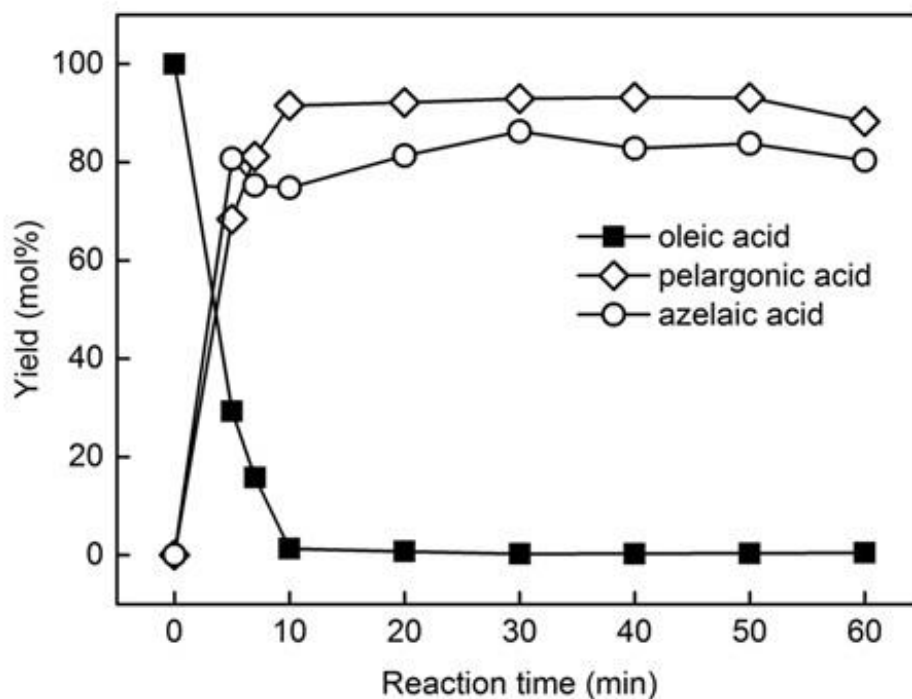


Figure 2-6 Yields of pelargonic and azelaic acids obtained by oxidative cleavage of oleic acid in aqueous KMnO_4 solution with 1.0 wt% emulsifier at 40 °C (KMnO_4 :oleic acid = 4:1, molar ratio).

2.3.2 Decarboxylation of pelargonic and azelaic acids into hydrocarbons

The effects of reaction pressure on fatty acid decarboxylation under N_2 or H_2 atmosphere were studied as shown in Figure 2-7. Various pressures of N_2 and H_2 in the range 0.1–10 MPa were applied for the decarboxylation of pelargonic and azelaic acids with Pd/C catalyst at 300 °C for 6h. Decarboxylation of pelargonic and azelaic acids will produce *n*-octane and *n*-heptane, respectively.

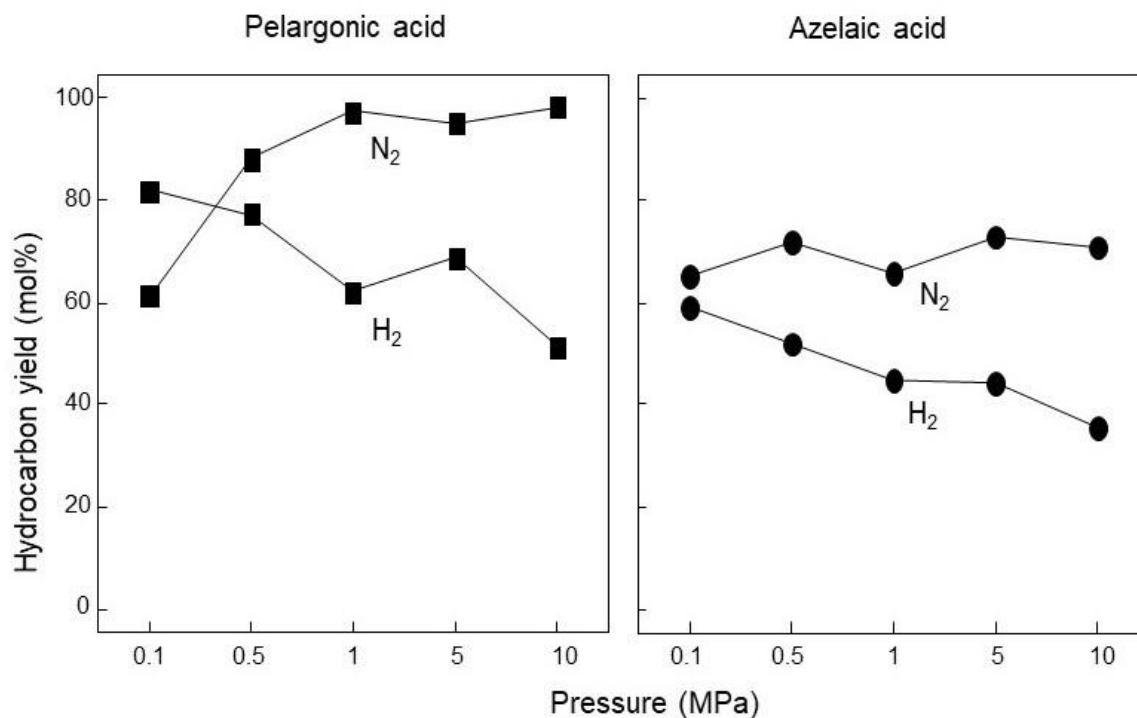


Figure 2-7 Product yields from decarboxylation of pelargonic acid with Pd/C catalyst at 300 °C for 6 h in N₂ and H₂ atmospheres.

Figure 2-7 revealed that in an N₂ atmosphere, the conversion of pelargonic acid increased with increasing pressure, and the *n*-octane selectivity was high at above 1 MPa. However, the decarboxylation of pelargonic acid in an H₂ atmosphere gave different products of the reaction. Although increasing the H₂ pressure increased pelargonic acid conversion, the hydrocarbon yield decreased. Under H₂ atmosphere, hydrogenation of carboxylic group occurred primarily, forming intermediate 1-nonanal. Due to the high rate hydrogenation of 1-nonanal to 1-nonanol and *n*-nonane, the presence of 1-nonanal was not detected in the reaction mixture. During the reaction, some of the pelargonic acid reacted with the produced 1-nonanol to form nonanoic acid nonyl ester. Plausible schemes for decarboxylation of pelargonic acid under N₂ and H₂ pressures are shown in Figure 2-8 [163, 164].

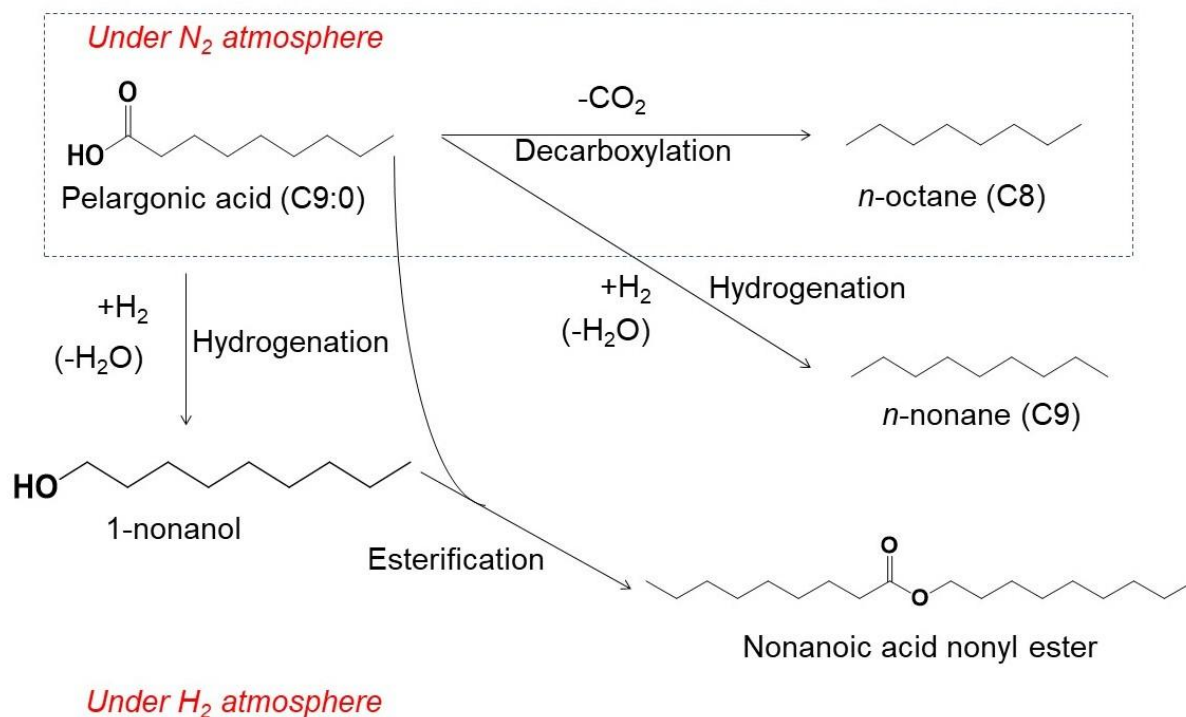


Figure 2-8 Possible reaction pathways for decarboxylation of pelargonic acid.

A similar study for azelaic acid (see Figure 2-7) indicates that in an N_2 atmosphere, selective decarboxylation of azelaic acid occurs, yielding *n*-heptane. Increasing the N_2 pressure drives the reaction toward completion, without significantly changing the obtained products. However, under H_2 pressurized conditions, various carboxylic acids, hydrocarbons, alcohols, and ester compound were produced. Similar to the case for pelargonic acid, the presence of H_2 causes the side reaction involving azelaic acid hydrogenation.

According to the obtained products, it can be concluded that decarboxylation of azelaic acid under H_2 atmosphere has a more complex reaction pathway. This might be caused by two carboxylic functional groups in azelaic acid. Hydrogenation of one side carboxyl functional group in azelaic acid generated pelargonic acid which could go for decarboxylation to form *n*-octane or hydrogenation to form 1-nonanol and *n*-nonane. Decarboxylation of one carboxyl

functional group of azelaic acid gave octanoic acid which was further decarboxylated to *n*-heptane or hydrogenated to 1-octanol and *n*-octane. A minor amount of octanoic acid octyl ester was present in the reaction mixture due to the esterification of octanoic acid and 1-octanol.

Figure 2-9 and Figure 2-10 show the time dependences of pelargonic and azelaic acids decarboxylation to produce hydrocarbons in the renewable gasoline range. For pelargonic acid (Figure 2-9), the reaction rate increased sharply up to 2 h, in which almost all the pelargonic acid had been consumed. Decarboxylation of pelargonic acid involve a one-step reaction (Reaction 2.3), generating *n*-octane and CO₂ as a by-product. In contrast, for azelaic acid (Figure 2-10), octanoic acid was formed during first hour along with the main decarboxylation reaction, but disappeared with the reaction time. Conversely, *n*-heptane was produced with the maximum yield after 3 h treatment. Such a trend suggests a two-step reaction involved in the decarboxylation of azelaic acid (Reactions 2.4 and 2.5).



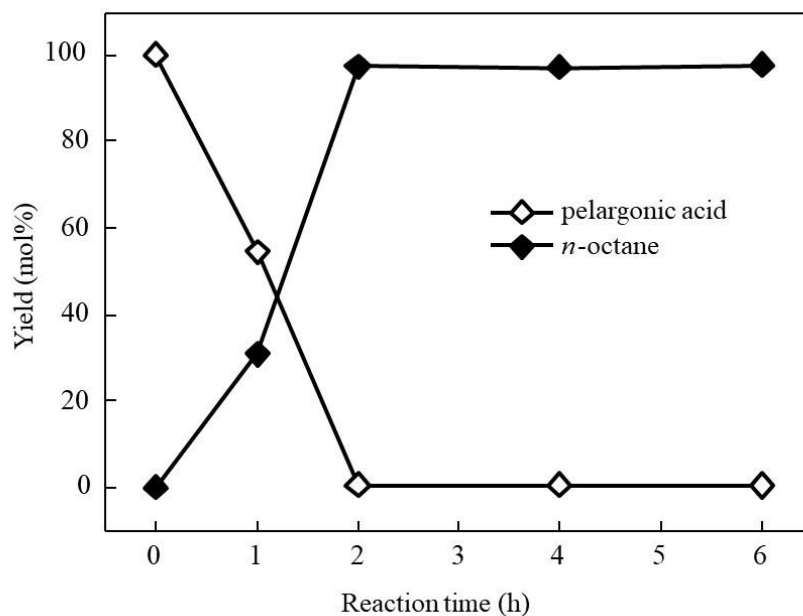


Figure 2-9 Time dependences of product yields in decarboxylation of pelargonic acid to *n*-octane with Pd/C catalyst at 300 °C/1 MPa N₂.

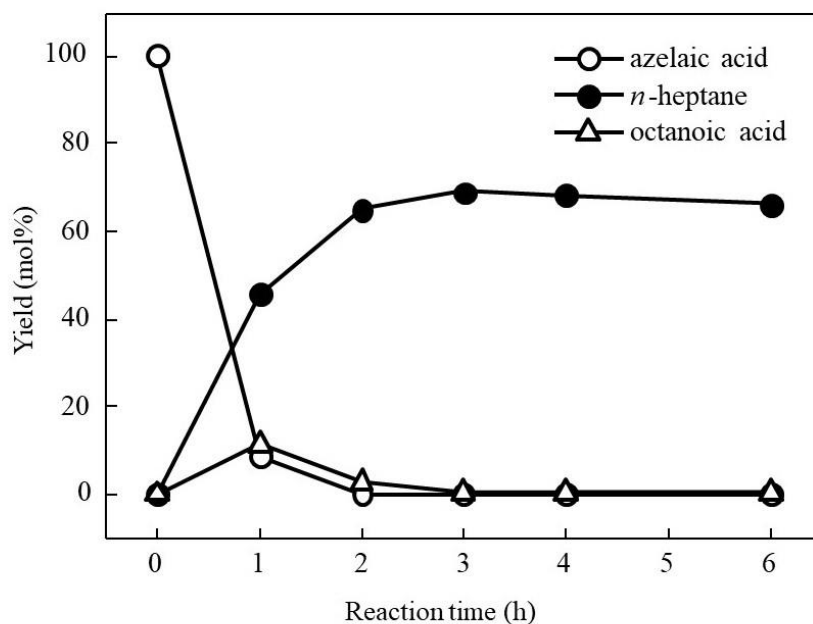


Figure 2-10 Time dependences of product yields in decarboxylation of azelaic acid to *n*-heptane and octanoic acid with Pd/C catalyst at 300 °C/1 MPa N₂.

In fact, the sum of the product yields from azelaic acid decarboxylation was not 100% although no other products were observed in the reaction mixtures. The product yield only reached the maximum at about 73.2 mol%. In this case, the deposition of hydrocarbon products on the catalyst surface and decomposition of hydrocarbons are suggested to occur.

To confirm the hydrocarbons deposition on the catalyst, FTIR analysis was performed to compare the spectra of fresh Pd/C catalyst and the used one after decarboxylation of pelargonic acid and azelaic acid (see Figure 2-11). Several absorption bands can be found only in the spectra of used Pd/C catalyst after decarboxylation of azelaic acid. Absorption bands between 1550–1300 cm^{-1} are related to the skeleton vibration of CH, CH₂ or CH₃ in aliphatic groups [165]. Furthermore, two peaks at 2855 and 2928 cm^{-1} were assigned to C-H stretching in CH₂ groups and were likely attributed to the adsorbed reaction products. In contrast, no peaks can be found at around 3400 cm^{-1} of OH bonding and 1000–1250 cm^{-1} of C–O–C bending vibration. This indicates that some of hydrocarbons formed in the catalyst cavities and cannot diffuse out, resulting in coke formation inside the catalyst. No evidence of hydrocarbon absorption bands on the used Pd/C catalyst of pelargonic acid decarboxylation revealed that the coke deposition only occurred for azelaic acid decarboxylation. Furthermore, the gas phase of azelaic acid decarboxylation analysis by Micro GC confirmed the decomposition of hydrocarbons to short-chain ones such as methane, ethane and propane. It is suggested that hydrocarbon decomposes, producing H₂ and shorter hydrocarbons and thereafter the presence of H₂ hydrogenated hydrocarbon to high volatile short-chain hydrocarbon (Reaction 2.6).



The overall decarboxylation network of azelaic acid is illustrated in Figure 2-12 [163, 166].

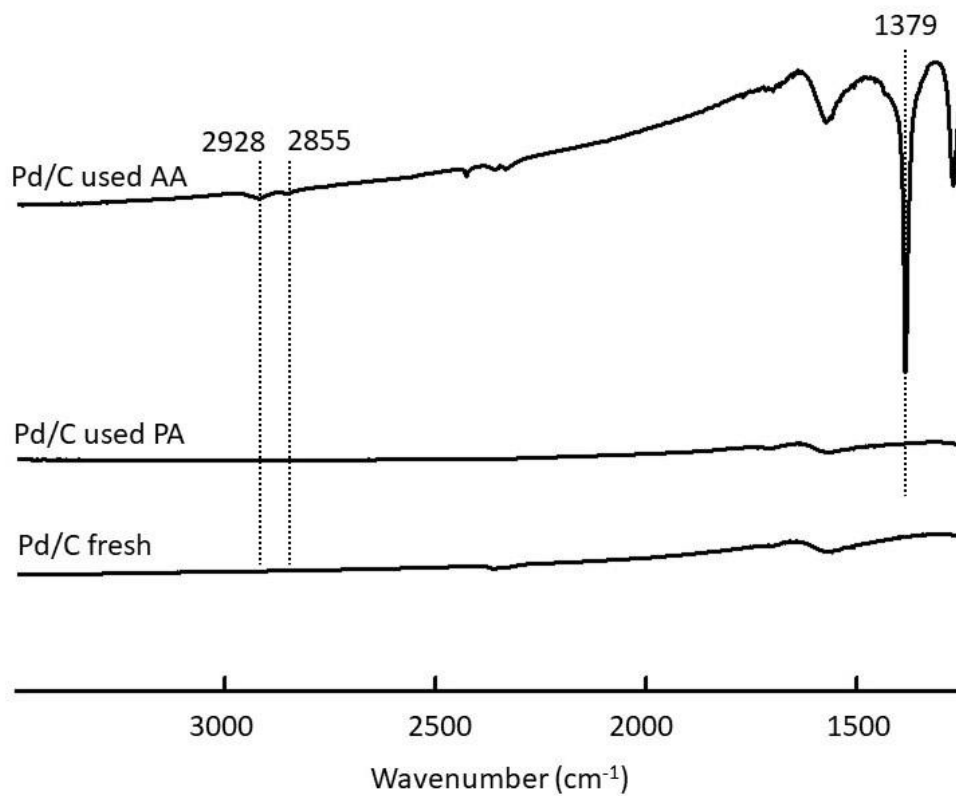


Figure 2-11 FTIR spectra of Pd/C fresh, Pd/C used for decarboxylation of pelargonic acid (PA), and Pd/C used for decarboxylation of azelaic acid (AA)

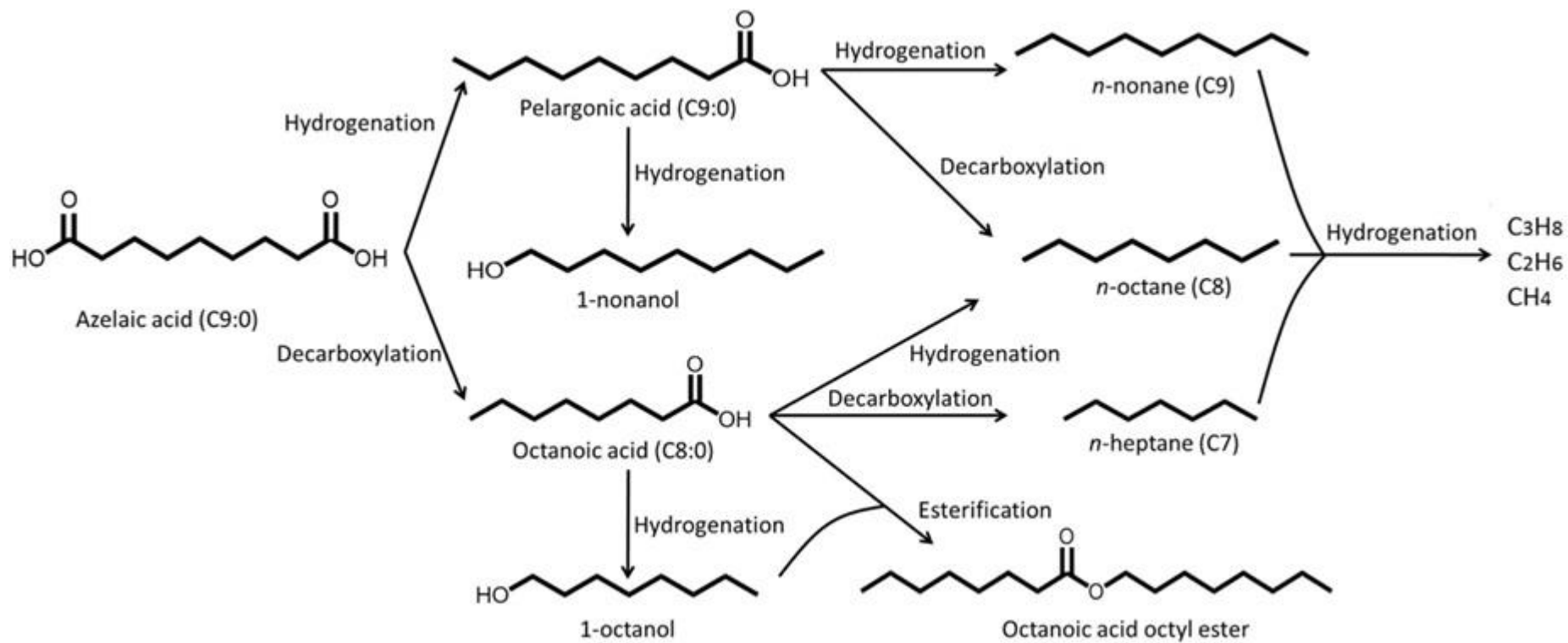


Figure 2-12 Possible reaction pathways for decarboxylation of azelaic acid

Based on results, pelargonic acid and azelaic acid were decarboxylated into 98.2 mol% of *n*-octane and 73.1 mol% *n*-heptane, respectively. The significant yield difference between theoretical and practical results in azelaic acid decarboxylation is due to hydrocarbon coke deposition in the catalyst with the formation of volatile products (methane, ethane and propane), which are not in a range of the carbon chain-length for gasoline, thus lost to the atmosphere. To minimize the formation of such volatile products requires further investigation with overcoming hydrocarbon deposition in the catalyst.

Regarding the oleic acid conversion, 100 mol of oleic acid was converted to 93 mol of pelargonic acid and 86 mol of azelaic acid by oxidative cleavage as in Figure 2-6, and based on decarboxylation performance, those short fatty acids were further decarboxylated into 91 mol of *n*-octane (93 mol \times 98.2%) and 63 mol of *n*-heptane (86 mol \times 73.1%), respectively.

2.4 Concluding remarks

In practical use of biofuels, some problems occur owing to corrosion of rubber, poor oxidation stability and poor cold-flow properties (for biodiesel application). To avoid such drawbacks, the new reaction route of producing hydrocarbons from plant oils through oxidative cleavage followed by decarboxylation was proposed in this study.

By using acid as a model of mono-unsaturated fatty acid, the appropriate reaction conditions were found for oxidative cleavage and decarboxylation. Oleic acid was successfully converted to 93 mol% pelargonic acid and 86 mol% azelaic acid under the condition of 1 wt% emulsifier, molar ratios of KMnO_4 to oleic acid was 4:1 (mol/mol), at 40 °C, for 30 min. Subsequently, pelargonic and azelaic acids were decarboxylated to give 98.2 mol% *n*-octane and 73.1 mol% *n*-heptane, respectively, under the condition of at 300 °C, 1 MPa N_2 , for 3 h.

Decarboxylation of azelaic acid resulted in a lower yield than pelargonic acid, because the deposition of hydrocarbon products on the catalyst and its decomposition occurred during the reaction. Nevertheless, this method has an advance to produce hydrocarbons equivalent to gasoline rather efficiently from renewable plant oils.

Chapter 3 Renewable Gasoline Production from Polyunsaturated Fatty Acids

3.1 Introduction

The potential of plant oils for renewable diesel or gasoline feedstocks has been discussed in Chapter 1. In Chapter 2, a two-step process was proposed for the conversion of monounsaturated fatty acid, oleic acid, to hydrocarbons as renewable gasoline. In the first step, unsaturated fatty acids are treated by oxidative cleavage with KMnO_4 at $40\text{ }^\circ\text{C}$ to obtain short-chain fatty acids. In the second step, the short-chain fatty acids are decarboxylated into hydrocarbons with a Pd/C catalyst at $300\text{ }^\circ\text{C}$. This reaction process resulted in high yield and selectivity to convert oleic acid as a model compound of unsaturated fatty acid into *n*-octane and *n*-heptane. The mild reaction conditions and high product selectivity are the main advantages of the proposed method.

Plant oils which consist of both saturated and unsaturated fatty acids, and each plant oil has an intrinsic fatty acid composition depending on its plant species. Unsaturated fatty acids are classified into monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) according to the number of unsaturated double bonds. The most common PUFA which usually found together with MUFA in plant oils are linoleic acid and linolenic acid. The difference in chemical structure of unsaturated fatty acid may affect the reaction conditions of the proposed two-step process. In this chapter, therefore, linoleic and linolenic acids were investigated as model compounds of PUFA for production of renewable gasoline (C4-C10) applying the same method as the previous work for MUFA in Chapter 2. Combination of the

results in Chapter 2 and Chapter 3 will deliver a comprehensive understanding of further application for real plant oils, which contain both MUFA and PUFA.

3.2 Materials and methods

3.2.1 Materials

Chemicals used in this Chapter 3 are the same as those listed in Chapter 2, except for the unsaturated fatty acid feedstocks. Reagent-grade of linoleic acid and linolenic acid were purchased from Nacalai Tesque (Kyoto, Japan) and used without purification.

3.2.2 Experimental procedures

(1) Oxidative cleavage

The procedure of oxidative cleavage is similar to that explained in Chapter 2. Approximately 0.1 g of linoleic acid or linolenic acid was subjected for each oxidative cleavage reaction. In this chapter, the molar ratio of KMnO_4 was not expressed based on the number of double bonds but the mole of fatty acid molecule.

(2) Decarboxylation

The procedure of decarboxylation was similar to that explained in Chapter 2. Amount of hexanoic acid (monocarboxylic acid, MW=116.16) and azelaic acid (dicarboxylic acid, MW=188.22) applied to the decarboxylation reaction were 0.18 and 0.15 g, respectively; the difference in amount came from the number of carboxyl groups in the reactant. The number of carboxyl groups in 0.18 g of hexanoic acid is 1.55 mmol ($0.18/116.16 \times 1$), while that in 0.15 g of azelaic acid is 1.59 mmol ($0.15/188.22 \times 2$); these are consistent each other against the same

amount of Pd/C catalyst. Decarboxylation was conducted only under N₂ pressure based on the result in Chapter 2.

(3) Analytical methods

All analytical methods were the same as those explained in Chapter 2. In addition, the hydrocarbon products were analyzed by GC-FID using a GC-214 system (Shimadzu) equipped with a CP-FFAP CB column (25 m × 0.32 mm i.d., 0.30 μm thick, Wilmington, US). The column temperature was programmed as follows: 0.2-min hold at 40 °C, ramp increasing to 100 °C at 15 °C/min, 2-min hold at 100 °C, ramp increasing to 240 °C at 7 °C/min. The injector and detector temperatures were set at 270 and 280 °C, respectively.

3.3 Results and discussion

3.3.1 Oxidative cleavage of PUFA

Linoleic acid has two double bonds at carbon numbers 9 and 12, while linolenic acid has three double bonds at carbon numbers 9, 12, and 15. Oxidative cleavage of these double bonds by KMnO₄ will produce monocarboxylic and dicarboxylic acids. The previous study in Chapter 2 showed that oxidative cleavage of oleic acid proceeded effectively in an emulsified system. Therefore, in this study, 1 wt% of emulsifier (PLE) was used in oxidative cleavage of linoleic and linolenic acids. The reaction conditions for oxidative cleavage of PUFA were investigated using various molar ratios of oxidizing agent (KMnO₄) to PUFA and at different reaction temperatures.

The products of oxidative cleavage were monocarboxylic acids and dicarboxylic acids; they are abbreviated by using the number of carbon atoms, followed by a colon and the number of double bonds as shown in parentheses.

(1) Oxidative cleavage of linoleic acid

Table 3-1 shows the major products of linoleic acid oxidative cleavage, which are hexanoic [monocarboxylic acid (C6:0)] and azelaic [dicarboxylic acid (C9:0)] acids, after the treatment for 60 min. In addition, minor compounds of monocarboxylic acids such as pentanoic (C5:0), heptanoic (C7:0), octanoic (C8:0), pelargonic (C9:0), dodecanoic (C12:0) acids; and dicarboxylic acids such as heptanedioic (C7:0) and octanedioic (C8:0) acids were observed in the reaction products, which might be produced from side reactions occurred during the oxidative cleavage.

The effect of the oxidizing agent (KMnO₄) concentration (Entries 1–4) was investigated. In a stoichiometric oxidative cleavage, 16 mol of KMnO₄ is needed to react with 3 mol of linoleic acid ($16/3 = 5.3/1$). When the molar ratios of KMnO₄ to linoleic acid was less than the stoichiometric amount (4:1, Entry 1), the yield of acid products was low. Excess amount of KMnO₄ increased the product yield, and the optimum reaction condition was found when the molar ratio of KMnO₄ to linoleic acid of 8:1 (Entry 3), yielding 90.3 mol% of hexanoic acid and 49.6 mol% of azelaic acid. With a more excessive amount of KMnO₄ (Entry 4), the product yield decreased. In this case, decomposition of products was considered to occur. Therefore, the molar ratio of 8:1 was applied to the following studies for linoleic acid.

The effect of reaction temperature on oxidative cleavage of linoleic acid (Entries 5–8) was also studied. The product yields were slightly affected by temperature. Increasing the temperature from 30 to 40 °C (Entries 5–6) slightly increased the acid products. However, further increasing the temperature to 60 °C caused a decrease of acid products because the emulsion system broke to some extent under such high-temperature condition. These results suggest that 40 °C was the optimal temperature for oxidative cleavage of linoleic acid.

Table 3-1 Yields of the product obtained by oxidative cleavage of linoleic acid with KMnO_4 in 1 wt% emulsifier for 60 min treatment.

Entry	Molar ratio of KMnO_4 to linoleic acid	Reaction temperature ($^{\circ}\text{C}$)	Acids product yield (mol%)		
			Hexanoic acid (C6:0)	Azelaic acid (C9:0)	Others ^a
1	4:1	40	64.1	32.7	5.6
2	6:1		74.6	46.4	12.9
3	8:1		90.3	49.6	17.1
4	10:1		73.4	53.8	13.0
5	8:1	30	88.9	50.0	15.3
6		40	90.3	49.6	17.1
7		50	82.5	52.9	16.3
8		60	82.2	50.0	15.3

^a Monocarboxylics of (C5:0), (C7:0), (C8:0), (C9:0), (C12:0) and dicarboxylics of (C7:0), (C8:0).

The time dependence in oxidative cleavage of linoleic acid was also investigated with 8:1 KMnO_4 at 40 $^{\circ}\text{C}$ and the results are summarized in Figure 3-1. When the molar ratio of KMnO_4 to linoleic acid was 8:1 at 40 $^{\circ}\text{C}$, the product yields (hexanoic, azelaic and others) increased rapidly during the initial stage of the reaction until 10 min, then reached plateau to give about 90 mol% hexanoic acid and 50 mol% azelaic acid.

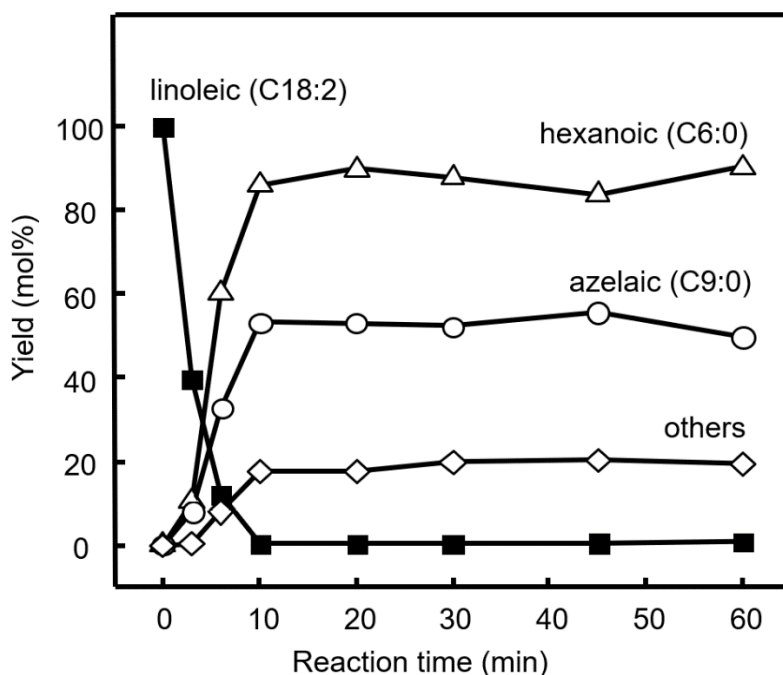


Figure 3-1 Yields of hexanoic, azelaic, and other acid products obtained by oxidative cleavage of linoleic acid in aqueous KMnO_4 solution with 1 wt.% emulsifier at 40 °C (KMnO_4 :linoleic acid molar ratio = 8:1)

In Table 3-1, the yield of azelaic acid was lower than that of hexanoic acid. The possible reason for this difference might be other undesirable reactions. Therefore, the stability of azelaic and hexanoic acids was investigated under similar condition for oxidative cleavage. The obtained result is shown in Table 3-2. In the case without KMnO_4 (Entry 1) at 50 °C, azelaic acid was stable and gave no degraded product. However, when it was mixed with KMnO_4 solution at designated conditions (Entries 2 and 3), azelaic acid was partly degraded into other products, such as butanedioic, pentanedioic, heptanedioic, and octanedioic acids. The higher temperature (Entries 3 and 4) and concentration of KMnO_4 caused more degraded products. On the other hand, hexanoic acid showed tolerance against further decomposition under the same condition (Entries 4 and 5). Although the degradation mechanism remained

unclear, these results suggest that KMnO_4 acts not only for the oxidative cleavage but also for the degradation of azelaic acid.

Theoretically, oxidative cleavage of linoleic acid will produce azelaic, hexanoic, and malonic acids. However, malonic acid (C3 dicarboxylic acid) is highly soluble in water, which is used as a medium for this oxidative cleavage reaction. After the reaction, malonic acid is expected to remain in the reaction mixture, but it would be difficult to collect malonic acid from the water phase. In addition, malonic acid has three carbon atoms, which cannot be expected to produce hydrocarbons in the composition range of gasoline. Figure 3-2 illustrates the oxidative cleavage of linoleic acid by KMnO_4 to produce hydrocarbons.

Table 3-2 Stability of azelaic and hexanoic acids under various KMnO_4 concentrations and temperatures.

Entry	Fatty acid	KMnO_4 : Fatty acid	Temperature (°C)	Degraded products (mol%)
1	Azelaic acid	0:1	50	0.0
2	Azelaic acid	4:1	50	26.5
3	Azelaic acid	6:1	50	38.0
4	Azelaic acid	4:1	40	16.2
5	Hexanoic acid	4:1	40	6.0

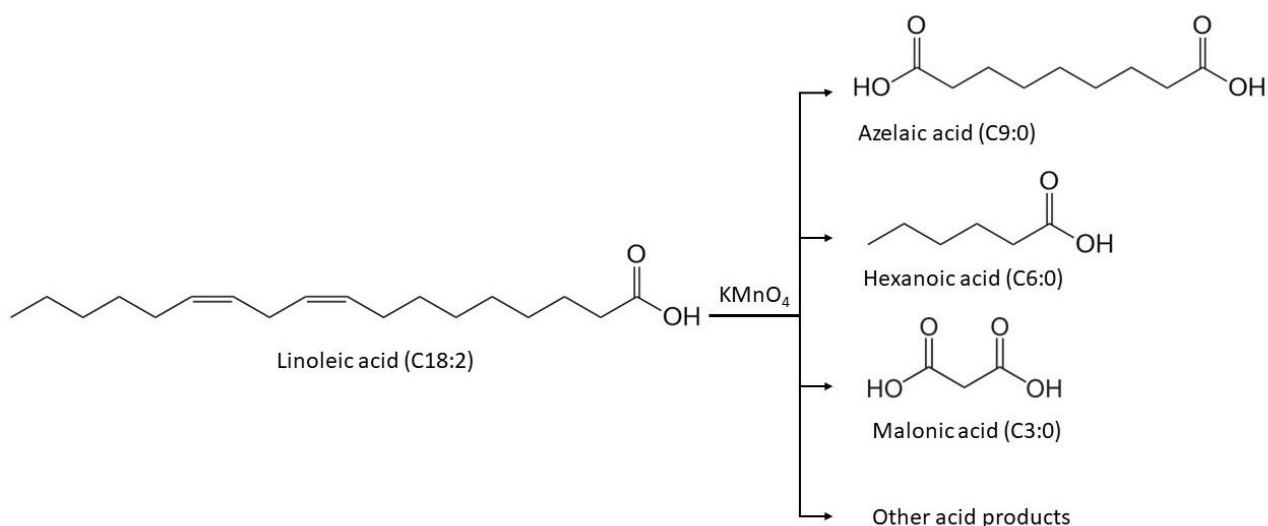


Figure 3-2 Oxidative cleavage of linoleic acid to produce short-chain fatty acids.

(2) Oxidative cleavage of linolenic acid (C18:3)

The same experiment was applied for linolenic acid to find out the optimum reaction conditions for oxidative cleavage, and the results are summarized in Table 3-3. Minor fatty acids were also observed in the product, such as hexanoic, dodecanoic, heptanedioic, octanedioic, and sebacic acids, which are shown as others in this table. This phenomenon is similar to the oxidative cleavage of linoleic acid. Although the main product is azelaic acid, the other fatty acids were produced by side reactions during the oxidative cleavage, or by the decomposition of azelaic acid.

Table 3-3 Yields of the product obtained by oxidative cleavage of linolenic acid with KMnO_4 in 1 wt.% emulsifier for 60 min.

Entry	Molar ratio of KMnO_4 to linolenic acid	Reaction temperature (°C)	Acid product yield (mol%)	
			Dicarboxylic acid (C9:0)	Others ^a
1	8:1	40	35.9	6.8
2	10:1		55.8	13.0
3	12:1		47.6	13.8
4	14:1		44.2	12.9
5	10:1	30	51.8	9.0
6		40	55.8	13.0
7		50	60.0	14.7
8		60	51.9	11.6

^aMonocarboxylics of (C6:0), (C12:0) and dicarboxylics of (C7:0), (C8:0), (C10:0).

Stoichiometrically, 24 mol of KMnO_4 will react with 3 mol of linolenic acid ($24:3 = 8:1$). To determine the optimum ratio of KMnO_4 for linolenic acid, experiments were conducted by changing the ratio from 8:1 to 14:1 (KMnO_4 : linolenic acid) as shown in Table 3-3 (Entries 1-4). The highest yield was achieved at 10:1 (Entry 2), producing 55.8 mol% of azelaic acid. Further trials were conducted at this molar ratio (10:1) to investigate the effect of reaction temperature (Entries 4-8). The reaction at 50 °C (Entry 7) gave the highest yield of azelaic acid (60.0 mol%).

Figure 3-3 shows the effect of reaction time for linolenic acid under the condition with the molar ratio of 10:1 (KMnO_4 : linolenic acid) at 50 °C. The product yields increased sharply at the early stage of the reaction until 30 min, and then slightly increased up to 60 min to yield 56 mol% of azelaic acid. Compared to linoleic acid, oxidative cleavage of linolenic acid had a lower reaction rate; therefore, it needed a longer treatment time.

The oxidative cleavage of linoleic acid, which has three double bonds, is theoretically expected to produce azelaic, malonic, and propionic acids. Propionic acid is also highly soluble in water as well as malonic acid as aforementioned. Therefore, malonic and propionic acids are difficult to be collected from the water phase. Even if they can be collected, we cannot convert them into renewable gasoline because of too short carbon length. Figure 3-4 illustrates the oxidative cleavage of linolenic acid by KMnO_4 to produce hydrocarbons.

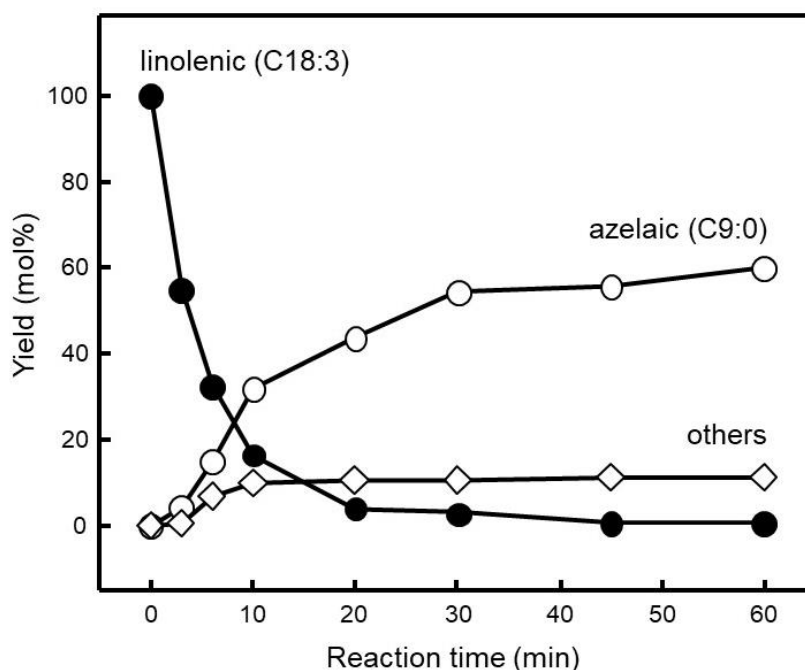


Figure 3-3 Yields of azelaic and other acid products obtained by oxidative cleavage of linolenic acid in aqueous KMnO_4 solution with 1 wt.% emulsifier at 50 °C (KMnO_4 :linoleic acid molar ratio = 10:1).

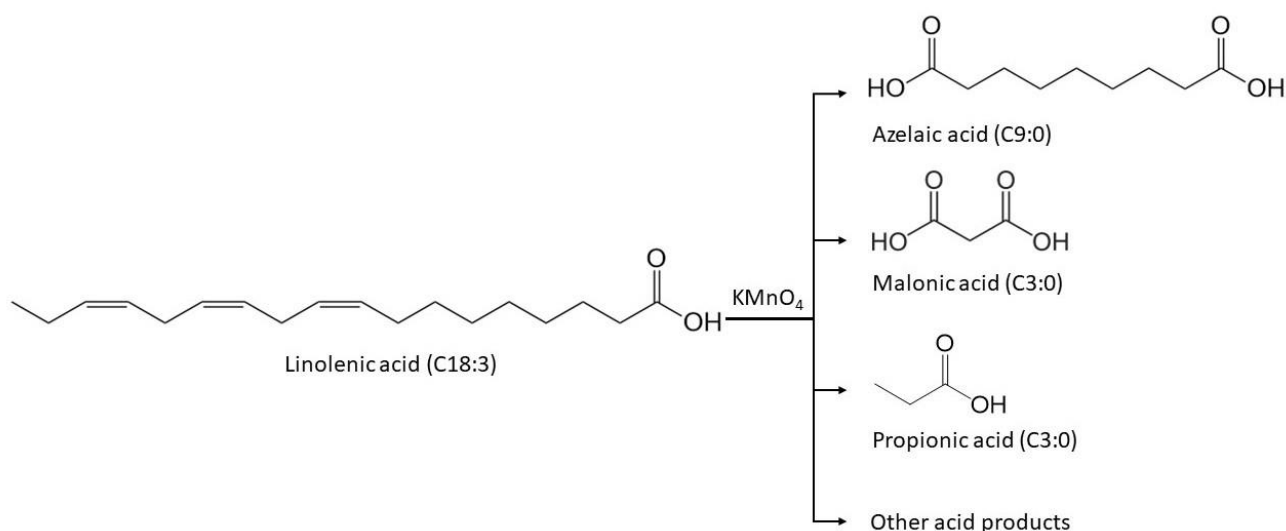


Figure 3-4 Oxidative cleavage of linolenic acid to produce short-chain fatty acids.

3.3.2 Decarboxylation of azelaic and hexanoic acids

The main products from the oxidative cleavage (azelaic and hexanoic acids) were then used to study the decarboxylation behaviors. Because the decarboxylation of azelaic acid into hydrocarbons was studied in Chapter 2 [118], the behavior of hexanoic acid was mainly examined in this chapter.

In the previous chapter, we understood that the decarboxylation of azelaic and pelargonic acids was more successful under N₂ atmosphere. For the current chapter, therefore, N₂ was used to pressurize the reaction vessel (0.1–10 MPa) for the decarboxylation of hexanoic acid. Figure 3-5 shows the N₂ pressure dependence on the hydrocarbon yield for decarboxylation of azelaic and hexanoic acids to *n*-heptane and *n*-pentane, respectively, with Pd/C catalyst at 300 °C for 6 h. The data of azelaic acid is taken from the previous work in Chapter 2 [118].

Figure 3-5 revealed that the N₂ pressure did not significantly affect the yield of *n*-heptane (C₇) from azelaic acid. The yield of *n*-heptane was around 70 mol% under wide range of N₂

pressure. For decarboxylation of hexanoic acid, the increase in N₂ pressure from 0.1 to 1 MPa increased the *n*-pentane (C₅) yield from 44.2 to 73.7 mol%.

One difference between hexanoic and azelaic acids is the number of carboxyl groups; hexanoic acid is mono-, and azelaic acid is dicarboxylic acid. At the applied reaction temperature (300 °C), hexanoic acid is most likely in gas phase when the pressure is less than 1 MPa, because its boiling point is 205 °C at 0.1 MPa and 310 °C at 1 MPa, which was estimated by using a steady-state process simulator Pro/II, ver 10.1 (Schneider Electric, Rueil-Malmaison, France). If the reactant becomes gas, the accessibility to the Pd/C catalyst will become poor compared with the liquid reactant. The low hydrocarbon yield from hexanoic acid at low pressures might be because of the low boiling point. However, the hydrocarbon yield from hexanoic acid decreased when the reaction pressure increased more than 1 MPa. Although the reason remained unclear, it is considered that a part of *n*-pentane might be volatilized and lost when recovering the reaction product, because the boiling point (36 °C at atmospheric pressure) is close to room temperature.

In contrast, two carboxylic groups in azelaic acid have more extensive association of intermolecular hydrogen bonding. Hence the boiling point of azelaic acid is high (360 °C at atmospheric pressure), so azelaic acid is always in the liquid phase at the given condition. That may be the reason why the hydrocarbon yield from azelaic acid did not depend on the pressure.

Figure 3-6 shows the time dependence of azelaic and hexanoic acids decarboxylation to *n*-heptane and *n*-pentane, respectively, as treated at 300 °C and 1 MPa (N₂). The reaction rate of azelaic acid (C₉ dicarboxylic acid) was rapid in the first 3 h and then plateaued to produce about 69 mol% *n*-heptane. In contrast, hexanoic acid (C₆ monocarboxylic acid) showed a steady reaction rate until almost all hexanoic acid had been consumed in 6 h to give about 73.5 mol% *n*-pentane. The decarboxylation rate of azelaic acid was higher than that of hexanoic acid.

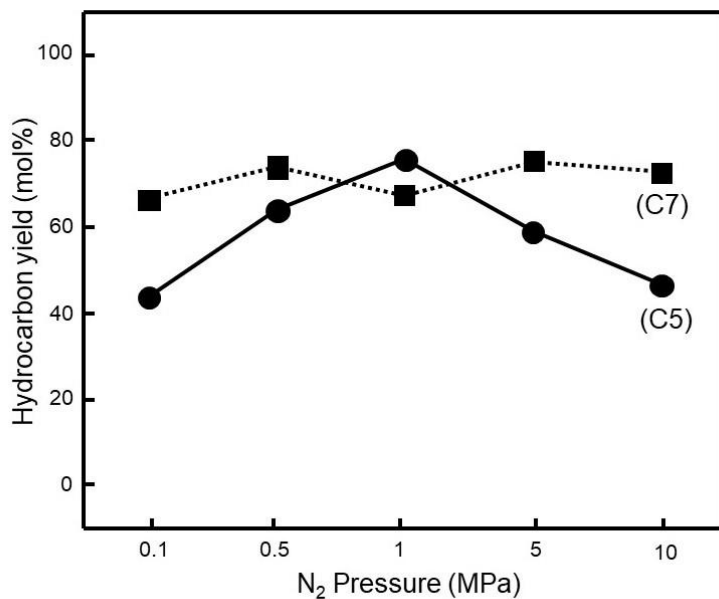


Figure 3-5 N₂ pressure dependence of product yields for decarboxylation of azelaic acid [118] and hexanoic acid to *n*-heptane and *n*-pentane, respectively, with Pd/C catalyst at 300 °C.

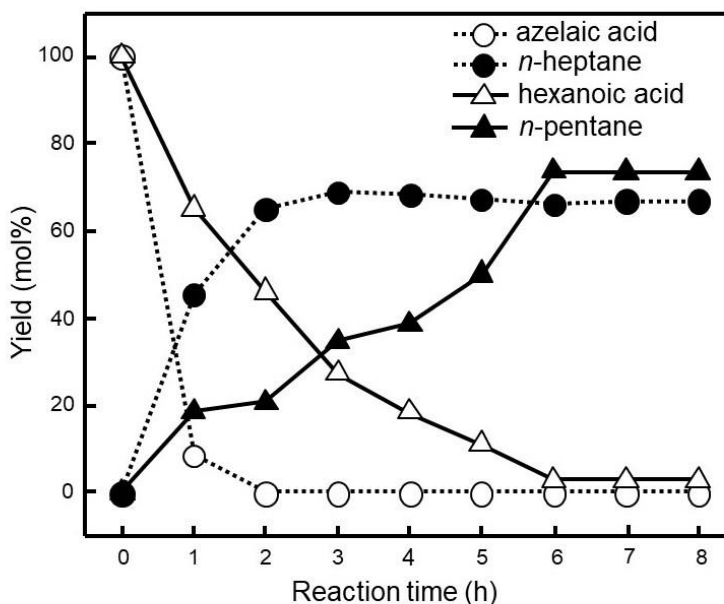


Figure 3-6 Time dependence of product yield for decarboxylation of azelaic acid [118] and hexanoic acid to *n*-heptane and *n*-pentane with Pd/C catalyst (300 °C, 1 MPa N₂).

Kipling and Wright [167], Jeffrey et al. [163], and Mohite et al. [168] reported that the lower decarboxylation rate was observed in the decarboxylation of shorter carbon chain acids. They found that fatty acids with shorter carbon chain have poorer adsorption onto the activated carbon support. In general, the number of methylene groups in the molecule is an important factor, but the polarity of the reactant could also play a role. In addition, as the estimated boiling point of hexanoic acid at 1MPa (310 °C) is close to the reaction temperature (300 °C), there is a possibility that a part of hexanoic acid may be still in gas phase. If the gas phase existed, the reactivity would decrease as aforementioned.

Furthermore, significant differences were observed between the theoretical and practical yields for the decarboxylation of azelaic and hexanoic acids; the product yields were not close to 100% (Figure 3-6). In this case, decomposition reactions and deposition of the hydrocarbon products on the catalyst were likely considered.

The decomposition reaction was confirmed by analyzing the gas phase of the decarboxylation products by Micro GC. For the azelaic acid decarboxylation, H₂ and short-chain hydrocarbons, such as methane, ethane, and propane were detected [118]. For the hexanoic acid decarboxylation, H₂ and methane were detected. These observations suggest that some hydrocarbon products decompose into H₂ and short-chain hydrocarbons during the decarboxylation reaction. These volatile hydrocarbon compounds are not in the composition range of gasoline (C₄–C₁₀), and will be lost to the atmosphere together with H₂.

To confirm deposition of the product on the catalyst, FTIR analysis was performed with fresh and used catalysts (Figure 3-7). Several absorption bands appeared in the spectra of the used catalysts that were not observed for the fresh catalyst. A strong absorption band at about 1384 cm⁻¹ was assigned to the skeleton vibration of CH in CH, CH₂, or CH₃ in aliphatic groups [165]. Another band at about 1716 cm⁻¹ was assigned to the C=O stretching peak of carboxylic acid groups [169]. Furthermore, two peaks at about 2858 and 2924 cm⁻¹ were assigned to C-H

stretching in CH₂ groups and were likely attributable to the adsorbed reaction products. Based on these lines of evidence, in azelaic acid decarboxylation, some unreacted carboxylic acid and hydrocarbon products did not diffuse out of the catalyst, resulting in a coke formation.

About 17% of other fatty acids from the oxidative cleavage of linoleic acid (Figure 3-1) are also expected to be decarboxylated into hydrocarbons in gasoline range. Similarly, 12 mol of other fatty acids from linolenic acid (Figure 3-3) will be converted into renewable gasoline. Therefore, the yield of hydrocarbons from linolenic and linolenic should be more than those mentioned above. When applying the proposed method to real plant oil, the yield of hydrocarbons will be higher because many plant oils are rich in monounsaturated fatty acid.

The two-step process for renewable gasoline production has several advantages, such as the reaction temperature is milder compared with the catalytic cracking and hydrotreating, and the selectivity for alkane hydrocarbons is very high without paraffin, isoparaffin, olefin, naphthenes and aromatics compounds in the product.

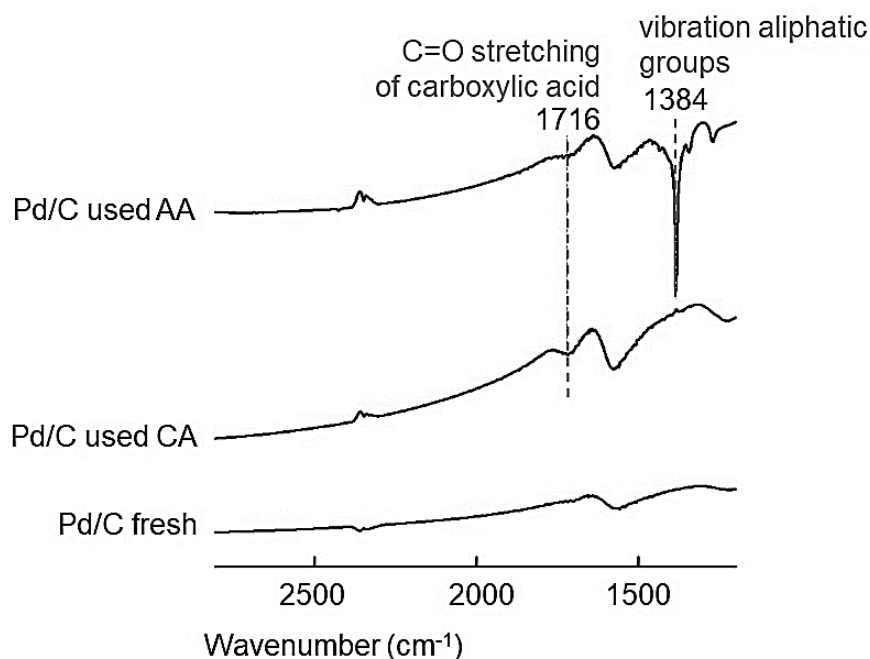


Figure 3-7 FTIR spectra of catalyst: Pd/C fresh, Pd/C used after decarboxylation of hexanoic acid (HA), and Pd/C used after decarboxylation of azelaic acid (AA).

3.4 Concluding remarks

The proposed method for hydrocarbon production from PUFA, which involves oxidative cleavage and decarboxylation, was successfully demonstrated. Oxidative cleavage of PUFA produced sufficient yields of target products (azelaic and hexanoic acids) even though malonic and propionic acids were also produced and lost. The hydrocarbon yield from azelaic and hexanoic acids by decarboxylation was around 70 mol% because of the decomposition and deposition of hydrocarbon products on the catalyst. Nevertheless, this method shows considerable potential for the production of hydrocarbons in the gasoline fraction from PUFA, which are found in abundance with MUFA in natural sources. For further application,

unsaturated fatty acids can be obtained from biomass by hydrolyzing the plant oils and then separated from its saturated fatty acids. Then, the unsaturated fraction, which contains MUFA and PUFA, can be treated with the proposed method to get hydrocarbons in the gasoline range.

Chapter 4 Renewable Gasoline and Diesel Production from Palm Oil

4.1 Introduction

Fossil fuel depletion is still a crucial issue in global energy security. The need for renewable biofuels is becoming urgent because of the threat of global climate change. Palm oil is a promising candidate to produce biofuels because of its large-scale production. Driven by high market demand in developing countries, the palm oil industry has grown rapidly. Indonesia and Malaysia dominate the global production of palm oil, accounting for about 85% of world production [170]. However, the European Union decided to ban palm oil-derived biofuels because of the deforestation that has accompanied palm oil cultivation [171]. Indonesia and Malaysia are thus looking for alternative routes to use palm oil; for example, palm oil producers in Indonesia intend to divert palm oil to domestic biofuel production.

Although biofuels, such as biodiesel and bioethanol, have been widely developed, they are oxygenated fuels, which lead to low calorific values, corrosion of engine components, and high affinities with water. Hydrocarbon biofuels are interesting alternatives to overcome these disadvantages of oxygenated biofuels. Hydrocarbon biofuels can be used in vehicles without engine modification because they are similar to fossil fuels. Hydrocarbons can be produced by removing oxygen atoms from triglycerides (TG) of plant oils through deoxygenation reactions [115, 116, 137, 172, 173]. The number of carbon atoms in a hydrocarbon molecule typically ranges from around C₄ to C₁₀ in gasoline and C₁₀ to C₂₀ in diesel derived from fossil fuels.

Conversion of plant oils into hydrocarbons is commonly conducted by catalytic cracking [91, 109] or hydrotreating [174–177]. Zeolite-based catalysts, such as HZSM5 and AlMCM-

41/ZSM5, are extensively used for catalytic cracking because of their acidic properties and large specific surface areas [96, 97]. Hydrotreating is typically performed using metal catalysts, such as Pd, Pt, Ni, Rh, Ir, Ru, and Os, supported on activated carbon or metal oxides [128], [129]. However, both catalytic cracking and hydrotreating are low-selectivity processes and yield a variety of hydrocarbons, particularly from unsaturated fatty acids (FA) [153],[154].

This study therefore developed a high-selectivity process, which involves hydrolysis of TG to FA, followed by oxidative cleavage of unsaturated FA and subsequent decarboxylation [118]. This process was designed with the intention of producing the diesel fraction (C10–20) from saturated FA, such as palmitic and stearic acids, and the gasoline fraction (C4–10) from unsaturated FA, such as oleic and linoleic acids, by cleaving unsaturated double bonds.

In Chapters 2 and 3, reaction conditions were optimized for oxidative cleavage and decarboxylation for oleic, linoleic, and linolenic acids as model FA [118]. Hydrocarbons between C4 and C10 were successfully produced from these FA. Based on these results, this chapter demonstrates the production of renewable gasoline and diesel from a real plant oil. Palm oil was used as the feedstock to produce renewable gasoline and diesel. Because palm oil is composed largely of C16 and C18 saturated and unsaturated FA, it should be possible to produce hydrocarbons in both gasoline and diesel composition ranges.

First, palm oil is hydrolyzed in subcritical water to obtain FA. The hydrolysis product is treated with potassium permanganate (KMnO_4) as an oxidizing agent to cleave double bonds in unsaturated FA, followed by decarboxylation with Pd/C to produce hydrocarbons including gasoline and diesel fractions. Moreover, if separation of saturated and unsaturated FA after hydrolysis is possible, it could allow separate production of gasoline and diesel fractions. This chapter attempt a separation step using the difference in melting points between saturated and unsaturated FA, and compare the results for cases with and without the separation process.

4.2 Materials and methods

4.2.1 Materials

Chemicals used in this Chapter 4 are the same as those listed in Chapter 2, except for the plant oil feedstock and chemical for separation process. In this chapter, refined palm oil was purchased from Fluka (Buchs, Switzerland) and used without purification.

4.2.2 Experimental procedures

(1) Hydrolysis of palm oil

Palm oil (1 mL) and water (4 mL) were charged into a 5-mL batch-type reaction vessel made of Inconel-625 [85]. Hydrolysis was conducted by immersing the vessel in a molten salt bath at the desired temperature (270–300 °C) for 20 min. Subsequently, the vessel was cooled in a water bath (25 °C) to terminate the reaction. The obtained product was extracted using hexane and then kept until the two phases separated. The upper portion containing FA was then evaporated by a rotary vacuum evaporator to remove hexane. The obtained hydrolysis product was analyzed by Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), and gas chromatography–mass spectrometry (GC–MS).

(2) Separation of hydrolysis product

The hydrolysis product (1.0 g) was added to 90 vol% aqueous acetonitrile (10 mL). The mixture was ultrasonically heated at 80 °C for 10 min to melt fully, and then cooled at –15 °C for 20 h to recrystallize saturated FA, which have higher melting points than unsaturated ones. The solid fraction, which was expected to be rich in saturated FA, was collected by using a 0.45- μm centrifugal filter (Nanosep, Pall Corporation, New York, US). The aqueous

acetonitrile was removed from the filtrate by vacuum evaporation to obtain the liquid fraction rich in unsaturated FA.

(3) Oxidative cleavage of unsaturated fatty acids

The procedure of oxidative cleavage was similar to that explained in Chapter 2. Approximately 0.1 g of liquid fraction or solid fraction or crude hydrolysis product was subjected for each oxidative cleavage reaction. The molar ratio of KMnO_4 was expressed based on the mole of fatty acid molecules.

(4) Decarboxylation of fatty acids to hydrocarbons

The procedure of decarboxylation was similar to that explained in Chapter 2. Amount of decarboxylation reactants (oxidative cleavage product of liquid fraction, solid fraction, and crude hydrolysis product) applied to the decarboxylation reaction were 0.15 g. The number of carboxyl groups in reactants are consistent each other against the same amount of Pd/C catalyst.

(5) Analytical methods

All analytical methods those have been explained in Chapter 3 were used in this chapter, except the FTIR spectroscopy method. In addition, gel permeation chromatography (GPC) was used for quantitative analysis of the hydrolysis product.

The hydrolysis product was examined by FTIR spectroscopy using an IRAffinity-1 spectrometer (Shimadzu, Kyoto, Japan) in reflection mode with a GladiATR attachment (Pike Technologies, Wisconsin, US). Furthermore, analysis with GPC was conducted using an LC-10VP system (Shimadzu) under the following conditions. Column: GF-310 HQ (Showa Denko K.K., Tokyo, Japan), oven temperature: 40 °C, eluent: acetone, flow rate: 1.0 mL/min, detector: refractive index detector (RID).

4.3 Results and discussion

4.3.1 Hydrolysis of palm oil

The hydrolysis reaction of palm oil was carried out at temperatures from 270 to 300 °C, and the FTIR spectra of the resulting hydrolysis products are shown in Figure 4-1. The main peaks and their assignment to functional groups are summarized in Table 4-1. For untreated palm oil, the absorption band at 1743 cm^{-1} originates from the C=O stretching vibration of ester groups. After hydrolysis, the absorption at this wavelength decreased, and a new band at 1712 cm^{-1} appeared that was assigned to the C=O stretching of carboxylic groups. A peak at 1166 cm^{-1} from the C-O bending of ester groups was observed for untreated palm oil; the intensity of this peak decreased gradually with rising reaction temperature. Absorption bands at 1292 cm^{-1} from C-O stretching and 941 cm^{-1} from O-H bending of carboxylic acid groups appeared in the FTIR spectra of hydrolysis products. The changes in the FTIR spectra indicate the effective formation of FA when hydrolysis was performed above 290 °C for 20 min.

Table 4-1 The main peaks in FTIR spectra of palm oil hydrolyzates.

Wavelength of untreated palm oil	Wavelength of hydrolyzed palm oil	Functional groups
1743	-	C=O stretching vibration (ester)
-	1712	C=O stretching vibration (carboxylic acid)
1463	1463	C-H scissoring and bending for methylene
-	1292	C-O stretching asymmetric (carboxylic acid)
1166	-	C-O bending vibration (ester)
-	941	O-H bending vibration (carboxylic acid)

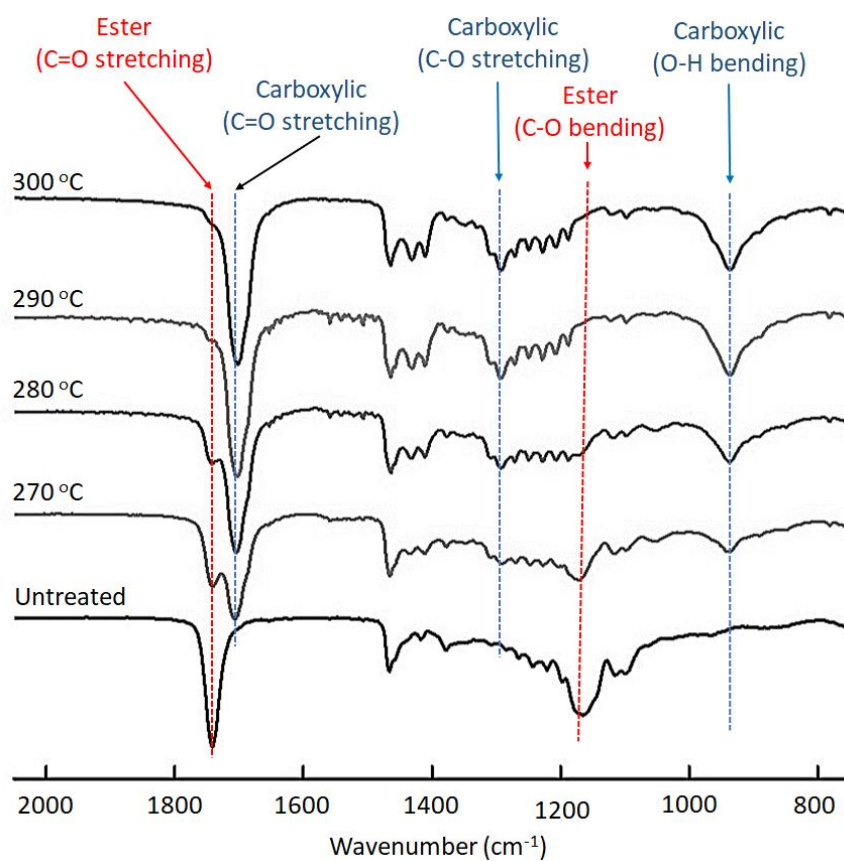


Figure 4-1 FTIR spectra of palm oil hydrolyzed in subcritical water at 270–300 °C for 20 min.

Figure 4-2 shows GPC results for palm oil treated in subcritical water at 270–300 °C for 20 min. The products were separated into three peaks; TG, diglycerides (DG), and a mixture of monoglycerides (MG) and FA. The results of GPC analysis are consistent with those of FTIR analysis. A higher hydrolysis temperature gave lower yields of unreacted TG and DG. The GPC data were used to quantify the hydrolysis products. However, because the peak from MG was overlapped with that from FA, the yields of MG and FA were determined by GC-MS analysis. The yield of each product is shown in Table 4-2. When the reaction temperature was increased from 270 to 300 °C, TG yield decreased from 13.2 to 0.5 wt%. The yields of DG and MG also decreased to only 1.1 and 2.0 wt%, respectively when the reaction temperature was raised from 270 to 300 °C. In contrast, FA yield increased monotonically from 52.2 to 88.8 wt% based on palm oil. The theoretical maximum yield of FA from palm oil is calculated to be 96.6 wt%; the decrease from 100 wt% is caused by the formation of glycerol as by-product. The FA yield of 88.8 wt% corresponds to about 92% conversion based on the theoretical maximum. The composition of FA obtained from the hydrolysis of palm oil is also listed in Table 4-2. The major saturated and unsaturated FA were palmitic and oleic acids, respectively. Hydrolysis of palm oil at 300 °C for 20 min gave the best results, so the product obtained under these conditions was used in the next step.

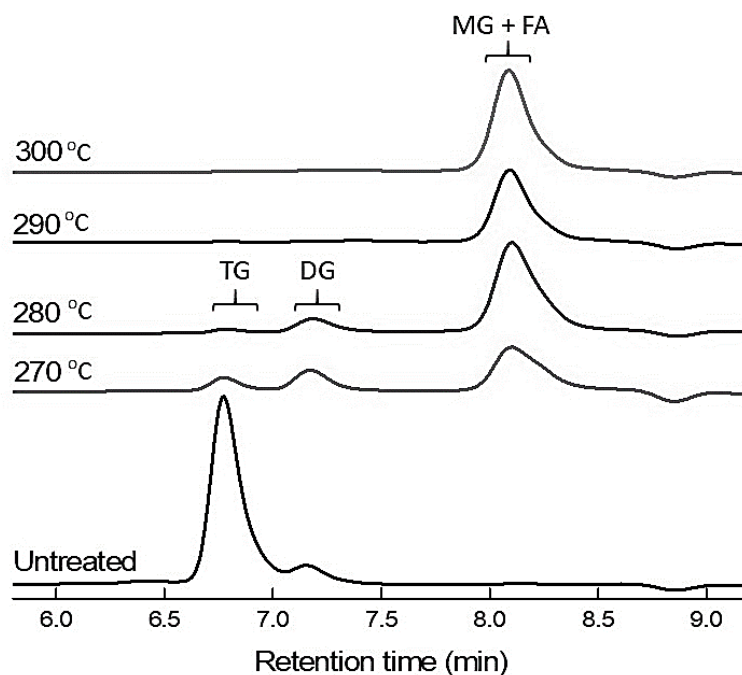


Figure 4-2 GPC traces of palm oil hydrolyzed in subcritical water at 270–300 °C for 20 min.

Table 4-2 Yields of the products obtained by subcritical water treatment of palm oil for 20 min at different temperatures.

Composition	Yield (wt% on palm oil)			
	270 °C	280 °C	290 °C	300 °C
Triglycerides	13.2	2.6	0.4	0.5
Diglycerides	10.6	9.0	2.5	1.1
Monoglycerides	14.1	10.0	7.6	2.0
Fatty acids	52.2	68.7	77.7	88.8
Myristic acid (C14:0)	1.2	0.0	1.8	2.1
Palmitic acid (C16:0)	22.9	30.6	33.8	38.9
Stearic acid (C18:0)	3.5	4.8	5.4	5.8
Arachidic acid (C20:0)	0.3	0.4	0.5	0.6
Oleic acid (C18:1)	20.1	27.3	30.5	35.9
Linoleic acid (C18:2)	4.2	5.6	5.8	5.5

4.3.2 Separation of saturated and unsaturated fatty acids

The product obtained from palm oil hydrolysis at 300 °C consisted of saturated and unsaturated FA with ratios of 47.4 and 41.4 wt%, respectively, as calculated from Table 4-2. Saturated FA are expected to be converted into renewable diesel, whereas the unsaturated ones are anticipated to provide the gasoline fraction. Therefore, the separation of saturated and unsaturated FA by recrystallization from aqueous acetonitrile was studied.

From 1.0 g of the hydrolysis product, 43.0 wt% solid and 49.5 wt% liquid fractions were recovered; the remaining 7.5 wt% was lost during the separation process. The solid fraction was rich in saturated FA as expected; the ratio of saturated to unsaturated FA was 89.8:10.2 (w/w) according to GC-MS analysis. The liquid fraction included a higher proportion of unsaturated FA; the ratio of saturated to unsaturated was 26.3:73.7 (w/w). Thus, only a rough separation was achieved by the recrystallization method. Because unsaturated FA remained in the solid fraction, both liquid and solid fractions were subject to oxidative cleavage.

4.3.3 Oxidative cleavage of hydrolysis product

Double bonds in oleic and linoleic acids can be oxidatively cleaved with KMnO_4 to give monocarboxylic (pelargonic and hexanoic acids) and dicarboxylic acid (azelaic acid). The previous study showed that oxidative cleavage proceeded effectively in an emulsified system (1 wt% aqueous PLE) and the appropriate molar ratios of KMnO_4 to unsaturated FA were found to be 4:1 and 8:1 for oleic (monounsaturated) and linoleic (diunsaturated) acids, respectively.

In this study, the oxidative cleavage of the liquid fraction was first examined with various molar ratios of KMnO_4 at 40 °C for 30 min. When the molar ratios of KMnO_4 to unsaturated FA were 4:1, 6:1, and 8:1, the quantified total yields of FA were 115.1, 112.8, and 114.0 wt%,

respectively, based on reactant FA; values higher than 100 wt% are caused by the introduction of oxygen atoms. Theoretically, 120.3 wt% yield is expected for the liquid fraction if complete oxidative cleavage occurs. These results indicated that a 4:1 molar ratio of KMnO_4 to unsaturated FA is sufficient to achieve a high conversion rate of 95.7% (115.1/120.3 wt%); this is because the amount of linoleic acid in palm oil is small. The high conversion might mean that saturated FA in the liquid fraction did not affect the oxidative cleavage of unsaturated FA.

Oxidative cleavage was therefore conducted with 4:1 of KMnO_4 to unsaturated FA for the separated liquid and solid fractions and crude hydrolysis product (without separation); the results are summarized in Table 4-3. The solid fraction exhibited a high conversion rate above 90 %, like the liquid fraction. In contrast, the crude hydrolysis product showed only 81.8% conversion. The low conversion might result from the degradation of long-chain FA (C16:0 and C18:0) by KMnO_4 as found previously. In the cases of liquid and solid fractions, the influence of the degradation of long-chain FA by KMnO_4 is thought to be limited. This is because the amounts of C16:0 and C18:0 in the liquid fraction were small; in addition, the solid fraction, which was low in unsaturated FA, only required a small amount of KMnO_4 to achieve effect oxidative cleavage.

Table 4-3 Yields of fatty acids obtained by oxidative cleavage of the hydrolysis products with KMnO_4 (KMnO_4 :fatty acid molar ratio of 4:1) at 40 °C for 30 min.

Composition	Yield (wt% on reactant fatty acids)		
	with separation		without
	Liquid fraction	Solid fraction	separation
Hexanoic acid (C6:0)	3.7	0.2	2.1
Azelaic acid (C9:0)	39.3	4.1	21.3
Pelargonic acid (C9:0)	28.8	3.3	17.1
Palmitic acid (C16:0)	20.8	73.6	34.1
Stearic acid (C18:0)	3.1	9.7	3.8
Other fatty acids	19.4	2.7	11.2
(a) Total fatty acids	115.1	93.6	89.6
(b) Theoretical maximum * ¹	120.3	101.7	109.5
Conversion (a/b, %)	95.7	92.0	81.8

*1: The theoretical maximum is the yield if all unsaturated fatty acids in the reactant are oxidatively cleaved.

4.3.4 Decarboxylation

In the previous work, the decarboxylation of model FA (hexanoic, pelargonic, and azelaic acids) was studied with Pd/C under 5 MPa of N_2 , and the results showed a shorter FA needed a longer reaction time [118]. Hexanoic acid (C6:0) required 6 h for decarboxylation, whereas pelargonic acid (C9:0) took only 3 h. In this study, the reaction time for the oxidative cleavage product from the liquid fraction was examined; the results are depicted in Figure 4-3.

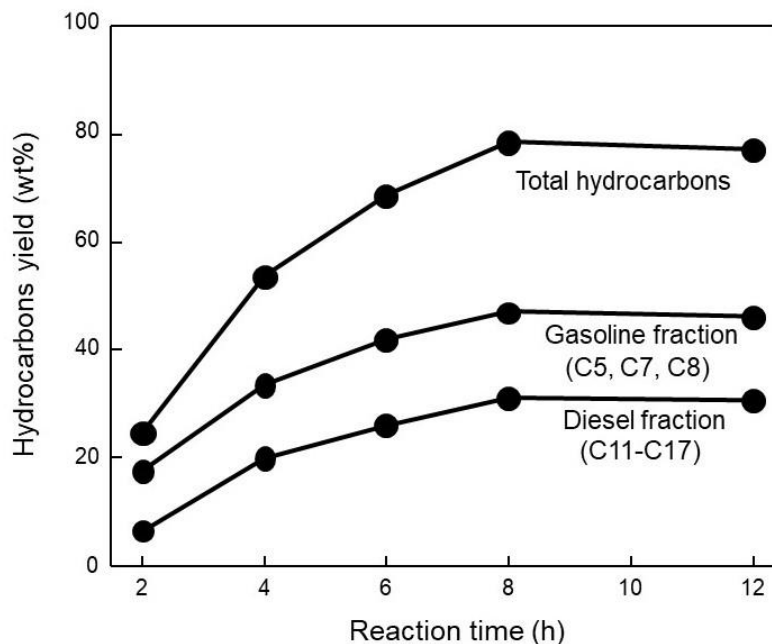


Figure 4-3 Yields of hydrocarbons from the oxidative cleavage product of the liquid fraction by decarboxylation with Pd/C at 300 °C / 5 MPa (N₂).

The hydrocarbons obtained were a mixture of gasoline and diesel fractions. In this study, C5, C7, and C8 hydrocarbons were assigned to the gasoline fraction and longer ones were assigned to diesel fraction. Figure 4-3 shows that the yields of both fractions increased with the reaction time until they reached a plateau after 8 h. The maximum yields were about 47 wt% of gasoline fraction and 31 wt% of diesel fraction after reaction for 8 h. The long reaction time might be related to the presence of short FA in the reactant. A reaction time of 8 h was then used for the other oxidative cleavage products; the results are summarized in Table 4-4.

The major hydrocarbons in the gasoline fraction were *n*-heptane (C₇H₁₆) and *n*-octane (C₈H₁₈), whereas the main component of the diesel fraction was *n*-pentadecane (C₁₅H₃₂). Furthermore, micro-GC analysis revealed the formation of gaseous products such as H₂, methane (CH₄), ethane (C₂H₆), and propane (C₃H₈). The formation of gaseous products

indicates that hydrocarbon decomposition occurred during decarboxylation to form lower hydrocarbons.

Although the solid fraction (after separation) and crude hydrolysis product (without separation) exhibited high conversion rates of 86.4 and 86.9 wt%, respectively, the sample from the separated liquid fraction showed slightly lower conversion. The reason for this remained unclear, but it is feasible that part of the gasoline fraction was lost during the experiment because the liquid fraction was rich in hydrocarbons in the gasoline fraction, which are volatile

Table 4-4 Yields of hydrocarbons obtained by decarboxylation at 300 °C/5 MPa N₂ with Pd/C for 8 h.

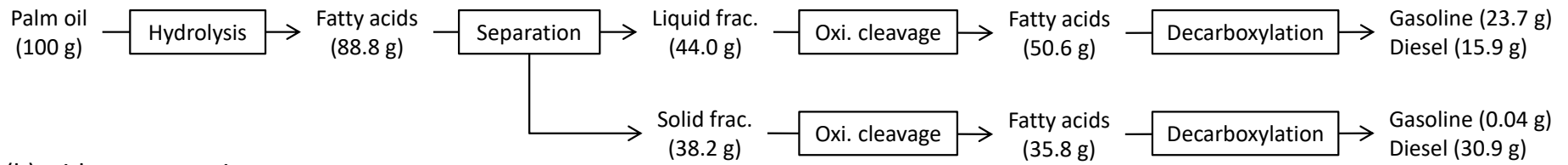
Hydrocarbons	Yield (wt% on oxidative cleavage product)		
	with separation		without separation
	Liquid fraction	Solid fraction	
Gasoline fraction	46.9	0.1	26.6
<i>n</i> -pentane (C ₅ H ₁₂)	2.7	0.0	1.6
<i>n</i> -heptane (C ₇ H ₁₆)	21.0	0.0	12.2
<i>n</i> -octane (C ₈ H ₁₈)	23.2	0.1	12.8
Diesel fraction	31.4	86.3	60.3
<i>n</i> -undecane (C ₁₁ H ₂₄)	2.8	0.1	0.0
<i>n</i> -dodecane (C ₁₂ H ₂₆)	1.0	0.3	3.1
<i>n</i> -tetradecane (C ₁₄ H ₃₀)	3.1	0.5	1.8
<i>n</i> -pentadecane (C ₁₅ H ₃₂)	16.6	70.0	48.3
<i>n</i> -hexadecane (C ₁₆ H ₃₄)	0.7	0.0	0.0
<i>n</i> -heptadecane (C ₁₇ H ₃₆)	7.2	15.4	7.1
Total hydrocarbons	78.3	86.4	86.9

4.3.5 Comparison of whole process between with/without separation

Figure 4-4 shows the schemes and product yields of the whole process from 100 g of palm oil, which were based on the conversion rate of each reaction step. The process with the separation step produced 23.7 g of gasoline and 15.9 g of diesel from the liquid fraction and 0.04 g of gasoline and 30.9 g of diesel from the solid fraction (Figure 4-4(a)). Therefore, 23.7 g of gasoline and 46.8 g of diesel are expected from 100 g of palm oil. Because the products are still mixtures of gasoline and diesel fractions, a distillation step is necessary to completely refine the products into gasoline and diesel fractions.

In the case without separation (Figure 4-4(b)), 21.2 g of gasoline and 48.0 g of diesel were produced, giving a total hydrocarbon weight of 69.2 g, which is almost the same as the case with separation. When the separation was conducted, the conversion rate in oxidative cleavage was high, but 7.5 wt% of the sample was lost during the separation, as mentioned in Section 4.3.2. Therefore, the advantage of separation process was not found in this study because the hydrocarbon yield was not improved. However, the effect of separation still remains unclear. In this study, the oxidative cleavage might be unnecessary for the solid fraction because it contained only small amounts of unsaturated fatty acids. In additions, if an efficient separation process were developed, it would benefit the production of renewable gasoline and diesel fuels.

(a) with separation



(b) without separation

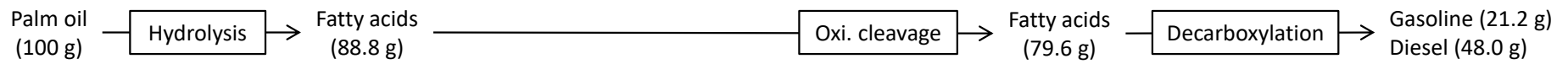


Figure 4-4 Comparison of the hydrocarbon production processes from palm oil between the cases with (a) and without (b) separation step.

The proposed separation process would be preferable for feedstocks rich in saturated fatty acids. As we know that only unsaturated fatty acids will react with KMnO_4 in the oxidative cleavage reaction. The presence of saturated fatty acids in the reaction system is unfavorable because it will require more energy to heat the reactants during oxidative cleavage. Furthermore, partial degradation by KMnO_4 is possible to occur, resulting in lower product yields in oxidative cleavage. Although the complete separation was not be achieved in Figure 4-4(a), a higher portion of unsaturated fatty acids was collected in liquid fraction and most of saturated fatty acids were in the solid fraction. Especially for the solid fraction, a small amount of unsaturated fatty acids is not a problem. The oxidative cleavage step might be omitted for the solid fraction, which can be directly subjected for decarboxylation to produce diesel fraction. Therefore, a general hydrocarbon production process from plant oils is proposed in Figure 4-5.

A common separation method of saturated and unsaturated fatty acids is recrystallization. To improve the phase separation, an organic solvent such as methanol, acetone, methyl formate, and propane can be used [178]. Urea inclusion method was also reported to perform effectively the separation of saturated and unsaturated fatty acids [179]. However, all those methods need very low crystallization temperatures, less than $0\text{ }^\circ\text{C}$, which will be a drawback in net energy balance in producing renewable energy. However, for the large scale application, these processes may be less preferred because evaporation is required to separate fatty acids and organic solvent. Multistage supercritical gas extraction can emerge as an alternative to separate saturated and saturated fatty acids in the future [180].

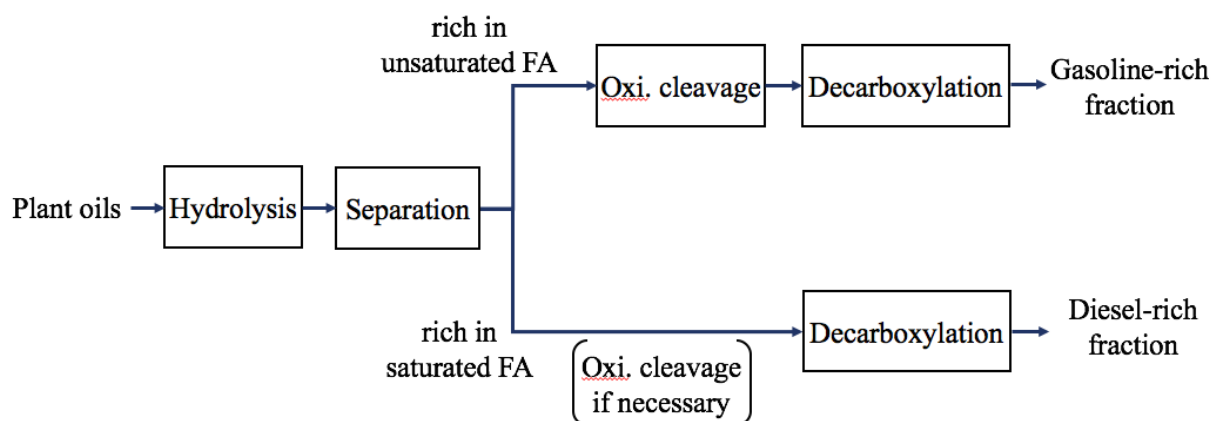


Figure 4-5 Hydrocarbon production process from plant oils.

The proposed method has advantages of the milder reaction temperature and high selectivity for alkane hydrocarbon products. Hydrocarbons obtained from the proposed method are in the form of straight-chain alkanes. In the case of diesel fraction, straight-chain alkanes are appropriate for diesel engine because they have high cetane numbers. The main components of the diesel fraction are *n*-pentadecane and *n*-heptadecane. Those two major compounds have a relatively high boiling point. Furthermore, the cold-flow properties such as pour point and cold filter plugging point are poor due to the form of straight-chain alkanes. To be used as fuel for diesel engine, the cold-flow properties should be improved to fulfill the standard diesel fuel. Blending the product of diesel fraction with fossil diesel until it meets all requirements of the specification standard is appropriate to achieve this purpose.

In the case of gasoline fraction, the major components are *n*-heptane and *n*-octane. These two major compounds have very low octane number. Three strategies can be suggested to use the product of gasoline fraction; first is to blend only a small volume of the gasoline fraction with a large amount of fossil gasoline. The second strategy is to blend the gasoline fraction with high octane compounds, such as aromatic compounds. The third strategy is to rearrange

the chemical structures of the gasoline fraction to get branched alkanes which have high octane numbers. Furthermore, although some of the component in gasoline fraction is in the range of jet fuel carbon number range, application for jet fuel is difficult. The requirements for jet fuel are more strict, because it must possess the right freezing point and boiling point distribution.

4.4 Concluding remarks

A proposed hydrocarbon production method involving hydrolysis, oxidative cleavage, and subsequent decarboxylation was successfully demonstrated using palm oil as the feedstock. All the reaction steps worked well for palm oil, producing hydrocarbons in gasoline and diesel fractions with yields of 21.2 wt% and 48.0 wt%, respectively. Although a separation process of saturated and unsaturated FA after hydrolysis was studied, the separation was not high enough, and the total hydrocarbon yield was not improved compared to the case without the separation step. Further investigations using highly unsaturated plant oils, such as sunflower, safflower, and soybean oils to produce gasoline-rich hydrocarbons should be conducted. In this study, KMnO_4 was used as the oxidant for oxidative cleavage, but it was consumed during the reaction. Thus, non-consumed and heterogeneous solid catalysts would be more preferable than KMnO_4 for oxidative cleavage, although such a prospect is challenging.

Chapter 5 Concluding Remarks

5.1 Conclusions

Interest in producing renewable energy from biomass sources has increased significantly. The most popular biomass-based liquid fuels to replace petroleum-based fuels are biofuels, such as bioethanol and biodiesel. Oxygen content is the main difference between biofuels and petroleum-based fuels. Biofuels contain 10-45 % of oxygen atoms in their molecules as hydroxy or ester group, whereas petroleum fuels consist of hydrocarbons, which are oxygen-free. The high oxygen content in biofuels causes low energy density and corrodes common metals. Thus, the need for renewable hydrocarbon fuels attracts high interest.

Plant oils mainly consist of triglycerides, which are triesters of one glycerol and three fatty acids. Because fatty acids molecules have alkyl chains similar to petroleum fuels, plant oils hold the potential to be converted into hydrocarbons by removing oxygen atoms. Up to present, the progress in direct upgrading of triglycerides into hydrocarbons has applied catalytic cracking and hydrotreating. These hydrocarbon fuels are called as ``renewable gasoline and renewable diesel``. However, high temperatures of more than 300 °C are necessary to conduct catalytic cracking and hydrotreating because of low reaction rate of triglycerides. The high reaction temperatures cause various side reactions, such as isomerization, cyclyzation, and aromatization, so that these conventional methods are low-selectively process for hydrocarbon production.

Given things mentioned above, a high selectivity reaction for hydrocarbons production from plant oils was proposed. This study proposed to hydrolyze plant oil triglycerides into fatty acids before hydrocarbons production because fatty acids are more reactive for hydrotreating than triglycerides; it allows lower reaction temperatures and high product selectivity.

Furthermore, the conventional catalytic cracking and hydrotreating process did not consider the presence of saturated and unsaturated fatty acids content. Since C=C double bonds in unsaturated fatty acids, such as oleic, linoleic, and linolenic acids, are very reactive, many side reactions can occur during the high-temperature process, which results in poor product selectivity, yielding a broad range of hydrocarbons. Therefore, this study proposed an oxidative cleavage reaction for unsaturated fatty acids to produce short-chain fatty acids under very low reaction temperatures. Subsequently, the obtained short-chain fatty acids are subjected to decarboxylation reaction at mild temperature (300 °C) to remove the oxygen atoms. The proposed process, which consist of hydrolysis, oxidative cleavage, and decarboxylation, will realize a high-selectivity hydrocarbons production in the composition range of gasoline (C4-C10). If the high-selectivity process is established, we can predict the composition of hydrocarbons from the fatty acid composition of feedstock plant oil.

In Chapter 1, the potential plant oils as feedstock for renewable hydrocarbon fuel production was studied. Advances and current knowledge of plant oils, their chemical composition, extraction methods, and their utilization for biofuels as well as renewable hydrocarbon fuels production were discussed.

Unsaturated fatty acid is the key factor to obtain hydrocarbons in renewable gasoline because the C=C double bond can be cleaved to get short-chain fatty acids which are suitable for hydrocarbons production in the composition range of gasoline. The most common MUFA in plant oils is oleic acid with 18 carbons and one double bond at the ninth carbon (C18:1). The investigation and study of oleic acid as a model MUFA to optimize the reaction condition for oxidative cleavage and decarboxylation were conducted in Chapter 2. An appropriate reaction condition for oxidative cleavage of oleic acid was at 1 wt% emulsifier, molar ratios of KMnO₄ to oleic acid was 4:1 (mol/mol), at 40 °C, for 30 min to obtain 93 mol% pelargonic acid and 86 mol% azelaic acid. Treating at 5 MPa N₂ atmosphere at 300 °C was appropriate for assisting

Pd/C catalyst to effectively produce 98.2 mol% *n*-octane (C8) and 73.1 mol% *n*-heptane (C7). Whereas H₂ atmosphere causes undesired hydrogenation reactions, which decrease the product selectivity.

Furthermore, in Chapter 3, investigation was conducted on the most typical PUFA in nature, linoleic and linolenic acids. Linoleic acid has two double bonds at carbon numbers 9 and 12 (C18:2), while linolenic acid has three double bonds at carbon numbers 9, 12, and 15 (C18:3). The study of the difference in chemical structure that may affect the reaction conditions of the proposed process was explored in Chapter 3. Oxidative cleavage of linoleic acid performed effectively at molar ratios of KMnO₄ to oleic acid was 8:1 and temperature reaction similar to oleic acid at 40 °C to get 90 mol% of hexanoic acid and 53 mol% of azelaic acid. But oxidative cleavage of linolenic acid needed higher temperature reaction at 50 °C at molar ratios of KMnO₄ to oleic acid was 10:1 to get 60 mol% of azelaic acid. Furthermore, the decarboxylation rate of hexanoic acid was lower compare to azelaic acid; the reason reminds unclear, but the difference in carbon chain length or chemical properties such as boiling point would affect the decarboxylation reaction. Catalytic decarboxylation with Pd/C catalyst 300 °C yielded hydrocarbons of 73.5 mol% *n*-pentane and 73.1 mol% *n*-heptane.

Based on the obtained results from the use of model compounds oleic, linoleic and linolenic acids, application of the proposed method for hydrocarbon production from real plant oil was discussed in Chapter 4, palm oil was selected as feedstock. Palm oil contains unsaturated and saturated fatty acids with carbon number between C14 and C20; therefore, hydrocarbons in the composition ranges of gasoline and diesel are possible to produce. The studies were more complicated because palm oil is needed to be hydrolyzed in subcritical water to get fatty acids and the obtained fatty acids are subjected to the hydrocarbon production. A separation process of saturated and unsaturated fatty acids was also investigated after hydrolysis, because if the separation was achieved, we can produce renewable gasoline and

diesel independently without distillation. The result showed that in the case of palm oil, hydrolysis reaction performed effectively to give high yield about 89 wt%. However, the complete separation was not achieved, and the only rough separation was possible with a higher portion of unsaturated fatty acids was collected in liquid fraction and most of saturated fatty acids were in the solid fraction. Especially for the solid fraction, a small amount of unsaturated fatty acids is not a problem. The oxidative cleavage step might be omitted for the solid fraction, which can be directly subjected for decarboxylation to produce diesel fraction. Total reaction with separation process could produce gasoline and diesel fractions with yields of 23.74 wt% and 46.8 wt%, respectively. While reaction without separation process could produce hydrocarbons in gasoline and diesel fractions with yields of 21.2 wt% and 48.0 wt%, respectively. The separation process did not improve the yield of hydrocarbons compared to the case without separation. Conclusively, this study emphasized the potential of plant oil for renewable hydrocarbon fuels production.

The proposed method produces hydrocarbons in the form of straight-chain alkanes. In the case of diesel fraction product, straight-chain alkanes are appropriate for diesel engine because they have high cetane numbers. Blending the product of diesel fraction with fossil diesel until it meets all requirements of the specification standard is appropriate to utilize it as fuel for diesel engine. In the case of gasoline fraction, the major hydrocarbon product has very low octane number. One of three strategies, which are blending a small volume of gasoline fraction with a large amount of fossil gasoline; blending the gasoline fraction with high octane compounds; or rearranging the chemical structures of the gasoline fraction to get branched alkanes which have high octane numbers can be selected to use the product of gasoline fraction.

5.2 Prospects for future research

This dissertation covers the behaviour of monounsaturated fatty acid and polyunsaturated fatty acids for hydrocarbon gasoline production by oxidative cleavage and decarboxylation as well as palm oil feedstock. A strong oxidizing agent of KMnO_4 is used in the oxidative cleavage step, however, in large scale application it may less interest because of fatty acids solubility in the reaction system can decrease the process efficiency and KMnO_4 is consumed during the reaction. Thus, the further step of this research is considering green alternatives for the oxidative cleavage of $\text{C}=\text{C}$ double bonds in fatty acid reactants. This field is valuable to be explored further to get a new alternative method with safer and more economically viable process. Furthermore, the investigation using highly unsaturated fatty acids of plant oil feedstocks, such as sunflower, safflower, and soybean oils, should be conducted to obtain gasoline-rich hydrocarbons. Further study of separation saturated and unsaturated fatty acids was also important for production of gasoline and diesel fractions separately.

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