[Review Paper]

Renewable Hydrocarbon Fuels from Plant Oils for Diesel and Gasoline

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The issues of global CO₂ emissions and depletion of non-renewable energy resources associated with fossil fuels encourage the use of plant oils (both edible and non-edible) as biofuel sources. This review summarizes the literature on renewable hydrocarbon fuel production, including feedstock choice, oil extraction, and production processes. Plant oils can be upgraded into hydrocarbon biofuels by catalytic cracking or deoxygenation reactions, such as hydrodeoxygenation, decarboxylation and decarbonylation. This review also covers current progress in renewable hydrocarbon fuel blending with fossil diesel or gasoline to meet the requirements of product quality for engine fuel applications.

Keywords

Renewable hydrocarbon fuel, Plant oil, Catalytic cracking, Deoxygenation, Fuel blending

1. Introduction

Petroleum fuel consumption has increased in recent decades due to rapid population growth and more industrialization. Unfortunately, greater use of these energy resources has resulted in serious problems, including national energy security, environmental pollution, and depletion of fossil fuel reserves^{1),2)}. Therefore, alternative sources of petroleum-based fuels are extremely desirable.

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 biomass³⁾. The most common biomass-based liquid fuels to replace petroleum-based fuels are biofuels such as bioethanol and biodiesel, which mainly consist of fatty acid methyl esters (FAME). Biofuels have many advantages, such as reduction of greenhouse gas emissions, sustainability, and security of supply^{4),5)}.

Oxygen content is the biggest difference between biofuels and petroleum-based fuels, at almost zero in petroleum-based fuels compared with about 10–45 % in biofuels³⁾, so many properties are very different. The high oxygen content in biofuels results in low energy density and tends to cause corrosion in common metals⁶⁾. Therefore, the need for renewable hydrocarbon

fuels has encouraged high interest in renewable energy sources other than bioethanol and biodiesel. Plant oils mainly consist of triglycerides, which have similar carbon chains to petroleum-based fuels. Therefore, the triglycerides in plant oils can be converted into hydrocarbons through removal of oxygen to produce renewable hydrocarbon fuels.

Production of renewable hydrocarbon fuels begins with the choice of feedstock, which depends on the oil content and fatty acid composition of the plant oils. Different plant oils with various fatty acid compositions can be used to produce different renewable hydrocarbon fuels. Edible plant oils are currently the main resources for study of renewable hydrocarbon fuels such as oils from soybean, sunflower, rapeseed, and oil palm. However, increasing the available supply of renewable fuels from industrialized agriculture as currently practiced could be problematic in the future because of the potential conflict between crop productions for energy as opposed to food⁷⁾. Therefore, the research focus should shift to non-edible resources.

Several methods for converting plant oils to renewable hydrocarbon fuels are available, including catalytic cracking^{2),8),9)} and deoxygenation^{10)–17)}, but all have specific advantages and disadvantages. Catalytic cracking can obtain a high yield of renewable hydrocarbon fuels at relatively low reaction temperature. Deoxygenation is widely used to upgrade plant oils by removing oxygen with or without the addition of hydrogen.

Therefore, this review presents an overview of renewable hydrocarbon fuel production by considering the use of various edible and non-edible plant oils in

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different treatment methods and production processes to emphasize the importance of the feedstock on the characteristics of renewable hydrocarbon fuels.

2. Feedstock Characteristics

Considerable effort is currently being committed to develop renewable hydrocarbon fuels using organic feedstocks, such as edible and non-edible plant oils, municipal solid wastes, algae, fats, greases, woody biomass, and waste cooking oils^{18)~20)}. The organic materials considered as potential feedstocks for renewable hydrocarbon fuels primarily consist of carbohydrates, lignins, and lipids²¹⁾. In particular, lipid-based plant oils are the main feedstock for biofuel production due to their high oil content; so are the primary interest of this review.

2.1. Edible and Non-edible Plant Oils

Plant oils are a promising basis for biofuels production because such feedstocks are naturally renewable and environmentally friendly. Many different plant oils are utilized in the oil chemistry or biofuel industries. However, few of these plant oils have the characteristics necessary for biofuel production, such as high oil content and well-structured supply chains. About 80 % of plant oils worldwide are produced from rapeseeds, sunflowers, soybeans, oil palms, and coconuts¹⁹⁾. Plant oil seeds are usually processed through cold-pressing or solvent-extraction techniques to obtain oil primarily consisting of triglycerides that can be converted into renewable hydrocarbon fuels²⁾. However, rapid population growth worldwide and extensive human consumption of edible oils has caused numerous problems, such as global imbalances in the food supply and demand market²²⁾. In addition, the large-scale expansion of oil crop plantations has caused ecosystem deforestation and destruction. Consequently, the significantly high demand for edible oils as food competes with the high demand for biofuels production, which have led to increases in the global price for plant oils. Therefore, non-edible oils have greater practicality as feedstock for biofuel production. However, land availability and the impact of plant oil crops on the environment are also very important in deciding which type of crop should be grown²³⁾.

This movement from edible to non-edible plant oils for biofuel production feedstock will solve many problems, such as food-versus-fuel, environmental, and economic issues²⁴⁾. Non-edible plant oils often contain toxic components and so are unsuitable for human consumption. Moreover, non-edible plant oils can be cultivated in unproductive areas, degraded forests, and on public lands, such as along railways, roads, and irrigation canals. Therefore, biofuels production from non-edible plant oils is considered to be a sustainable source to archive global energy security in general²⁵⁾.

Previous research to use pure edible and non-edible plant oils as diesel fuel has processed oil such as jatropha, karanja, soybean, rapeseed, sunflower, and oil palm oils by preheating, blending with diesel fuel, or dual gaseous and liquid fuels^{26)~32)}. However, such plant oils have high oxygen content and low heating value and storage stability³³⁾. Furthermore, major problems occurred with carbon deposit formation in internal combustion engines during long-term usage³⁴⁾. Therefore, methods to upgrade plant oils into renewable hydrocarbon fuels are very important.

2.2. Plant Oil Yield

Biofuel production will depend on the availability of an ample supply of the feedstock in any specific region. Therefore, different plant oils are generally used as raw materials to produce biofuels in different countries. The key factor to determine the suitability of a feedstock for renewable hydrocarbon fuels production is the oil yield; so clearly plant oils with higher yields are preferable.

Table 1 shows the oil yield and content for various edible and non-edible plant oils. Edible plant oils have yields from 147 to 5000 kg oil per hectare (kg/ha). The oil palm (*Elaeis guineensis*)⁴⁰⁾ has the highest oil yield with 5000 kg/ha, followed by coconut (*Cocos nucifera*)⁴⁰⁾ and walnut (*Juglans regia*)⁴⁹⁾, which can produce 2260 kg/ha and 2160 kg/ha oil yield, respectively, among the various edible plant oils that can be considered as biofuels feedstock. Edible plant oils are found in large amounts in the seeds and occasionally in the kernel part. Oil palm oil is present in high amount in both seed and kernel with oil contents of 30-60 wt% and 44-65 wt%, respectively^{24),38)}. Oil palm is mainly cultivated in Malaysia and Indonesia, coconut oil in the Philippines, soybean (*Glycine max*) oil in the United States, and rapeseed (*Brassica napus*) and sunflower (*Helianthus annuus*) oils are widely grown in many European countries⁶³⁾.

Non-edible plant oils, except for green algae (*Botryococcus braunii*), have yields from 80 to 3621 kg/ha. Mahua (*Madhuca indica*)^{35),38)} has the highest oil yield of 3621 kg/ha, followed by neem (*Azadirachta indica*)¹⁾, karanja (*Pongamia pinnata*)⁵⁸⁾, and jatropha (*Jatropha curcas*)^{40),56)}, which can produce 2670, 2250, and 1590 kg/ha, respectively. **Table 1** summarizes many other promising feedstocks for biofuel production obtained from non-edible plant oils. Jatropha is the most studied non-edible plant oil feedstock for producing biofuels. Jatropha is a fast-growing tree capable of producing high amounts of oil from its seed (30-50 wt%) and kernel (45-60 wt%), and can be cultivated in tropical and semitropical regions, and even on marginal land^{52),64)~67)}. Jatropha originates from South America, but has spread throughout Africa and Asia. Mahua and karanja grow in India and have been successfully introduced to humid, tropical regions of

Table 1 Oil Yield and Content in Various Edible and Non-edible Plant Oils

Plant	Oil yield [kg/ha]	Oil content [wt%]		Ref.
		Seed	Kernel	
Edible oils				
Almond (<i>Prunus dulcis</i>)	1500	55	-	35),36)
Canola (<i>Brassica campestris</i>)	1190	38-45	-	37),38)
Cashew (<i>Anacardium occidentale</i>)	148	43-50	11.8	39),40)
Coconut (<i>Cocos nucifera</i>)	2260	-	65-75	37),40)
Corn (<i>Zea mays</i>)	147	40-55	-	35),37),40),41)
Cotton (<i>Gossypium hirsutum</i>)	273	15-25	-	37),40)
Hazelnut (<i>Corylus avellana</i>)	405	-	51.4-75.1	40),42)
Hemp (<i>Cannabis sativa</i>)	305	30-35	-	40),43)
Jojoba (<i>Simmondsia chinensis</i>)	1528	43-49	-	38),40),44)
Oil palm (<i>Elaeis guineensis</i>)	5000	30-60	44-65	24),38),40)
Peanut (<i>Arachis hypogaea</i>)	890	36-56	-	35),40)
Pumpkin (<i>Cucurbita pepo</i>)	449	31.6	-	45)
Rapeseed (<i>Brassica napus</i>)	1000	38-46	-	24),38),40)
Safflower (<i>Carthamus tinctorius</i>)	665	17.5-32	-	35),40),46)
Sesame (<i>Sesamum indicum</i>)	585	48.5-60	-	40),47),48)
Soybean (<i>Glycine max</i>)	375	16-22	-	35),37),40)
Sunflower (<i>Helianthus annuus</i>)	800	25-50	-	35),38),40)
Walnut (<i>Juglans regia</i>)	2160	54.2-72.2	-	35),49)
Non-edible oils				
Castor (<i>Ricinus communis</i>)	1188	45-53	-	24),35),38),40)
Country almond (<i>Terminalia catappa</i>)	-	49-57.5	-	50)
Croton (<i>Croton tiglium</i>)	900	30-45	50-60	35)
Cuphea (<i>Cuphea painter</i>)	144-446	10-39.5	-	51),52)
Desert date (<i>Balanites aegyptiaca</i>)	1816	36-47	-	35)
Ethiopian mustard (<i>Brassica carinata</i>)	481	42	2.2-10.8	35),53)
Green algae (<i>Botryococcus braunii</i>)	> 15000	25-75 ^{a)}	-	54)
Jatropha (<i>Jatropha curcas</i>)	1590	30-50	45-60	35),37),40),55),56)
Kapok (<i>Ceiba pentandra</i>)	1167	28.7	-	57)
Karanja (<i>Pongamia pinnata</i>)	225-2250	25-50	30-50	35),38),58)
Kokum (<i>Garcinia indica</i>)	570	45-45.5	-	52),59)
Kusum (<i>Schleichera triguga</i>)	500-800	-	55-70	35),52)
Linseed (<i>Linum usitatissimum</i>)	402	28-44	-	37),40),52)
Mahua (<i>Madhuca indica</i>)	3621	35-50	50	35),38)
Milkweed (<i>Asclepias syriaca</i>)	1100	20-25	-	35),38)
Moringa (<i>Moringa oleifera</i>)	1230	33-41	2.9	1)
Nahor (<i>Mesua ferrea</i>)	-	58-75	-	35)
Neem (<i>Azadirachta indica</i>)	2670	20-30	25-45	1)
Oleander (<i>Thevetia peruviana</i>)	1575	8.41	60-67	1),60)
Rubber (<i>Hevea brasiliensis</i>)	80-120	40-60	40-50	1),24)
Sea mango (<i>Cerbera odollam</i>)	-	54	-	61)
Soapnut (<i>Sapindus mukorossi</i>)	-	51.8	-	55)
Sugar apple (<i>Annona squamosa</i>)	314	15-23	-	35),62)
Syringa (<i>Melia azedarach</i>)	-	10	-	1)
Tobacco (<i>Nicotiana tabacum</i>)	100	30-43	-	38)
Tung (<i>Aleurites fordii</i>)	790	16-40	-	35),38),40)

a) In the cell.

Australia, New Zealand, China, and the USA⁵²⁾. Neem is native to India, Pakistan, and Sri Lanka, and can grow in almost all soil types including clay, saline, alkaline, and even dry soils^{1),52)}. Many non-edible plant oils are extracted from both seed and kernel parts.

Microalgae are another important source of non-edible plant oil, with superior growth rates, short maturity, high lipid productivity, and potential to cultivate on marginal or nonarable land areas^{54),68),69)}. The lipid content of several microalgae species may exceed 70 % of dry weight⁷⁰⁾. For example, *Botryococcus braunii*,

a species of green algae, has very high oil yield of greater than 15,000 kg/ha and the oil content can range from 25 to 75 dry wt% (**Table 1**). However, oil extraction from microalgae is tedious and expensive, involving high energy consumption^{71),72)}, which is one of the key reasons why production of biofuels from microalgae has not yet entered the commercial stage⁷³⁾.

2. 3. Plant Oil Composition

Feedstock characteristics, mainly the fatty acid composition, are other important criteria to determine the suitability of plant oils for producing hydrocarbon bio-

fuels. The oil composition will determine the type of processing required to produce hydrocarbon biofuels and the properties of the resultant hydrocarbon biofuels.

Fatty acids in the oils are categorized into saturated and unsaturated fatty acids. Unsaturated fatty acids contain one or more double bonds in the carbon chain. **Table 2** shows the fatty acid composition of various types of edible and non-edible plant oils. Fatty acids are specified by two numbers in parentheses and separated by a colon. The first number is the number of carbon atoms, and the second is the total number of double bonds present.

The type of fatty acid and the content mainly depend on the plant species and growth conditions. The major fatty acid composition in both edible and non-edible plant oils is generally similar, except for coconut⁷⁴, castor (*Ricinus communis*)³⁸, and tung (*Aleurites fordii*)³⁷ oils, with palmitic, stearic, oleic, and linoleic acids as the main fatty acids. Coconut oil has the highest composition of lauric acid (47.5-52.0 wt%)⁷⁴, castor oil contains the specific unsaturated ricinoleic acid (86-90 wt%)³⁸, which is soluble in most organic solvents, and tung oil has a high content of trienoic α -eleostearic acid (84 wt%)³⁷.

3. Plant Oils Extraction

Extraction of the oils from seeds and kernels first requires drying to the appropriate moisture level. Oil extraction methods include mechanical, chemical, and enzymatic methods⁵², but mechanical and chemical methods are the most commonly used for commercial oil processes. Mechanical extraction using expellers can extract oils directly from seeds or kernels or mixtures, whereas chemical extraction requires pretreatment of the materials^{86,87}.

3.1. 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 physically squeeze the oil out of the seeds or kernels. 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 no supplemental heat is added to the process. This method is reported to extract 60-86 % of the available oil^{52,88} and can process many oil seeds, including soybean, sunflower, sesame (*Sesamum indicum*), Ethiopian mustard (*Brassica carinata*), and jatropha seeds^{67,89}. A hydraulic press expeller was used to extract the oil from jatropha seeds, successfully recovering about 86 wt% of oil^{88,90}, a screw press expeller recovered around 70 wt% oil from soybean seeds⁹¹ and successfully recovered oil from sunflower seeds⁹².

The advantages of the mechanical extraction method

are the simple and available for processing small capacities. The absence of solvent residues in the oil results in a high-quality clean and pure oil rich in color and flavor. However, the machine design might not be suitable for different 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 through solvent extraction.

3.2. Chemical Extraction

Chemical extraction is a method for processing oil from seeds or 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%⁵². Chemical extraction can be used to extract jatropha, neem, soybean, and safflower (*Carthamus tinctorius*) oils, among others^{78,79,94}.

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^{52,89,93~95}. The water content of the seed is important because the water could wet the seed surface, which will interfere with penetration of the solvent into the seeds. However, a certain degree of moisture is needed to maintain the elasticity of the seed flakes and prevent disintegration. Furthermore, the particle size and shape must allow the optimum extraction from each individual particle by minimizing diffusion pathways. Selection of the solvent is important, as the viscosity should be sufficiently low to allow free circulation. The most commonly used solvent is hexane because of the specific characteristics, such as high volatility, which facilitate separation from the solid and oil with low energy input. In addition, hexane is immiscible with water, so that the water will remain in the seed or oil whereas the hexane will continue in the system during the extraction process. Furthermore, hexane dissolves and mixes well with plant oils so that the desired oils can be easily extracted from the seeds or kernels.

The oldest type of chemical extraction method is the soxhlet equipment. Many recent studies have explored the application of ultrasound to improve the extraction rate and product quality, and to reduce the extraction time⁹⁶. Furthermore, studies have developed 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)⁹⁷. Moreover, a 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% from hydraulic cold pressing⁹⁸. Therefore, evaluation of

Table 2 Fatty Acid Compositions in 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	Ref.
Edible oils														
Almond	-	-	-	4.5-6.0	-	1.7-2.0	61.3-72.1	17.5-19.8	0.5	-	-	-	-	75)
Canola	-	-	-	4.3	0.2	1.9	61.5	20.6	8.3	0.5	1.1	0.2	-	37)
Cashew	-	-	-	14.1	0.4	10.2	57.3	17.2	0.2	-	-	0.5	-	39)
Coconut	5.5	47.7-52.0	19.9	-	-	2.7	6.2	1.6	-	-	-	-	-	74)
Corn	-	-	-	11.3	0.1	1.9	32.2	52.5	1.0	0.4	0.3	0.1	-	37)
Cotton	-	-	0.6	19.6	0.6	2.5	22.1	52.3	0.6	-	-	0.6	-	76)
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	-	42)
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	-	43)
Jajoba	-	-	0.2	6.21-9.1	-	-	13.5-24.3	0.3-0.5	0.7-1.1	-	-	53.1-71.8	-	44)
Oil palm	-	-	0.5-2.0	32.0-45.0	-	2.0-7.0	38.0-52.0	5.0-11.0	-	-	-	-	-	38)
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	-	-	-	-	-	55),74)
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	-	-	-	-	-	45)
Pumpkin	-	-	-	15.6-16.4	-	4.1-5.2	43.5-44.8	33.8-35.8	-	0.1-0.8	-	-	-	38),74)
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	-	37)
Safflower	-	-	0.1	6.4	-	2.2	13.9	76.0	0.2	0.4	0.2	0.2	-	48)
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	-	38)
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	-	37)
Sunflower	-	-	-	6.1	-	4.2	24.0	63.5	0.4	0.3	0.1	0.8	-	77)
Walnut	-	-	0.19	5.82	-	1.9	22.7	51.6	17.8	-	-	-	-	
Non-edible oils														
Castor	-	-	-	2.0	-	1.0	7.0	5.0	-	-	-	-	Ricinoic 86-90	38)
Country almond	-	-	-	32.3-33.9	-	5.7-6.3	22.7-26.7	30.0-32.0	-	0.8	-	-	-	50)
Croton	-	1.1	1.5	30.7	2.9	4.9	34.1	18.5	2.9	0.5	-	1.4	-	78)
Cuphea	28.1	64.7	2.9	0.2	-	-	0.9	1.9	-	-	-	-	-	51)
Desert date	-	-	-	15.4-16.1	-	18.6-19.3	25.6-27.0	38.5-40.8	-	-	-	-	-	79)
Ethiopian mustard	-	-	-	4.3	-	0.5	7.4	18.2	24.9	4.7	-	-	-	53)
Green algae	-	0.7	0.8	21.0	2.0	2.9	3.2	13.6	33.0	0.2	-	0.2	Ricinoic 35-40	70)
Jatropha	-	-	0.5-1.4	12.0-17.0	-	5.0-9.5	37-63	19-41	-	0.3	-	-	Hexadecatrienoic 15	57)
Kapok	-	-	0.1	22.6	-	5.2	30.1	37.5	-	1.7	-	0.3	-	57)
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	-	-	38)
Kokum	-	-	-	8.0	-	5.5	50.2	26.0	-	-	-	-	-	59)
Kusum	-	-	-	5.0-8.0	-	2.0-6.0	57.0-62.0	-	-	20.0-25.0	-	-	-	80)
Linseed	-	-	-	6.7	-	3.7	21.7	15.8	52.1	-	-	-	-	37)
Mahua	-	-	-	20.0-25.0	-	20.0-25.0	41.0-51.0	10.0-14.0	-	0.1-3.3	-	-	-	38)
Milkweed	-	-	-	15.1	5.7	2.6	27.1	49.6	1.0	0.3	-	-	-	81)
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	-	82)
Nahor	-	-	-	15.3	-	12.0	53.2	17.0	-	2.0	-	0.5	-	83)
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	-	-	-	38)
Oleander	-	-	0.2	20.2	0.3	7.7	46.1	15.9	0.4	-	-	-	-	60)
Rubber	-	-	-	8.8	0.2	6.2	39.0	42.1	2.4	0.7	-	-	-	84)
Sea mango	-	-	-	30.3	-	3.8	48.1	17.8	-	-	-	-	-	61)
Soapnut	-	-	-	4.7	0.4	1.5	52.6	4.7	2.0	7.6	-	23.9	-	55)
Sugar apple	-	-	-	12.1	-	13.6	47.4	22.9	-	0.9	-	-	-	62)
Syringa	-	-	-	10.1	-	3.5	21.8	64.1	-	-	-	-	-	85)
Tobacco	-	-	-	9.6	-	6.3	21.7	55.6	-	-	-	-	-	38)
Tung	-	-	-	3.0	-	2.0	4.0	9.0	-	-	-	-	α -eleostearic 82	37)

other solvents for extracting plant oils could achieve important advances.

3.3. Enzymatic Extraction

The oil is contained in the vacuoles within seed cells, so that the walls of both vacuoles and cell walls 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 yield⁹⁹. Oil extraction with aqueous enzymes usually uses a mixture of cell wall-degrading enzymes, such as pectinase, cellulase, and hemicellulose with water as 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 technology¹⁰⁰. Consequently, 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 extraction¹⁰¹. 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 accessibility¹⁰⁰. Furthermore, the parameters of temperature and pH are important. The optimum incubation temperature varies for different oil seeds and enzymes. High temperatures will cause gradual loss of enzyme activity due to denaturation of proteins and darken the oil¹⁰², whereas low temperatures lead to slow enzymatic hydrolysis and low oil extraction. For example, the optimum temperature for olive oil extraction is 40 °C and that for linseed is 35 °C^{103,104}, and the maximum yield of peanut oil was obtained at 40 °C¹⁰⁵. 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 °C and 55 °C¹⁰⁶.

Preparation of plant oil for biofuel production is simpler, compared to that for food grade oil. Crude oil will undergo the processes of refining or degumming, bleaching, and finally deodorizing for food use¹⁰⁷. The refining or degumming step is designed to remove the phospholipids, proteins, carbohydrates and free fatty acids from crude plant oil. The bleaching and deodorizing processes are required to remove 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 hydrocarbons¹⁰⁸.

4. Renewable Hydrocarbon Fuel Production

4.1. Catalytic Cracking

Interest in producing biofuels using catalytic cracking has increased in recent years. Catalytic cracking consist of both thermal and catalytic reactions, but the catalytic reaction becomes more important for smaller molecules. The catalysts can be acidic or basic catalysts. The conventional basic catalyst for continuous cracking is Na₂CO₃ or K₂CO₃¹⁰⁹. Such catalysts can produce hydrocarbon biofuels from soybean oil over 80 wt% yield of diesel and gasoline fractions¹⁰⁹. However, exhaustion of these catalysts results in contamination of the hydrocarbon biofuel product by the corresponding salt, which leads to corrosion of the equipment. Therefore, the development of new basic solid catalysts is very desirable.

Catalytic cracking of plant oils is typically conducted in the temperature range between 360 °C and 525 °C. The reaction will always produce a solid fraction (coke), a liquid bio-oil product, and a gaseous stream of biogas^{110,111}, which are highly dependent on both temperature and residence time. Lower temperatures and longer residence times will yield higher quality coke product, 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.

The last operational condition is well known as the fast pyrolysis process, which has the potential to produce large amounts of hydrocarbon biofuels. The type of the catalyst is also important in the formation of specific fractions (gas, gasoline, or diesel) due to the selectivity characteristics¹¹². Zeolites are widely used in catalytic cracking due to their high acidity and porosity which are key in determining the selectivity¹¹³. Catalytic cracking of bio-oil over a HZSM-5 catalyst could obtain the maximum biofuel yield with a minimum coke yield at 450 °C¹¹⁴. Therefore, the requirement for high temperatures can be suppressed by carrying out the reaction at different pressures from 2 to 11 MPa¹¹⁵.

Various reaction conditions for the catalytic cracking of plant oils to obtain hydrocarbon biofuels are summarized in **Table 3**. A fixed-bed reactor is the most common equipment for catalytic cracking of plant oil. This reactor configuration has good mass and heat transfer distributions of the oil feed to avoid clogging, entrainment, and channeling, which are the major issues in catalytic cracking reactions¹¹⁶. In addition, zeolite-based catalysts are extensively used in catalytic cracking reactions due to their activity, selectivity, acid properties, ion-exchange properties, and large specific surface areas^{117,118}. Hydrocracking of canola (*Brassica campestris*) oil using a bifunctional catalyst of NiMo/ γ -Al₂O₃ catalyst obtained a maximum 80 % yield of

Table 3 Several Reaction Conditions for Catalytic Cracking of Plant Oils to Yield Renewable Hydrocarbon Fuels

Plant oil	Catalyst	Operation condition	Reactor	Main product	Yield [wt%]	Coke [wt%]	Ref.
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	-	119)
Castor	HZSM-5	400 °C	Fixed-bed	Bioliquid	38	1.5	121)
Coconut	HZSM-5	400 °C	Fixed-bed	Bioliquid	27.6	2.2	121)
Euglena	Zeolite Y	470 °C, 0.7 MPa	Fixed-bed	Gasoline	40	5	6)
Jatropha	AlMCM-41/ZSM-5	400 °C	Fixed-bed	Bioliquid	70	-	120)
Jatropha	Ni-W/SiO ₂ -Al ₂ O ₃	450 °C, 6 MPa	Fixed-bed	Biokerosene	25-30	-	122)
Neem	HZSM-5	400 °C	Fixed-bed	Bioliquid	16.7	1.4	121)
Oil palm	Microporous HZSM-5; mesoporous MCM-41; micromesoporous zeolite	450 °C	Fixed-bed	Gasoline	48	1.7	123)
Rapeseed	Ni-Ecat-H; Pt-Ecat-H	525 °C, 0.1 MPa	Microriser	Gasoline	29-41	5-8.2	124)
Soybean	NiMo/ZSM-5	360-450 °C, 4.5 MPa	Fixed-bed	Hydrocarbon biofuel	50	-	125)
Sunflower	ZSM-5	450-550 °C, 0.1 MPa	Fixed-bed	Bio-jet fuel (C7-C12)	77.3	-	2)
Sunflower	Pt/HZSM-22/Al ₂ O ₃	280-370 °C, 3.5-8 MPa	Flow reactor	Bioliquid	>90	-	126)

Scheme 1 Catalytic Cracking of Plant Oils to Produce Renewable Hydrocarbon Fuels^{125)~127)}

diesel-like hydrocarbon under reaction conditions at 350 °C and 9 MPa¹¹⁹⁾. Catalytic cracking of jatropha oil with AlMCM-41/ZSM5 obtained hydrocarbon products carbon chains lower than 18 at 70 wt% yield of bioliquid fuel with 61 wt% of selectivity of renewable gasoline¹²⁰⁾. 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 phase¹²¹⁾. Catalytic cracking of oil from *Euglena* (*Euglena gracilis*) produced about 40 wt% of hydrocarbons in gasoline chain lengths among a large amount of paraffins and olefins instead of aromatics. Edible sunflower and canola oils, and non-edible jatropha oil can be converted to biofuel with this method to obtain more than 60 % in yield^{2),119),121)}.

Reactions in the catalytic cracking of plant oils to produce renewable hydrocarbon fuels are shown in **Scheme 1**^{127)~129)}. Cracking of triglycerides might be initiated with thermal cracking, which usually produces free radicals of ester carbonyl groups. These free radicals 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 esters¹²⁷⁾. Further cracking of the C-C bonds of oxygenated hydrocarbon molecules followed by deoxygenation reactions then occur, resulting in the liquid products, *i.e.*, renewable hydrocarbon fuels (diesel and gasoline). The renew-

able hydrocarbon fuel composition depends on the reactions that are triggered by the acid catalysts in the system, such as β -scission, hydrogen transfer, isomerization, cyclization, or aromatization. The various examples in **Table 3** suggest that the cracking of C-C bonds will produce more hydrocarbons with lower carbon numbers, such as gasoline (C4-C13). However, this process is highly nonselective because a large range of oxygenates and hydrocarbons could be formed. CO, CO₂, and H₂O are derived from this oxygen-removal reaction. Side reactions associated with the deoxygenation reactions of the heavy oxygenated hydrocarbons resulted in formation of light hydrocarbons (*i.e.*, CH₄, C₂H₆, C₂H₄). Furthermore, coke is formed from the polymerization of oxygenated hydrocarbon molecules¹³⁰⁾. Coke formation usually creates the problem of catalyst deactivation, by physically covering the active surface of the catalysts or blocking the catalyst pores. However, loading metals on zeolites to increase selectivity and optimizing the catalytic cracking conditions can reduce coke formation²⁾.

4. 2. Deoxygenation

The greatest concern during the catalytic cracking process is the water and oxygen content in biofuels, which can be lowered through catalytic hydroprocessing using a heterogeneous catalyst, *i.e.*, deoxygenation¹³¹⁾. The resulting (oxygen-free) hydrocarbons are compatible with fossil fuels. This hydrotreating process involves oxygen removal through hydrodeoxygen-

Table 4 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	133)
	Lauric	Pt/Nb ₂ O ₅	180-250 °C, 0.8 MPa (H ₂)	Batch	Dodecane	99	133)
	Myristic	Pt/Nb ₂ O ₅	180-250 °C, 0.8 MPa (H ₂)	Batch	Tetradecane	89	133)
	Oleic acid	MoO ₂ C/graphene oxide	350 °C, 5 MPa (H ₂)	Continuous flow	Octadecane	60	134)
	Palmitic	MoO ₂ /CNTs	190-260 °C, 4 MPa	Batch	Hexadecane	4.1-92	135)
	Stearic	Pt/Nb ₂ O ₅	180-250 °C, 0.8 MPa (H ₂)	Batch	Octadecane	96	133)
Decarboxylation	Stearic	PdO _x /zeolite	360 °C, 2 MPa (H ₂)	Batch	Octadecane	89	136)
	Stearic	Pd/C	300 °C, 1.7 MPa (He)	Semibatch	Heptadecane	82	17)
	Stearic	Pd/C	300 °C, 0.6 MPa (He-H ₂)	Semibatch	Heptadecane	98	137)
	Stearic	Pd/C	300 °C, 1 MPa (H ₂)	Batch	Heptadecane	90	15)
	Palmitic	Pd/C	300 °C, 1 MPa (H ₂)	Batch	Pentadecane	53	16)
	Stearic	Ni/C	370 °C	Batch	Heptadecane	81	138)
Decarbonylation	Pelargonic	Pd/C	300 °C, 10 MPa (N ₂)	Batch	Octane	98	14)
	Azelaic	Pd/C	300 °C, 5 MPa (N ₂)	Batch	Heptane	73	14)
	Stearic	[(C ₆ H ₅) ₃ P] ₂ Rh(CO)Cl	280 °C	Batch	Heptadecene	81	139)
	Stearic	Pd/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	90.1	140)
	Stearic	Cu/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	77.6	140)
	Stearic	Pt/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	45	140)
	Stearic	Ni/γ-Al ₂ O ₃	350 °C, 1.4 MPa (N ₂)	Batch	Heptadecene	36	140)

Scheme 2 Deoxygenation of Plant Oils to Hydrocarbon Biofuels^{2),14),15)}

ation to form hydrocarbon and H₂O combined with hydrogenation of double bonds or aromatic rings. Such double bonds can also be converted to saturated fatty acids with lower carbon number¹⁴⁾. Deoxygenation of saturated fatty acids will result in liquid products of renewable hydrocarbon fuels (diesel and gasoline). Deoxygenation can refer to different chemical reactions, including hydrodeoxygenation, decarboxylation, and decarbonylation, depending on the reaction conditions and the type of catalyst used^{11)~17),132)}.

The main reaction path in the conversion of plant oils into hydrocarbon biofuels via deoxygenation is shown in **Scheme 2**^{2),14),15)}. Hydrodeoxygenation yields hydrocarbons with the same chain length as the reactant, whereas decarboxylation and decarbonylation result in hydrocarbon chains with one carbon atom less than in the starting compounds. **Table 4** summarizes the deoxygenation process for fatty acids to yield renewable hydrocarbon fuels.

4.2.1. Hydrodeoxygenation

Hydrodeoxygenation reduces the oxidation state of the carbon atom in the carboxylic group of fatty acids

by using molecular H₂ to form H₂O as well as hydrocarbons with the same number of carbon atoms substrate. This reaction only occurs in the presence of H₂ (Eq. (1)). Selective hydrodeoxygenation reactions have been reported using Ni-loaded zeolites, Pt-Re/ZSM-5, and tungsten and molybdenum carbide catalysts at 260-350 °C under 1-5 MPa H₂^{141)~144)}. Furthermore, Nino Rinaldi *et al.*¹⁴⁵⁾ 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 problem¹⁴⁴⁾.

Several different catalysts have obtained higher product yields for hydrodeoxygenation of fatty acids (**Table 4**). Hydrodeoxygenation of capric, lauric, myristic, and stearic acids using Pt/Nb₂O₅ at 180-250 °C under 0.8 MPa resulted in 88-99 wt% yield of the corresponding products. Partial blocking of Pt by Nb₂O₅ increases the Lewis acidity of the suboxide and the co-

operation of metal (Pt)-Lewis acid significantly enhances the selectivity in C–O and C=O bond reduction by the hydrodeoxygenation reaction¹³³. Furthermore, a low-cost Mo-based catalyst is believed to have potential for hydrodeoxygenation due to its high activity for C–O bond scission and conversion of oleic and palmitic acids into hydrocarbons with up to 92 wt% yields at 190–350 °C under 4–5 MPa^{134,135}. Functionalized PdO_x/zeolite was developed to convert oleic acid into 89 wt% yield of octadecane at 360 °C under 2 MPa¹³⁶.

The hydrodeoxygenation method is relatively carbon-efficient because hydrocarbons are formed with the same carbon number as the fatty acid substrates. 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 method¹⁴⁶.

4. 2. 2. Decarboxylation and Decarbonylation

Decarboxylation removes the oxygen in fatty acids as CO₂ to form hydrocarbons with one atom carbon less than the corresponding fatty acid. In principle, this process does not involve a reaction with hydrogen (Eq. (2))^{14,147}. However, the presence of hydrogen at low partial pressure was found to be beneficial for catalyst stability in some cases¹⁷.

Decarboxylation of fatty acids was first successfully demonstrated obtaining heptadecane from stearic acid through a homogeneous selenium catalytic reaction¹⁴⁸. The needs for greener processing and recovery of the new catalyst to obtain greater product purity resulted in investigation of various supported metal catalysts to develop promising heterogeneous catalysts with activity for the decarboxylation of fatty acids.

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 showed that Pd supported on carbon demonstrated high activity and selectivity for the desired product of heptadecane¹³⁷. Therefore, most decarboxylation studies have used Pd catalyst, and some examples are presented in **Table 4**. In addition, study of the effect of hydrogen concentrations in decarboxylation reactions showed that hydrogen in the reaction atmosphere could reduce undesirable aromatization and increase the product yield from 82 to 98 wt% for stearic acid decarboxylation^{17,137,149}. Solvent-free decarboxylation of stearic acid and palmitic acid under hydrogen with Pd/C catalyst obtained the corresponding saturated hydrocarbons with 90 wt% and 53 wt% yields, respectively, without by-product^{15,16}. In contrast, decarboxylation under an inert atmosphere could also achieve outstanding results. Low cost and abundantly available supported Ni-based catalyst allowed decarboxylation of stearic acid to 81 %

heptadecane without hydrogen¹³⁸. Solvent-free decarboxylation of pelargonic and azelaic acids under N₂ atmosphere yielded 98 % and 73 % yields of the corresponding hydrocarbons¹⁴⁴. Decarboxylation under hydrogen caused a side reaction involving fatty acid hydrogenation to form aldehyde and alcohol. The positive effect of hydrogen can generally be attributed to 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 can reduce capital and operational costs. In addition, the catalytic stability is higher because water is not formed in the reaction. Consequently, high-selectivity decarboxylation can release relatively pure CO₂.

Decarbonylation is known to occur with the decarboxylation reaction under certain conditions, which eliminates the oxygen in fatty acids in the form of carbon monoxide (CO), yielding the corresponding alkene with one less carbon atom and H₂O as by-product. An early study of decarbonylation reactions converted stearic acid into heptadecene using a homogeneous transition metal complex rhodium with triphenylphosphine ligand [(C₆H₅)₃P]₂Rh(CO)Cl, to obtain 81 wt% yield (**Table 4**)¹³⁹. The presence of excessive ligand preserves catalyst activity by preventing metal reduction. Furthermore, study of the quantum chemical behavior of stearic acid decarbonylation using Pd, Cu, Pt, and Ni supported on γ-Al₂O₃ found that the free energy of activation decreased in the series Ni > Pt > Cu > Pd, which resulted in higher yields of the desired product¹⁴⁰. Several deoxygenation reactions can occur through these two parallel pathways of decarboxylation and decarbonylation. However, decarboxylation is thermodynamically more favorable¹⁵⁰.

4. 3. Isomerization

Straight chain hydrocarbons tend to ignite rapidly during spark ignition in internal combustion engines, resulting in engine knocking caused by excessive pressure inside the cylinder. However, branched chain and cyclic hydrocarbons are burned smoothly to eliminate this engine knocking. Therefore, branched and cyclic hydrocarbons are valuable in commercial gasoline because of their superior characteristic to straight hydrocarbon isomers^{151,152}. In addition, branched and cyclic hydrocarbons are desirable for jet fuel because of the required properties of high energy density to maximize aircraft range and low freezing point to avoid the crystallization of the wax during high-altitude flights¹⁵³. Therefore, isomerization technologies are gaining significant attention because the straight hydrocarbon molecules can be reformed into branched or cyclic hydrocarbons with the same carbon numbers¹⁵⁴.

The isomerization process generally depends on the feedstock. For a liquid phase of C5–C6 isomerization,

Table 5 Typical Chemical and Physical Properties of Biodiesel and Renewable Diesel¹⁶⁵⁾

Property		Biodiesel (FAMES)	Renewable diesel
Carbon	[wt%]	76.2	84.9
Hydrogen	[wt%]	12.6	15.1
Oxygen	[wt%]	11.2	0
Density	[kg/m ³]	880	780
Cetane number		45-55	79-90
$T_{90}^a)$	[°C]	330-360	290-300
Viscosity at 40 °C	[mm ² /s]	4-5	3-4
Energy content (LHV)			
Mass basis	[MJ/kg]	39	44
Mass basis	[BTU/lb]	16,600	18,900
Vol basis	[1000 BTU/gal]	121	122

a) Temperature at which 90 vol%/vol% of diesel compounds evaporate.

the process aims to convert straight chain hydrocarbon to *i*-hydrocarbon. For C7+ hydrocarbons isomerization, the reaction is intended to obtain di- and multi-branched isomeric hydrocarbons. Isomerization reactions are generally performed using bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acidic sites for isomerization via carbenium ions¹⁵⁵⁾. Isomerization of *n*-hexane, *n*-octane, and *n*-hexadecane over Pt-SAPO (silicoaluminophosphate) found that the major products were mono-methyl isomer hydrocarbons¹⁵⁵⁾. Furthermore, isomerization of *n*-heptane over Pd-SAPO obtained high selectivity for 80 wt% yield of 2,3-dimethylpentane¹⁵⁶⁾. Hydroisomerization of *n*-decane, *n*-nonadecane, and pristene over Pt/ZSM-22 resulted in their corresponding isomer yields of approximately 67 wt%¹⁵⁷⁾. In general, the isomerization process is conducted using a catalyst of Pt-chlorinated alumina, metal oxides (zirconia-based), zeolite, or sulphated oxide at temperatures 120-270 °C under 1-3.5 MPa (H₂)^{158),159)}.

5. Renewable Hydrocarbon Fuel Products

5.1. Renewable Hydrocarbon Diesel

Biodiesel, which consists of fatty acid methyl esters (FAMES), is the most widely used diesel alternative. The conventional method of biodiesel production is transesterification of triglycerides using alkaline catalysts, but more advanced methods of biodiesel production have been established with catalyst-free supercritical methanol technologies by a one-step method through transesterification of triglycerides to FAMES and a two-step method through hydrolysis of triglycerides and esterification of the obtained fatty acids to FAMES with excellent results^{160)~164)}. However, interest in diesel hydrocarbons derived from plant oils, referred to as renewable diesel, is now increasing.

Both biodiesel and renewable diesel can be made from the same feedstock, but the chemical and physical properties are quite different¹⁶⁵⁾. The typical proper-

ties of biodiesel and renewable diesel are summarized in **Table 5**. Renewable diesel has about 10 % higher mass energy content (44 MJ/kg) compared to biodiesel (39 MJ/kg) due to its higher carbon and hydrogen contents and considerably lower oxygen content. Renewable diesel is less dense than biodiesel, but has a significantly higher cetane number. Those advantages have led to an increasing number of studies of renewable diesel production.

Renewable diesel has varied physical and chemical properties, which depend on various factors, such as the feedstock, the fatty acid composition of the feedstock, and production method. However, renewable diesel should be usable in conventional diesel engine without modifications. However, renewable diesel must be analyzed using advanced analytical equipment to ensure it meets the international standards for commercial use. ASTM International in the US and the European Committee for Standardization (CEN) in Europe have established the ASTM D975 and EN 590 standard specifications for renewable diesel, respectively. The properties of renewable diesel may vary significantly depending on their fatty acid composition, as discussed previously in section 4.^{2),119)~121),123)~125)}. The physical and chemical properties of various renewable diesels from edible oils, such as coconut, oil palm, rapeseed, and sunflower oils, and non-edible oils, such as castor and jatropha, are shown in **Table 6**.

Water content is one of the important properties of renewable diesel. The presence of water in fuel will reduce the combustion heat and cause corrosion in engine components, and the insoluble sediment consisting of dirt particles as insoluble compounds formed by fuel oxidation can cause clogging during combustion¹⁷⁰⁾. The amounts of water and sediment property for all renewable diesels is under the standard limit (0.05 vol% in ASTM D975) as shown in **Table 6**. The highest value is for oil palm oil (0.045 vol%) and the lowest for castor oil (0.01 vol%). Unfortunately, the data for coconut and rapeseed oils are not available.

Another important property of renewable diesel is its

Table 6 Physical and Chemical Properties of Renewable Diesel from Several Plant Oils

Property		International standard renewable diesel		Renewable diesel from plant oil					
		ASTM D975	EN 590	Edible oil				Non-edible oil	
				Coconut ¹⁶⁾	Oil palm ¹⁶⁶⁾	Rapeseed ¹⁵⁾	Sunflower ¹⁶⁷⁾	Castor ¹⁶⁸⁾	Jatropha ¹⁶⁹⁾
Water and sediment	[vol%, max.]	0.05	0.02	-	0.045	-	0.03	0.01	-
Kinematic viscosity at 40 °C	[mm ² /s]	1.9-4.1	2.0-4.5	1.6	2.17	4.5	2.65	3.51	3.6
Flash point	[°C, min.]	52	55	42	78	153	49	78	-
Cetane number ^{a)}	[min.]	40	46	-	61.3	-	65	110	60
Density	[kg/m ³]	-	820-845	750	761	770	806	772	834
Cold filter plugging point	[°C, max.]	-	-15	-22	16	22	-14	22	-

a) Cetane number is estimated from the cetane index.

kinematic viscosity, which refers to the fluidity of the viscous fuel. This property affects the injection process, particularly at low temperatures at which the viscosity increases and affects the fluidity of the fuel⁵²⁾. A high viscosity value leads to formation of engine deposits because of insufficient fuel atomization. All the renewable diesels studied here had standard viscosity (1.9-4.1 mm²/s in ASTM D975, 2.0-4.5 mm²/s in EN 590), except for coconut oil diesel. The highest kinematic viscosity is that of rapeseed oil diesel (4.5 mm²/s), and the lowest for coconut oil diesel (1.6 mm²/s). High carbon number and branched chains in the hydrocarbon renewable diesel result in higher kinematic viscosity.

Flash point is another important property, which is the lowest temperature at which the renewable fuel will ignite when exposed to a flame. The flash point of renewable diesel from coconut oil is 42 °C, which is lower than the lower limit (52 °C) specified at ASTM D975, possibly due to its high content of volatile compounds.

Cetane number is a characteristic that can provide information about the ignition delay time of the fuel at injection into the combustion chamber; low cetane number fuel will cause engine knocking and produce gaseous and particulate emissions. Therefore, the high cetane number of renewable diesel is one of its advantages. All cetane numbers shown in **Table 6** for renewable diesel are above the standard required values (40 in ASTM D975, 51 in EN 590).

Density is another important property that can influence the efficiency of fuel atomization in combustion systems. All renewable diesels in **Table 6** have a lower density than standard diesel fuel (820-845 kg/m³ in EN 590), except for jatropha oil diesel (834 kg/m³). This low density is probably caused by the low concentration of aromatics and the high concentration of alkanes¹⁶⁷⁾. Cold filter plugging point (CFPP) is an important property which identifies the temperature at which the test filter starts to plug due to the crystallization of fuel components caused by cooling of the fuel. This is an important characteristic for cold weather performance. The fuel system will clog more easily at high CFPP. The reported data suggests that the CFPP of renewable

diesels is poor, except that from castor oil. The renewable diesel from oil castor has a CFPP value of -22 °C, which is comparable with the CFPP value of a standard diesel fuel (max. -15 °C).

5. 2. Renewable Hydrocarbon Gasoline

Development of renewable gasoline is less well studied than renewable diesel. These studies have usually focused on gasoline additives, such as ethanol, butanol, butane, ethyl *t*-butyl ether (ETBE), and methyl *t*-butyl ether (MTBE)^{171),172)}. All these additives have the advantage of high octane rating, but the oxygen content, especially in aliphatic alcohol additives, has the previously mentioned problems. Renewable hydrocarbon gasoline has recently been considered as a promising alternative, and many studies are exploring different approaches to create chemical compounds that are nearly identical to standard gasoline.

International standards for renewable hydrocarbon gasoline (here called renewable gasoline) have been established in ASTM D4814 (**Table 7**). The chemical and physical properties of renewable gasoline from jatropha and oil palm oils obtained through a catalytic thermal cracking process^{173),174)} are also summarized in **Table 7**.

The chemical and physical properties of renewable gasoline from jatropha are comparable with those of petroleum gasoline¹⁷³⁾. The manufacturing process applied a nanocrystalline ZSM-5 catalyst. The moderate acidity and presence of mesopores in this catalyst were responsible for increased aromatization of olefins, so the liquid hydrocarbon products contained major amounts of aromatics. High content of aromatics results in high octane, low olefins content, and zero sulfur content which are suitable for commercial gasoline blending. Manufacture of renewable gasoline from oil palm oil over a sodium carbonate catalyst showed high olefins content, but low aromatics content¹⁷⁴⁾. Furthermore, the density of the renewable gasoline was lower than that of the standard specification, so the characteristic of renewable gasoline needs to be optimized.

Table 7 Properties of Renewable Hydrocarbon Gasoline from Jatropha and Oil Palm Oils

Property		International standard renewable gasoline	Renewable gasoline from plant oil	
		ASTM D4814	Jatropha ¹⁷³⁾	Oil palm ¹⁷⁴⁾
Flash point	[°C]	− 30	-	2.1
Octane number		> 87.0	94.6	-
Density at 15 °C	[kg/cm ³]	750-850	720-760	690
Kinematic viscosity	[mm ² /s]	< 1	-	0.72
Initial boiling point	[°C]	35	37	40
Final boiling point	[°C]	210	215	175
Sulfur content	[wt%]	0.005	nil	nil
Reid vapor pressure at 38 °C	[kPa]	60	64	-
Aromatics	[vol%]	42	63.4 [wt%]	1.94
Olefins	[vol%]	21	15.6 [wt%]	31.54

5.3. Blending Renewable Hydrocarbon Fuels with Petroleum-based Fuels

The world is beginning to shift from fossil fuels to cleaner energy sources. Hydrocarbon-based biofuels are expected to become important replacements for petroleum-based fuels. However, some properties of renewable hydrocarbon fuels (renewable diesel and renewable gasoline) differ from those of the conventional types. In particular, the products must achieve acceptable characteristics for engine fuel applications before delivery to the end user.

The use of straight plant oils to power a specially designed diesel engine was first attempted by Rudolf Diesel in 1893¹⁷⁵⁾. However, modern engines now incorporate advanced modifications such as the injection pump, high-pressure fuel system, and various high tolerance parts that require less-viscous fuel. Unsuitable properties of the fuel will result in carbon deposits inside the engine, higher coking index, and reduced engine life span⁵²⁾. Furthermore, the relatively low yield and high cost of new technologies to produce renewable fuels cannot meet the increasing demand for fuels in the future. Therefore, the current strategy is to blend renewable fuels, such as renewable diesel and renewable gasoline, with petroleum-based fuels to avoid the need to modify engine technologies.

Renewable diesel from coconut oil has lower flash point, kinematic viscosity, and CFPP compared with commercial petrodiesel (Table 6). To meet the standard requirements, this renewable diesel must be blended with petrodiesel in concentrations of less than 30 vol%¹⁶⁾. Renewable diesel was blended with petrodiesel to improve the CFPP of renewable diesel to around 20 vol%¹⁵⁾. Blending of renewable diesel from sunflower oil with petrodiesel found that 10-50 wt% of renewable diesel satisfied the diesel fuel specification¹³⁵⁾. Renewable diesel from castor oil met most of the standard specifications, except for its low-temperature properties¹⁴¹⁾. Blending the renewable diesel with petrodiesel at 20 vol% decreased the CFPP to a value that satisfied petrodiesel requirements.

Table 7 shows that some properties of hydrocarbon

gasoline from jatropha and oil palm are less suitable for automotive gasoline, such as flash point, density, and Reid vapor pressure. Blending technology was employed to associate reformulated gasoline with the new fuel. Gasoline blending must meet two important specifications octane number and Reid vapor pressure (RVP)¹⁷⁶⁾. The RVP is the volatility of the gasoline blend at 37.8 °C (100 °F), which affects the starting and warm-up of the internal combustion engine. Too high or low volatility of the gasoline prevents fuel pump operation due to negative suction pressure¹⁷⁷⁾. Gasoline contains many different hydrocarbons, which contribute to the final properties of blended gasoline, but the light hydrocarbons of butane, pentane, and isopentane are important for high RVP pressure, so must be limited to control the appropriate vapor pressure in gasoline blending. Therefore, the hydrocarbon composition must be considered in blending hydrocarbons to achieve the required octane number for gasoline. Straight chain hydrocarbons have a very low octane number of about 63 and were used as the bulk component for gasoline in the 1970 s when lead tetraethyl was added to boost the octane number¹⁷⁷⁾. Mono-aromatic compounds were found to have higher octane number of 89, and have since been used as one of the major blending components in gasoline. Isooctane has the highest octane number of 96, so is used to boost the octane number in gasoline.

Very limited data on blended gasoline properties or performance are available. Blending of up to 10 vol% renewable gasoline, which mainly contains C5-C6, resulted in a fuel with no restrictions on its final properties and application¹⁷⁶⁾. Furthermore, for applications in advanced homogeneous charge compression ignition (HCCI) engine technology, blending of *i*-propanol and *n*-heptane in 30 : 70 by vol is suitable for HCCI combustion systems¹⁷⁸⁾. This blended fuel had high calorific value and showed significant resistance to knocking.

6. Conclusions and Future Prospects

Both edible and non-edible plant oils have great potential for use as renewable hydrocarbon fuels. The production of renewable hydrocarbon fuels from non-edible plant oils will be vital in overcoming the land use problem because plants with non-edible oils can be grown in marginal areas. Moreover, the issue of imbalanced market demand and endangered food supply caused by using edible plant oils as energy sources can be avoided.

Production of renewable fuels from plant oils is affected by several factors, including the fatty acid composition of the oils, processes, and the operational conditions of the selected process. Catalytic cracking and deoxygenation are two promising pathways for renewable fuels from plant oils. Zeolite-based catalysts, alumina-based catalysts, Pd, Cu, Ni, and Pt metal catalysts are usually used for these processes. However, deoxygenation through decarboxylation or decarbonylation is now important because of the low-pressure conditions and high catalytic stability due to the absence of water in the products. Furthermore, isomerization can be applied to produce high-octane components from low-octane straight hydrocarbons by structurally changing the hydrocarbon molecules.

Application of the renewable fuels in engines is the main challenge because required standards must be reached for direct application in engines without special modification. The current scenario is to blend renewable fuels with petroleum-based fuels to meet the international standards for biofuels.

Present knowledge of renewable fuels, especially for gasoline, is very limited. The present review of the fatty acid composition of potential edible and non-edible plant oils could be used to select suitable candidates as feedstocks for renewable diesel and renewable gasoline production. Diversified resources for renewable fuel feedstocks will also ensure that the quality of the obtained renewable fuels is suitable for each region. For example, renewable diesel with poor cold flow properties can be produced for hot-weather countries and renewable diesel with good cold flow properties can be produced for cold-weather countries.

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要 旨

軽油およびガソリンに代わる植物油からの再生可能炭化水素燃料

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地球規模での CO₂ 排出と化石資源の枯渇の問題に取り組むために、食用および非食用の植物油がバイオ燃料資源として使用されている。この総説では、可食性および非可食性植物油原料の選択、油の抽出、および再生可能な炭化水素製造プロセスを含む、有望なバイオマス起源の炭化水素燃料の製造に関する文献情報を取りまとめた。植物油は、触媒を用いた接触分解ま

たは水素化脱酸素、脱炭酸および脱カルボニルといった脱酸素反応によって炭化水素系バイオ燃料へとアップグレードされる。これによって、エンジン用途での燃料品質の要件を満たし、軽油またはガソリンと混合しての利用が可能となる。このような炭化水素バイオ燃料について、これまでの研究の進歩を総括的に紹介する。