



CHAPTER II

LITERATURE REVIEW

2.1 Biodiesel and Hydrogenated Biodiesel : What's the Difference?

Biodiesel is defined as any diesel-equivalent biofuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and other biomass-derived oils that meets the diesel fuel specification requirements of the American Society of Testing and Materials (ASTM) D6751 and European Committee of Standardization (CEN) standard EN14214. In each standard, an important specification is a limit on the amounts of free glycerin and glycerides in biodiesel. In an article on proposed ASTM standards, biodiesel was defined as “the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines.” Biodiesel can be used as a pure fuel (B100). Moreover, it can be blended with the conventional diesel. Biodiesel blends are denoted as “BXX” with “XX” representing the percentage of biodiesel contained in mixing process, such as B5 in Thailand, a blend of 5% biodiesel with 95% conventional diesel.

Renewable diesel or hydrogenated biodiesel is defined in the Internal Revenue Code (IRC) as diesel fuel produced from biological material using a process called “thermal depolymerization” that meets the registration requirements for fuels and fuel additive established by the Environmental Protection Agency (EPA) under section 211 of the Clean Air Act (42 U.S.C. 7545); and meets the requirements of the American Society of Testing and Materials (ASTM) D975 (petroleum diesel fuel) or D396 (home heating oil). Normally, hydrogenated biodiesel is referred to hydrocarbons that do not contain oxygen in their molecular structure.

Thermal depolymerization is a process for the reduction of complex organic materials through the use of pressure and heat to decompose long-chain polymers of hydrogen, oxygen, and carbon into short-chain hydrocarbons with a maximum length of around 18 carbon atoms. A process may qualify as thermal depolymerization even if catalysts are used in the process. The structure of biodiesel and hydrogenated biodiesel are shown in Figure 2.1.

Biodiesel has lower heating value because of its oxygen content. Biodiesel also has other undesirable properties such as high density, and high NO_x emissions. Overall, hydrogenated biodiesel appears to be a superior product (Marker *et al.*, UOP, 2005).

2.2 Feedstocks for Biodiesel and Hydrogenated Biodiesel

Vegetable oils and animal fats are considered as raw materials for the production of biodiesel and hydrogenated biodiesel because they are broadly available from a variety of sources, and they are renewable. The example of vegetable oils use for production are palm oil, sunflower oil, corn oil, coconut oil, jatropha oil, olive oil, canola oil, cottonseed oil, castor oil, soybean oil, etc. As well as animal fats, recycled cooking oil, trap grease (from restaurant grease traps), and float grease (from waste water treatment plants), are also available as raw materials for biodiesel and hydrogenated biodiesel production.

Both oils and fats are composed of molecules called triglycerides. Fat generally refers to the triglycerides in solid form at room temperature, whereas oils are liquid at room temperature. The molecule of triglyceride is composed of three long-chain fatty acids of 8 to 22 carbons attached to a glycerol backbone. The chemical structure of a triglyceride is shown in Figure 2.2 where R₁, R₂, and R₃, which may be the same or different, represent long chain fatty acids which are mostly palmitic, stearic, oleic, linoleic, and linolenic acids. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water.

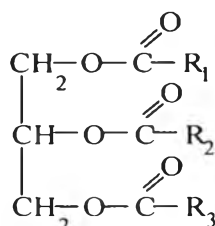


Figure 2.2 A chemical structure of triglyceride.

Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats are listed in Table 2.2. Besides these fatty acids,

numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower.

Table 2.2 Selected properties of some common fatty acids (Gerhard *et al.*)

Trivial (Systematic) name ; Acronym ^b	MW	m.p. (°C)	b.p. (°C)	Formula	Heat of Combustion (kg-cal/mol)
Caprylic acid (Octanoic acid); 8:0	144.22	16.5	239.3	C ₈ H ₁₆ O ₂	-
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	C ₁₀ H ₂₀ O ₂	1453.07 (25°C)
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131 ¹	C ₁₂ H ₂₄ O ₂	1763.25 (25°C)
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5 ¹⁰⁰	C ₁₄ H ₂₈ O ₂	2073.91 (25°C)
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350	C ₁₆ H ₃₂ O ₂	2384.76 (25°C)
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360	C ₁₈ H ₃₆ O ₂	2696.12 (25°C)
Oleic acid (9Z-Octadecenoic acid); 18:1	282.47	16	286 ¹⁰⁰	C ₁₈ H ₃₄ O ₂	2657.4 (25°C)
Linoleic acid (9Z,12Z- Octadecadienoic acid); 18:2	280.45	-5	229-230 ¹⁶	C ₁₈ H ₃₂ O ₂	-
Linolenic acid (9Z,12Z,15Z- Octadecatrienoic acid); 18:3	278.44	-11	230-232 ¹⁷	C ₁₈ H ₃₀ O ₂	-
Erucic acid (13Z-Docosenoic acid); 22:1	338.58	33-4	265 ¹⁵	C ₂₂ H ₄₂ O ₂	-

a) Z denotes cis configuration.

b) The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Superscripts in boiling point column denote pressure (mm Hg) at which the boiling point was determined.

Palm oil is the major feedstock for the production of biodiesel and hydrogenated biodiesel in Thailand. In year 2011, the harvests area of palm suppose to have about 5,648 million square metre and the production of 10.49 million tons increase 10.31 percentage from year 2010. This is due to the government has the policy to give the agriculturist expands to grow the palm. The requirement of palm oil for consuming has about 920,000 ton, for biodiesel production about 460,000 ton resulting the total of 1,380,000 ton increase 8.24 percentage from year 2010. Table 2.3 shown balance of crude palm oil in Thailand from year 2006 to 2011.

Table 2.3 Balance of crude palm oil in Thailand from year 2006 to 2011 (ton/year)

Year	2006	2007	2008	2009	2010	Rate(%)	2011
Stock (begin of year)	151,122	113,669	164,521	88,916	107,947	-8.75	246,539
Produce	783,953	1,167,126	1,051,089	1,543,761	1,463,529	16.51	1,782,767
Import	-	-	-	28,385	-	-	-
Total	935,075	1,280,795	1,215,610	1,661,062	1,571,476	13.86	2,029,306
Export	-	163,180	219,700	288,054	50,000	-1.87	150,000
Consume	821,406	953,094	844,812	989,061	914,937	2.56	920,000
Biodiesel production	-	-	62,182	276,000	360,000	2.10	460,000
Stock (end of year)	113,669	164,521	88,916	107,947	246,539	13.83	499,306
Total	935,075	1,280,795	1,215,610	1,661,062	1,571,476	-	2,029,306

(Office of Agricultural Economics, Thailand, 2010)

2.3 Biodiesel

Biodiesel refers to as a diesel-equivalent biofuel derived from vegetable oils or animal fats and other biomass-derived oils. Normally, biodiesel is defined as mono-alkyl ester which is a liquid varies in color, golden to dark brown, depending on type of feedstock. It is immiscible in water. Most of mono-alkyl ester has high boiling point (in the range of 620-630 K) and low vapor pressure (less than 1 mm Hg). Its flash point is higher than 130 °C, significantly higher than that of the conventional diesel (64 °C), and its density is in the range of 0.86 to 0.90 g/cm³, less than the density of water. The production of biodiesel from bio-oils is a chemical reaction called transesterification.

2.3.1 Chemistry of Transesterification Process

Normally, mono-alkyl ester is produced via the transesterification of vegetable oils or animal fats (triglycerides). In this process, triglycerides react with alcohols, generally methanol or ethanol, in the presence of a catalyst to produce mono-alkyl esters (biodiesel) and glycerol (Jon Van Gerpen *et al.*, 2004). The transesterification reaction can be catalyzed by bases, acids, or enzymes. The most common catalysts used are strong bases, such as sodium hydroxide, potassium hydroxide, and sodium methoxide. The typical transesterification process is shown in Figure 2.3.

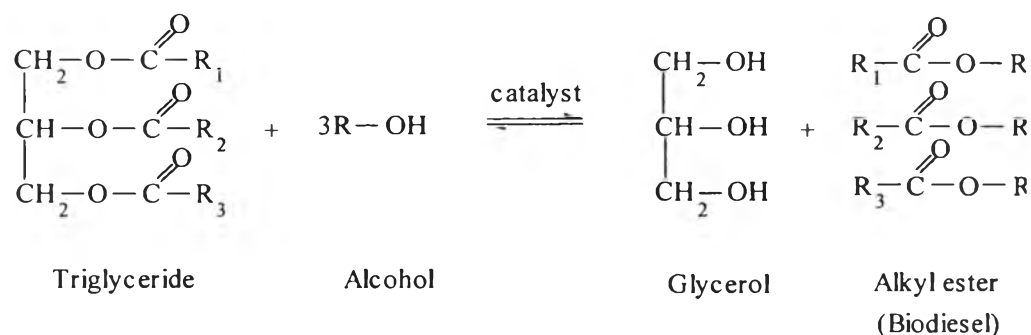


Figure 2.3 The production of biodiesel via transesterification of triglyceride.

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. These reactions are given in Figure 2.4.

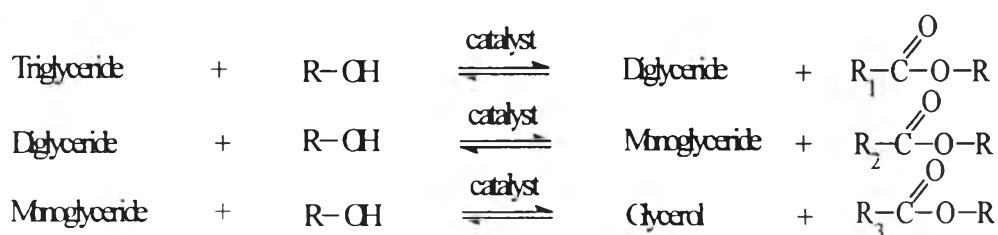


Figure 2.4 The transesterification reactions of triglyceride with alcohol to ester and glycerol.

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. In the last step, the conversion of monoglycerides to glycerol, yielding one methyl ester molecule from each step. (Srivastava A. *et al.*, 2000)

The stoichiometric relation between triglyceride and alcohol is a one mole of triglyceride reacts with three moles of alcohol. However, for the transesterification to occur, usually 6 moles of alcohol are used for every mole of triglyceride, which is more than the equation indicates. The reason is that the equilibrium of the reaction needs to be shifted toward the right side of the equation. To force the equilibrium in the direction of the desired products, one or more

parameter(s) of the reaction may need to be changed such as the molar ratio, temperature, pressure, and catalyst type.

The most popular mono-alkyl ester is methyl esters, resulting from the reaction of triglyceride with methanol, shown as Figure 2.5.

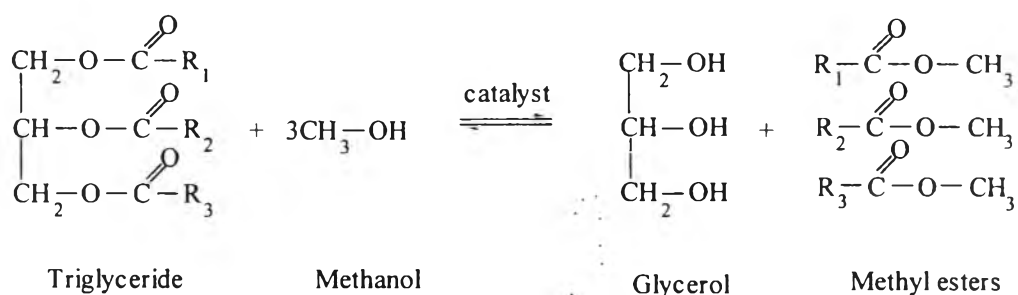


Figure 2.5 A chemical reaction of triglyceride with methanol.

The conversion of triglycerides into mono-alkyl esters through the transesterification reaction reduces the molecular weight to one-third that of the triglyceride and slightly increases the volatility.

2.3.2 Homogeneous Alkali-catalyzed Process

The homogeneous alkali-catalyzed system has been well studied and applied industrially. For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol. The alcohol-to-oil molar ratio that should be used varies from $N = 1:1$ – $6:1$. However $N = 6:1$ is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w. The standard value for the reaction to take place is 60 °C, but depending on the type of catalyst different temperatures will give different degrees of conversion, and for that reason the temperature range should be from 25 to 120 °C (Marchetti *et al.*, 2007). The optimum conditions at 1 atm pressure (60 °C, 1 wt. % catalyst, six-to-one alcohol-to-oil molar ratio), was introduced by Alex *et al.*, (1984). The kinetics of the alkali-catalyzed system was also studied by Freedman *et al.* (1986), Based on their results, approximately 90–98% oil conversion to methyl esters was observed within 90 min.

In order to prevent saponification during the reaction, the free fatty acid (FFA) and water content of the feed must be below 0.5 wt. % and 0.05 wt. %, respectively (Freedman *et al.*, 1984). Because of these limitations, only pure vegetable oil feeds are appropriate for alkali-catalyzed transesterification without extensive pre-treatment.

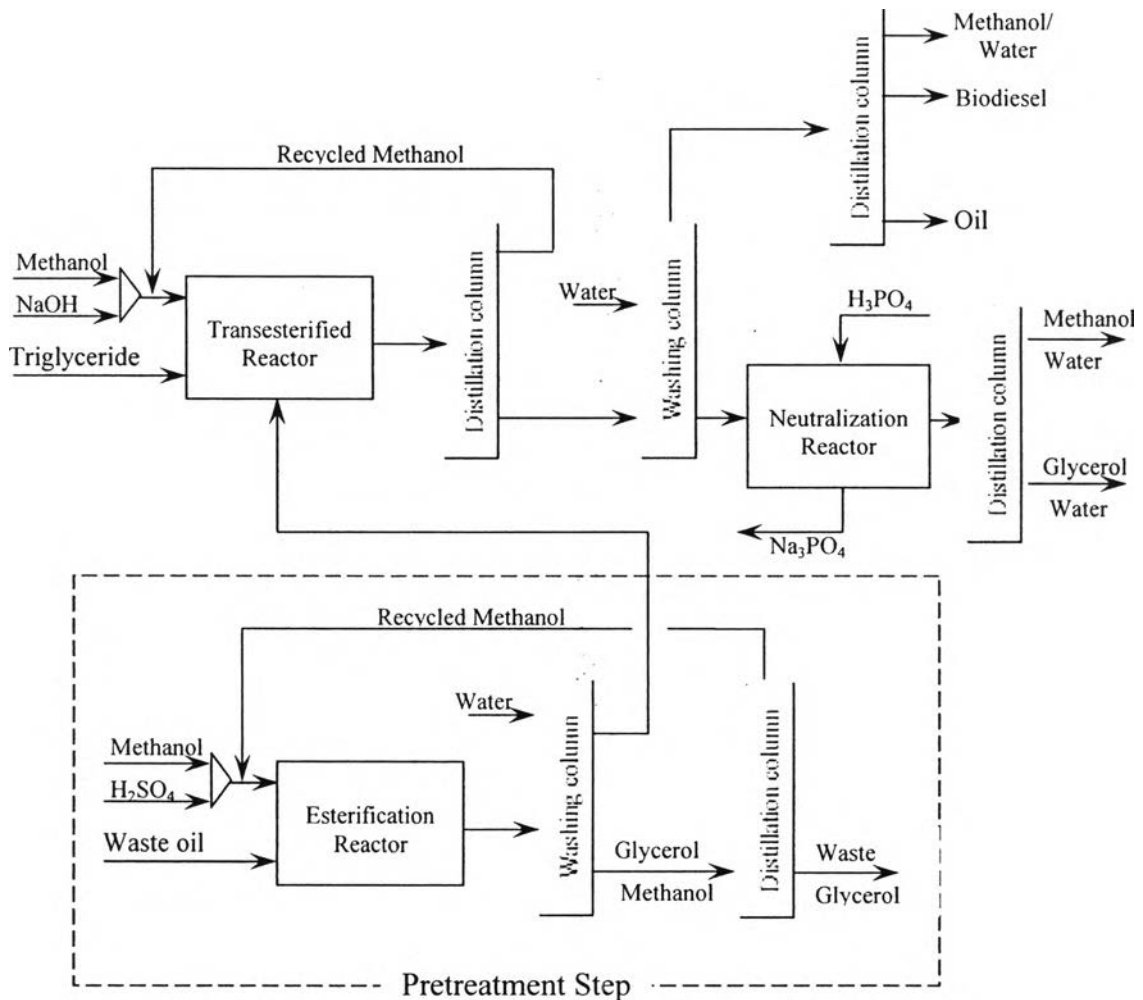


Figure 2.6 A homogeneous alkali-catalyzed pure vegetable oil process and a two step process to treat waste vegetable oil.

Zhang *et al.*, (2003) developed a HYSYS-based process simulation model to assess the technological feasibility of a homogeneous alkali-catalyzed pure vegetable oil process and a two step process to treat waste vegetable oil. Process flowsheet is presented in Figure 2.6. The vegetable oil was transesterified in the first step, and then sent for downstream purification. Downstream purification consisted

of the following steps: methanol recovery by distillation; glycerol separation; catalyst neutralization and removal (where appropriate); glycerol and methyl-ester purification by distillation.

In conventional industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Sodium hydroxide or sodium methylate is often used as catalyst. Sodium is recovered after the transesterification reaction as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase which must be isolated after neutralization by decantation as fatty acids. An acidic neutralization step with, for example, aqueous hydrochloric acid is required to neutralize these salts. In that case, glycerol is obtained as an aqueous solution containing sodium chloride. Depending on the process, the final glycerol purity is about 80–95%. The loss of esters converted to fatty acids can reach as high as 1% of the biodiesel production. These operations are illustrated in Figure 2.7 (Bournay L. *et al.*, 2005).

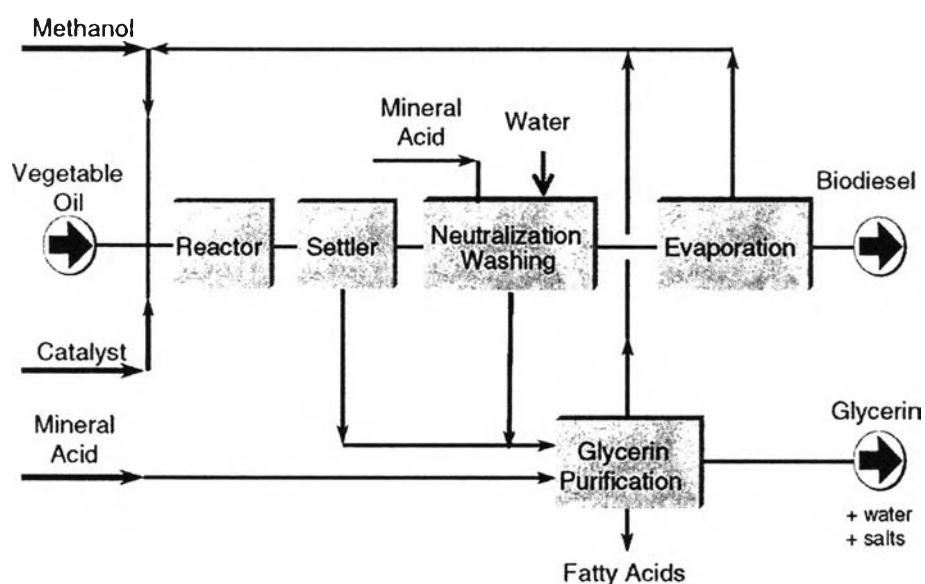


Figure 2.7 Global scheme for a typical continuous homogeneous catalyzed process.

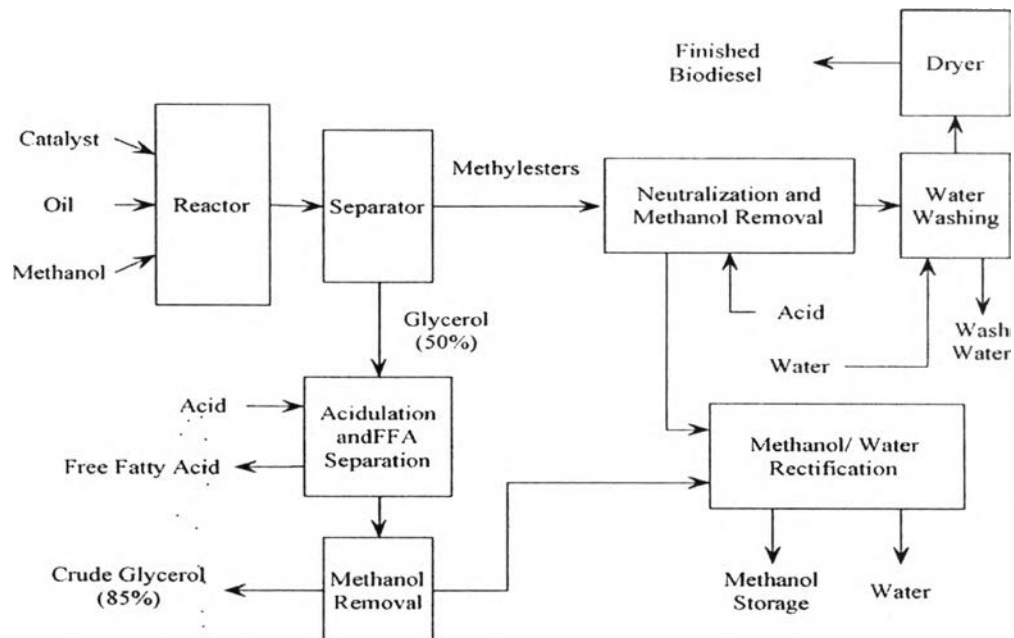


Figure 2.8 Process flow schematic for biodiesel production (Byung-Hwan Um *et al.*, 2009)

The above industrial manufacturing information on biodiesel production formed the principle basis for the design of the alkali-catalyzed processes in this study.

2.3.3 Drawbacks of Biodiesel Use

Although mono-alkyl ester is considered as a potential sustainable alternative fuel but there are still disadvantages associated with its use. There are several properties of mono-alkyl ester that limit their uses. First, mono-alkyl ester has cloud point and pour point higher than conventional diesel, the performance of biodiesel in cold conditions is poorer than petroleum diesel, which might be caused engine problems and increased nitrogen oxide emissions. Biodiesel has been shown to increase nitrogen oxide (NO_x) emissions in many engines on engine stand tests. Biodiesel does not contain nitrogen so the increasing NO_x phenomenon is not related to fuel nitrogen content. NO_x is created in the engine as the nitrogen in the intake air reacts with oxygen at the high in-cylinder combustion temperatures. Second, mono-alkyl ester is a good solvent, it can dissolve rubber and some plastics, remove paint, and oxidize the metals. Third, the hydrophilic property of mono-alkyl ester might cause the corrosion of the engine. Lastly, mono-alkyl ester contains oxygen which

may be undesirable for certain applications. The presence of oxygen lowers the heat content as shown by the volumetric heating values of it, which are 9-13% lower than conventional diesel (Demirbar, 2003). Moreover, this production route has several economic considerations mainly attributed to the price and availability of the main byproduct glycerin. Another drawback is the demand for large biodiesel production units requiring large investments (Knothe *et al.*, 2005).

Therefore, the deoxygenation of triglyceride becomes an alternative process of hydrogenated biodiesel production because there are a lot of advantages of this process over transesterification, including compatibility with infrastructure, engines and fuel standards, lower processing costs and raw materials flexibility (Stumborg *et al.*, 1996). Moreover, the obtain products from this process have high quality and have similar property to the conventional diesel fuel.

2.4 Hydrogenated Biodiesel

Hydrogenated biodiesel can be produced via the hydrodeoxygenation of vegetable oils or animal fats, resulting in straight-chain hydrocarbons in diesel range. The deoxygenation reaction may be carried out in the presence of homogeneous or heterogeneous catalysts under controlled hydroprocessing conditions, known as hydrotreating or hydrocracking processes.

2.4.1 Chemistry of Hydrodeoxygenation Process

Hydrogenated biodiesel can be produced by hydrotreating of vegetable oils at standard hydrotreating conditions (i.e. 300 °C to 450 °C) with conventional hydrotreating catalysts (sulfided NiMo/Al₂O₃, NiMo/γ-Al₂O₃). Avelino Corma *et al.*, (2007) studied hydrotreating of pure sunflower oil in a fixed bed reactor with a sulfided NiMo/γ-Al₂O₃ catalyst. The reaction were done at temperature ranging from 300 °C to 450 °C, pressure of 50 bar, LHSV 4.97 h⁻¹ and H₂ to feed ratio of 1600 ml H₂ /ml liquid feed. A reaction pathway for conversion of triglycerides into alkanes or hydrogenated biodiesel is shown in Figure 2.9.

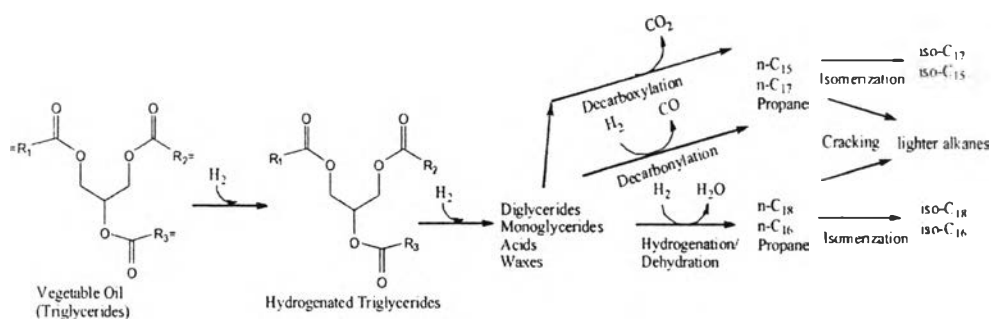


Figure 2.9 Proposed reaction pathway for conversion of triglycerides to hydrogenated biodiesel (Avelino Corma *et al.*, 2007).

In the first step of this reaction pathway, the triglyceride is hydrogenated and broken down into various intermediates which are monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes by three different pathways: decarboxylation, decarbonylation and hydrodeoxygenation (or dehydration/hydrogenation). Moreover, the straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes.

There are several possible reaction pathways for a production of straight-chain hydrocarbons, shown as Figure 2.10. Carboxylic acids have used to represent feedstock and similar equations can be written for alkane production from mono, di or tri-glycerides. Fatty acids can be directly decarboxylated or decarbonylated. Direct decarboxylation removes the undesired oxygen by releasing carbon dioxide and producing aliphatic hydrocarbon chains with one carbon atom less than in the original feed, while direct decarbonylation removes the undesired oxygen by forming carbon monoxide and water, as explained by reactions I and II. Moreover, the fatty acid can be deoxygenated by adding hydrogen leading to a production of straight-chain hydrocarbons and undesired oxygen will be removed through formation of water, as explained by reactions III (Murzin D.Yu. *et al.*, 2006). This pathway involves bifunctional catalysis that contains sites for hydrogenation reactions (possibly NiMo sites) and for dehydration reactions (acid catalytic sites). It is possible that the free fatty acid intermediates are catalyzing the dehydration reaction. The hydrogen requirements decreases as hydrodeoxygenation > decarbonylation pathway > decarboxylation pathway (Avelino Corma *et al.*, 2007).

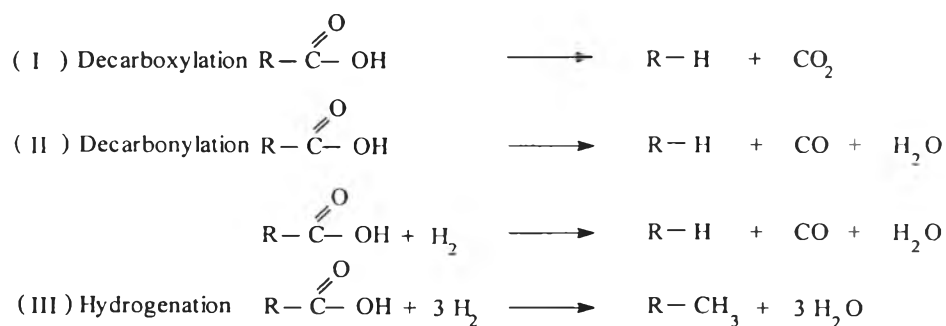


Figure 2.10 The possible liquid-phase reaction pathways for production of straight-chain hydrocarbons from fatty acids.

In addition to the liquid-phase reactions, the water gas shift and methanation reaction are occurred with a number of carbon monoxide, carbon dioxide, hydrogen, and water formed during decarbonylation/decarboxylation reaction. The water-gas-shift reaction may balance the concentrations of CO and CO₂, while methanation reaction of fatty acids gives methane and water, shown as Figure 2.11.

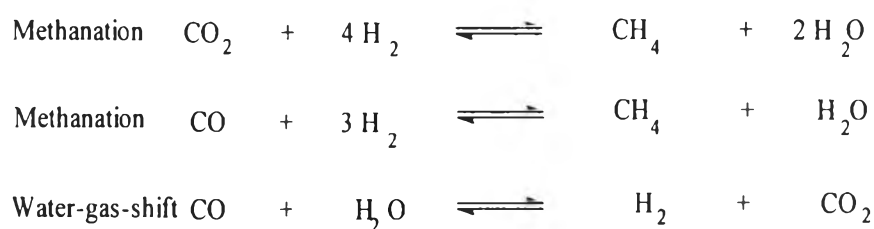


Figure 2.11 Gas phase reactions of CO or CO₂ with H₂ or H₂O.

Neste Oil Corporation has developed a technology called NExBTL technology that uses to produce high quality renewable diesel. The product obtained from this technology is called NExBTL renewable diesel or Green diesel. Chemically, NExBTL renewable diesel is produced via direct catalytic hydrogenation of vegetable oil, which is triglyceride, into the corresponding alkane. The glycerol chain of the triglyceride is hydrogenated to propane, the corresponding C₃ alkane. The reaction of NExBTL renewable diesel production is shown as Figure 2.12. This process removes oxygen from the oil; the product is not oxygenating like traditional biodiesel. The product is clear and colorless paraffin, with a high cetane number (85 to 95) and better properties than even petroleum-based diesel.

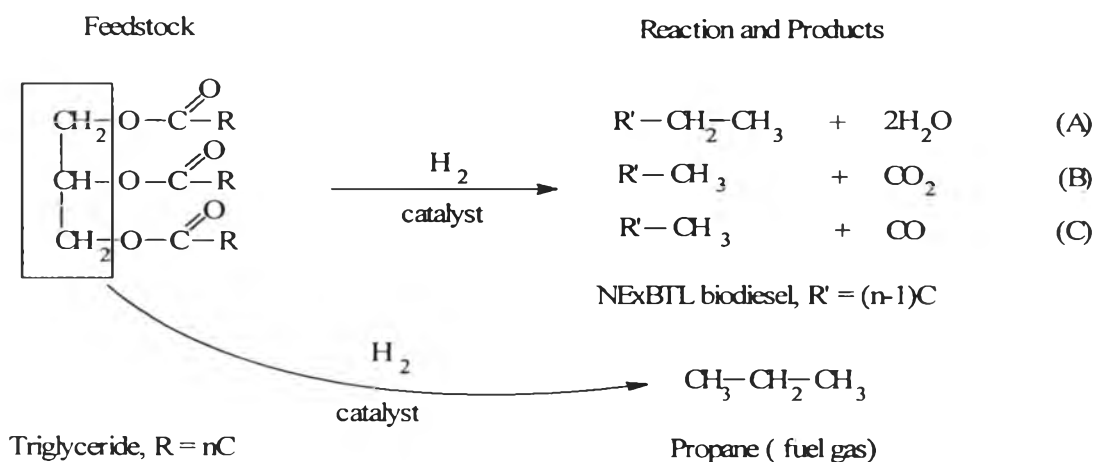


Figure 2.12 The reaction of NExBTL renewable diesel production.

2.4.2 Hydrogenated Biodiesel Production Process

Hydrotreating is a process traditionally used by petroleum refineries to remove sulfur impurities from diesel fuel. Hydrogenated biodiesel produced using this process can either be produced in a “bio-only” unit that uses only vegetable oils or animal fats as feedstock or where oils or fats are co-processed with the distillate fractions (diesel fuel) derived from petroleum. Both processes produce a mixture of hydrocarbons that has been reported to meet the ASTM standard for petroleum diesel (D975). The hydrogenated biodiesel fuel produced through these processes, consequently, could utilize the existing infrastructure currently used for blending and transporting petroleum fuels. Any fuels containing the products produced from either process must be registered with the EPA as a fuel or fuel additive before being sold as diesel fuel in the U.S.

2.4.2.1 Co-processing with Petroleum

The process unit for the biofeedstock co-processing is a distillate hydrotreater for ultra-low sulfur diesel (ULSD) as shown in Figure 2.13. The objective of the co-processing is to produce a “G5” diesel pool in which 5% of the diesel pool contains “green diesel”. The hydroprocessing conditions are assumed to completely favor hydrodeoxygenation (HDO). In other words, oxygen in the biofeedstock is removed by reaction with hydrogen to form water and the C_{18} n-paraffin.

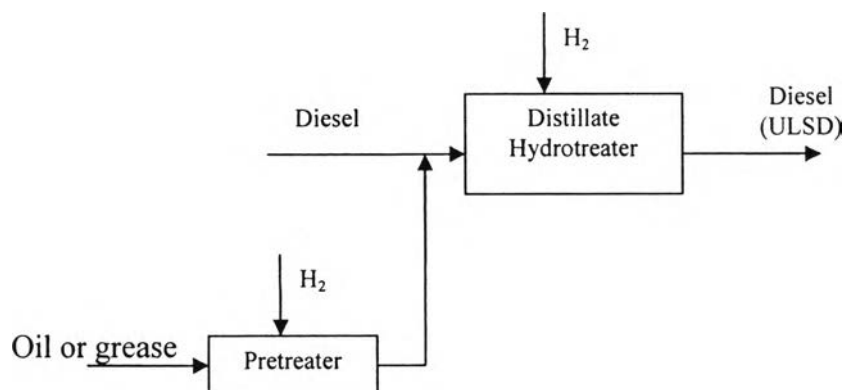


Figure 2.13 Pretreater and co-processing oil or grease in an existing hydroprocessing unit (Marker *et al.*, UOP, 2005).

From the experiments, co-processing of vegetable oil in a typical refinery distillate hydrotreating unit has some drawbacks for green diesel production such as the chemical nature of the biofeedstocks significantly increases hydrogen requirements under conditions that favor hydrodeoxygenation, the heat release from these feeds substantially reduces the catalyst cycle length, typical hydrotreating unit configurations do not permit remediation of increased cloud point due to n-paraffins in the green diesel component of the diesel pool, and the process conditions for hydrotreating units for ultra-low sulfur diesel production favor HDO, producing water that may adversely affect catalyst performance. In conclusion, standard refinery distillate hydrotreating units do not appear to be suitable for green diesel production in a co-processing scheme (Marker *et al.*, UOP, 2005).

2.4.2.2 Processing in a Stand-alone Process Unit (“Bio-only” Hydrotreating)

Neste Oil, a company that is 50% owned by the Finnish government, has developed a “bio-only” process that produces non-ester diesel fuel through its NExBTL™ technology, a thermal/hydrotreating process. The process uses vegetable oils and/or animal fats as sole feedstock. The product obtained from this technology is called NExBTL renewable diesel or Green diesel.

NExBTL renewable diesel, which is a mixture of hydrocarbons similar to petroleum diesel fuel, is essentially sulfur, oxygen, nitrogen and aromatic free. It can be combined with petroleum diesel at any blend level but requires a lubricity additive, as do very low sulfur petroleum diesels. Using NExBTL also helps improve overall air quality, as it generates significantly less nitrogen oxide and particulate emissions as well. The schemes for NExBTL process is shown in Figure 2.14. The production process can apparently be adjusted to produce a fuel with a cloud point anywhere between $-5\text{ }^{\circ}\text{C}$ and $-30\text{ }^{\circ}\text{C}$.

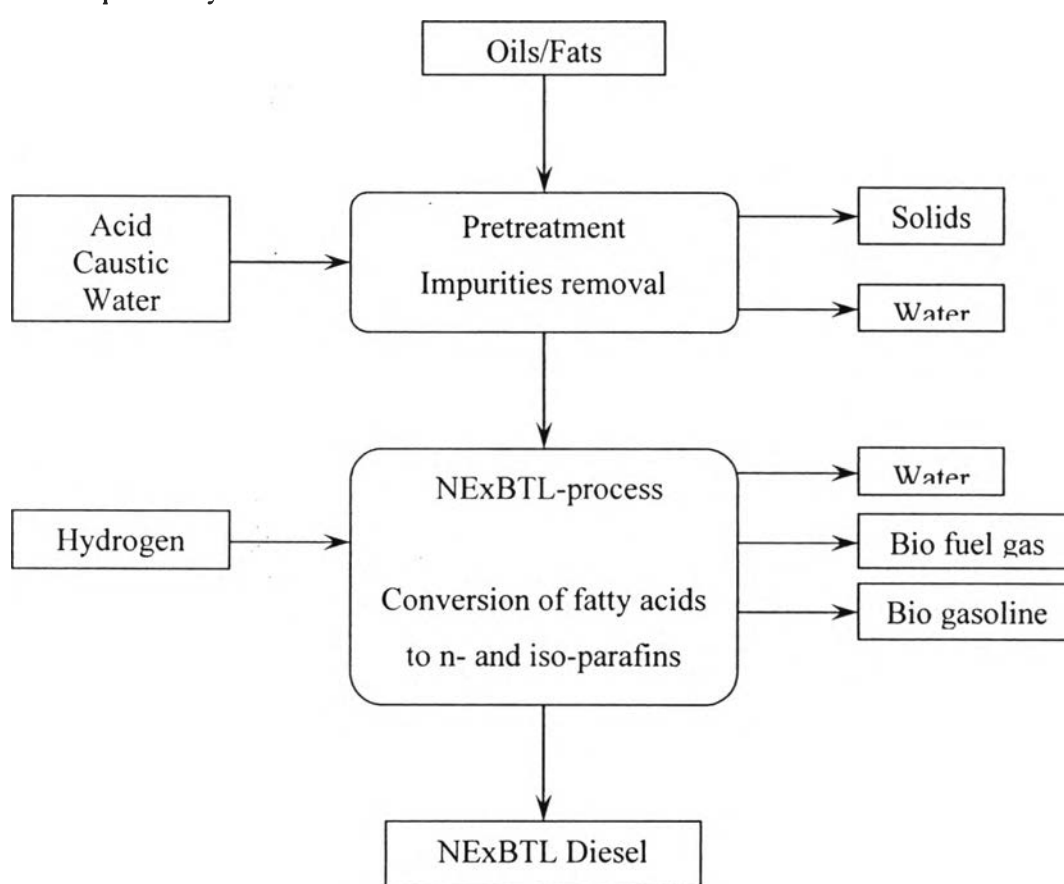


Figure 2.14 The scheme for NExBTL process.

Dynamic Fuels, a joint venture between Tyson Foods and Syntroleum, has recently announced plans to construct a 75 million-gallon per year facility to produce renewable diesel using catalytic hydrotreating of fats and oils feedstock, with production expected in 2010. The fuel produced from this process is presumably similar in composition to the NExBTL fuel produced by the Neste process.

UOP, a Honeywell company, also recently announced that ENI, an Italian refining company intends to build a production facility at an existing refinery in Italy using UOP catalytic hydrotreating technology to convert vegetable oils to hydrogenated biodiesel. It is expected to begin production in 2009, at a capacity of about 95 million gallons per year.

The potential for using bio renewable feedstocks in oil refineries was studied. The study considered the production green diesel from vegetable oils and greases via catalytic hydrotreating technology.

In a standalone unit, a pre-processing step would remove contaminants from the biofeedstock by using a combination of technologies such as hydrocyclones, desalting, acid washing, ion exchange, or fixed guard bed catalyst systems. One possible flow scheme for standalone production of green diesel is shown in Figure 2.15. Feed and a hydrogen-rich gas are contacted with a regenerable hydrotreating catalyst in vessel at typical hydrotreating conditions, e.g., temperature of 350 °C to 400 °C, and 500 psia to 2000 psia then reactor products and unreacted hydrogen are cooled and separated. The liquid product is stripped to remove light components and hydrogen sulfide, or fractionated to recover multiple liquid products (R.L. Bain, UOP, 2007).

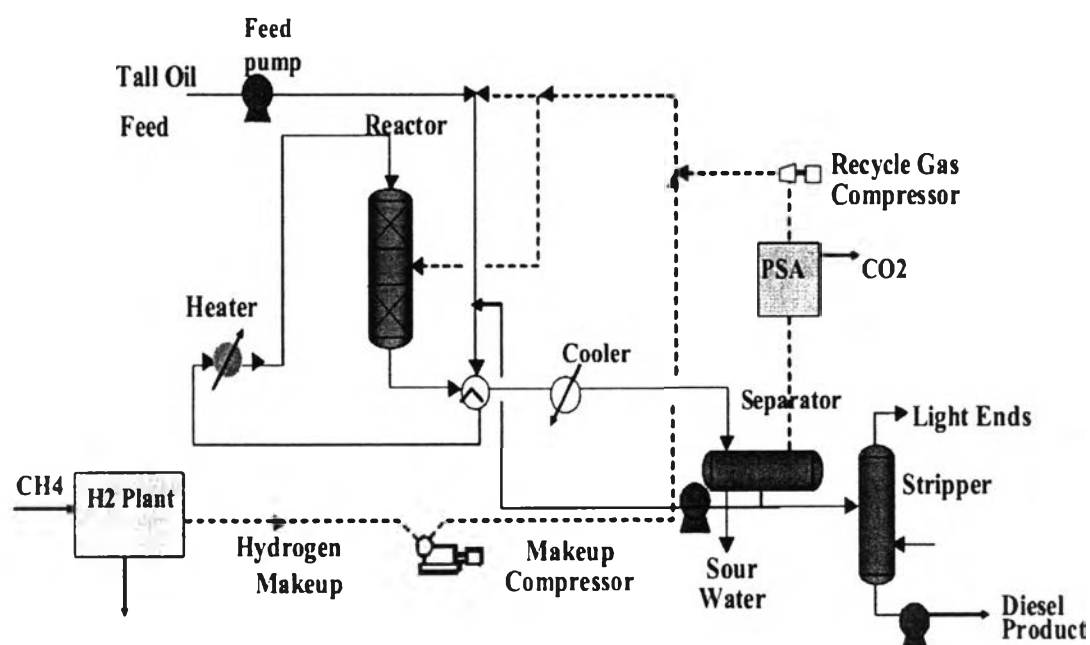


Figure 2.15 Proposed flow scheme for standalone production of green diesel (Marker *et al.*, UOP, 2005).

The experiments performed in this project showed that both hydrodeoxygenation and decarboxylation occur, with the results summarized in Table 2.4. Decarboxylation is favored at lower pressures and hydrodeoxygenation increased with increasing pressure. Decarboxylation (DeCO₂) results in odd number paraffin production and CO₂ formation whereas hydrodeoxygenation (HDO) results in even carbon number paraffin production; therefore the ratio of n-C17 to n-C18 is a measure of the DeCO₂/HDO ratio. Standard hydrotreating catalysts of NiMo, CoMo and Pd all showed activity for both reactions. Furthermore it was demonstrated that the process could be run at lower temperatures than cited in the Arbokem patent and heavy material boiling above diesel range, which Arbokem produced, could be eliminated or reduced with proper choice of catalyst and conditions. Also, most experiments were done at 500 psi which is well below the pressures cited in the Arbokem patent. (Marker *et al.*, UOP, 2005)

Table 2.4 Green diesel experimental summary

Items	Experiment			
	524	531	1316-C3	1316-C4
Feed	Vegetable oil	Vegetable oil	Vegetable oil	Vegetable oil
Catalyst	HCT	N200	HCT	HCT
Test Unit	Autoclave	Autoclave	Plt 1316-B1	Plt 313-B1
WHSV	1.9	1.7	0.8	0.3
Temperature (°c)	300-350	300-350	325	310
Pressure (psia)	500	500	500	500
Products				
% water	1.7	1.2	4.9	9.9
% CO ₂ + CO	12.7	13.4	2.6	1.9
% Light HC	7.0	5.2	3.4	3.9
% diesel +	79.0	80.0	88.3	84.0
% heavy	0	3.2	0.3	0.3
% deoxygenation	90+	91+	85.0	99.0
n C17/ nC18	3.0	2.1	0.6	0.49

Terry *et al.*, UOP, a Honeywell company, studied green diesel production by hydrotreating renewable feedstocks indicates the UOP/Eni Ecofining process for green diesel production.

The Ecofining process is an integrated two stage hydrotreating process. A simplified block flow diagram of the process is shown in Figure 2.16. In the process, feedstock is pumped to process pressure, mixed with recycle hydrogen then sent to a multi-stage adiabatic, catalytic hydrodeoxygenation reactor (R1), where the renewable oil is saturated and completely deoxygenated. Gas recycle to R1 is set to achieve a minimum hydrogen partial pressure at the reactor outlet. Conversion of feed is complete and the volumetric yield of deoxygenated hydrocarbon products is greater than 100%. Selectivity to diesel boiling-range paraffin is very high. The primary deoxygenation reaction by-products are propane, water and carbon dioxide. The effluent from R1 is immediately separated at reactor pressure to remove carbon dioxide, water and low molecular weight hydrocarbons. The resultant diesel is mixed with additional hydrogen gas and then routed to an integrated catalytic hydro-isomerisation reactor (R2), where a branched paraffin rich diesel fuel is produced. In this manner, the cold flow properties of the diesel are adjusted to meet required specifications. The isomerisation reaction is also selective and, as a result, consumes very little hydrogen.

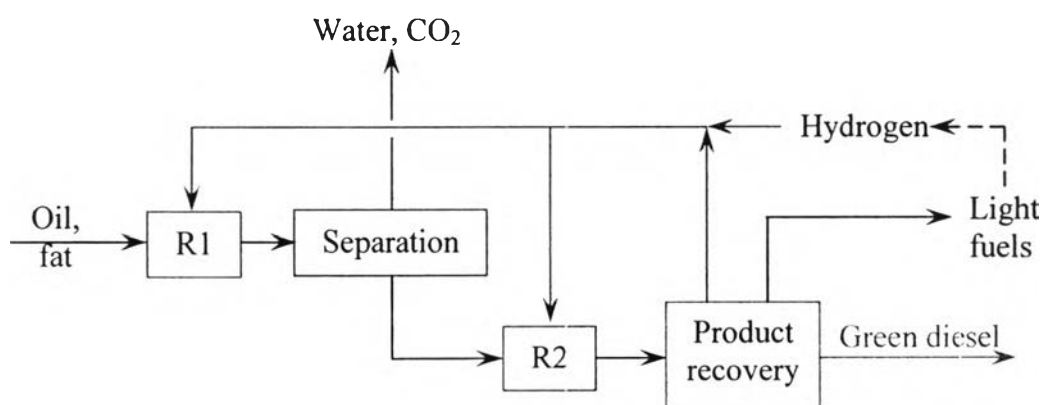


Figure 2.16 Simplified Ecofining process diagram.

Isomerised product is separated from excess hydrogen in a conventional gas/liquid separator. After purification, the excess hydrogen is recycled back to R1 and R2 to maintain the minimum required hydrogen partial pressure. Make-up hydrogen is added to the process to balance both chemical consumption and solution losses. The liquid product is sent to the product recovery section of the process, where conventional distillation steps are employed to separate co-products such as propane and naphtha. The process for producing green diesel operates in mild conditions and integrates well within existing petroleum refineries. If required, a portion of the light fuel co-product can be steam reformed to generate all of the hydrogen consumed in the process.

Miron *et al.*, (2006) studied the production of diesel fuel from vegetable and animal oils. A process for producing a fuel composition from vegetable and/or animal oil comprises hydrodeoxygenating and hydroisomerizing the oil in a single step. The fuel composition has acceptable lubricity and comprises a mixture of C_{14} to C_{18} paraffins having a ratio of iso to normal paraffins of 2 to 8 and less than 5 ppm sulfur.

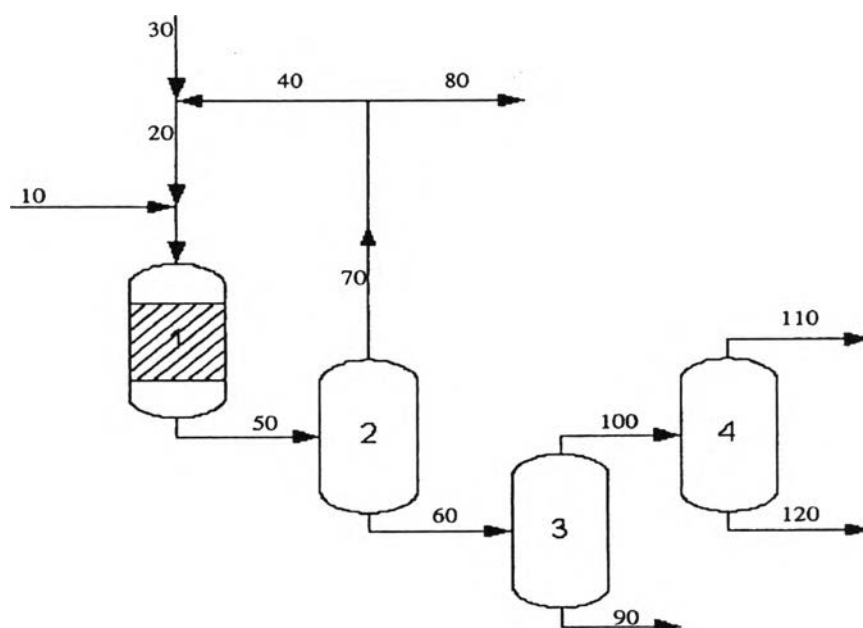


Figure 2.17 Simplified process flow scheme for production of diesel fuel from vegetable and animal oils (Miron *et al.*, 2006).

The process is carried out at relatively mild conditions, for example, at an LHSV in range of 0.8 h^{-1} to 1.2 h^{-1} , at a temperature in the range of $350 \text{ }^{\circ}\text{C}$ to $420 \text{ }^{\circ}\text{C}$., at a pressure of 10 atm to 60 atm, and a H_2/oil ratio of about 800 NL/L to 1200 NL/L. Figure 2.17 depicts an exemplary process schematic. The vegetable and/or animal oil (10) fed to a fixed-bed hydrodeoxygenation/hydroisomerization reactor (1) with a hydrogen stream (20). The hydrogen stream (20) may be comprised of fresh hydrogen (30) as well as recycled hydrogen (40). The reactor (1) could be wall-cooled, multi-bed with interim cooling, or an adiabatic configuration. The effluent (50) from the reactor (1) flows to a first high pressure separator (2) that separates the liquid products (60) and gas (70) containing hydrogen and light components (C_1 to C_4 hydrocarbons and carbon oxides). Hydrogen (40), separated from the light components (80) by a selective membrane or a pressure swing absorption unit (not shown), may be recycled back to the reactor (1). The liquid products (60), containing two phases, an organic phase and water, enters a second separator (3) that separates the water (90), and the organic phase (100) is fed to a third separator (4) for separating the lighter components (110) and C_{14} to C_{18} paraffin products. The lighter components (110) may comprise a naphtha composition of a mixture of C_6 to C_{13} paraffins, aromatics and naphthenes with a boiling point of $< 150 \text{ }^{\circ}\text{C}$.

Refined soybean oil was fed to a fixed-bed reactor packed with a granulated NiMo catalyst operated at an LHSV of 1.0 h^{-1} , $375 \text{ }^{\circ}\text{C}$., 40 atm, and an H_2/oil ratio of 1200 NL/L (Stage 1). The total liquid product was separated into two phase, water and organic phase. The organic phase was fed to a fixed-bed reactor packed with a granulated 1 wt % Pt/SAPO-11 catalyst operated at an LHSV of 3.0 h^{-1} , $380 \text{ }^{\circ}\text{C}$., 50 atm, and an H_2/oil ratio of 500 NL/L (Stage 2). The organic phase from Stage 1 and the diesel product from Stage 2 were analyzed according to ASTM methods and their compositions were measured by GC-MS and confirmed by NMR. The results can be found in Table 2.5.

Table 2.5 The results of production of diesel fuel from soybean oil

	Comparative Stage 1	Comparative Stage 2
Oil	Soybean	Soybean
Temperature	375 °C	380 °C
Catalyst	Granulated	Granulated
LHSV, hr ⁻¹	1.0	3.0
Pressure, atm	40	50
H ₂ /oil ratio, NL/L	1200	500
Composition, wt%		
Linear paraffins	51	14
Branched paraffins	28	76.8
Alkyl cyclohexane	9.2	5.5
Alkyl benzene	2.2	0.6
Olefins	2.7	0.3
Acids	0.2	Not detected*
Others	6.7	2.8

*Detection limit of 0.1 wt%

2.5 Economics Assessment

Economics comparisons for the various processing options are shown in Figure 2.18 (Marker *et al.*, UOP, 2005). The results shown that with greases as the feedstock, the capital cost of biodiesel process is significantly higher than that of grean diesel process and the overall cost of biodiesel production is projected to be nearly twice that of green diesel.

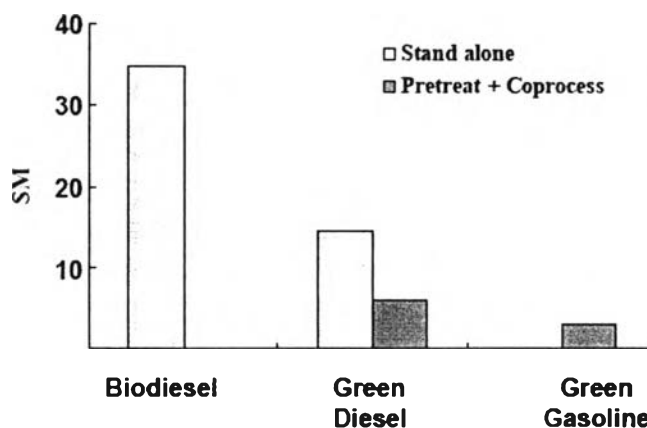


Figure 2.18 Capital costs of biofuels production from oils and greases (Marker *et al.*, UOP, 2005)