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Hydroconversion of Triglycerides into Green Liquid Fuels

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1. Introduction

Due to the depletion of crude reserves and the increasing demand for clean hydrocarbon fuels the production of renewable materials-based fuels has emerged to solve at least partially this problem in the past decade and it is expected to continue [1,2]. Green fuels can be classified as naphtha, jet fuel, and diesel. In the case of green diesel, its increasing demand could reach 900 million tons by 2020 [3].

The common ways to produce diesel-type fuel from biomass are a) by transesterification of triglycerides to obtain biodiesel, and b) by hydroprocessing to synthesize green diesel. Biodiesel is a mixture of fatty acid methyl esters (FAME) while green diesel is a mixture of hydrocarbons, mainly heptadecane and octadecane. Both fuels can be used as additives to petro-diesel. FAME can be used to enhance the lubricity of petro-diesel while green diesel can boost the cetane number. Biodiesel can be obtained with an alkaline liquid catalyst at 60 °C and atmospheric pressure, while green diesel requires a bifunctional solid catalyst (acid/metal), temperatures around 300 °C and ca. 5 MPa of hydrogen in a continuous flow process.

The technology for producing green fuels from triglycerides has been used in petroleum refineries for about 60 years, for instance the same catalyst, reactor type and separation equipment used in the hydrotreating of vacuum gas oil can effectively be used for hydrotreatment of fats and vegetable oils. Thus, during the last decade it has been an increasing interest in research and development for their optimal production, trying to find the best catalyst and the most favorable operating conditions. Many countries and major petroleum companies are nowadays considering the use of vegetable oils and fats as raw materials for production of hydrogenated green fuels. The main drawbacks seem to be the availability of raw material and the large consumption of hydrogen during the process,

which increases the production cost. However there are positive aspects of this technology that overcome the technical difficulties. In what follows these aspects are comprehensively reviewed, starting from the raw material and closing with the current commercial processes.

2. Triglycerides

Triglycerides make up the structure of all vegetable oils and fats found in nature. They are primarily composed of long chains of fatty acid esters as shown in Figure 1. The side chains of triglycerides are either saturated, monounsaturated or polyunsaturated. They can be classified by the length and saturation degree of their side chains. The acid portion of the ester linkage (fatty acids) usually contains an even number of carbon atoms in a linear chain of 12 to 24 carbon atoms with up to three unsaturated bonds usually in the position 9, 12 and 15 with cis orientation, and prevalently in the 9 and 12 position such as in a linoleic oil [4].



Figure 1. Basic structure of a triglyceride and a fatty acid commonly present in fats and vegetable oils

The properties of triglycerides depend on the fatty acid composition and on the relative location of fatty acids on the glycerol. Both fats and oils are composed of triglycerides. The difference between them is simply one of melting point: fats are solid at room temperature (20 °C) whereas oils are liquids. Thus, natural fats and oils are designated as the triglyceride type in terms of saturated and unsaturated acids and isomeric forms. Saturated oils have better oxidation stability and higher melting points than unsaturated ones. A higher degree of unsaturation also means a higher reactivity [5].

The vegetable oil composition is commonly described by its content of fatty acids as it is shown in Table 1 for palm, canola, jatropha, soybean and sunflower oils. This composition is usually determined by derivatization of the esters obtained by total esterification of the oil with a strong acid, e.g. boron trifluoride, as it is shown elsewhere [10]. The molecular weight is given for the fatty acid and for the triglyceride that contains three side chains of the corresponding acid. The average molecular weight of the vegetable oils listed in this table

Source	Structure	Molecular weight (MW)		Typical composition, wt.%				
		Fatty acid	Triglyceride	Jatropha	Palm	Canola	Soybean	Sunflower
Capric	C10:0	172.3	554.8	0.0	0.0	0.6	0.0	0.0
Lauric	C12:0	200.3	639.0	0.0	0.0	0.0	0.0	0.0
Myristic	C14:0	228.4	723.2	0.0	2.5	0.1	0.0	0.0
Palmitic	C16:0	256.4	807.3	15.9	40.8	5.1	11.5	6.5
Palmitoleic	C16:1	254.4	801.3	0.9	0.0	0.0	0.0	0.2
Stearic	C18:0	284.5	891.5	6.9	3.6	2.1	4.0	5.8
Oleic	C18:1	282.5	885.4	41.1	45.2	57.9	24.5	27.0
Linoleic	C18:2	280.4	879.4	34.7	7.9	24.7	53.0	60.0
Linolenic	C18:3	278.4	873.3	0.3	0.0	7.9	7.0	0.2
Arachidic	C20:0	312.5	975.6	0.0	0.0	0.2	0.0	0.3
Eicosenoic	C20:1	310.5	969.6	0.2	0.0	1.0	0.0	0.0
Behenic	C22:0	340.6	1059.8	0.0	0.0	0.2	0.0	0.0
Erucic	C22:1	338.6	1053.8	0.0	0.0	0.2	0.0	0.0
Estimated MW:				869.7	847.0	876.9	871.9	876.7

Table 1. Typical composition of various vegetable oils.

Nomenclature: Cn:m describes a fatty acid with n carbon atoms and m double bonds. Adapted from refs. [6-9].

was estimated by considering that the concentration of a given triglyceride in the oil is the same as the concentration of its corresponding fatty acids, i.e. the three side chains of the triglyceride come from this fatty acid. Thus the estimated average molecular weight for jatropha oil is ca. 870. Another way to determine the molecular weight of a vegetable oil includes the acid and saponification values [11]. The properties of vegetable oils and fats can be modified by hydrogenation.

Hydrogenation of edible vegetable oils has been around for about 100 years in the fat and oils industry, the hydrogenation takes place in a multi-phase catalytic reactor (e.g. slurry type) on a supported Ni catalysts in which the side chains of the triglycerides present in the oil are saturated and converted into a solid or semisolid product [12]. Thus the oil gets a better oxidation stability, and if it is partially hydrogenated it can be used as margarine. This chapter does not focus on food applications, but on the use of vegetable oils for production of liquid transportation fuels by means of a hydrogenation highly enough to crack the triglycerides into hydrocarbons, i.e. hydrocracking.

3. Fundamentals of hydroconversion processes

Hydroprocessing is an important class of catalytic processes in a refinery scheme that comprises a set of reactions in which hydrogen is passed through a bifunctional catalyst

(metal/acid). Hydroprocessing is used to convert a variety of petroleum distillates into clean transportation fuels and heating oil. The reactions that occur in hydroprocessing can be classified in two groups: a) hydrocracking, and b) hydrotreating.

Hydrocracking involves destructive hydrogenation and is characterized by the conversion of the higher molecular weight components in a feedstock to lighter products. Isomerization and cracking of C-C bonds in bigger molecules occur at some extent to produce hydrocarbons within the boiling range of gasoline and diesel. Such treatment requires high temperature and the use of high hydrogen pressures to minimize the condensative chain polymerization reactions that lead to coke formation [5]. From a catalytic viewpoint, hydrocracking is carried out on acid supports, i.e., amorphous supports (alumino-silicates), silicoaluminophosphates (SAPO), and crystalline supports (zeolites) [13]. Figure 2 shows schematically an example of hydrocracking of a model molecule present in vacuum gas oil.

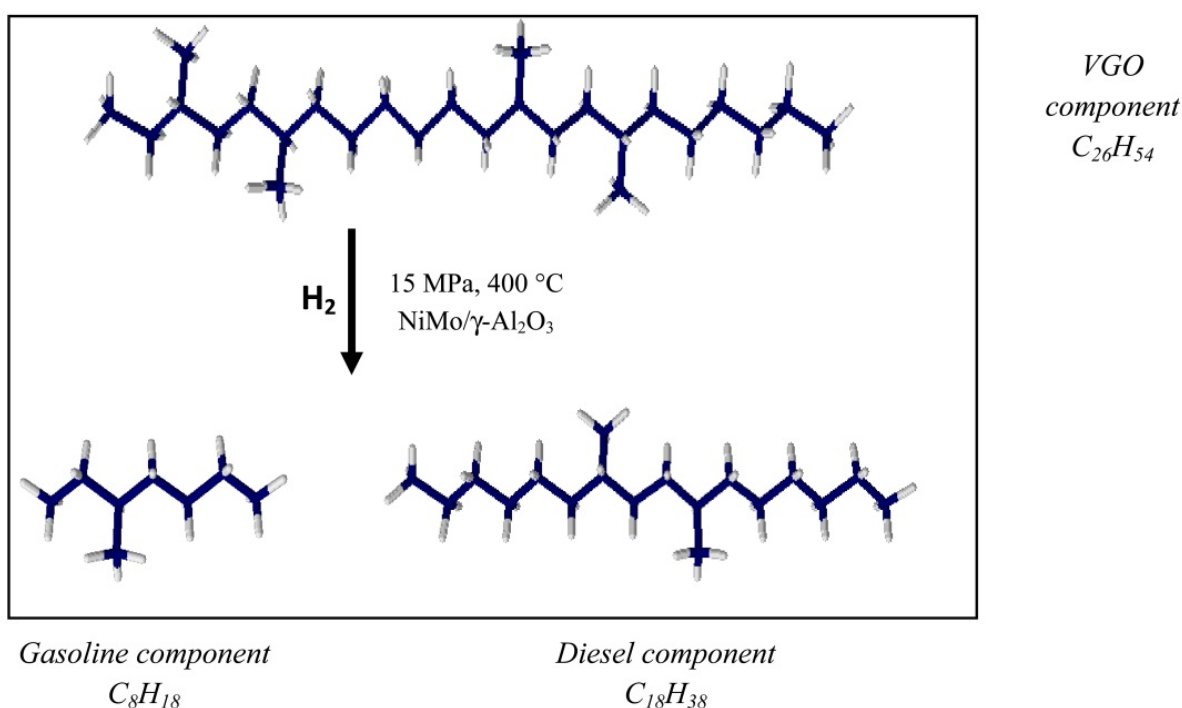


Figure 2. Hydrocracking of gas oil into gasoline and diesel on a bifunctional catalyst

Hydrotreating or hydrofining involves non-destructive hydrogenation and is used to improve the quality of petroleum distillates without significant alteration of the boiling range. Nitrogen, sulfur, and oxygen compounds undergo hydrogenolysis to remove ammonia, hydrogen sulfide, and water, respectively. Mild temperature and hydrogen pressures are employed so that only the more unstable compounds that might lead to the formation of gums, or insoluble materials, are converted to more stable compounds [5]. Hydrotreating takes place on the metal active sites of a catalyst, e.g., NiMo or CoMo in sulfide state supported on $\gamma-Al_2O_3$ [13]. Other catalysts different to metal sulfides have been used in hydrotreating, such as supported noble metal catalysts [14] and Ni-Mo/ $\gamma-Al_2O_3$ catalyst in which its acidity was improved with addition of fluorine [15]. The NiMo/ $\gamma-Al_2O_3$

is actually one of the most commonly used catalysts in the hydroprocessing of middle and heavy distillates at petroleum refineries. This catalyst has a high hydrogenation activity and mild acidity which are also appropriate for the hydroconversion of triglycerides into diesel hydrocarbons [16].

4. Hydroprocessing of triglycerides

As an alternative renewable raw material, the triglycerides present in fats and vegetable oils can be industrially hydroconverted at the petroleum refineries.

Five of the most common approaches for upgrading hydrotreaters for clean-fuels production are (1) upgrading feedstock and integrating processes, (2) implementing a higher-activity catalyst, (3) replacing reactor internals for increased efficiency, (4) adding reactor capacity, and (5) increasing H₂ partial pressure. Refiners also have the option to implement advanced process control, and simulations to optimize operation and commercial catalyst developments have been accelerating [17].

4.1. Green fuels from triglycerides: Technological advantages

The hydroprocessing of triglycerides involves the hydrogenation of the double bonds of the side chains and the removal of oxygen on the metal sites of the catalysts. The hydrotreating of most vegetable oils leads to the production of C₁₅-C₁₈ hydrocarbons, i.e. a liquid mixture within the boiling point range of diesel which is commonly called "green diesel", "renewable diesel" or "bio-hydrogenated diesel", and therefore with the same chemical nature than petroleum-derived diesel [18].

In comparison with the process to produce fatty acid methyl esters (FAME or biodiesel), the hydroprocessing of vegetable oils for production of green diesel has the following advantages[19]:

- The product is compatible with existing engines.
- Flexibility with the feedstock, e.g. the content of free fatty acids in the vegetable oil does not matter.
- Higher cetane number.
- Higher energy density.
- Higher oxidation stability (zero O₂ content).
- It does not increase the emissions of NO_x.
- It does not require water.
- There are not byproducts that require additional treatment (e.g. glycerol).
- The distribution of the renewable diesel does not cause additional pollution since it can be transported through the same pipelines that are currently used for distribution of petrodiesel.
- Better performance in cold weather.

To obtain lighter hydrocarbons such as those within the boiling point range of jet fuel or gasoline, catalysts with stronger acid sites (e.g. zeolites) can be used. The zeolite supported

catalysts usually contain higher acidity and therefore a more severe cracking activity than those supported on alumina. The acid sites of the catalyst increase also the isomerization degree of the molecules, thus boosting the properties of the green liquid fuels, such as a lower pour point and a higher octane number.

4.2. Raw materials used as source of triglycerides

Different sources of triglycerides have been hydrotreated using bifunctional catalysts to produce green fuels such as palm, sunflower, jatropha, rapeseed, and soybean oils among others. Waste cooking oils have also been used to produce green fuels. Some of these vegetable oils and its composition are shown in Table 1. Most of the vegetable oils found in nature contain linear paraffinic side chains with 16 and 18 carbon atoms, predominantly monounsaturated chains (C18:1). The hydroprocessing of long-chain triglycerides highly unsaturated requires higher hydrogen consumption than that required for less unsaturated triglycerides to reach the same level of hydroconversion into liquid fuels. This fact is also dependent on the catalyst used and reaction conditions at which triglycerides are processed.

Hydroconversion of triglycerides can be carried out in two ways. The first one consists in hydroprocessing of triglycerides only and the second one in co-feeding to the process triglycerides and (petroleum-based) vacuum gas oil.

4.2.1. Hydroprocessing of triglycerides only

During hydroprocessing of triglycerides, the type of catalyst is one of the most important factors to determine the yield and composition of liquid products, such as green naphtha (C₅-C₁₀), green jet fuel (C₁₁-C₁₃), and green diesel (C₁₄-C₂₀), and even green liquid petroleum gas (LPG). A severe hydrocracking catalyst would lead to a high production of green naphtha whereas a mild-hydrocracking catalyst is prone to produce mainly green diesel. The reaction temperature plays an important role for the yield and quality of hydroprocessed oils as well. It has been observed that diesel selectivity decreases with increasing reaction temperature while naphtha selectivity increases as result of the thermal cracking of diesel hydrocarbons. Therefore, high temperatures and strong acid catalysts are preferred if naphtha is the desired product. Conversely, moderate temperatures and catalysts with mild acid sites are needed if middle distillates are the desired products [20]. The yield of green gasoline can also be increased by using a two-step process, i.e. hydrotreating followed by hydrocracking. In the first one, oxygen is removed from biomass as water. The deoxygenated product is then separated by distillation, and the heavier fractions are further brought to the second step to convert them into (lighter) molecules within the boiling range of naphtha, as reported elsewhere [21]. Figure 3 shows a schematic two-step process in which green naphtha, jet fuel, and diesel are obtained. The first reactor is packed with a hydrotreating catalyst to remove oxygen. A low extent hydroisomerization also occurs in the first reactor. Then, the oxygen-free product is processed in a second reactor packed with a selective hydrocracking catalyst where both cracking of larger molecules and hydroisomerization take place. Distillation of the product yields three major liquid streams, i.e. naphtha, jet fuel, and diesel.

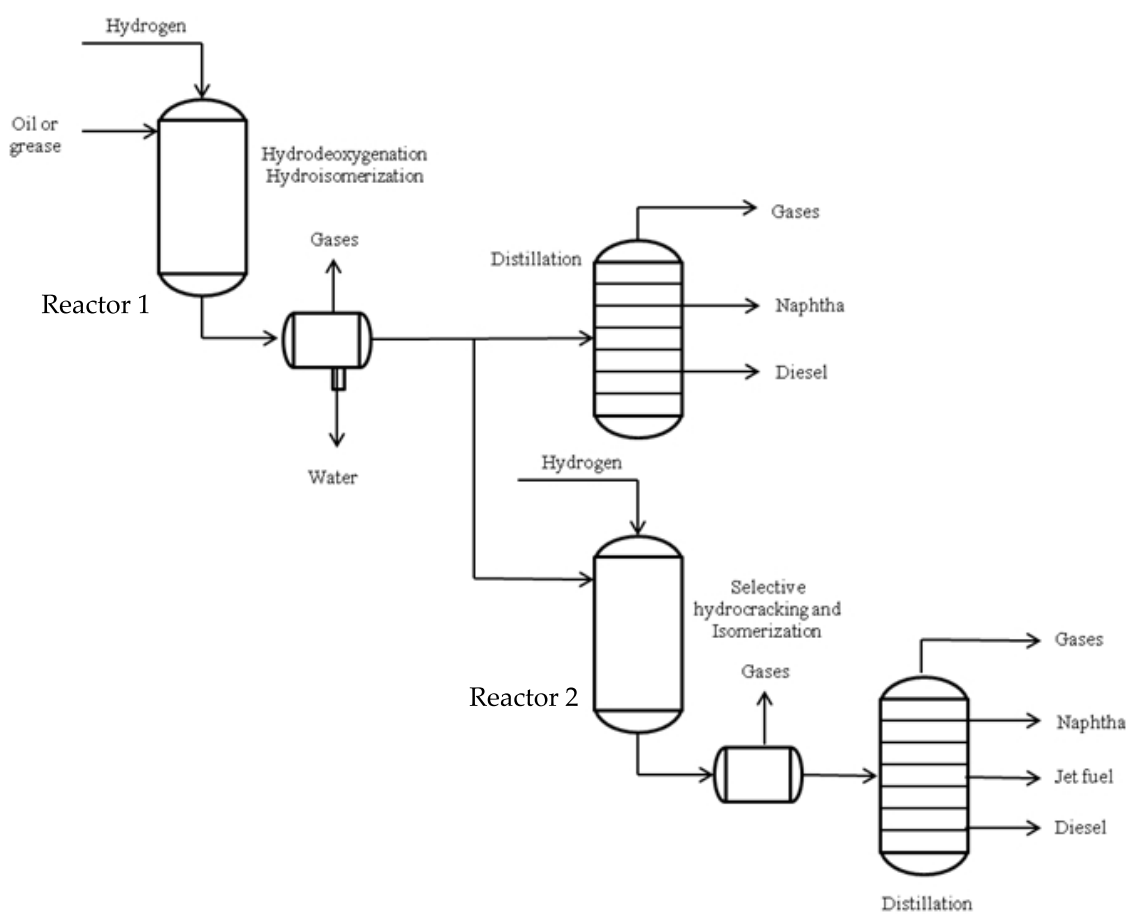


Figure 3. Schematic representation of a two-step process for obtaining green naphtha, jet fuel, and diesel coupling hydrodeoxygenation and selective hydrocracking.

In comparison with the use of different catalysts to produce green jet fuel or diesel, the use of catalysts for production of green naphtha through simultaneous cracking and hydrogenation has not been abundantly reported in literature. It has been stated that green gasoline is obtained when using NiMo/zeolite (klinoptilolite type) at 300-320 °C in a batch reactor after 1-2 h of reaction time. The strong acid sites in the zeolite favored the cracking of the large molecules in the vegetable oil into naphtha; however, middle distillates (C₁₃-C₁₉) were also obtained at some extent [22]. Another acidic support able to produce green naphtha is HZSM-5 zeolite. It has been reported that a synthesized zeolite having a SiO₂/Al₂O₃ ratio of 30 readily produces a high amount of gasoline from palm oil due to the large number of available Brønsted acid sites that increase the selectivity toward cracking reactions [23].

The green diesel obtained directly by hydrodeoxygenation is mainly composed by C₁₇ and C₁₈ n-paraffins that have a high cetane number but poor cold flow properties as these hydrocarbons have a high melting (freezing) point in between 20 and 28 °C. Therefore, its quality needs to be boosted by bringing the hydrodeoxygenated product through a second process in which selective hydroisomerization and cracking take place [14,15,24]. In this process, not only quality-improved diesel is obtained but also jet fuel, as the acid sites of the catalyst promote the conversion of larger alkyl chains into smaller chains.

Hydroisomerization is a key parameter to obtain methyl-branched paraffins mainly. This goal is achieved by using a shape-selective catalyst such as zeolites or other acidic supports. Normal paraffins in the boiling point range of diesel have generally a higher cetane number than that of their branched isomers. Conversely, iso-paraffins have lower freezing points than n-paraffins. Thus there is a trade-off in the quality of a fuel rich in paraffins, i.e. either with good combustion properties or with good cold flow properties.

Several studies have reported green diesel having a cetane numbers higher than petrodiesel and biodiesel, with values from 65 to 104 [24-27]. Hancsók et al. [24,26] and Simacek et al.[27] have studied the influence of the reaction temperature on the cetane number. As the reaction temperature was increased the cetane number of the liquid product was observed to decrease. This can be related with an increasing thermal cracking and therefore a reduced concentration of large paraffins in the diesel. Though green diesel is evidently a premium quality diesel and could be used as an effective additive enhancer, improved cold flow properties are also necessary for both jet and diesel fuels to be used at very low temperatures (e.g. below 0 °C).

Hydroisomerization is desirable for green diesel to have a lower freezing point though with lower cetane number. The hydroisomerization of a green diesel for instance containing mainly n-C₁₇ and n-C₁₈ paraffins and with a cetane number close to 100 and a freezing point close to 20 °C may produce a green diesel with a cetane number close to 70 and a freezing point lower than -5 °C, as it is shown by the variation of these two properties as function of carbon number in Figure 4. It is also observed that 5-methyl iso-paraffins have better cold flow properties than 2-methyl iso-paraffins.

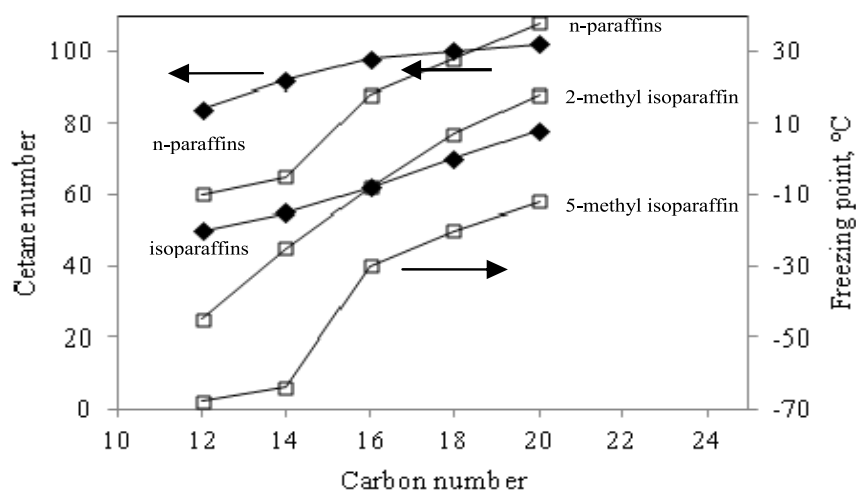


Figure 4. Cetane number and freezing points as function of carbon number in linear and methyl-branched paraffins. (Adapted from ref. [28]).

The interest for the production of both green jet fuel and diesel has been constantly increasing during the last decade, and gained such an importance nowadays that two-step processes are industrially available. Neste Oil in Europe and UOP Honeywell in America

have built plants based on these types of processes to convert distinct vegetable oils into green jet fuel and green diesel. Obviously, these green fuels need to accomplish with quality standards to be used along with current fossil fuels in conventional engines. Table 2 presents some of the most important properties of jet fuel and diesel.

Green jet fuel specifications			
Property	Value	Test method	
		ASTM	IP
Total acidity, mg KOH/g	0.10 (Max.)	D3242	354
Distillation temperature, °C	Report	D2887, D86	123
Flash point, °C	38 (Min.)	D56, D3828	34
Density @15°C, kg/m ³	775-840	D1298, D4052	365
Freezing point, °C	-40 Jet A (Max.)	D2386, D5972, D7153,	16
	-47 Jet A-1 (Max.)	D7154	
Viscosity @ -20°C, cSt	8.0 (Max.)	D445	71
Neat heat of combustion, MJ/kg	42.8 (Min.)	D3338, D4529, D4809	12, 355, 381
Diesel fuel specifications			
Property	Value	Test method	
		ASTM	EN
Flash point, °C	38 (Min.)	D93	2719
Kinematic viscosity, mm ² /s @40°C	1.9 (Min.)	D445	3104
	4.1 (Max.)		
Ash, wt%	0.01 (Max.)	D482	6245
Cetane number	40 (Min.)	D613	5165
Cloud point, °C	Report	D2500	ISO 3015

Table 2. Some properties of green jet fuel and diesel specified in test methods (Adapted from test methods ASTM D-975-11b, ASTM D-7566-11a).

Once green diesel has an improved performance in cold weather it may be used directly in vehicles or it can be mixed with petro-diesel. In the case of jet fuel, it has been mixed at 50% with petroleum-derived jet fuel or other percentages in one turbine and used in some documented commercial flights as shown in Table 3. The green jet fuel produced by UOP/ENI technology has been proved to meet all the main properties of petroleum-derived aviation fuels such as flash point, cold temperature performance, and good air oxidation stability [29].

The studies regarding to one-step process in which a catalyst is able to enhance both hydroisomerization and cracking are scarce and only a few reports have appeared in the literature. Microporous silicoaluminophosphates (SAPO) have been reported to possess acid sites of sufficient strength to be highly selective toward hydroisomerization. Methyl isoparaffins are the predominant products obtained with Pt/SAPO-11 and Pt/SAPO-31 catalysts [30] and Pd/SAPO-31 [2]. In this case, it was possible to obtain hydrodeoxygenated and hydroisomerized liquid products over only one type of catalyst, which it would be more

desirable and economical at industrial scale. NiMo/Al₂O₃-SiO₂ catalyst has also been used to hydrogenate unsaturated carbons of jatropha oil followed by deoxygenation to produce propane and C₁₅-C₁₈ n-paraffins, which were further hydroisomerized and cracked to generate C₁₅-C₁₈ iso-paraffins. All products were synthesized in a one-step process [7].

Airline company	Jet model	Date	Oil source	Percentage of blend in one motor
Virgin Atlantic	B747	Feb. 23, 2008	Coconut, babassu	20%
Air New Zealand	B747	Dec. 30, 2008	Jatropha	50%
Continental Airlines	B747	Jan. 9, 2009	Jatropha	50%
Japan Airlines	B747	Jan. 30, 2009	Camelina	50%
Aeromexico	B777	Aug. 2, 2011	Jatropha	30%

Table 3. Different demonstration commercial flights employing mixtures of green jet fuel mixed with aviation turbine fuel from petroleum (Adapted from several web pages of different airlines companies).

4.2.2. Hydroprocessing of triglycerides plus petroleum gas oil simultaneously

Vegetable oils can be mixed with petroleum fractions such as straight run gas oil and/or vacuum gas oil to be hydroprocessed on conventional hydrotreaters used in refineries to reduce operation costs by using the existing installations. In this case, two main reactions would occur, e.g. hydrodeoxygenation of triglycerides and hydrodesulfurization of gas oil. Both reactions are carried out on the same hydrotreating catalyst. It has been observed that NiMo/Al₂O₃ catalysts promote hydrodeoxygenation having high selectivity toward diesel range products compared with NiW/SiO₂-Al₂O₃; however, the NiW sulfides reduced the hydrogen consumption and increased the production of jet fuel. In a mixture of soybean oil and gas oil, it was observed that hydrodeoxygenation of soybean and hydrodesulfurization of gas oil were not competing reactions. In spite of similarities in active sites for both reactions their number is high enough to avoid inhibition among them [31]. In other studies it was reported that simultaneous hydrodeoxygenation of gas oil with high sulfur content with vegetable oil had a synergistic effect up to 15% of oil in the blend. With higher contents of vegetable oil in the mixture, desulfurization of the petroleum stream was reduced [32]. The mixture of rapeseed oil and light gas oil after being hydroprocessed yielded high conversions of sulfur and oxygen to obtain a diesel fuel with improved properties [33]. The addition of sunflower oil to gas oil to be simultaneously processed showed an enhancement of cetane number by 1-7 units when hydroprocessing took place at 420 °C and 18 MPa by which the fuel obtained can be considered as an excellent bio-component for the diesel fuel blending [27]. Figure 5 shows the co-feeding of vegetable oil of 5 to 20 wt% and vacuum gas oil (VGO) in a reactor operating at typical hydroprocessing conditions in a refinery. The cetane number is expected to be higher than that of the diesel obtained by only processing VGO, for about 10 to 20 units.

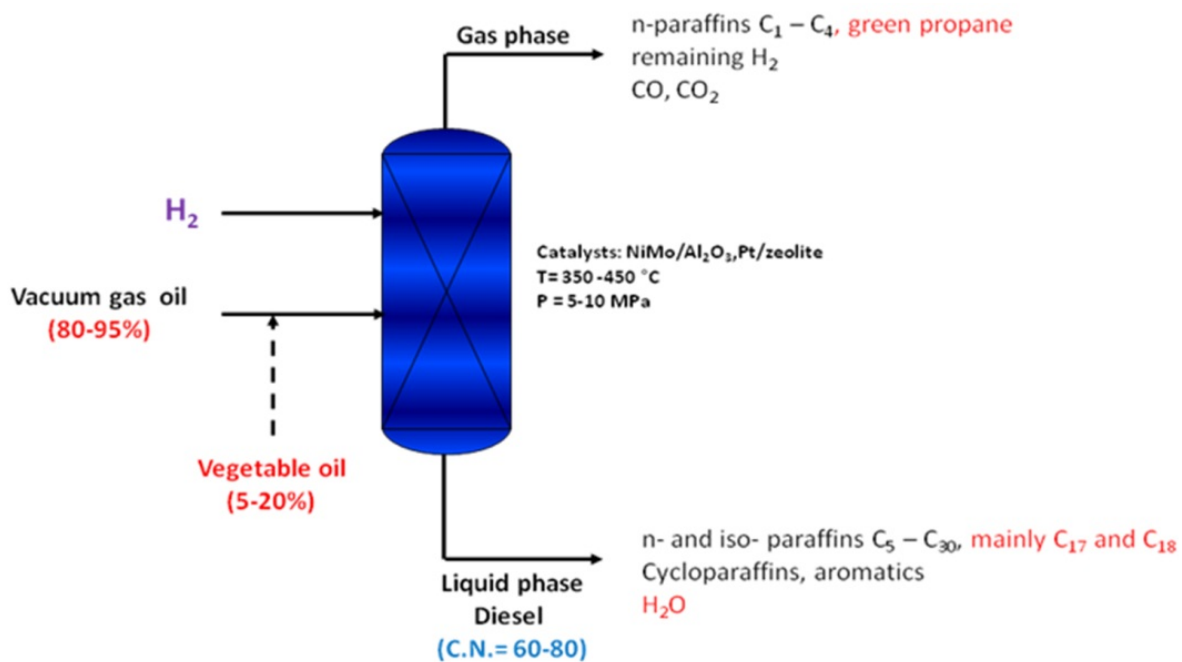


Figure 5. Co-feeding of vacuum gas oil and vegetable oil in a hydrotreater.

5. Chemistry of the hydrotreating of vegetable oils

The understanding of the chemistry of the hydroprocessing of triglycerides is essential to formulate a kinetic model that could lead to the design of the reactor and its subsequent simulation and optimization. The triglycerides are converted into hydrocarbons, mainly to n-paraffins at the temperatures between 300 and 450 °C and hydrogen pressures above 3 MPa leaving CO, CO₂ and water as by-products. The mechanism of the reaction is complex and consists of a series of consecutive steps (Viz Fig. 6). Oxygen removal from triglycerides occurs through different reactions such as hydrodeoxygenation, decarboxylation, and decarbonylation and influences on the distribution of hydrocarbon products [33,34].

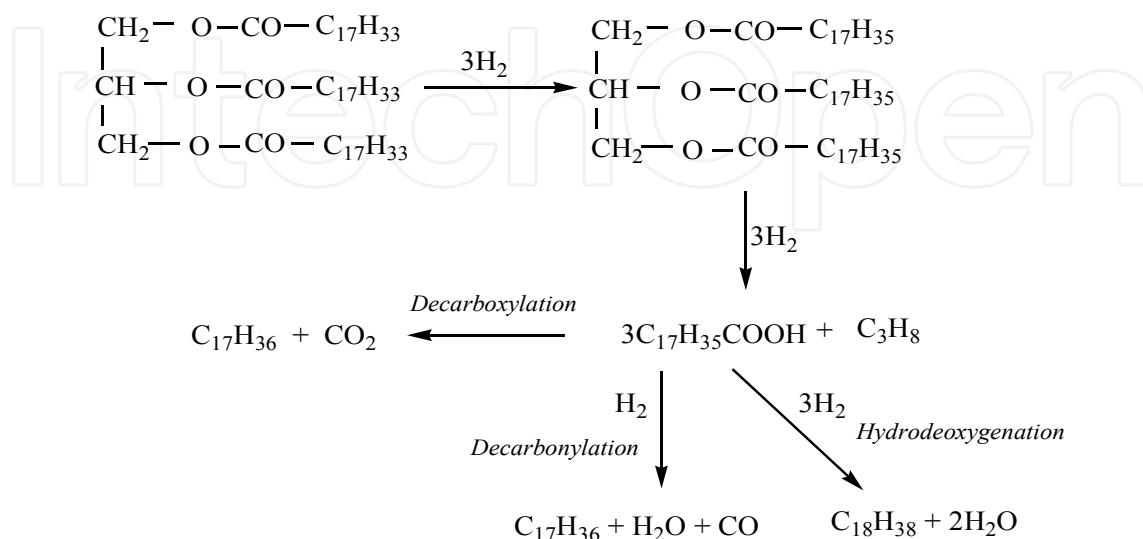


Figure 6. Molecular reactions occurring in the hydroconversion of a triglyceride (e.g. triolein)

The production of 2 moles of n-heptadecane, 1 mole of n-octadecane and 1 mole of propane requires 10 moles of hydrogen per each mole of triolein in the feedstock (Viz Figure 6). More unsaturated triglycerides will require a larger amount of hydrogen to produce heptadecane and octadecane. Hydrocarbons having one carbon atom less than the parent fatty acid chain, i.e., pentadecane and heptadecane, are the products of the decarboxylation and decarbonylation (with CO and CO₂ as gaseous by-products), whereas the liquid hydrocarbons with the same carbon number as the original fatty acid, i.e., hexadecane and octadecane, are the products of hydrodeoxygenation reaction (with H₂O as secondary product). In most cases, the extent of both pathways is elucidated from the liquid hydrocarbon distributions and knowing the value of the C₁₇/C₁₈ ratio is consequently a common way to determine the dominant path of the reaction [16,31,35]. The product distribution is also influenced by the reaction pressure since at a high hydrogen pressure the hydrodeoxygenation will be the preferred pathway. On the other hand, at a lower hydrogen pressure the decarboxylation reaction will be enhanced. Thus, the CO₂/CO ratio in the product distribution could also be used to determine the selectivity for decarboxylation to decarbonylation reactions.

Under reaction conditions it is likely that limitations by diffusion take place, i.e., by hydrogen mass transfer through the stagnant liquid film formed by reactants and/or products on the catalyst surface [36]. Figure 7 shows a probable mechanism in which triglycerides are converted into linear paraffins. In this case, the oil is considered to be composed by triolein, tripalmitin, and trilinolein having distinct unsaturations. As first step, free fatty acids are formed by scission of propane from the glycerol backbone of the triglyceride molecules in presence of hydrogen. Three moles of oleic, palmitic, and linoleic acid are formed, respectively. In the second step, hydrogenation takes place to saturate the oleic and linoleic acids. The side chain of palmitic acid is already completely saturated. Then, the three common reported reactions to eliminate oxygen may occur. Decarbonylation and decarboxylation form hydrocarbons having one carbon atom less than the parent free fatty acid (FFA) whereas hydrodeoxygenation removes the oxygen atom keeping the same carbon atoms as in the original FFA. In this way, the linear paraffins are comprised in the range of C₁₅-C₁₈.

Thermodynamic data for production of linear C₁₇ hydrocarbons from stearic acid at 300 °C indicated that Gibbs free energy and standard enthalpy of reaction for decarboxylation were -83.5 kJ/mol and 9.2 kJ/mol, respectively. Whereas these values for decarbonylation were -7.0 kJ/mol and 179.1 kJ/mol, respectively, and for hydrogenation of -86.1 kJ/mol and -115.0 kJ/mol, respectively. Apart from deoxygenation reactions, it is likely that other reactions, i.e., hydroisomerization, dehydrogenation, and cyclization occur simultaneously. However, the extent of these reactions depends on the catalyst type and hydroprocessing reaction conditions [37]. Formation of alcohols and esters has also been reported to take place during hydroprocessing of triglycerides [38]. The use of sulfided catalysts during hydrodeoxygenation of triglycerides under typical hydrotreating conditions (P=50-100 MPa, T=320-420 °C and NiMo/Al₂O₃ or CoMo/Al₂O₃ as catalyst) typically produces carboxylic acids as intermediates [39]. However, during deoxygenation, some degree of cracking of the fatty acid chains is carried out in order to form more hydrocarbons from triglycerides in

which C-C bond scission is involved to produce lower hydrocarbons. The deoxygenation of tristearin on carbon-supported Ni, Pd, and Pt catalysts produced n-pentadecane through β - and γ - scissions [40].

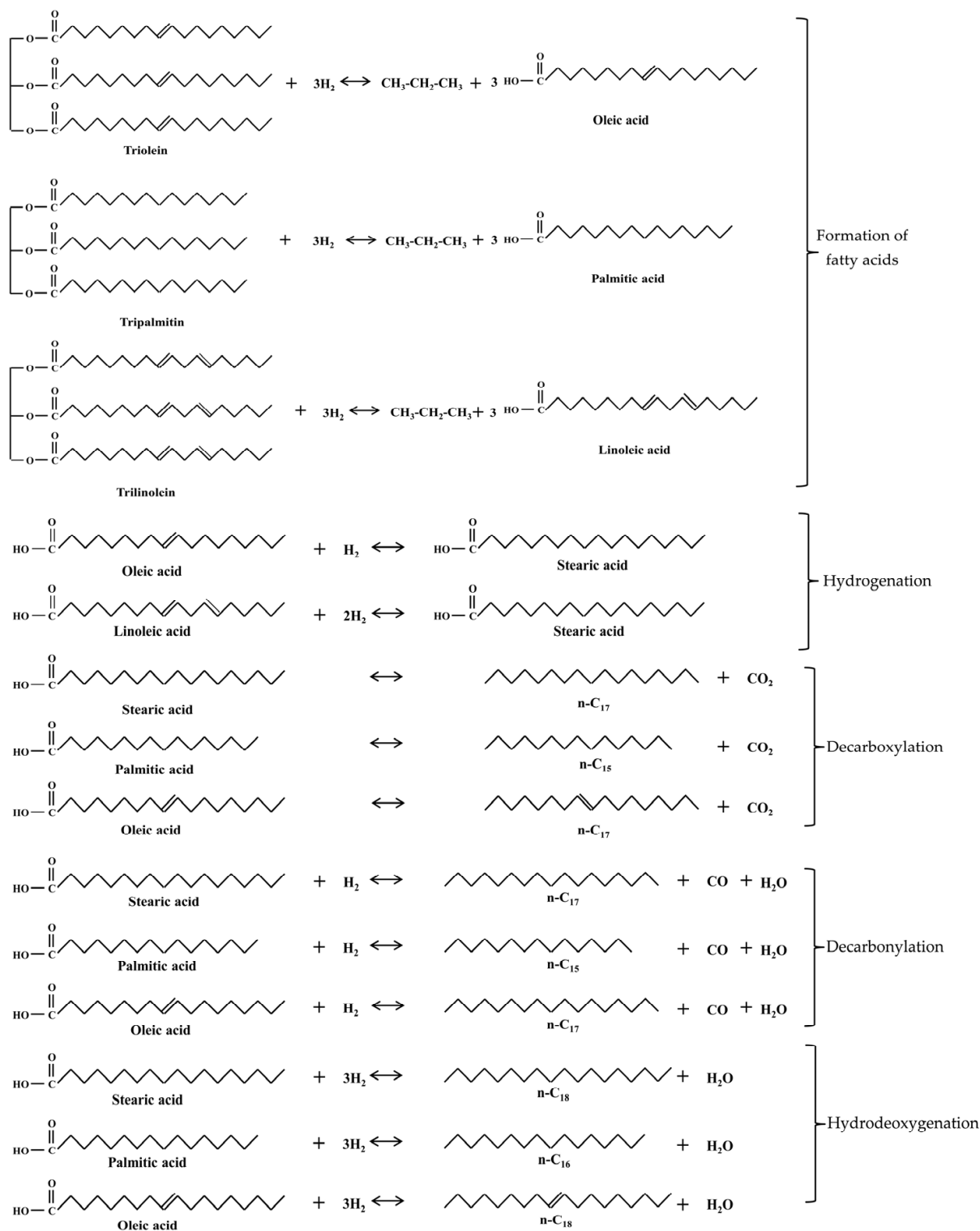


Figure 7. Reaction pathways during hydroprocessing of three triglycerides (Adapted from Ref. [38]).

The products from hydrotreating of fats and vegetable oils will rather be linear paraffins. As explained in Section 4.2.1, the hydroisomerization of these n-paraffins is needed to improve the cold properties of green fuels. For hydroisomerization to take place a bifunctional catalyst is needed, thus the saturation of the intermediate iso-olefins is carried out on the metal sites. It is generally acknowledged that isomerization of paraffins takes place by a mechanism involving carbenium ions as intermediate with protonated cyclopropane (PCP) isomerization as the rate determining step. When secondary or tertiary carbocations are formed, cracking of the paraffin by β -scission would also appear. Thus, a catalyst with a suitable high acid activity would both isomerize and crack these carbenium ions on the acid sites yielding after hydrogenation on the metal sites, lighter hydrocarbons such as propane and gasoline range hydrocarbons.

6. Catalysts used for the hydrotreating of vegetable oils

There are three methods to crack long chain of hydrocarbons to short chain of hydrocarbons. The first method is known as thermal cracking and occurs with the aid of heat to produce a lighter product. The second process is the catalytic cracking that is conducted in the presence of an acid catalyst without the use of hydrogen and needs less thermal energy than thermal cracking. The third method is known as catalytic hydrocracking and occurs in the presence of a bifunctional catalyst and a high hydrogen pressure. The catalytic hydrocracking process consumes less thermal energy and the presence of hydrogen minimizes coke formation and therefore reduces catalyst deactivation by pore blockage [41].

In spite of having so far optimized the different factors that improve the conversion of triglycerides into green fuels, the properties of the catalyst for upgrading vegetable oils still need to be enhanced. While the current commercial catalysts used in obtaining renewable fuels have been optimized to process petroleum feedstocks, the new catalysts to process vegetable oils may be synthesized taking into account the following considerations: a) high activity toward deoxygenation, b) minimization of coke formation, c) water resistance, d) capability to regenerate in single processes, e) high tolerance to chemical poisons, f) scalability in any commercial process [18].

The first study on hydrocracking of vegetable oils was presented by Nunez [42] in 1984 in his Doctoral thesis and in which he reported the use of rhodium and ruthenium supported catalysts for the hydrocracking of soybean oil in a batch reactor. Two years later, Nunez et al. [43] reported that the hydrocracking of soybean oil was observed to begin at about 400 °C. At this temperature, they observed the decarbonylation/decarboxylation of fatty acids to take place with a marked hydrogenolysis on a bifunctional catalyst, yielding mainly normal paraffins and an overall conversion of 83 wt% (including the gas fraction CO, CO₂, C₁-C₄) under favorable conditions of pressure and temperature. Since then and especially in the last 6 years, many types of catalysts have been used to crack the long chain of hydrocarbons of vegetable oils to produce short chain of hydrocarbons, such as paraffins, olefins and aromatics by catalytic cracking. Several of these studies on hydrocracking of vegetable oil (Viz Table 4) have involved the use of zeolites and conventional hydrotreating catalysts

used in petroleum refining as well. The strong acidity of zeolites promotes the hydroisomerization and cracking of triglycerides up to gasoline range hydrocarbons.

Charusiri et al. [44] have studied the catalytic conversion of waste cooking vegetable oil in the temperature range of 380 to 430 °C and hydrogen pressure about 1-2 MPa with reaction time from 45 to 90 min, using catalysts of zeolite HZSM-5, sulfated zirconia and a hybrid catalyst HZSM-5-sulfated zirconia. Their results showed that the catalyst with the higher conversion to gasoline fuel was the hybrid catalyst with a yield of 26.57 wt% at 430 °C. In the process, three parallel reactions were observed to occur: hydrogenation, hydrodeoxygenation and decarboxylation of carboxylic acids as it is shown in Figure 7. By the hydrodeoxygenation path, n-paraffins with an even number of carbon atom, i.e. n-C₁₆ and n-C₁₈, corresponding to the side chains of the fatty acids originally present in the triglycerides, were formed along with water and propane. In a similar experiment carried out in a 70 cm³ batch micro-reactor over a temperature range of 400 to 430 °C and reaction time from 30 to 90 min over sulfated zirconia, Charusiri et al. [45] found that longer reaction times than 90 minutes favored the production of light gases and aromatics. They worked at a range of initial hydrogen pressures between 10 and 30 bar and reported a maximum conversion to gasoline at the lower limit of 10 bar. Due to the strong acid sites of the zirconia catalyst the conversion of vegetable oil into gasoline was possible at a relatively low hydrogen pressure. High temperature favored the production of liquid hydrocarbons consisting mainly of gasoline. They concluded that initial hydrogen pressure was responsible for the catalytic cracking step, and hydrogenation and hydrocracking were possible for the cracking and rearrangement to yield light hydrocarbon molecules.

A study to produce biogasoline from palm oil through simultaneous catalytic cracking and hydrogenation reactions was conducted for Nasikin et al. [22], using a batch reactor at atmospheric pressure in presence of hydrogen. The reaction was studied at 300 and 320 °C, while the reaction times were 1, 1.5 and 2 hours for each temperature. A catalyst with cracking and hydrogenation activity, i.e. NiMo/zeolite (klnoptilolite type) was used in a feed/catalyst ratio of 75 wt/wt. Biogasoline containing C₈ to C₁₀ was produced, with a volumetric yield of 11.93%. Green diesel was also obtained with a volumetric yield of 13.1%.

In another study [46], the hydroprocessing of two mixtures 80:20 and 60:40 wt% of gas oil:sunflower oil, respectively, with sulfided NiO (3%)–MoO₃ (12%) as precursors supported on γ -Al₂O₃ incorporating β -zeolite (BEA) in concentrations of 0, 15 or 30 wt% was carried out at 320-350 °C; 3–6 MPa, and weight hourly space velocities (WHSV) of 1–4 h⁻¹. The catalyst containing 30 wt% BEA achieved nearly 100% conversion into diesel hydrocarbons, compared to 95.5% conversion obtained by using the Ni–Mo/alumina catalyst without β -zeolite.

Hancsók et al. [24] used Pt/HZSM-22/ γ -Al₂O₃ catalysts for the isomerization of pre-hydrogenated sunflower oil for production of diesel over catalysts containing 0.25–1.1% platinum on HZSM-22 at temperatures of 280 to 370 °C, total pressures of 3.5 to 8 MPa and liquid hourly space velocities (LHSV) of 1.0 to 4.0 h⁻¹. Under favorable conditions, they obtained a yield of liquid products higher than 90 %, with a cetane number in the range 81–

84, and with a *cold filter plugging point* (CFPP) in between -18 and -14 °C. The ratio of iso- to n-paraffins was in the range 3.7:1–4.7:1. This catalyst seems to be very efficient to produce an excellent green diesel fuel with not only a high cetane number, but also a low freezing point.

Some studies conducted by Simacek et al. [47], showed that hydroprocessing of rapeseed oil can be converted into diesel fuel. The study was carried out at various temperatures (260–340 °C) under a pressure of 7 MPa in a laboratory continuous flow reactor. Three Ni-Mo/alumina catalysts with different concentrations of NiO and MoO₃, respectively, i.e. A (3.8 and 17.3 wt%), B (2.6 and 15.7 wt%) and C (2.6 and 8.8 wt%), were used. At reaction temperatures higher than 310 °C, an organic liquid product was obtained containing only hydrocarbons of the same nature as those found in diesel fuel.

Recently, Liu et al. [7] produced bio-hydrogenated diesel by the hydrotreatment of vegetable oils over Ni-Mo based catalysts in a high pressure fixed bed flow reactor system at 350 °C under 4 MPa of hydrogen. *Jatropha curcas L.* oil was converted into paraffins by one step hydrotreatment process. Ni-Mo/SiO₂ catalyst favored the production of n-C₁₈H₃₈, n-C₁₇H₃₆, n-C₁₆H₃₄ and n-C₁₅H₃₂. These long normal hydrocarbons have a high melting point and thus the liquid hydrocarbon product has poor cold properties (pour point higher than 20 °C). The use of Ni-Mo supported on zeolites, i.e. Ni-Mo/H-Y or Ni-Mo/H-ZSM5, resulted in the production of a large amount of gasoline hydrocarbons.

Sotelo-Boyás et al. [16] studied the hydrocracking of rapeseed oil on three different types of bifunctional catalysts: Pt/H-Y, Pt/H-ZSM-5, and sulfided NiMo/γ-Al₂O₃. Experiments were carried out in a batch reactor over a temperature range of 300 to 400 °C and initial hydrogen pressures from 5 to 11 MPa. The reaction time was limited to 3 h to prevent a high degree of cracking. The Pt-zeolite catalysts had a strong catalytic activity for both cracking and hydrogenation reactions, and therefore a higher severity was required to reach a relatively high oil conversion into liquid hydrocarbons. Among the three catalysts, hydrocracking on Ni-Mo/γ-Al₂O₃ gave the highest yield of liquid hydrocarbons in the boiling range of the diesel fraction, i.e., green diesel, containing mainly n-paraffins from C₁₅ to C₁₈, and therefore with a high cetane number but poor cold flow properties. While for both zeolitic catalysts, hydrotreating of rapeseed oil produced more iso- than n-paraffins in the boiling range of C₅ to C₂₂, which included significant amounts of green gasoline.

On the other hand, Liu et al. [48], worked on the production of bio-hydrogenated diesel by hydrotreatment of high-acid-value waste cooking oil over a ruthenium catalyst supported on Al-polyoxocation-pillared montmorillonite at 350 °C and 2 MPa. Free fatty acids and the triglycerides in the waste cooking oil were simultaneously deoxygenated. The predominant hydrocarbon products (98.9 wt %) were n-C₁₈H₃₈, n-C₁₇H₃₆, n-C₁₆H₃₄ and n-C₁₅H₃₂.

Silicoaluminophosphates materials (SAPO), have also been tested [2] in the hydroconversion of sunflower oil on a bifunctional Pd/SAPO-31 catalyst as a perspective technological way for single-stage production of hydrocarbons in the diesel fuel range. Transformation of sunflower oil was performed at temperatures of 310 to 360 °C and WHSV of 0.9 to 1.6 h⁻¹, under a pressure of 2.0 MPa in a laboratory flow reactor. At temperatures in between 320

and 350 °C, the liquid phase product contained only hydrocarbons, and the main components were identified as C₁₇ and C₁₈ n- and iso-paraffins. The Pd/SAPO-31 catalyst demonstrated a high initial activity for the hydroconversion of the feed and good isomerization activity, but its deactivation occurred after several hours of operation.

Murata et al. [49] obtained renewable green diesel-type alkanes by hydrotreating jatropha oil at standard hydrotreating conditions (i.e. 270-300 °C, 2 MPa) with Pt/H-ZSM-5 and rhenium-modified Pt/H-ZSM-5 catalysts. The non-modified Pt/H-ZSM-5 was not effective to produce a high amount of C₁₅-C₁₈ paraffins at high oil/catalyst ratios. Rhenium-modified Pt/H-ZSM-5 catalysts were found to be much more effective for hydrotreating jatropha oil even at a high oil/cat ratio of 10, and 80% conversion and 70% selectivity to C₁₈ were achieved. The deoxygenation activity of the catalyst was therefore improved with the addition of rhenium.

The above results show that vegetable oils using hydrocracking catalyst can be converted into liquid fuels and research continues to find the best catalyst that promotes a high selectivity to liquid fuels with high cetane number and good cold flow properties.

As summary, different oil sources, reactor type, reaction conditions, catalysts, and main products obtained during the hydroprocessing of vegetable oils are shown in Table 4.

Only oil as feedstock						
Oil source	Reactor type	Reaction conditions	Catalyst	Main products	Performance	Ref.
Jatropha	Fixed bed	T=350°C P=4 MPa LHSV=7.6 h ⁻¹ H ₂ /oil ratio=800 Nm ³ /m ³	NiMo/Al ₂ O ₃ - SiO ₂	C ₁₅ -C ₁₈ n-paraffins LPG	Conversion: 100 % Yield: 83.5 wt%	[7]
	Batch	T=270°C P=6.5 MPa t=12 h Catalyst/oil wt ratio=1	NiMo/SiO ₂ NiMo/γ-Al ₂ O ₃ NiMo/H-Y NiMo/H-ZSM-5	C ₁₁ -C ₂₀ C ₁₁ -C ₂₀ C ₁₁ -C ₂₀ C ₅ -C ₁₀		
			Pt/H-ZSM-5 Pt/USY	C ₁₀ -C ₂₀ n-paraffins C ₁₀ -C ₂₀ n-paraffins	Conversion:83.8% Yield: 67.7 wt % Conversion: 100% Yield: 90 wt%	[49]
Soybean	Batch	T=400°C P=9.2MPa t=1 h Catalyst/oil wt ratio=0.044, 0.088	NiMo/γ-Al ₂ O ₃ Pd/ γ-Al ₂ O ₃	C ₁₅ -C ₁₈ n-paraffins C ₁₅ -C ₁₇ n-paraffins	Conversion:92.9% Yield C ₁₅ -C ₁₈ : 64.45 wt % Conversion:91.9% Yield C ₁₅ -C ₁₇ : 79.22 wt%	[50]

Only oil as feedstock						
Oil source	Reactor type	Reaction conditions	Catalyst	Main products	Performance	Ref.
	Batch	T=350°C P=0.7 MPa N ₂ t=4 h Stirring rate=1000 rpm	CoMo/ γ -Al ₂ O ₃	C ₁₅ -C ₁₇ n-paraffins	Conversion:78.9% Yield C ₁₅ -C ₁₇ : 33.67 wt%	[40]
			Ni/Al ₂ O ₃ -SiO ₂	C ₁₅ -C ₁₇ n-paraffins	Conversion:60.8% Yield C ₁₅ -C ₁₇ : 39.24 wt%	
			Pt/ γ -Al ₂ O ₃	C ₁₅ -C ₁₇ n-paraffins	Conversion:50.8% Yield C ₁₅ -C ₁₇ : 37.71 wt %	
			Ru/ γ -Al ₂ O ₃	C ₁₅ -C ₁₇ n-paraffins	Conversion:39.7% Yield: 32.00 wt%	
			Ni/Al ₂ O ₃	≥ C ₁₈	Conversion: 68% Yield ≥ C ₁₈ : 51.20 wt%	
			NiAl/LDH	C ₈ -C ₁₇	Conversion :74% Yield C ₈ -C ₁₇ : 52.90 wt%	
			MgAl/LDH	C ₈ -C ₁₇	Conversion: 72% Yield C ₈ -C ₁₇ :47.80 wt%	
Rapeseed	Fixed bed	T=340°C P=4.0 MPa LHSV=1 h ⁻¹ H ₂ /oil ratio=500- 1000 Nm ³ /m ³	NiMo/ γ -Al ₂ O ₃	C ₁₅ -C ₁₈ n-paraffins	Conversion:93% Yield C ₁₅ -C ₁₈ n-paraffins: 54.52 wt%	[51]
	Batch	T=300-400°C P=5-11 MPa t=3 h	NiW/TiO ₂ NiMo/TiO ₂ NiW/ZrO ₂ NiW/NaY			
			NiMo/Al ₂ O ₃	C ₇ -C ₁₈ n-paraffins	Yield: 70-80 % wt%	[16]
			Pt/H-Y Pt/H-ZSM-5	C ₅ -C ₂₂ n- and i-paraffins	Yield: 20-40 %	
Sunflower	Fixed bed	T=360-420°C P=18 MPa Oil flow=49 g/h H ₂ flow=0.049 Nm ³ /h	Sulfided catalyst (not specified)	C ₁₅ -C ₂₀ n- and iso-paraffins	Yield: 64.7 wt% (360 °C)	[27]

Only oil as feedstock						
Oil source	Reactor type	Reaction conditions	Catalyst	Main products	Performance	Ref.
	Fixed bed	T=360-380°C P=6-8 MPa LHSV=1.0-1.2 h ⁻¹ H ₂ /oil ratio=450 Nm ³ /m ³	CoMo/Al ₂ O ₃ NiMo/Al ₂ O ₃ NiW/Al ₂ O ₃	Gases C ₅ -C ₁₀ n-paraffins C ₁₁ -C ₁₉ n- and iso-paraffins	Conversion: 94-99.8 Yield: 63.1-71.5 wt% Conversion: 81.8-97.4% Yield: 42-51.9 wt% Conversion: 86.7-95.6 % Yield: 9.4%-49.3%	[28]
	Fixed bed	T=350-370°C P=2-4 MPa LHSV=1.0 h ⁻¹ H ₂ /oil ratio=500 Nm ³ /m ³	NiMo/Al ₂ O ₃ -F	C ₁₅ -C ₁₈ n-paraffins	Yield: 73.2-75.6 wt%	[15]
	Fixed bed	T=380°C P=4-6 MPa LHSV=1.0 h ⁻¹ H ₂ /oil ratio=500-600 Nm ³ /m ³	CoMo/Al ₂ O ₃	C ₁₄ -C ₁₉ n-paraffins	Conversion: 100% Yield: 73.7-73.9%	[52]
	Fixed bed	T=310-360°C P=2 MPa LHSV=0.9-1.2 h ⁻¹ H ₂ /oil ratio=1000 Nm ³ /m ³	Pd/SAPO-31	C ₁₆ -C ₁₈ n- and iso-paraffins	Yield: 89.3-73.4 wt%	[2]
Safflower	Batch	T=340°C P=0.98 MPa H ₂ -N ₂ H ₂ -N ₂ ratio: 1:4 Cat./oil wt ratio=0.0025 t=3 h	Pt/SBA-15 NiMoC/SBA-15 CoMoC/SBA-15 Triflic acid/SBA-15	Gases C ₅ -C ₉ n-paraffins C ₁₀ -C ₁₄ n-paraffins C ₁₅ -C ₂₃ n-paraffins	Conversion: 25% Conversion: 99%	[53]
Palm	Fixed bed (pilot plant)	T=350°C P=4-9 MPa LHSV=2 h ⁻¹ TOS=0-14 days	NiMo/Al ₂ O ₃	C ₁₆ -C ₁₈ n-paraffins	Molar yield: 100%	[38]

Only oil as feedstock						
Oil source	Reactor type	Reaction conditions	Catalyst	Main products	Performance	Ref.
	Batch	T=300-320°C Atm. pressure t=1-2 h Catalyst/oil wt ratio=0.0133	NiMo/zeolite (klinoptilolite type)	C ₈ -C ₁₉ n-paraffins	Vol. yield: 11.93 %	[22]
	Fixed bed	T=450°C WHSV=2.5 h ⁻¹	HZSM-5 MCM-41	Naphtha, kerosene, and diesel-range paraffins		[54]
Waste cooking oil	Fixed bed	T=350°C P=2 MPa LHSV=15.2 h ⁻¹ H ₂ /oil ratio=400 Nm ³ /m ³	Ru/Al13-montmorillonite	C ₁₅ -C ₁₈ n-paraffins	Conversion: 100% Yield: 82.1-84%	[48]
	Batch	T=380-430°C P=1-2 MPa Catalyst/oil wt ratio=0.0028 t=0.75-1.5 h	HZSM-5 Sulfated zirconia	Naphtha, kerosene, and diesel-range paraffins	Yield:79.17 wt%	[44]
Mixture of gas oil + oil as feedstock						
Rapeseed	Fixed bed	T=300°C P=4.5 MPa LHSV=1.5 h ⁻¹ H ₂ /oil ratio=250 Nm ³ /m ³	NiMo/Al ₂ O ₃	C ₁₅ -C ₁₈ n-paraffins	Conversion: 97%	[33]
	Fixed bed	T=400-420°C P=18 MPa WHSV=1 h ⁻¹ H ₂ /oil ratio=1000 Nm ³ /m ³	NiMo/Al ₂ O ₃	C ₁₅ -C ₂₀ n-paraffins	At 420 °C Yield: 55.4 wt %	[55]
Palm	Fixed bed	T=310-350°C P=3.3 MPa WHSV=0.7-1.4 h ⁻¹ H ₂ /oil ratio=1500 Nm ³ /m ³	CoMo/Al ₂ O ₃	Diesel-range paraffins	Conversion 100%	[56]
		T = 300-320 °C, P = 1 atm	NiMo/zeolite klinoptilolite type	Diesel-range paraffins	Yield: 11.93 wt%	[22]
Sunflower	Fixed bed	T=360-380°C P=8 MPa LHSV=1 h ⁻¹ H ₂ /oil ratio=600 Nm ³ /m ³	NiMo/Al ₂ O ₃	C ₁₁ -C ₂₂ n-paraffins	Yield: 82-90 wt%	[32]

Mixture of gas oil + oil as feedstock						
Oil source	Reactor type	Reaction conditions	Catalyst	Main products	Performance	Ref.
	Fixed bed	T=350°C P=13.8 MPa LHSV=1.5 h ⁻¹ H ₂ /oil ratio=1060 Nm ³ /m ³	Hydrotreating catalyst (not specified)	Diesel-range paraffins	Conversion: 85 % Yield: 42 wt%	[57]
	Fixed bed	T=350°C P=6.9 MPa LHSV=1.5 h ⁻¹ H ₂ /oil ratio=1068 Nm ³ /m ³	Hydrocracking commercial catalysts (not specified)	Naphtha, kerosene, and diesel-range paraffins	Conversion catalyst B: 64 % Conversion catalyst C: 37.5 %	[20]
	Fixed bed	T=300-450°C P=5 MPa LHSV=4.97 h ⁻¹ H ₂ /oil ratio=1600 Nm ³ /m ³	NiMo/Al ₂ O ₃	C ₁₅ -C ₁₈ n-paraffins	Yield: 54 – 75wt%	[35]
	Fixed bed	T=320-350°C P=3-6 MPa WHSV=1-4 h ⁻¹ H ₂ /oil ratio=1068 Nm ³ /m ³	NiMo/Al ₂ O ₃ -β-zeolite	C ₁₇ -C ₁₈ n-paraffins	Conversion: >90%	[46]
Soybean	Fixed bed	T=340-380°C P=5 MPa LHSV=2.4 h ⁻¹ H ₂ /oil ratio = 1500 Nm ³ /m ³	NiW/Al ₂ O ₃ -SiO ₂ NiMo/Al ₂ O ₃	C ₁₅ -C ₂₀ n-paraffins	Yield: 85-95 wt%	[31]
Waste cooking oil	Batch	T=325°C P=2 MPa Stirring=900 rpm t=1, 2, 5, 20 h	Pt/ γ-Al ₂ O ₃ Ni/ γ-Al ₂ O ₃ Pt/γ-Al ₂ O ₃	C ₁₅ -C ₁₈ n-paraffins	Conversion: 100% Yield: 60 molar% Conversion: 76.8% Conversion: 100%	[58]
	Fixed bed	T=330-398°C P=8.3 MPa LHSV=1 h ⁻¹ H ₂ /oil ratio=710 Nm ³ /m ³	Hydrotreating catalyst (not specified)	C ₈ -C ₂₉ n- and iso-paraffins	At 350°C Conversion: 72.62% Yield: 71 wt% At 390 °C Conversion 81.88%	[59]

Table 4. Summary of type of oil, reactor, reaction conditions, catalyst, and main products obtained during hydroprocessing of pure oil and oil plus gas oil mixture (Adapted from several references).

7. Current commercial processes

During the last 10 years, several petroleum related companies have had an increasing interest in producing renewable green liquid fuels from the hydroprocessing of various lipid feedstocks, and just recently the developed technology has started to be commercialized.

UOP Honeywell Co. with its 90 years of refining technology experience is offering an alternative process to produce green fuels from various biofeedstocks. The UOP/ENI Ecofining process [29] has been designed to convert non-edible second generation natural oils to green diesel, which can be used in any percentage in the existing fuel tanks. Since green diesel has the same chemical properties of petro-diesel, it can be used in today's tanks, pipelines, trucks, pumps and automobiles without major infrastructure changes. UOP have agreements in place with China, India and the United Arab Emirates for biofuel development projects that will utilize Ecofining process along with green jet fuel technology to introduce new energy solutions and develop new biofuel economies [29]. The UOP/Eni Ecofining process is based on the hydrotreating of triglycerides along with free fatty acids, which results in deoxygenation via hydrodeoxygenation and decarboxylation [60,61]. After the hydrotreating step, an isomerization process is performed to produce an isoparaffin rich diesel fuel to obtain a fuel with good cold flow properties. In a life cycle analysis reported in a 2009 [25], the renewable diesel produced by the Ecofining process has been reported to be economically and environmentally competitive with biodiesel production.

Haldor Topsøe, a Danish catalyst company, has also developed a new hydrotreating technology for production of green diesel and jet fuel from raw tall. In contrast to other feedstocks used for renewable diesel production, tall is a non-edible material, and thus the process does not raise the problems of global food shortage. The basic engineering for applying the process in Preem Gothenburg Sweden Refinery has been completed by Topsøe[62].

The Neste Oil Co. has claimed to have developed a technology capable of producing high-quality diesel fuel from vegetable oils and animal fats as well. The NExBTL process produces renewable diesel by hydrotreating vegetable oils or waste fats, resulting in a 40-80% lifecycle reduction in CO₂ depending on the feedstock. Neste Oil recently opened a plant in Singapore using NExBTL technology that is intended to produce more than 800,000 tons per year of renewable diesel from feedstocks such as palm oil and waste animal fat [63]. Neste Oil's own tests, together with those carried out by engine and automotive manufacturers, have shown that NExBTL renewable synthetic diesel-based fuel performs very well in both car and truck engines [64], as it is shown by the following properties:

- A high cetane value in between 84 and 99 means that NExBTL can be used to upgrade off-spec diesel fuel and make it suitable for on-road use; and also to create a superior diesel product.
- A low cloud point value (as low as 30 °C below zero) allows NExBTL to be used year round, even in the colder northern states and Canada, without any concern.
- NExBTL is a stable hydrocarbon that can be stored for extended periods.

Another company is Tyson Foods, Inc., which is taking a strategic step in its quest to be a leader in renewable energy. Tyson and Syntroleum Corporation, a based synthetic fuels technology company, have developed a technology to produce synthetic fuels targeting the renewable diesel, jet, and military fuel markets. Dynamic Fuels, which is a joint venture between Syntroleum and Tyson Foods, recently opened a plant in Geismar, LA USA for the production of renewable diesel through hydrotreating from non-food grade animal fats. The animal fat includes beef tallow, pork lard and chicken fat. Syntroleum reported that the carbon footprint of the renewable diesel produced at the plant is 75% less than that of petroleum diesel. The plant was designed to produce up to 75 million gallons of renewable diesel fuel per year [65].

Valero Energy Corporation announced that a new plant at St. Charles Refinery in Norco LA., will be utilized to convert used cooking oil and animal fat into renewable diesel via hydrogenation and isomerization processes [66]. The fat and oil feedstocks will be supplied by Darling International, who is Valero's partner in the venture [67].

ConocoPhillips has begun commercial production of renewable diesel fuel at the company's Whitegate Refinery in Cork, Ireland. The production process, developed by ConocoPhillips, hydrogenates vegetable oils to produce a renewable diesel fuel component that meets European Union standards. The refinery is producing 1,000 barrels per day of renewable diesel fuel for sale into the Irish market. The fuel is produced with vegetable oil as feedstock using existing equipment at the refinery, and is being blended and transported with petrodiesel. In December 2006, ConocoPhillips conducted a successful renewable diesel production test at Whitegate. Soybean oil was intended to be the primary feedstock, although the plant can use other vegetable oils and animal fats. It has been reported that this renewable diesel burns cleaner than conventional diesel, it has a lower sulfur content and emits less nitrous oxide [68,69]

Toyota Motor Corporation (TMC), Hino Motors, the Tokyo Metropolitan Government and Nippon Oil Corporation (NOC) started a joint project aimed at commercializing what they are calling bio hydrofined diesel (BHD), a second-generation renewable diesel fuel produced by hydrogenating a vegetable oil feedstock. Nippon Oil and Toyota have worked jointly on the development of BHD technology since 2005. At the 16th Annual Catalysts in Petroleum Refining & Petrochemicals symposium in Saudi Arabia, Dr. Akira Koyama of Nippon Oil presented NOC's findings on the reactivity, distillate yields, evaluation of the fuel (now called BHD) and its applicability as an automotive fuel. The use of refinery-based hydrogenation processes to produce a synthetic, second-generation renewable diesel is driven by several issues, including some technical considerations over the properties and effects of first-generation fatty acid methyl ester biodiesel (storage, oxidation, possible effect on fuel handling systems). In its studies, Nippon Oil explored reaction temperatures ranging from 240 °C to 360 °C, with reaction pressures of 6 MPa and 10 MPa, and used a common hydrodesulfurization catalyst. The resulting fuel is claimed to be aromatics- and sulfur-free, with a cetane number of 101 [70].

Technology	Process	Feedstock	Product
UOP/Eni (Ecofining process)	Hydrotreating and Isomerization	Triglycerides and/or free fatty acids	Green diesel and jet fuel
Haldor Topsøe	Hydrotreating	Raw tall oil	Green diesel and jet fuel
The Neste Oil. (NExBTL process)	Hydrotreating	Palm oil and waste animal fat	Green diesel
Tyson Foods Inc. and Syntroleum Corporation	Hydrotreating	Animal fat includes beef tallow, pork lard, chicken fat and greases	Green diesel and jet fuel
Valero Energy Corporation	Hydrogenation and Isomerization	Used cooking oil and animal fat	Green diesel
ConocoPhillips	Hydrotreating	Vegetable oil like soybean oil, grape seed oil and other vegetable oils and animal fats	Green diesel
Toyota Motor Corporation, Hino Motors, Nippon Oil Corporation.	Hydrotreating	Vegetable oils	Green diesel

Table 5. Main commercial processes to produce green fuels.

8. Conclusions

Hydroprocessing of vegetable oils and fats in green transportation fuels is a prominent technology that will probably continue to develop in the present decade, as different countries or petroleum companies realize that it is both an economical and environmentally efficient way to produce energy and decrease the accelerated consumption of fossil fuels. Green fuels are currently not a substitute of fossil fuels, but they can be used effectively as additives to boost the properties of their corresponding fossil fuels. The use of green jet fuel is projected to increase as the European Union introduces strict environmental regulations in the use of transportation fuels.

Technologically there are some factors that need to take into consideration when dealing with different raw materials. The catalyst for instance plays an important role in the reaction process, and it is a key point to optimize the process. In this context, the use of simulation and in general computer-aided tools can be used for optimization of the hydroconversion process of vegetable oils. This however needs the use of kinetics models, which at the same time requires a deep understanding of the chemistry involved in hydrocracking, hydroisomerization and hydrodeoxygenation. This is clearly not an easy task, and in spite some authors [45,71,72] have derived kinetic models for oxygenated molecules, they do not represent a comprehensive kinetics occurring in the hydrocracking of vegetable oils. A

deeper study on the hydrocracking chemistry and the subsequent development of a suitable kinetic model seems the way to follow for future work in this outstanding technology.

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