

## An overview of catalytic conversion of vegetable oils/fats into middle distillates

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Due to scarce conventional petroleum fuel, there is a need to search for alternative renewable fuel that can be adopted for use in place of fossil fuel oil. Even the ester-based biodiesel has many limitations, such as low energy content, oxidative stability etc. Renewable hydrocarbon-based diesel obtained by hydroprocessing of vegetable oils/fats (2nd generation biodiesel) is one of the alternatives that is getting attention from both academia and industry. The present paper reviews the emerging processes, catalysts and operating conditions for the catalytic conversion of vegetable oils/fats into hydrocarbon-based diesel via hydroprocessing. Hydroprocessing of vegetable oils is similar to petroleum hydroprocessing, but requires slight modification and optimization in the catalyst, as well as process parameters. The current status and future scope of the catalyst and process for hydroprocessing of vegetable oil are discussed.

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### 1. Introduction

The main sources of fuel and energy for transportation and manufacturing sectors are natural gas, petroleum and coal. These are non-renewable fossil fuels with limited sources and are depleting fast under the pressure of high energy and fuel demand. Besides this, carbon dioxide emission from fossil fuels is another issue. Fulfilling energy demand while keeping the emission under control is a major challenge. Improving energy efficiency, reducing carbon dioxide emission, energy saving and developing clean and fuel efficient vehicles are a few options in this direction. Besides these, alternative renewable energy sources are the other option. Among renewable energy resources, vegetable oils/fats are a good source for liquid transportation fuel due to their high energy density. Vegetable oil occupies a prominent position in the development of alternative fuels. India, being an agriculture-based country, produces around  $6.7 \times 10^6$  tons of non-edible oils, such as Jatropha, linseed, castor, karanj (*Pongamia Pinnata*), Neem (*Azadirachta indica*), Palash (*Butea monosperma*) and Kusum (*Schelchera Trijuga*). These oils can be used as alternative fuels in compression ignition engines after modifying the fuel structure or properties or modifying the engine.<sup>1–5</sup>

In the literature, mainly the research work is aimed at ester-based biodiesel, which is obtained by transesterification of

vegetable oils/fats with methanol.<sup>6–11</sup> Oxidative stability, low energy content and cold-flow properties are the major factors that work against the use of ester-based biodiesel. A different processing route to convert vegetable oils into a high quality diesel fuel or diesel blend stock that is fully compatible with petroleum-derived diesel fuel is desired.<sup>12</sup> The new types of bio-renewable fuels entering the fuel market must satisfy the following conditions:<sup>13</sup>

- (1) It can be used in existing engines without any modification.
- (2) Engine power should not be affected.
- (3) It must be blended with petro-diesel in any proportion and can be easily integrated into the existing market structure.
- (4) It should be of high quality and should form environmentally cleaner combustion products.

Conversion of vegetable oils directly into deoxygenated liquid fuel addresses most of the above discussed issues. Hydrodeoxygenation or hydroconversion of triglycerides directly results in diesel-like hydrocarbon fuel. Hence, it is most ideal and also the shortest route to arrive at biofuel that will have identical properties to those of conventional diesel fuels. Hydrocarbons can be prepared from vegetable oils by the following pathways:<sup>14</sup>

- (a) Conversion of vegetable oils to soaps (sodium salt) by hydrolysis, followed by dry distillation of the soap in the presence of soda lime<sup>15</sup>
- (b) Hydrolysis of vegetable oils into fatty acids and then decarboxylation of the fatty acids in the presence of catalysts
- (c) Thermal/catalytic pyrolysis
- (d) Hydroprocessing of vegetable oils.

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Routes generally used for obtaining deoxygenated biofuel from triglycerides include thermal and catalytic pyrolysis,<sup>16–19</sup> but these processes provide low atom economy, poor selectivity due to uncontrollable side reactions, such as cracking or polymerization of the hydrocarbons, and formation of undesired hydrocarbon gases coupled with a poor yield of diesel range product.<sup>20</sup>

The emerging technology for the conversion of triglycerides into hydrocarbon-based diesel fuel is the hydroprocessing of vegetable oils. The hydroprocessing process requires hydrogen gas to selectively eliminate the linkage oxygen as water and saturate the double bonds present in vegetable oils. The resulting products are the respective diesel-like hydrocarbons. Paraffins obtained by hydroprocessing of vegetable oil and fats is sometimes termed as *second generation biodiesel* or *green diesel*.<sup>21</sup> Unlike the first generation (ester-based biodiesel), this new generation biodiesel (hydrocarbons) is more favorable for industrial applications, being compatible with the current engines, even avoiding the need to be blended with diesel if isomerised.<sup>22,23</sup>

## 2. Production of deoxygenated biofuel from vegetable oil

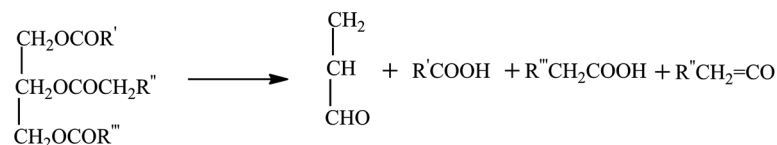
### 2.1. Thermal/catalytic pyrolysis

Pyrolysis of vegetable oil is well-studied and its use to produce fuels dates back 100 years.<sup>24,25</sup> Similar to biodiesel, pyrolysis will work on a variety of feedstocks, both edible and non-edible. However, pyrolysis only requires a pre-drying step for use with soybean soapstock.<sup>26</sup> The fuel obtained by pyrolysis of different triglycerides was used in different countries during the First and Second World Wars. For instance, a Tung oil pyrolysis batch system was used in China as a hydrocarbon supply during World War II.<sup>27</sup> These hydrocarbons were used as raw materials for gasoline and diesel-like fuel production in a cracking system similar to the petroleum process now in use. Since then, several studies on vegetable oil pyrolysis as an alternative method to obtain chemicals and fuels have been reported in the literature.<sup>28–32</sup> Pyrolysis of triglycerides can be divided into direct thermal cracking and catalytic cracking. Complex mixtures of products are obtained by thermal cracking. In thermal cracking, distribution of product constituents significantly depends upon reaction variables such as the reactor type, residence time, the composition of feedstock and reaction temperature, as well as the collection procedure and analytical techniques used.<sup>33</sup> The results of these studies provide an idea about the type of products can be achieved from this process. It is evident that liquid mixtures with high percentages of hydrocarbons can be obtained, but in many of these studies, the presence of undesirable oxygenated compounds, such as carboxylic acids and ketones, was also reported.<sup>33</sup> The effect of reaction conditions on the final product distribution needs to be studied more extensively so that the reaction may be optimized to obtain the desired product.

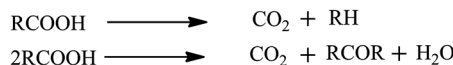
Vegetable and plant oils contain a complex mixture of unsaturated and saturated triglycerides. Idem *et al.* studied the thermal cracking of canola oil in the presence and absence of steam and postulated a reaction scheme to account for the thermal cracking of both the unsaturated and saturated components.<sup>32</sup> The reaction in Scheme 1 proposed by Chang *et al.*<sup>34</sup> consists of various steps and reactions involved in thermal pyrolysis. Other researchers, such as Alencar,<sup>35</sup> Kitamura,<sup>36</sup> Nawar,<sup>37</sup> Nichols and Holman,<sup>38</sup> have also proposed the mechanisms for this reaction. The mechanism proposed by Schwab *et al.*<sup>28</sup> also accounts for the formation of heavy oxygenated compounds, including ketones, aldehydes and esters, carbon monoxide and carbon dioxide, C1–C5 straight and branched chain hydrocarbons, alcohols and dimethyl ether, diolefinic, cyclic and acetylenic hydrocarbon gases, C6+ aliphatic hydrocarbons, aromatics, heavy hydrocarbons, coke and hydrogen during the cracking of canola oil in the absence of a catalyst. The degree of unsaturation of the triglyceride has a significant effect on the cracking behavior. Decarboxylation and decarbonylation can occur before or after the C–C bond cleavage. If the triglyceride is unsaturated, the cleavage most likely occurs before the decarboxylation and decarbonylation. It has also been shown that C–C bond cleavage for unsaturated and saturated molecules results in different products.<sup>32</sup> Thermal decomposition of triglycerides produces different compounds, which include alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Scheme 2 outlines a scheme that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from pyrolysis of triglycerides.<sup>28</sup> Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of the many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism.<sup>35</sup> Formation of a homologous series of alkanes and alkenes can be accounted for by the generation of the “RCOO•” radical from the triglyceride cleavage and subsequent loss of carbon dioxide. The “R•” radical, upon disproportionation and ethylene elimination, gives the odd-numbered carbon alkanes and alkenes. The presence of unsaturation enhances cleavage at a position  $\alpha$ ,  $\beta$  to the unsaturation. Positional isomerization and subsequent cleavage could account for the higher amounts of C<sub>5</sub>–C<sub>10</sub> alkanes obtained from safflower compared with soybean oil.<sup>40</sup> The formation of aromatics is supported by a Diels–Alder addition of ethylene to a conjugated diene formed in the pyrolysis reaction.<sup>37</sup> Carboxylic acids formed during the pyrolysis of vegetable oils probably result from cleavage of the glyceride moiety.

Pyrolysis studies were carried out in the absence of a catalyst using oil from soybean,<sup>28</sup> palm tree,<sup>35</sup> babassu,<sup>35</sup> pequi,<sup>35</sup> macauba,<sup>30,31</sup> and canola<sup>32</sup> as raw materials. Thermal cracking of vegetable oils is generally carried out at temperatures of 350–500 °C or higher and at moderate pressures (atmospheric to several bar) to yield around 70% hydrocarbons. As a rule,

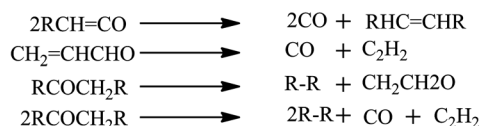
## 1. Decomposition of glyceride



## 2. Decomposition of fatty acids



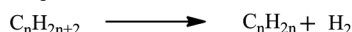
## 3. Decomposition of ketenes and acrolein



## 4. Decomposition into elements



## 5. Dehydrogenation of paraffins

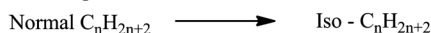


## 6. Splitting decomposition of paraffins

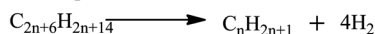


## 7. Alkylation of paraffins reverse of 6

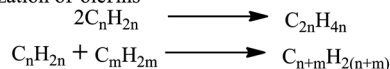
## 8. Isomerization of paraffins



## 9. Aromatic cyclization of paraffins



## 10. Polymerization of olefins



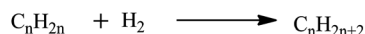
## 11. Depolymerization of olefins, reverse of 10

## 12. Decomposition of olefins to diolefins

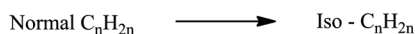
## 13. Decomposition of olefins to acetylenic hydrocarbons

## 14. Aromatisation or cyclization of olefins

## 15. Hydrogenation of olefins



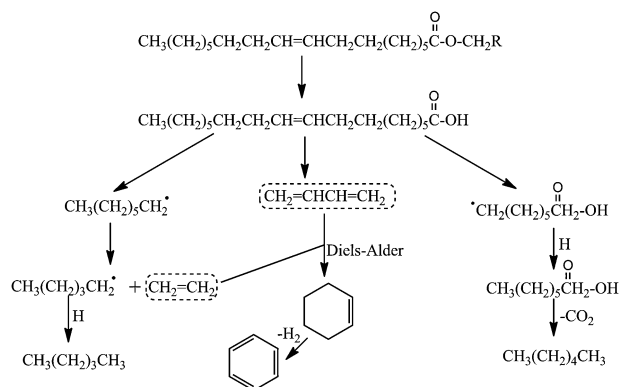
## 16. Isomerization of olefins

Scheme 1 Decomposition of vegetable oils.<sup>33</sup>

an increase in pyrolysis temperature leads to an increase in the selectivity towards the formation of light hydrocarbons. The liquid fractions of the thermally decomposed vegetable oil are similar to diesel fuels. The pyrolyzed soybean oil contains 79% carbon and 12% hydrogen.<sup>28,40</sup>

To improve the yield and selectivity of the desired product, triglycerides are treated at high temperature in the presence of a catalyst. Processing of vegetable oil at high temperature is divided into two categories; in the presence of hydrogen or in the absence of hydrogen. Processing in the presence of hydrogen is known as hydroprocessing or hydrotreatment of vegetable oils, which will be discussed in detail in the next

section. By processing in the absence of hydrogen, more gasoline-type products are obtained containing significant amount of aromatics and gaseous products. Pyrolyzed oil has low viscosity and a high cetane number compared to pure vegetable oils. The cetane number of pyrolyzed soybean oil is enhanced to 43 from 37.9 and the viscosity is reduced to 10.2 cSt from 32.6 at 38 °C,<sup>28,41</sup> but it exceeds the specified value of 4.5 cSt (IS 1460: 2005). The pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values, but unacceptable ash, carbon residue amounts and pour point. Gas and liquid products characterization has been reported in the literature<sup>30–32,40</sup> and



**Scheme 2** Pyrolysis of vegetable oils.<sup>27</sup>

some reaction pathways have also been proposed. Many studies have focused on improving the performance of standard catalytic cracking procedures for application to vegetable oils using standard or modified cracking catalysts, such as those based on basic oxides,<sup>42</sup> activated alumina,<sup>43</sup> aluminosilicates,<sup>44–46</sup> zeolites<sup>47–49</sup> and pillared clays.<sup>50</sup> In recent years, some new types of catalysts based on H-ZSM-5<sup>51</sup> and MCM-41<sup>52,53</sup> have been developed and used in a pyrolysis reaction. It was observed that the product in this case has lower viscosity and a higher cetane number (>50) compared to pure soybean oil.<sup>54</sup> It is worth mentioning that the pyrolytic oils exhibited high carboxylic acid content (acid number 116–133). These undesired products have great effects on the corrosion value, cold filter plugging point and freezing point of the biofuel. Pyrolyzed oil also contains significant amount of olefins, which increase the oxidative instability and it needs to be upgraded by hydrogenation. Low yield 45–65% and selectivity to the desired hydrocarbon range are the major issues with pyrolysis.<sup>55</sup>

## 2.2. Hydroprocessing

Renewable hydrocarbon-based diesel obtained by hydroprocessing is also termed as second generation biodiesel or green diesel. Table 1 compares various properties of ester-based and hydrocarbon-based renewable diesel. Hydroprocessing of vegetable oils was proposed several years ago, using processes and catalysts similar to those used for middle distillate hydrotreatment.<sup>56</sup> There is renewed interest for this route for several reasons. The primary product is straight-chain paraffins, which can be hydroisomerized to high quality diesel or hydrocracked to kerosene. The gas

by-product propane is feedstock for the petrochemical industry and also used as motor fuel.<sup>57</sup> A large variety of vegetable oils, including edible, non-edible and animal fats, can be processed to yield the same high quality diesel product. Finally, co-processing with crude oil-derived middle distillates is possible and even favorable.

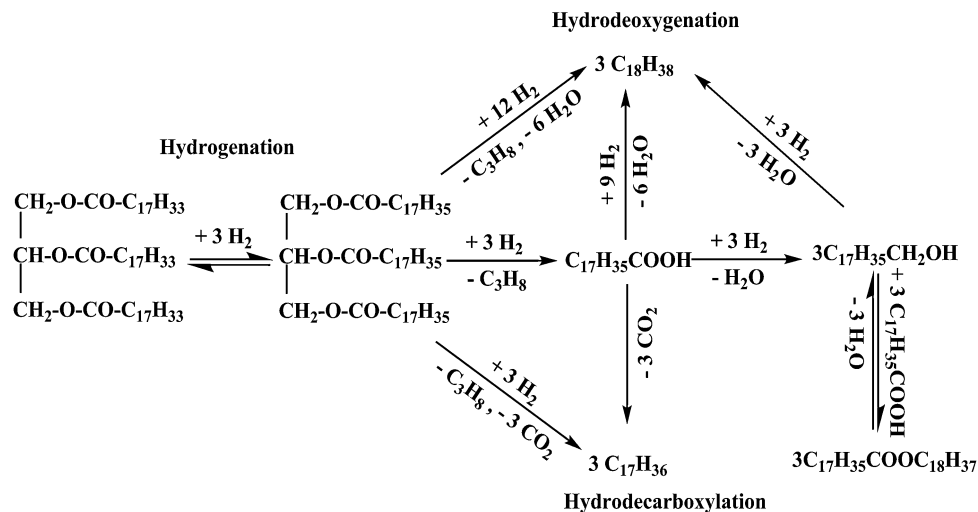
This is an emerging area and several authors have reviewed the work in this area<sup>58,59</sup> and have tried to elucidate the mechanism of the hydroprocessing of vegetable oils into diesel. It is generally acknowledged that the triglycerides are first get saturated on their side chain, followed by scission of the C–O bond, leading to the formation of diglycerides, monoglycerides, carboxylic acids and waxes. Then, these are transformed into hydrocarbons by hydrotreatment. Removal of oxygen is accomplished through hydrodeoxygenation (HDO) and other direct mechanisms, such as hydrodecarbonylation (HDCN), hydrodecarboxylation (HDCX) and hydrogenation (Scheme 3).<sup>39</sup>

The predominant hydroconverted products are *n*-heptadecane and *n*-octadecane and byproducts, carbon monoxide, propane, carbon dioxide and water, are obtained. Due to the acid function of the catalyst, isomerization and cyclization of the olefin intermediates can occur, leading to the formation of isoparaffins and naphthenes. Aromatics may also be observed when low severity hydrogenation reactions are carried out. Dehydrogenation is favored at high temperature and low pressure.<sup>60</sup>

Hydroprocessing is used in the refinery to remove S, N and metals from petroleum-derived feedstock, including heavy gas-oil or vacuum gas-oil. These processes and existing refinery facilities can be used for vegetable oils and fats hydroprocessing. These processes can be sometimes called hydrodeoxygenation when applied to oxygenated hydrocarbons, such as vegetable oils or FFAs, as they lead to the removal of oxygen by hydrogenation, decarboxylation and decarbonylation. Therefore, fully deoxygenated high cetane hydrocarbons suitable for use in diesel engines are formed. In hydroprocessing, maximum hydrocarbon yield is obtained *via* hydrodeoxygenation as compared to decarboxylation, where one carbon is lost as carbon dioxide. With respect to the fractional composition, the products of thermo-catalytic cracking represent a suitable alternative to gasoline rather than to diesel. Even if the catalytic cracking process is optimized, the yields of biodiesel are relatively low. Furthermore, these products often contain carboxylic acids and other oxygenates, which could complicate their use with

**Table 1** Comparisons of ester-based biodiesel and hydrocarbon-based green diesel

Properties	Biodiesel	Green diesel
Chemical composition	Methyl or ethyl ester of fatty acids	Saturated hydrocarbons
Oxygen content	10–12%	Nil
Density (g ml <sup>-1</sup> )	0.880	0.780
Heating value (KJ g <sup>-1</sup> )	38	45
Cloud point (°C)	–5	–5 to +30
Sulfur content (ppm)	<1	<1
Oxidative stability	Unstable	Stable
Cetane number	50–65	70–90
Feedstock flexibility	Good quality	More feedstock flexibility
Production facility	Production require new facility	Can be produced in existing refinery
Engine modification	Some changes required in existing diesel engine	No change is required



**Scheme 3** Hydroprocessing of vegetable oils.<sup>38</sup>

respect to storage and distribution and also with respect to their combustion in engines. On the other hand, hydroprocessing as compared to pyrolysis provides high conversion of vegetable oils, as well as high yields of hydrocarbon middle distillates, which can be used as an alternative diesel fuel.

**2.2.1. CATALYSTS FOR HYDROPROCESSING OF VEGETABLE OILS.** In hydrotreatment, the reaction mechanism and rate depend on the type of oxygen compounds present. Reactions using model compounds or directly different fatty acids and their esters or triglycerides have been studied in the literature. Efforts have been focused on the HDO of vegetable oils/fats on transition metal sulfide catalysts and noble metal catalysts. A list of these catalysts is presented in Table 2.<sup>61–92</sup> It has been found that conventional hydrotreating catalysts, such as CoMo or NiMo, are suitable for hydrodeoxygenation of triglycerides. Gusmao *et al.* found that only double bonds were hydrogenated in soybean oil at low reaction temperatures (less than 200 °C) and corresponding saturated triglycerides, *i.e.*, tristearin and tripalmitin, were formed. The decomposition of triglycerides is accompanied by the hydrogenation of the decomposition products at temperatures above 290 °C. In contrast to reduced Ni catalyst, sulfided Ni–Mo catalysts requires higher reaction temperatures (in the range of 230–280 °C) to achieve double bond hydrogenation. On the other hand, the transformation of the carboxylic groups is achieved under similar reaction temperatures (around 300 °C) on both catalysts.<sup>91</sup> The main products for both catalysts are aliphatic hydrocarbons that correspond either to total hydrogenation (hydrodeoxygenation) *i.e.* they have the same carbon number as the acids, or hydrodecarboxylation *i.e.* their carbon atom number is smaller by one than the corresponding carboxylic acid. If the reaction conditions are severe enough, all carboxylic acids (reaction intermediates) are converted into the hydrocarbons and negligible cracking of the hydrocarbon chains is observed. In comparison with a metal sulfide catalyst, high cost is the primary disadvantage of noble metal catalysts. Metal sulfide catalysts were investigated extensively because of good hydrodeoxygenation activity, but the sulfidation process of these catalysts needs high temperature and a

sulfiding agent. Moreover, an additional sulfiding agent was required to be added in the feed to maintain the sulfidation level of the metal sulfide catalyst because the negative effect of oxygen would significantly decrease the catalytic activity.<sup>93</sup> Hence, it is very important to develop a new kind of non-sulfur-based, cheap and more active catalyst for the HDO of vegetable oils. Compared to sulfided CoMo and NiMo on Al<sub>2</sub>O<sub>3</sub>, relatively few studies have been attempted with noble metal-based catalysts.

Supported metal catalysts<sup>61–64,70</sup> have been reported to convert fatty acids and their esters into hydrocarbons mainly by decarboxylation and, because of this, the product contains more odd number hydrocarbons as compared to even ones, while sulfided catalysts provide more even number hydrocarbons resulting from hydrodeoxygenation of fatty acid feedstock. Despite their high cost, noble metal catalysts possess several advantages over conventional sulfide catalysts: (1) high reactivity at moderate temperature, achieving an energy efficient HDO process, (2) no sulfur stripping and (3) flexible catalyst design by tailoring the active phase and support.<sup>63,64</sup> Zeolites have also been used for the hydroprocessing of vegetable oils, but a small pore diameter and cracking due to acidity lead to lower yield.<sup>70</sup>

Mesoporous materials show great potential as catalyst supports.<sup>78,80,81</sup> Moreover, mesoporous supports, such as mesoporous molecular sieves (MCM-41, SBA-15) or organized mesoporous alumina (OMA), offer several advantages over the alumina supports used in traditional hydrosulfurization catalysts. In contrast to standard alumina supports and similar to microporous molecular sieves (zeolites), organized mesoporous aluminas have very high specific surface areas that can be used to achieve very high dispersions of the supported active phase<sup>80</sup> and high loadings of the active phase. Moreover, larger pore diameters as compared to zeolites make mesoporous supports excellent candidates for applications where large organic molecules have access to the well dispersed active sites located inside the pores. The molecular size of triglycerides suggests that mesoporous supports could be used advantageously in catalytic transformations of triglycerides. Nava *et al.* recently



**Table 2** Catalysts for hydroprocessing of vegetable oils

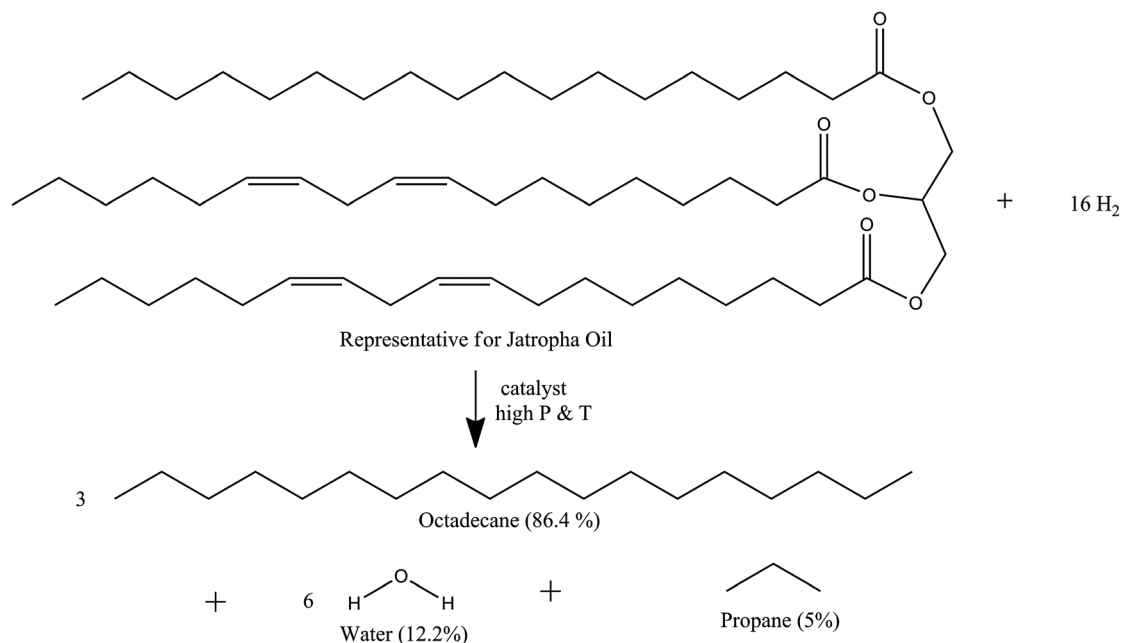
S. no.	Catalyst	Feed	Conditions	Ref.
1	5% Pd/C (Aldrich)	Oleic acid	$P = 15\text{--}27$ bar, $T = 573\text{--}633$ K, time = 6 h	61
2	4% Pd/C mesoporous	Stearic and palmitic acid	$T = 573$ K, $P = 17$ bar (5% $H_2$ in Ar),	62
3	1% Pt-Re/H-ZSM-5	Vegetable oil	$P = 65$ bar (85% $H_2$ in $N_2$ ), $T = 543$ K, time = 12 h	63
4	1% Pt/ $Al_2O_3$	Methyl stearate	$P = 6.9$ bar ( $H_2$ ), $T = 598$ K, time = 5 h	64
5	Ni-Mo/ $SiO_2$ or $Al_2O_3$	Jatropha oil	$H_2$ /oil = 800 mL/mL, LHSV = $7.6\text{ h}^{-1}$ , $T = 623$ K	65
6	Topsøe TK-575 Ni-Mo/ $\gamma$ -alumina	Rapeseed (15% in <i>n</i> -heptane)	$P = 45$ bar, $T = 623$ K, LHSV = $1.5\text{ h}^{-1}$ ,	66
7	PtSnK/silica PtSn/silica Pt/silica	Methyl ester and triglyceride	$P = 24.1$ bar, $T = 350$ °C,	67
8	Pd/SAPO-31	Sunflower oil	$T = 310\text{--}360$ °C, $P = 20$ bar, WHSV = $0.9\text{--}1.6\text{ h}^{-1}$ .	68
9	Ni-Mo/ $Al_2O_3$	Waste cooking oil	$T = 25\text{--}450$ °C, $P = 0\text{--}150$ bar, LHSV = $1\text{ h}^{-1}$ .	69
10	Pt/Zelite (HY & H-ZSM-5), sulfided Ni-Mo/ $Al_2O_3$	Rapeseed oil	$T = 300\text{--}400$ °C, $P = 50\text{--}110$ bar, time 3 h	70
11	Mo, W, V nitrides/ $Al_2O_3$	Oleic acid and canola oil	$T = 380\text{--}410$ °C, $P = 71.5$ bar, LHSV = $0.45\text{ h}^{-1}$	71
12	Sulfide Ni-W supported on mesoporous $SiO_2\text{--}Al_2O_3$ and Ni-Mo/ $Al_2O_3$	Waste soybean oil and refinery oil mixtures	$T = 340\text{--}380$ °C, $P = 50$ bar, LHSV = $2.4\text{ h}^{-1}$	72
13	Sulfided Co-Mo/ $Al_2O_3$	Rapeseed oil	$T = 310$ °C, $P = 35$ bar, WHSV = $2\text{ h}^{-1}$	73
14	Sulfided Co-Mo/ $Al_2O_3$	Cotton seed oil in petroleum diesel	$T = 305\text{--}345$ °C, $P = 30$ bar, WHSV = $5\text{--}25\text{ h}^{-1}$ .	74
15	Ni-Mo, NiW and Co-Mo/ $Al_2O_3$	Waste cooking oil trapped grease	$T = 30\text{--}350$ °C, $P = 70$ bar, time-3 h	75
16	Ni-Mo/ $Al_2O_3$	Rapeseed oil	$T = 260\text{--}340$ °C, $P = 70$ bar, WHSV = $1\text{ h}^{-1}$ .	76
17	Ni-Mo/ $Al_2O_3$	Crude Palm oil	$T = 260\text{--}340$ °C, $P = 40\text{--}90$ bar, LHSV = $2\text{ h}^{-1}$ .	77
18	Pd/mesoporous C	Stearic acid	$T = 360$ °C, $P = 10$ bar, WHSV = $0.45\text{ h}^{-1}$ .	78
19	Co-Mo/ $Al_2O_3$	Gas oil and palm oil	$T = 310\text{--}350$ °C, $P = 33$ bar, WHSV = $0.7\text{--}1.4\text{ h}^{-1}$ .	79
20	Co-Mo/MCM-41	Rapeseed oil	$T = 300$ and $320$ °C, $P = 20\text{--}110$ bar, WHSV = $1\text{--}4\text{ h}^{-1}$ .	80
21	Co-Mo/mesoporous alumina	Rapeseed oil	$T = 250\text{--}350$ °C, $P = 7\text{--}70$ bar, WHSV = $1.5\text{ h}^{-1}$ .	81
22	Sulfided commercial hydrocracking catalyst	Sunflower oil	$T = 360\text{--}420$ °C, $P = 180$ bar, WHSV = $1.5\text{ h}^{-1}$ .	82
23	Commercial hydrotreating catalyst	Waste cooking oil	$T = 330\text{--}398$ °C, $P = 82$ bar, WHSV = $1\text{ h}^{-1}$	83, 84
24	Ni-Mo/ $Al_2O_3$	Waste cooking oil	$T = 300\text{--}400$ °C, $P = 35$ bar, W/F = $0.7\text{ h}^{-1}$ .	85
25	Ni-Mo/ $Al_2O_3$	Sunflower oil-heavy vacuum oil (HVO) mixtures	$T = 300\text{--}450$ °C, $P = 50$ bar, LHSV = $5\text{ h}^{-1}$	86
26	Ni-Mo/ $Al_2O_3$	10 and 20% rapeseed oil in diesel oil	$T = 300\text{--}380$ °C, $P = 30$ and $50$ bar, LHSV = $2\text{ h}^{-1}$	87
27	Ni-Mo/ $Al_2O_3$ and NiW/ $Al_2O_3$	6.5 Vegetable oil + gas oil	$T = 320\text{--}360$ °C, $P = 35\text{--}55$ bar, LHSV = $1\text{ h}^{-1}$	88
28	Three commercial hydrocracking catalysts	Vacuum gas oil (VGO) - vegetable oil mixtures	$T = 250\text{--}450$ °C, $P = 0\text{--}150$ bar, liquid flow = $6.5\text{--}50\text{ mL min}^{-1}$	89
29	Sulfided Ni-Mo/ $\gamma\text{--}Al_2O_3$ , sulfided CoMo/ $\gamma\text{--}Al_2O_3$ , Ni/ $SiO_2\text{--}Al_2O_3$ , Pd/ $\gamma\text{--}Al_2O_3$ , Pt/ $\gamma\text{--}Al_2O_3$ , Ru/ $\gamma\text{--}Al_2O_3$	Soybean oil	$T = 400$ °C, $P = 92$ bar, catalyst/oil weight ratio of 0.044 batch mode	90
30	Ni/ $SiO_2$ and sulphided Ni-Mo/ $\gamma\text{--}Al_2O_3$	Vegetable oils	$T = 350\text{--}400$ °C, $P = 10\text{--}200$ bar,	91
31	Co-Mo/SBA-15, Co-Mo/HMS, Co-Mo/SBA-16, Co-Mo/DMS-1	Olive oil	$T = 250$ °C, $P = 30$ bar, TOS-5 h	92

investigated the effect of mesoporous silicate supports (SBA-15, HMS, SBA-16, DMS-1) on the hydroprocessing of an olive oil by-product.<sup>92</sup> The selectivity for paraffin production for the reported catalysts was found to decrease in the following order: CoMo/SBA-15 > CoMo/HMS > CoMo/SBA-16 ~ CoMo/DMS-1. The SBA-15, SBA-16- and DMS-1-based catalysts were reported to be more active in hydrodeoxygenation than a HMS-supported catalyst.<sup>92</sup>

Besides the above mentioned catalysts, nitrides of molybdenum, tungsten and vanadium supported on  $\gamma\text{-}Al_2O_3$ <sup>71</sup> and metals supported on carbon<sup>61,62,78</sup> have also been reported to catalyze hydrodeoxygenation of fatty acids and vegetable oils.

In hydrotreatment of vegetable oils, hydrogen has to be taken in excess to avoid decarboxylation. Excess hydrogen flow helps in removing water (a by-product of hydrodeoxygenation) and thereby avoids deactivation of the catalyst. The excess hydrogen can be recycled after purification. Since hydrogen also removes the sulfur from the catalyst, therefore keeping the active metals in sulfided form, up to 1–2% sulfiding agent is added to the feed, which generates  $H_2S$  by decomposition at the reaction temperature in the presence of hydrogen and keeps the catalyst activity.

Product yield and its composition depend on various factors, such as nature and quality of the feedstock, operating



**Scheme 4** Hydrodeoxygenation of vegetable oils.

conditions (flow, temperature, pressure *etc.*) and the type of catalyst. Boda *et al.*<sup>93</sup> showed that hydrotreatment of a model compound for vegetable oils, tricaprinn (TC), proceeds in consecutive steps: hydrogenolysis (HYS) of TC to capric acid (CA) and propane, followed by hydrodeoxygenation (HDO) of the CA intermediate. The overall reaction rate was governed by the rate of the HDO reaction. Over Pd/C the prevailing reaction route of CA hydroconversion was the decarbonylation giving mainly C7 alkane and CO, whereas the HDO over the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts proceeded in consecutive H<sub>2</sub> addition and dehydration steps giving predominantly C18 alkanes and water. In other side reactions, alcohol and traces of aldehyde are also detected as acid-to-alkane intermediates. Hydrodeoxygenation is the preferred scheme for the production of hydrocarbons as in this path there is no loss of carbon as carbon dioxide, which results in higher yield (86 wt%) as compared to decarboxylation (81 wt%) only (Scheme 4).

**2.2.2. EFFECT OF PROCESS PARAMETERS.** Hydroprocessing of vegetable oils is very complex and involves consecutive and parallel reactions, which are influenced by a variety of process parameters, such as temperature, pressure, sulfiding agents, nature and flow of feedstock *etc.* In this section, some important reaction parameters are discussed.

**Influence of sulfidation.** Sulfided catalysts are the most active and widely used catalysts for the hydroprocessing of the vegetable oils. However, the presence of oxygenates tends to remove the sulfur from the catalysts, thereby making it inactive or less active. To keep the catalysts in active sulfided form some sulfiding agents have to be added into the vegetable oil feedstock as the sulfur content of these bio feedstocks is very low. Various studies have indicated that sulfiding agents affect the HDO process differently depending on feed composition and process conditions. For example, the addition of a sulfiding

agent to a bio-oil has generally been found to suppress the HDO of phenolic and furanic compounds on sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts,<sup>94,95</sup> but a promoting effect has been demonstrated in HDO studies with aliphatic oxygenates, such as esters and carboxylic acids on similar catalysts.<sup>96,97</sup> As water forms as the by-product in hydrodeoxygenation and inhibits the catalyst's activity, Senol *et al.* reported that addition of H<sub>2</sub>S (or H<sub>2</sub>S generated from sulfiding agent) not only keep the catalysts in sulfided state, but also compensates for activity loss due to water.<sup>97</sup>

**Influence of hydrogen pressure and flow.** Hydrogen pressure and flow is a very crucial in hydrotreatment of vegetable oils as it is not only a reactant, but also helps in removal of water from the catalyst, thereby preventing it from deactivation. Relative activities of catalysts towards decarboxylation and hydrodeoxygenation are very important in hydroprocessing of triglycerides as these reactions decide the hydrogen consumption, product yields, heat balance and catalyst inhibition.<sup>66</sup> Higher hydrogen pressure decreases decarboxylation and favors hydrodeoxygenation of triglycerides and also suppresses cracking of the products, thereby helping to obtain higher yield. A higher H<sub>2</sub>/oil ratio also favors the hydrodeoxygenation over decarboxylation, which can be confirmed by more even number hydrocarbons being obtained in the products.<sup>66</sup>

**Influence of temperature.** One of the most dominant effects of hydrotreatment temperature is on the product yields. At low temperatures, the oxygen removal is low and higher temperatures favor the oxygen removal from the final products. With the increase in temperature, a decrease in diesel range product is observed, which is expected as increasing temperature favors the undesirable hydrocracking reactions competing with the

**Table 3** Fatty acid profile of common edible and non-edible vegetable oils/fats<sup>28,97,98</sup>

		Fatty acid composition (wt%)							
Vegetable oil	Iodine value	C12	C14	C16	C18	C18:1	C18:2	C18:3	Other
<i>Edible oils</i>									
Soybean oil	128–143	—	—	12	3	27	52	6	—
Sunflower oil	125–140	—	—	7	5	19	68	1	—
Rapeseed oil (mustard oil)	98–110	—	—	4	1	65	22	8	—
Palm oil	48–58	—	1	45	4	40	10	—	—
Cotton seed oil	103–115	—	1	22	3	19	54	1	—
Coconut oil	7–11	51	18	9	3	6	2	—	C10:0 (6), C8:0 (5)
Rice bran oil	90–108	—	—	15	2	43	39	1	—
Corn (maize) oil	103–128	—	—	2	11	28	58	1	—
Peanut/ground nut/arachis oil	84–100	—	—	11	2	48	30	2	—
Tucuma oil	12–17	47	26	6	3	13	3	—	C8:0 (1), C10:0 (1)
Buriti oil	81–90	—	1	—	4	72	2	2	C16:1 (19)
Babassu oil	14–20	50	20	11	4	15	—	—	—
<i>Non-edible oils</i>									
Karanja oil	81–90	—	—	6	7	62	17	—	C20:0 (3), C22:0 (4)
Jatropha oil	82–98	—	1	15	6	55	23	—	—
Rubber seed oil	132–148	—	—	10	9	25	40	16	—
Mahua oil	58–70	—	—	28	23	50	9	—	—
Tung oil	160–175	—	—	4	1	8	4	3	C18:3(ZEE) (80) <sup>a</sup>
Maracuja oil	105–145	0	8	2	12	77	1	—	—
Neem oil	65–80	—	—	16	10	50	16	8	—
<i>Animal Fats</i>									
Chicken fat (poultry fat)	75	—	1	23	6	42	17	1	C16:1 (8), C20:1 (2)
Fish oil (menhaden)	167	—	11	20	3	15	2	1	C16:1 (15), C20:1 (1), C18:4 (4), C20:5 (5), C20:6 (12)
Beef tallow	35–48	1	3	27	17	42	3	1	C16:1 (4), C17:0 (2)

<sup>a</sup> C18:3(ZEE) – 9Z,11E,13E – Octadecatrienoic (α-eleostearic) acid.

<sup>a</sup> C18:3(ZEE) – 9Z,11E,13E – Octadecatrienoic ( $\alpha$ -eleostearic) acid.

desirable hydrotreatment reactions. An increase in alkanes with an odd number of carbon atoms was also observed as the reaction temperature was raised. As the hydrotreating temperature increases, diesel selectivity gradually drops. The cold flow properties, such as cloud point and pour point, were found to improve with increasing temperature, as expected from the increase in iso-alkanes content. But it should be noted that higher reactor temperatures are more attractive when gasoline production is of interest, while lower reaction temperatures are more suitable when diesel production is important. Sulfur and nitrogen are most effectively removed in all cases (over 99.4%), while oxygen removal is favored by hydrotreating temperature.<sup>83,84</sup>

**Influence of feedstocks.** The fatty acid composition of different vegetable oils is shown in Table 3.<sup>29,98,99</sup> Generally, vegetable oil contains fatty acids that have carbon numbers from C14 to C18 with few exceptions, such as coconut oil. Hydroprocessing studies have shown that the product alkanes contain equivalent or one less carbon than the parent fatty acids. The renewable diesel product composition of the vegetable oil hydroprocessing reaction can thereby be roughly estimated based on the fatty acid composition of the feed. However, depending on the chain length and degree of saturation of the vegetable oils, some differences have been observed in the product yields. The soybean, buriti and maracuja oils contain fatty acids that have a longer chain length and are more unsaturated compared to tucuma and babassu oils.<sup>100,101</sup> Gaseous products were found to increase with a decrease in chain length and degree of

unsaturation of the vegetable oils. Some authors have also reported getting some amount of cycloalkane and aromatics.<sup>102</sup> This generally happens in cases of low hydrogen pressure or low hydrogen to oil ratio, then side reactions, such as cracking, cyclization and aromatization, increase. Cycloalkane also increases when there is a higher degree of unsaturation in the feedstock and alkane selectivity increases with an increase in the degree of saturation.<sup>103</sup> But these products are not generally found in hydrotreating, where at process conditions of temperature and pressure most of the unsaturation becomes saturated and does not lead to cyclisation or aromatization.

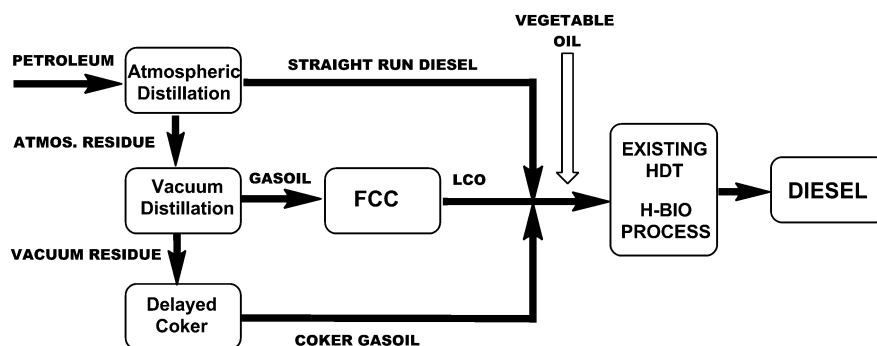
### 3. Co-processing of vegetable oil with petroleum feed

Renewable diesel that is produced when an oil company adds small amounts vegetable oils or animal fats to the traditional petroleum refining process while producing diesel fuel is termed co-processing. Co-processing is a relatively cheap option to produce renewable fuels because it avoids setting up new units. Advantages of co-processing are: (1) increases cetane number of the diesel fraction, (2) reduction in CO and hydrocarbon emission, (3) reduction in sulfur content and (4) reduces dependence on petroleum. While some studies have considered co-processing of vegetable oils with vacuum gas oil (VGO) boiling range petroleum, others have investigated co-processing with light gas oil (LGO) fractions. Corma and



**Table 4** Some commercial/pilot scale units for green diesel production

Company	Feedstock	Country/plant location
Neste oil	Vegetable oils/animal fats	Finland, Singapore, Netherlands
UOP and ENI	Vegetable oils	Italy
Dynamic Fuels (Syntroleum/Tyson)	Non-food grade animal fats and greases	USA
Petrobras	Vegetable oils/animal fats	Brazil
British Petroleum	Vegetable oils/animal fats co-processed with petroleum diesel	Australia
ConocoPhillips/Tyson	Vegetable oils/animal fats co-processed with petroleum diesel	Ireland

**Fig. 1** Hydroconversion in hydrotreating units (HDT) developed by Petrobras (H-bio process).<sup>104</sup>

co-workers have reported that the kinetics of oxygen removal from sunflower oil was much faster than that of sulfur removal from VGO.<sup>101</sup> The conversion of sunflower oil at 350 °C was 100%, while the corresponding sulfur conversion was only 41%, and up to 50% sunflower oil has no influence on the rate of desulfurization over the sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. In general, it has been observed that an increase in vegetable oil content is detrimental to the cold flow properties of the diesel product. An increase in the rapeseed oil content in the feed from 0% to 25% resulted in an increase in the cloud point product from 4.4 °C to 10.5 °C.<sup>66</sup> Knudsen *et al.* also reported that in LGO-rapeseed oil co-processing studies, decarboxylation selectivity and hydrogen consumption increases with an increase in rapeseed oil content, but a decrease in aromatic conversion was observed due to inhibition of the hydrogenation of mono-ring aromatic compounds by CO formed from the rapeseed oil conversion.

#### 4. Commercial units

Industrial hydrogenation plants are under development and presented in Table 4.<sup>104</sup> Neste Oil<sup>105,106</sup> has developed the NExBTL<sup>®</sup> process for which the first commercial plant has started in Finland. UOP/Eni Ecofining<sup>™</sup> is another commercialized process to convert non-edible, second generation natural oils to Honeywell Green Diesel<sup>™</sup>, a drop-in diesel fuel for use in any percentage.<sup>107</sup> Co-processing of vegetable oils with middle distillates, the H-Bio process (Fig. 1),<sup>108</sup> has been started in Brazil by Petrobras. However, several problems still need to be addressed. The presence of a large amount of water in the hydrotreatment reactor could have adverse effects on the sulfided catalyst performance. To make this process attractive, it should be optimized to

consume minimum hydrogen and the catalyst should be robust enough to tolerate high concentrations of free fatty acids present in non-edible oils and water produced as a by-product. Even hydrogen can be produced by steam reforming from light fraction produced as a side reaction or from biomass.<sup>107</sup> Companies are concentrating more on non-edible oil sources to avoid the food vs. fuel issue and reduce the production cost. Renewable diesel is becoming more attractive than conventional biodiesel due to its higher feedstock flexibility, lower cost, high oxidative stability, high blendability and used in existing fuel distribution systems.<sup>107,108</sup> For stand-alone processing, since vegetable oils do not have a high sulfur content, new non-sulfided hydrotreating catalysts could be used.

For co-processing, carbon monoxide, formed by hydrogenolysis of vegetable oils, has an inhibiting effect on hydrodesulfurization activity. In the hydrotreatment conditions, unsaturated fatty chains are hydrogenated. The resulting straight chains, mainly C<sub>12</sub>–C<sub>18</sub>, are completely paraffinic. Such fully saturated compounds have an excellent cetane index, but generally bad cold flow properties compared to corresponding esters,<sup>109,110</sup> which may require an additional hydroisomerization step. In this type of process, there are no longer any constraints on the chemical composition of the vegetable oils or fats (length of the fatty chains, degree of unsaturation).

If, as it seems today (average crude oil price in 2012 is > \$100/barrel), oil prices stay at a high level, then the incentive for manufacturing fuels from renewable resources will become attractive, especially from non-edible vegetable oils/fats and biodiesel will gradually emerge in the market place. This essentially sulfur-free fuel could, eventually, have a moderating effect on the growth of the hydrotreating industry. The use of bio-based feeds will lead to the presence of oxygen atoms in

feed molecules and hydrodeoxygenation (HDO) or any other technique for the removal of oxygen may be needed. In that case, more basic knowledge of HDO is necessary.

## 5. Conclusions

Hydroprocessing of vegetable oils to obtain hydrocarbon-based diesel fuel is becoming more attractive due to its stability and feedstock (low quality high FFA) flexibility over ester-based biodiesel and compatibility with the petroleum distribution system and diesel engine. Although many reported studies advanced the knowledge of vegetable oil hydroprocessing, still the stability of the catalyst in long duration runs with various feedstocks and optimization of process parameters need more detailed understanding for its wider commercial use. High hydrogen consumption in the process is another issue to be addressed as it is crucial to develop and optimize quality catalysts and process conditions. This process is a two-step process that results in a higher operating cost and lower yield. Therefore, a single step process for conversion of vegetable oil into hydrocarbons would be more desirable.

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