



Catalytic hydrodeoxygenation of triglycerides: An approach to clean diesel fuel production



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ABSTRACT

The catalytic upgrading of vegetable oil to green diesel is one of the distinct research subjects in biorefineries. The catalytic conversion of triglycerides entails the method of hydrotreating such as hydrogenation, hydrodeoxygenation, decarboxylation and decarbonylation as well as isomerization. The product derived is renewable green diesel (straight chain hydrocarbon), of which its production addresses the sustainability of the future energy. The main challenges faced by hydrodeoxygenation are the selection and synthesis of suitable catalysts, selection of appropriate feedstocks, optimization of the thermodynamic parameters, and the reaction pathways. The literature on the selection of feedstock and model compounds is discussed in the sub-section. This review also includes the evaluation on several potential catalysts such as bimetallic solid acid, sulphided, non-sulphided, nitrides, phosphided, isomerization and hydrocracking catalysts as well as the noble metal catalysts. The selection of the metal supports catalysts, the catalyst designed practice and the overall performance is also reviewed and discussed. The most common supports used for the hydrodeoxygenation is solid acid composites such as Al_2O_3 and zeolites. In addition, the promoters tested yield different results with different reaction mechanisms demonstrated. The research on the hydrodeoxygenation pathways and the product distribution related with all kinds of catalysts are also addressed. In addition, the advancement of co-hydroprocessing of mix-vegetable oil and vacuumed gas oil is addressed and summarized as well. Overall, this review provides a comprehensive discussion on the hydrodeoxygenation issues and challenges in all relevant technical aspects.

1. Introduction

A dynamic, clean and economical energy production is a strategic way to ensure a healthy and effective global economics [1]. The key tasks to be addressed in cleaner and sustainable energy production are the consumption of energy in the transportation sector and the loss of energy during conversion and transportation [2]. The consumption of energy is increasing day by day due to the ballooning of the world's population. The major energy consumption area is the transportation sector that demands huge amount of fuel and it is unavoidable in the future. The fossil fuels in the form of hydrocarbons are liquid and gaseous fuels (petroleum, diesel, and natural gas). These fuels are the vital source for the transportation industry. The excessive use of fossil fuel had caused severe global issues such as the increase in CO_2 emission in the atmosphere that is ultimately responsible for the greenhouse effect and global warming. Most of the scientists therefore

have the primary interest to work for renewable energy sources such as solar, hydroelectric, wind, geothermal and bioenergy. Nevertheless, the more economical, sustainable and abundantly available energy resource is the biomass from woods, lignocellulosic materials, oils, and fats [3].

In most of the reported works, the main researches intensively developed the ester-based biodiesel obtained by the conventional transesterification of edible or non-edible oil. The major issues with the biodiesel are oxidative stability, cold flow properties, and low energy content. To encounter these gaps, different routes for conversion of vegetable oil to efficient quality fuel need to be studied, which should also be compatible with the petroleum based fuels. Another prevalent dilemma reported with the transesterified vegetable oil is high kinematic viscosity, which ultimately causes the quandary in pumping the atomization, carbon deposition on piston, ring sticking, carbon deposition on the cylinder head, ring grooves and etc. [4]

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However, the viscosity of the vegetable oils can be minimized by several methods that include blending of oils, microemulsion, pyrolysis, transesterification and hydrodeoxygenation as shown in Fig. 1.

Esterification and hydrodeoxygenation (HDO) are the most considered commercial routes for producing biodiesel and hydrocarbon from vegetable oil, respectively. One of the major advantages to select the HDO route as compared to other is the ability of HDO to produce the diesel range fuel (C_{16} – C_{18}) [5,6]. The fuel derived from biomass is oxygen free and of high-quality fuel that should be completely compatible with conventional fuel based on refinery [7]. This renewable green diesel fuel has efficiently- same energy densities as petroleum – derived fuels due to removal of oxygen contents and equal carbon-carbon percentage. The detail discussion have been reported by Berghthorson et al. [8] in a critical review on combustion and emission properties of biofuels. The deoxygenated products of vegetable oil mainly consist of C_{15} – C_{18} . These alkanes have high cetane numbers (above 98). However, other fuel properties such as cold flow properties are not favourable enough. To deal with these kind of problems, the isomerization of *n*- paraffin to branched isomers is regarded as more feasible method [9,10]. Therefore, extensive research works are made of recent trend to enhance the fuel properties of green diesel. The co-processed triglycerides is found to be nearly identical in blended form with the fossil fuel to enhance the fuel properties and evidently, these triglyceride feeds can be hydroprocessed as the renewable fuels [11]. The hydrogenolysis reaction is also an important route for the production of certain type of value added chemicals derived from the intermediate compounds of the biomass. The removal of the oxygen contents from the biomass can be achieved by hydrogenolysis, decarboxylation, decarbonylation and dehydration of C-O bond. The most significant mode of deoxygenation is hydrogenolysis process that can also be used for depolymerisation of biomass [5].

The triglycerides and fatty acids are the potential feedstocks for the production of renewable and sustainable fuel. These feedstocks do not only produced diesel and gasoline range hydrocarbons via hydroprocessing but they can also produce alcohols, aldehydes and alkenes as the reaction intermediates [12,13]. The presence of these intermediates also enhanced the fuel properties such as viscosity, flash point, cetane number etc. A commendable efforts have been made by many

researchers for the extensive studies on hydrodeoxygenation/deoxygenation of vegetable oils or model compounds with the adaptation of common industrial hydrodesulphurization process. This technology in addition, does not require any further amendment of the reactor designed, but it gives significant conversion and yield of gasoline and diesel range hydrocarbon.

Nevertheless, another key issue to for this process, is the development of catalyst to enhance the fuel properties. To understand the reaction mechanism on the catalyst surface in depth, during the last few years, the well-defined nanocatalysts have been developed for the hydrogenolysis of C-O bond [14,15]. These catalysts can be classified into two major groups: catalysts based on pure metal alloys and bi-functional catalysts combined with the nano-metallic site with acid or base catalysts [16]. These catalysts are being used actively for the hydrodeoxygenation, hydrogenation and hydrocarboxylation of model compounds, representing triglycerides of edible oil and non-edible oil [7,14,15,17–20]. The process of converting triglycerides to the hydrocarbons is usually carried out under high pressure and high temperature in the presence of catalysts [21]. Consequently, the final product comes in the form of *n*-alkane, *iso*-alkane or long chain hydrocarbon and water as shown in Fig. 2 [18,20,21]. This comprehensive critical review is therefore an effort to highlight the hydrodeoxygenation process in terms of selection of the feedstocks, catalysts design processes, optimized reaction conditions and investigation of the reaction pathways.

2. Triglycerides selection

Among all renewable energy sources, the oils and fats from the biomass sources such as vegetable oils, are the significant source of energy fuel for the transportation industry due to their high energy density. Yet, the direct use of vegetable oil as fuel is not compatible with the current combustion engine due to its high viscosity. Various type of vegetable oils are being used as the feedstock for biofuel but to date, only sunflower, cottonseed, peanut oil, soybean, palm, safflower, and rapeseed have shown a potential production for biofuel [22,23]. Other potential source such as camelina, only need low water and nitrogen supply for cultivation. Camelina crop can be easily rotated for wheat

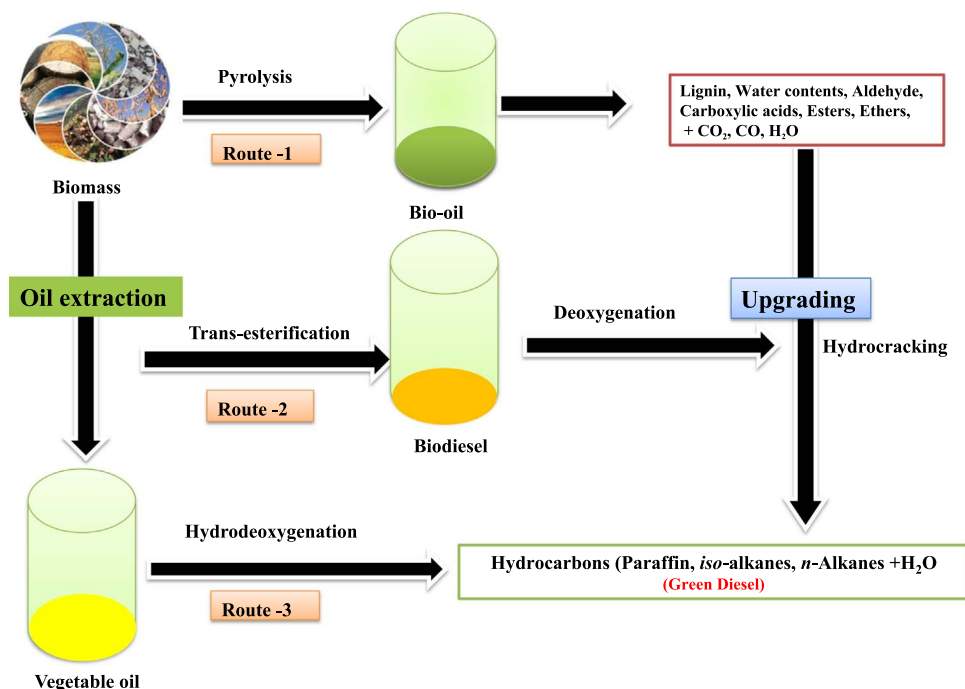


Fig. 1. The conversion routes from biomass to direct hydrocarbons. **Route-1** shows the pyrolysis of biomass and followed by HDO to hydrocarbon conversion. **Route-2** shows the trans esterification of vegetable oil to biodiesel and then its upgrading to green diesel. **Route-3** shows HDO of vegetable oil directly to green diesel fuel.

with less amount of fertilizer during the rotation process [24]. Approximately 19 pounds of camelina seeds can produce almost a gallon of oil. The main focus on camelina plant for biofuel production is due to its vast irrigation distribution [25]. These vegetable oils and fats can be used as a green source of fuel in engines after some modifications in the fuel structure or properties [26]. The most commonly used edible oil is sunflower oil containing 40–50% oil. The Ukraine, Russian Federation, Turkey, Argentina and The Europe-27 are the countries, which highly produced sunflower oil. The sunflower and the rapeseed oils are used as the main feedstock for biofuel mainly in Europe [27]. The cultivation period for sunflower is very short as compared to other oil-producing crops. The worldwide sunflower oil production is only (10%) as compared to the rapeseed (55%), cotton seed (10%) and soybean (55%) [28]. Among all edible oils, the rapeseed oil, which is also known as canola oil is widely used as the feedstock for biofuel production. The most familiar countries like Canada, India, China and Northern Europe are the main producers of the rapeseed oil. These countries produced approximately 7 to 10 million tonnes of canola oil per year [25]. In other part of the world, soybean is largely produced in the United States. The soybean oil production worldwide is thirty-five million tonnes and 47% of the global soybean oil is fulfilled by the United States [29]. The capability of nitrogen fixation is higher in soybean in a symbiotic relationship, and hence, it requires low amounts of nitrogenous fertilizers [30]. In the tropical climate areas, coconut and palm oil are the main sources for biofuel production [25]. Both palm oil and coconut plants have high percentage of oil contents, steady ripening periods, small conservation and the foundation of eco-friendly waste material during the whole process of oil extraction [25,31]. Malaysia is one the major producers of palm oil and the Malaysian Palm Oil Board (MPOB) has performed systematic studies for the production of alternative fuels from palm oil and its derivative [7,31–33]. Malaysia has planned to use the palm oil for fuel production and reduced the imports for crude oil [31,33].

The production of fuels from edible oil is not eminent in Asian sub-continent, therefore, the use of non-edible oil is favourable as an alternative energy source [34]. In addition, the price of edible oil is much higher than the commercial diesel due to its extensive use for food purpose. One of the non-edible plants is jatropha, which grows in

infertile soil because of the presence of phorbol esters [35]. It grows mostly in the south and Central America, Asia and Africa [36]. As compared to the conventional fuels, jatropha oil possesses high flash point, kinematic viscosity, solidifying point and ignition point [37]. Waste cooking oil (WCO) is another inexpensive feedstock, easily available in catering places. WCO possesses high acid value due to the high contents of free fatty acids [38]. China produces WCO approximately 500 million tonnes/year due to large catering sector. The fatty acid value of WCO affects the biodiesel production but not the hydrodeoxygenation process [39,40].

There are various type of oils that had been extensively studied on the hydrodeoxygenation such as soybean oil [41,42], rapeseed oil [43–46], sunflower oil [47–50], palm kernel oil [51], jatropha oil [52–56], waste cooking oil [57–61] and algal oil [62]. Some other inexpensive non-edible oil like pongamia, madhuca, karanji, jatropha, linseed, castor, rice bran, cotton seed, azhadirachta and rubber seed are available as abundant feedstocks for paraffin fuels production [63]. The selection of the feedstock for the hydrodeoxygenation also depends on the fatty acid composition and the relative bonding location of the glycerol. The fats and oils are composed of triglycerides. These vegetable oils mainly composed of triglycerides, which consist of the structure as shown in Fig. 3. The triglycerides are categorized in saturated and unsaturated isomeric form, whereas the saturated fatty acids have higher oxidative stability with higher melting point. The unsaturated triglycerides are highly reactive towards hydrogenation [43]. The most common vegetable oil composition is listed in Table 1 as adopted from Ashraf et al. and Lee et al. [63,64]. These compositions have been determined by derivatization of esters by esterification of oil with strong acid e.g. Boron trifluoride (BF₃) or oxalic acids etc. [64].

3. Catalysts selection

The future biorefineries are aimed to improve the sustainable and integrated chemical production. Therefore, catalyst plays an important role in ensuring a high conversion of triglycerides and high yield of the intended products. There are various studies, which discussed the catalytic work in the hydroprocessing of variety of feedstocks including vegetable oil, model compounds and co-hydroprocessing with petro-

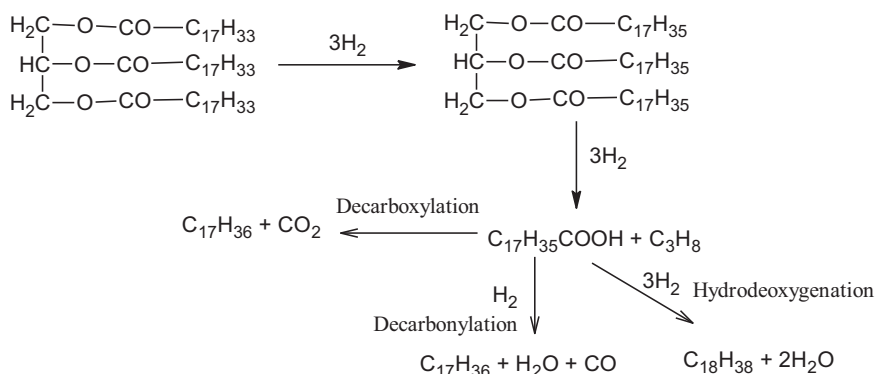


Fig. 2. Stoichiometric reactions in the hydrocarbon conversion of a triglyceride to green diesel, adopted from [14].

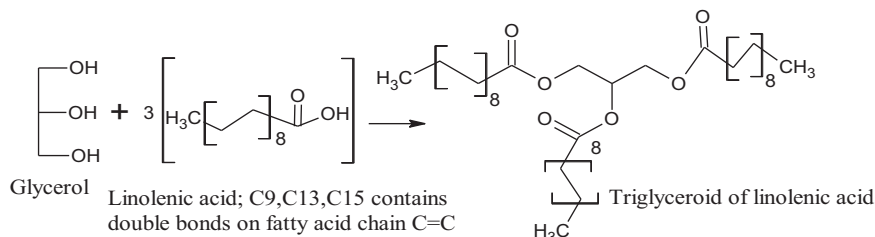


Fig. 3. Triglyceride structure of linolenic acid (triolein).

Table 1

The fatty acid composition of various vegetable oils.

Source: Adapted from Refs. [63,64].

Source	Structure	Typical fatty acid composition, wt%					
		Jatropha	Palm	Canola	Soybean	Sunflower	Rubber seed
Capric	C10:0	0.0	0.0	0.0	0.0	0.0	0.0
Lauric	C12:0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic	C14:0	0.0	2.5	0.1	0.0	0.0	0.0
Palmitic	C16:0	15.9	40.8	5.1	11.5	6.5	10.2
Palmitoleic	C16:1	0.9	0.0	0.0	0.0	0.2	0.0
Stearic	C18:0	6.9	3.6	201	4.0	5.8	8.7
Oleic	C18:1	41.1	45.2	57.9	24.5	27.0	24.6
Linoleic	C18:2	34.7	7.9	24.7	53.0	60.0	39.6
Linolenic	C18:3	0.3	0.0	7.9	7.0	0.2	16.3
Arachidic	C20:0	0.0	0.0	0.2	0.0	0.3	0.0
Eicosenoic	C20:1	0.2	0.0	1.0	0.0	0.0	0.0
Behenic	C22:0	0.0	0.0	0.2	0.0	0.0	0.0
Erucic	C22:1	0.0	0.0	0.2	0.0	0.0	0.0

Note: Nomenclature: Cn:m describes a fatty acid with n carbon atoms and m double bonds.

leum fractions distillates. The oils studied are from edible and non-edible oils, and these were tested for hydrodeoxygenation.

The summarized work by worldwide researchers on hydrodeoxygenation of vegetable oil is illustrated in Table 2. This includes soybean oil, jatropha oil, sunflower, crude algal oil, oleic acid, rapeseed oil, waste fat, microalgal oil, canola oil, camelina oil and some others. These oils have been tested for the production of green diesel via HDO. The choice of the catalysts for the hydrodeoxygenation depend upon the activity, stability and importantly the selectivity of metal and support catalyst as well as its high surface area and extensive range of high porosity. For the hydrodeoxygenation of different feedstocks, many catalysts including noble metal, transition metal, sulphided, non-sulphided, phosphided, nitride, reduced and oxides of metal catalysts have been tested [65]. From the previous findings, it is proven that the hydrocarbon conversion of triglycerides does not merely depend on the catalysts activities but also the selectivity and nature of the catalysts. The extent of the hydrodeoxygenation and the product selectivity also depends on the reaction conditions i.e. temperature, pressure, liquid space hour velocity (LSHV)/ weight hour space velocity (WHSV) and H₂ to oil (volume/volume) ratio [66]. The water vapors produced during the HDO reaction are also responsible to reduce the activity, stability, and selectivity of the catalysts, which ultimately reduce the degree of the deoxygenation [66]. Consequently, for hydrodeoxygenation, the removal of water vapors is also considered as one of the main issues. The elimination of water is important during HDO reaction because its existence in reaction mixture is ultimately responsible for catalysts deactivation especially when the batch reactors are used.

3.1. Sulphided/non-sulphided catalysts

The most commonly used catalysts for HDO are the noble metal, transition metal catalysts in sulphided and reduced form with bimetallic solid acid catalysts [67]. A generalized category of solid acid catalysts for hydrodeoxygenation is shown in Fig. 4. From earlier studies, sulphided Ni-Mo/ γ -Al₂O₃ and Co-Mo/ γ -Al₂O₃ had been used widely for the hydrodeoxygenation and also considered as more active hydrodesulphurization (HDS) catalysts (the catalytic chemical process commonly used to remove sulphur (S) from natural gas and refined petroleum products) [68]. In catalytic activities, the nature of support plays an important role for the hydrodeoxygenation. Tiwari et al. [69] tested mesoporous SiO₂-Al₂O₃ and Al₂O₃ as supports for Ni-W and Ni-Mo catalysts. They used sulphided catalysts for hydroprocessing of soybean oil and refinery oil. Among all the catalysts, the Ni-W/SiO₂-Al₂O₃ catalyst showed high hydrocracking activity and selectivity for paraffinic hydrocarbon fuels via decarboxylation and decarbonylation

pathways. The Ni-Mo/Al₂O₃ catalyst was found to be more selective for HDO and produced diesel range hydrocarbon fuels. The obtained hydrocarbon fuels were characterized by high cetane number with low density. This property of hydrocarbon showed an addition of mesoporous support [69].

It was reported that the sulphidation creates active sites on the catalysts surface [68,70,71]. Although the use of sulphided catalyst produced good hydrocarbon conversion but the products are usually contaminated by sulphur, hence sulphided catalysts are less favourable for hydrodeoxygenation [72]. The researchers, therefore, strongly involved in developing the non-sulphided transition metal catalysts [67,72]. Krar et al. [47] treated the non-sulphided Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ with sunflower oil and observed that these catalysts possess a high deoxygenating activity for hydrocarbon conversion of sunflower oil. The same research group extended their work using reduced catalysts. They used reduced Co-Mo/Al₂O₃ catalysts at a temperature range of 573.15–653.15 K and under the pressure of 40–60 bar with 1 h⁻¹ LSHV. The catalysts remain active by reduction. The reduced catalysts showed 100% hydrocarbon yield with 73.7–73.9% high paraffin fuel. The mixture of high paraffin fuel contained *iso* and *n*-alkane mixture, which possessed higher cetane number and excellent cold flow properties than the conventional diesel fuel i.e. 103–104 at 573.15 K [47].

The activity of monometallic Ni/Al₂O₃, Mo/Al₂O₃, and Ni-Mo/Al₂O₃ sulphided catalysts were studied for comparative hydroprocessing activity of sunflower oil [73]. Due to the contamination of sulphur in paraffinic fuel, many researchers investigated the process of HDO with non-sulphided catalysts. Harnos et al. [73] compared the activity of sulphided catalysts with the non-sulphided catalysts. They tested both the sulphided and non-sulphided Pd/activated C, Pd/Al₂O₃, Ni/Al₂O₃ and bimetallic solid acid catalysts Ni-Mo/Al₂O₃. The reaction conditions were set at 613.15 K under the pressure of 21 bars of H₂ gas. The major products distribution were found to be C₁₇, C₁₈ and small alkanes with different catalysts depending on the two main routes of HDO i.e. decarboxylation/decarbonylation and hydrodeoxygenation. It is reported by Harnos et al. that Pd and Ni catalysts on supported alumina, are proven to be more dominant in the product distribution of decarboxylation route. The other main products obtained by Ni-Mo/Al₂O₃ catalyst contained similar alkane chain with high *i*-paraffin/*n*-paraffin ratio. Ni-Mo/Al₂O₃ gives higher yield of linear alkanes with higher *i*-paraffin/*n*-paraffin ratio. The comparative studies on sulphided and non-sulphided catalysts for hydrodeoxygenation showed that the non-sulphided catalysts are more suitable for the reaction, which also indicate a higher activity [73]. Sulphided catalyst deactivates during HDO due to sulphurization, thus, the addition of

Table 2
Few examples on studies of hydrodeoxygenation of various sources of triglycerides.

S. No.	Feed	Catalyst	Press. (bars)	Temp. (K)	Time (h)	Reactor	Remarks	Ref
1.	Crude palm oil	Ni-Mo/Al ₂ O ₃	40–90	533–613	[*] LHSV = 1 h ⁻¹	trickled-bed reactor	Catalyst showed slight deactivation	[51]
2.	Vegetable oil and Jatropa oil	1% Pt / H-ZSM-5 Re/Al ₂ O ₃	65, 85% H ₂ in N ₂	543–573	[*] LHSV = 1–2 h ⁻¹	fixed bed reactor	67%, C ₁₅ –C ₁₈ with Re/Al ₂ O ₃	[69]
3.	Rapeseed oil	Co-Mo/MCM-41	20–110	573–593	^{**} WHSV = 1–4 h ⁻¹	fixed-bed reactor	Conversion was lower than alumina supported Co-Mo.	[79]
4.	Refined and acidic vegetable oil	Ni-Mo/γ-Al ₂ O ₃ , Co-Mo/γ-Al ₂ O ₃	33	583.15–623.15	^{**} WHSV = 1.4 h ⁻¹	bench-scale trickle-bed reactor	52 ± 3% hydrocarbon conversion	[80]
5.	Soybean oil	Sulfided Ni-Mo/γ-Al ₂ O ₃ , Ni/SiO ₂ -Al ₂ O ₃ , Pd/γ-Al ₂ O ₃ , Pt/γ-Al ₂ O ₃ , Ru/γ-Al ₂ O ₃	92	673	Catalyst/oil weight ratio of 6.044	high-pressure batch reactor	NiMo, CoMo favoured the HDO pathway	[77]
6.	Rapeseed oil	Ni-Mo/Al ₂ O ₃	70 and 150	583.15, 633.15	^{**} WHSV = 1 h ⁻¹	laboratory flow reactor	Good yield of hydrocarbon product	[82]
7.	Rapeseed oil	Co-Mo/Mesoporous Al ₂ O ₃	7–70	523–623	^{**} WHSV = 1.5 h ⁻¹	fixed-bed reactor	The extent of HDC increased with high temperature and low pressure	[84]
8.	Rapeseed oil	Sulfided Ni/Al ₂ O ₃ , Mo/Al ₂ O ₃ , Ni-Mo/Al ₂ O ₃	35	583	^{**} WHSV = 2 h	fixed-bed reactor	NiMo/Al ₂ O ₃ yielded HDC HDO hydrocarbon, Ni/Al ₂ O ₃ yielded DC product and Mo/Al ₂ O ₃ yielded exclusively HDO products	[86]
9.	Oleic acid and canola oil	Mo, W, V nitrides/Al ₂ O ₃	715	653–683	[*] LHSV = 0.45 h ⁻¹	quartz tubular reactor	oxygen removal exceeded 90%	[87]
10.	Vegetable oil	Ni-Mo/SiO ₂ or Al ₂ O ₃	H ₂ /oil = 800 mL/mL,	623	[*] LHSV = 7.6 h ⁻¹	fixed-bed flow reaction system	n-C ₁₈ H ₃₈ , n-C ₁₇ H ₃₆ , n-C ₁₆ H ₃₄ , and n-C ₁₅ H ₃₂ as predominant products	[104]
11.	Rapeseed oil	Pt/zeolite(HY-H-ZSM-5) sulfide Ni-Mo/Al ₂ O ₃	50–110	573–673	[*] LHSV = 3 h ⁻¹	batch reactor	Highest yield of liquid hydrocarbons was observed	[46]
12.	Sunflower oil	Sulfide commercial hydro cracking catalyst	180	633–693	^{**} WHSV = 1.5 h ⁻¹	fixed bed reactor	good low heating properties	[50]
13.	Waste cooking oil	commercial hydro cracking catalyst	827 and 965	603–671	[*] LHSV's (0.5, 1.0, and 1.5 h ⁻¹)	small-scale pilot plant unit of CPERI/CERTH	Sulphur and nitrogen removal exceeded 99% oxygen removal was (> 90%).	[61]

^{*} LHSV: Liquid Hour Space Velocity.

^{**} WHSV: Weight Hour Space Velocity.

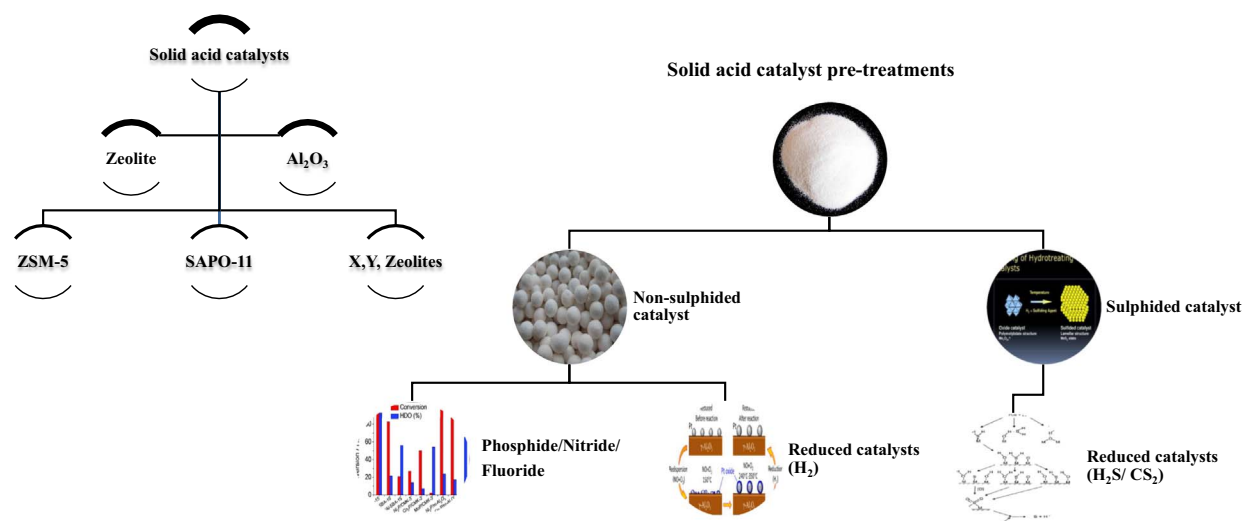


Fig. 4. The general categorized solid acid catalysts for hydrodeoxygenation.

sulphiding agent is required to keep these catalysts active during HDO process as shown in Fig. 5 [74–76]. Veriansayah et al. [77] investigated the HDO using soybean oil in the presence of a series of sulphided noble metal catalysts. The catalysts such as Ni-Mo/ γ - Al_2O_3 , Ni/ SiO_2 - Al_2O_3 , Pd/ γ - Al_2O_3 , Pt/ γ - Al_2O_3 , Ru/ γ - Al_2O_3 were used at 92 bars and 673 K. The catalyst/oil weight ratio of 6.044 was used in the batch reactor. The activity of all catalysts yield the following results in the order of highest active catalysts to lower: NiMo > Pd > CoMo > Ni > Pt > Ru, at the catalyst/oil weight ratio of 0.044 and Ni > NiMo > Pd > CoMo, at the catalyst/oil weight ratio of 0.088 [77].

On the other hand, more advance researches have been carried out using sulphided catalysts. Sankaranarayanan et al. [78] carried out HDO consisted of a mixture of sunflower and gas oil over sulphided Ni-Mo/ γ - Al_2O_3 fused with 30 wt% of beta zeolite. The reaction was carried out between 593.15 and 623.15 K under the pressure of 30–60 bar with LHSV of 2 h^{-1} . Ni-Mo/ γ - Al_2O_3 fused with 30 wt% of beta zeolite showed 100% hydrocarbon conversion at 60 bars, 603.15 K and LHSV of 2 h^{-1} as compared to Ni-Mo/ γ - Al_2O_3 , which suggested that beta zeolite demonstrates a higher tendency to improve the hydrodesulphurization capacity of the catalysts. The major component produced was found to be octadecane (C_{18}) in the presence of zeolite beta at 15 wt%. Octadecane yield increases by lowering the temperature, and high pressure with high oil to H_2 (feed) ratio. The catalysts give efficient activity and high conversion towards the selected oil [78].

Palm oil is abundantly found in tropical areas and currently focused for biomass research. The paraffinic diesel range fuel (C_{16} - C_{18}) was obtained using the most common hydroprocessing catalyst by Guzman

and colleagues. Guzman et al. [51] used crude palm oil as feedstock for HDO in the presence of Ni-Mo/ Al_2O_3 between 40 and 90 bars and 533–613 K in a fixed bed reactor. They observed the diesel range of high paraffinic fuel with excellent cetane index. In addition, there was only slight deactivation of the catalysts. Donniss and his fellows studied the same process on rapeseed oil. Kubicka et al. [79] conducted HDO by using rapeseed oil over Co-Mo/MCM-41 catalyst, between 20 and 110 bar at 573 and 593 K in a continuous flow reactor. It was found that the conversion of the triglycerides was lower by using Co-Mo/MCM-41 as compared to CoMo/ Al_2O_3 catalysts [79]. An average hydrocarbon conversion was reported by Vonortas et al. [80]. They used refined acidic vegetable oil for HDO in the presence of Ni-Mo/ γ - Al_2O_3 and Co-Mo/ γ - Al_2O_3 at 33 bars and the range of temperature of 583.15–623.15 K using bench scale trickle bed reactor. The maximum conversion was found to be about 52–53% [80]. Gusmao et al. [81] used vegetable oil for HDO in the presence of Ni/ SiO_2 and sulfide Ni-Mo/ γ - Al_2O_3 for 10–200 bars pressure at 623–673 K temperature for 2 h in batch reactor, which showed the maximum conversion (100% molar yield of hydrocarbon) has taken place from reactant to product [81]. As a result of previous studies, it is obvious that bimetallic NiMo and CoMo-based catalysts demonstrate good catalytic activity for hydrocarbon conversion over sulphided and non-sulphided catalysts.

Simacek et al. [82] experimented hydroprocessing with pure sunflower oil over conventional hydrocracking sulphided metal supported catalysts. The activity of the catalysts was observed under the optimum reaction conditions i.e. temperature range 633.15–693.15 K and 180 bars. The hydrocarbon products were observed altogether with

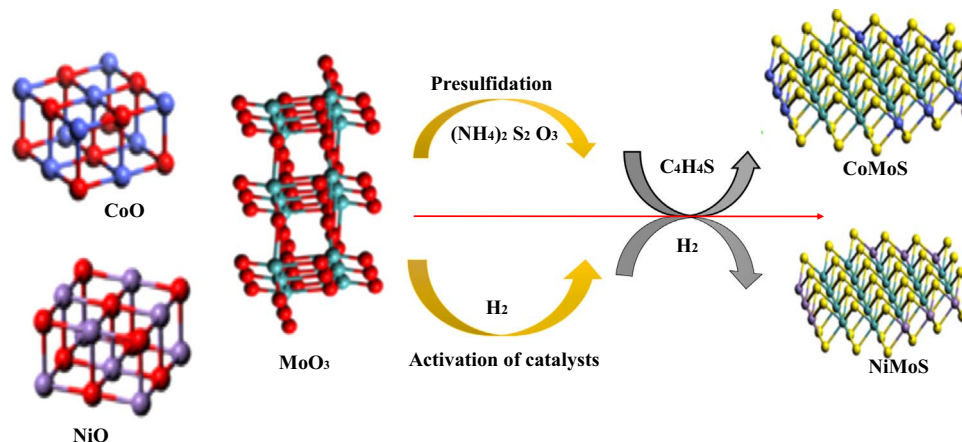


Fig. 5. Pre-sulphidation process of bimetallic solid acid catalysts for activation of catalysts adopted from [76].

low aromatic contents. It was perceived by the research team that by increasing the temperature from 633.15 to 693.15 K, the concentration of *n*-alkane in a range of C_{17} – C_{18} decreased from 53 wt% to 5 wt%. However, the hydrocarbon composition at 693.15 K was found to be similar with petroleum-based diesel fuels, which possesses good cold flow properties i.e. cold filter plugging point 287.15 K and cloud point of 284.15 K [82]. In a different study, it was found that by varying the percentage of precursor and active metal catalysts, the hydrocarbon conversion varies [82]. Simacek et al. [82] used commercial catalysts for hydrotreatment of oil at the temperature range of 583.15–633.15 K under varied hydrogen pressure of 70–150 bars. The major hydrocarbon products is obtained at 634.15 K and 70 bars of hydrogen, which are approximately 75 wt% of *n*-alkane, *n*-heptadecane, and *n*-octadecane. The product was characterized using cetane numbers index and cold flow properties. It was investigated that the product exhibited poor cold flow properties but with high cetane number, it showed that the product can be blended with other conventional diesel that requires slight modification in flow modifier [82]. Simacek et al. [83] treated rapeseed oil with different percentage sulphided Ni-Mo/Alumina catalysts for the hydrodeoxygenation. The reaction condition was set up for each formulation at the range of 533.15–643 K with the H_2 pressure of 70 bars. The product obtained contained C_{17}/C_{18} *n*-alkane and *iso*-alkane. It was examined that at a low temperature, the reaction was found to be incomplete. As the temperature is increased above 583.15 K, the product is found to have more similarity with the conventional diesel fuel. The increase in temperature of the obtained product also had an increasing trend in *iso*-alkane with all catalysts formulation i.e. NiO (2.6 wt%) MoO_3 (15.7 wt%) [83].

It is obvious from previous studies that the process of deoxygenation includes three types of main reaction pathways, namely decarboxylation (DCO), decarbonylation (DCN) and hydrodeoxygenation (HDO) with the resulting by-products are CO_2 , CO and H_2O respectively. A study on single step reaction mechanism of the deoxygenation of rapeseed oil was investigated by Kubicka et al. [84] using sulphided Co-Mo/ Al_2O_3 catalyst. The feedstock contained phospholipids and alkalis caused the deactivation of the catalyst due to the coke formation. Kubicka et al. [84] confirmed that the coke was formed due to the high concentration of alkali and phospholipids in the feedstock. The reaction conditions for deoxygenation were set up at 623.15 K, 35 bars, and $2\ h^{-1}$ LSHV. The product with the varied ratio of C_{17}/C_{18} as a results of sulphidation, also increased the product ratio. However there is an increase in acidity of the catalyst, which ultimately decreased the HDO and decarboxylation ratio. Kubicka et al. [84] also reported the use of Co-Mo supported on organized mesoporous alumina (Co-Mo/OMA) for the process of hydrodeoxygenation. Co-Mo/ Al_2O_3 and Co-Mo/MCM-41 showed slightly less activity than Co-Mo/OMA for the deoxygenation. The process of deoxygenation followed a decarboxylation or HDO depends on reaction conditions like temperature, pressure, nature of catalysts and support. The reaction performed had an optimum selectivity of triglycerides into hydrocarbon conversion at 583.15 K and 70 bars. The decarboxylation reaction was favoured at high temperature and low pressure and in the result of this reaction, the C_{17}/C_{18} ratio decreased and C_{17} alkane became the major product [84,85]. Furthermore, Kubicka and Kaluza [86] investigated the deoxygenation reaction using Ni-Mo/ Al_2O_3 and Ni-Mo sulphided catalysts between 533.15 and 553.15 K at 35 bars with the LHSV of 0.25 – $4\ h^{-1}$. The bimetallic Ni-Mo/ Al_2O_3 with Ni/Ni-Mo ratio of 0.2–0.4%, which was prepared by wet impregnation method was found to have the highest catalytic activity. The catalysts also showed the variety in the product with C_{17}/C_{18} *n* and *iso*-alkane selectivity. The decarboxylation and hydrodeoxygenation routes are prominent whenever Ni-Mo/ Al_2O_3 is used, which give HDO to decarboxylation related products. The molar ratio increases with the increase in conversion due to the formation of intermediates of fatty acid esters. Nonetheless, Ni/ Al_2O_3 and Mo/ Al_2O_3 selectively demonstrates good activity for decarboxylation and HDO routes respectively [86]. Toba et al. [57]

investigated the hydrodeoxygenation reaction using waste cooking oil over sulphided Ni-Mo/ Al_2O_3 , Co-Mo/ Al_2O_3 , and Ni-W/ Al_2O_3 catalysts. Among these catalysts, Ni-Mo/ Al_2O_3 and Ni-W/ Al_2O_3 are more active for HDO reaction, as compared to Co-Mo/ Al_2O_3 since the latter is prone to deactivation. The most suitable reaction temperature is found to be at 523.15 K. The main decarboxylation products such as *n*-paraffin, *iso*-paraffins and fewer extent of olefins are obtained by using of Ni-W/ Al_2O_3 catalysts as compared to Ni-Mo/ Al_2O_3 and Co-Mo/ Al_2O_3 . However, the sulphur contents are very low in hydrocarbon product. This research group also tested other catalysts in addition to different supports. The Ni-Mo/ B_2O_3 - Al_2O_3 was also tested for its activity for HDO. The activity of Ni-Mo/ B_2O_3 - Al_2O_3 is enhanced due to the increasing in acidity of support and formation of *iso*-paraffinic products, which is the main factor affecting the cold properties of diesel range hydrocarbon fuels [57].

3.2. Nitride/phosphide/reduced-catalysts

Nitration and phosphatization also improve the active sites like sulphided catalysts. Unfortunately, there were insufficient research works that had been carried out to investigate the effects of nitrides and phosphide catalysts for hydrocarbon conversion, and thus become an area of interest for further research. Monnier et al. [87] used the nitrides of Mo, W, and V supported on alumina and verified the activity of these catalysts for HDO of canola oil and oleic acid. Among all the catalysts tested, molybdenum nitride (Mo_3N/Al_2O_3) demonstrates higher hydrocarbon conversion. The oxygen removal activity reaches 100% at 573.15 K and 71.5 bars. In addition, *n*-alkane is produced with high cetane number. It was concluded from their research that the nitride catalysts are effective for selective deoxygenation via HDO route while Vanadium catalysts selectively shows high activity for decarboxylation route [87]. Similarly, in recent research the Ni_2P/SiO_2 catalysts were used for HDO of guaiacol, in a continuous flow fixed-bed reactor between 523 to 573 K, either at atmospheric or 8 atm and an LHSV of $2.0\ h^{-1}$. The comprehensive and combined X-ray absorption fine structure spectroscopy (XAFSS) and density functional theory (DFT) studies exposed that the active site of Ni_2P catalysts is made up of three-fold heavy Ni and P sites, which highlighted the adsorption of H or OH groups. This comprehensive results suggest that the relatively occupied surface of catalysts (Ni_2P) with H or OH groups on Ni or P sites surface have an influence on complete reaction mechanism [88].

Ni/P is another efficient hydrodeoxygenation catalyst with different molar ratio of Ni with P was investigated for hydrodeoxygenation of guaiacol. Wu et al. [89] successfully studied the effect of P on both active phase composition and catalytic activities of Ni/P. It was discerned from activities that highly rich P exhibited the lower guaiacol conversions than deoxygenation with less coke formation than the phosphorus lean samples. From the kinetic analysis of guaiacol using phosphorus-containing catalysts, Wu et al. [89] observed that the phosphorus showed negative effect on guaiacol conversion. With a variable composition of phosphorus and Ni catalysts, different conversion routes were observed and proposed for demethylation, demethoxylation, direct deoxygenation, hydrogenation, and trans-alkylation. A comprehensive study by Wu et al. [89] showed that the bifunctional properties of hydrogen on Ni and protonation on PO-H of Ni_2P/SiO_2 and Brønsted acidity of Ni_2P_5/SiO_2 and Ni_3P/SiO_2 improved their catalytic activities and performances. The catalyst deactivation is attributed to coking and phosphide leaching during HDO nonetheless by using these catalysts, the duration for the catalysts to deactivate become longer. The Ni/P=1 gives the highest guaiacol conversion up to 78% but with Ni/P=3, it gives the lowest i.e. 46% [89]. It is concluded that all three types of phosphide catalysts with Ni are not suitable for high conversion of guaiacol. Coke formation becomes more noticeable as higher percentage of phosphide catalyst being used.

Another work was established by Shi et al. [90] as they investigated the effect of supports (SiO_2 , CeO_2 , TiO_2 , and SAPO-11) for deoxygena-

tion of methyl laurate (model compound) to gasoline products via HDO route over Ni-based phosphide catalysts (Ni/P). With Ni/P = 1.0, Ni₂P were doped on SiO₂, CeO₂, TiO₂ and SAPO-11 and Ni₃P and Ni₂P₅ were doped on γ -Al₂O₃ HY zeolite. Shi et al. [90] reported that the conversion of methyl laurate and selectivity for gasoline products decreased following this order: Ni₂P/SiO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/TiO₂ > Ni₂P/SAPO-11 > Ni₂P-Ni₁₂P₅/HY > Ni₂P/CeO₂. Additionally, while C₁₁ and C₁₂ were the desired products for their research work, they observed that the C₁₁/C₁₂ molar ratio is in the order of Ni₂P/CeO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/SiO₂ > Ni₂P/SAPO-11 > Ni₂P/TiO₂ > Ni₂P-Ni₁₂P₅/HY. Hence, it was concluded with their results that the supports yield results in terms of their reducibility and acidity. It is also discussed that the reaction pathways mainly depends on the catalysts activity and selectivity towards hydrocarbon conversion, which is correlated with Ni sites on the surface of supports, the Ni₂P crystallite size and interaction between acid sites of supports and Ni active sites [90]. Another series of catalysts such as titania supported molybdenum carbide, phosphide, nitride, and oxide were also tested for hydrodeoxygenation of phenol. Eiras et al. [91] investigated all the titanium supported molybdenum based catalysts on fixed bed reactor at 20 bars and the highest activity was observed at 15 wt% MoC/TiO₂. Based on their investigation, it was concluded that Mo-based catalysts are highly active and likely to be used to achieve high selectivity in HDO of converting phenolic compounds to hydrocarbon [92].

Phosphide catalysts do have an impact on enhancing the catalytic activity. Zarchin et al. [93] used 25% Ni₂P/SiO₂, and 25% Ni₂P/H-Y zeolite catalysts, which was the first attempt for the HDO of soybean oil. The reaction was conducted at normal hydroprocessing operating conditions in a trickle bed reactor. Both catalysts showed high activity generally but NiP/SiO₂ is not prone to hydrocracking activity. Otherwise, Ni₂P/H-Y zeolite demonstrates high hydrocracking and isomerization activity. The physicochemical characterization of freshly prepared and used catalysts showed that by exposing the catalysts with water vapors produced during HDO, this would reduce the catalysts acidity, which ultimately reduced the hydrocracking activity of the catalysts. The oxygen removed from the soybean oil in deoxygenation was observed to reach 99.5%. Moreover, Ni₂P/H-Y zeolite is more stable at the designed operating conditions for more than 250 h and gives yield of up to 50 v% of light hydrocarbon fraction [93].

Yan et al. [94] prepared a series of high-performance Ni-based Phosphide SBA-15 supported catalysts via TPR of Nickel phosphate impregnated in mesostructure SiO₂ support. The loading of active phase was varied from 10% to 20% for Ni, while Ni/P ratios ranged from 0.5 to 3. The different active phase Ni₂P, Ni₁₂P₅, and Ni₃P ratio depend on the P/Ni proportion. All the Ni-based phosphide catalyst were investigated for HDO of methyl oleate at 30 bars and from 523 to 613 K in the continuous flow reactor. Yan et al. [94] reported that the lower contact time and reaction temperature decreased the hydrocarbon conversion but favoured the desired product, which is octadecane formation. Furthermore, this study revealed that the activity and the selectivity are affected exceptionally by the change of Ni/P ratio. The highest conversion achieved is for the catalysts Ni₂P/SBA-15, whereas the highest selectivity for C₁₈ (40% yield) is interestingly found to be for MoP/SBA-15. It was concluded that the catalyst based on metal phosphide nanoparticles are more favourable to enhance the deoxygenation properties of triglycerides [94].

Ayodele et al. [95] studied an interesting combination of bimetallic solid acid fluoride based catalysts (NiMoFO_x/Zeolite) for the hydrodeoxygenation of oleic acid to paraffin. The catalysts with added fluoride reduce the crystalline and particle size but give an increment in pore volume and pore area, which ultimately increase the surface area. Ayodele et al. [95] studied the effect of pressure, temperature and metal loading. The best-optimized conditions to produce *n*-octadecane and *iso*-octadecane are observed at 633 K, 20 bars and 100 mLH₂/min. This catalyst with 45 mL of oleic acid converted into 75% *n*-octadecane

and 23% *iso*-octadecane and it is concluded by the authors that the formation of *iso*-octadecane was due to fluoride ion participated in functionalization. Besides the activity of fluoride based catalyst, the catalysts reusability also showed the positive results with only few percent losses of activity after using it for the third time [95]. Therefore, a proper protocol for the synthesis of catalysts balancing with the organometallic precursors is needed to be further investigated on industrial scale to commercialize the HDO technology.

3.3. Active metals for HDO

Ni catalysts play an important role in the hydrogenation pathways. The selectivity and the activity of Ni-based catalyst can be enhanced with metal loading in combination with different supports. The activity and the selectivity of Ni Cu-SiO₂ catalysts with 90 wt% metal loading were studied for the hydrodeoxygenation of model compound anisole [96]. The reaction conditions were set based on the hydrotreatment parameters at 553 K and 60 bars in a batch reactor. The material composition and the methods for catalysts' synthesis had different effects on the catalytic activity. For anisole, the research group used the decomposition of metal salts with 10 wt% of SiO₂ for the NiCu-SiO₂ catalysts synthesis. The results based on the investigation on the kinetic studies as reported by Khoromova et al. [97] confirms that a certain catalytic activity in the HDO route is enhanced with the loading of the nickel content in the entire range of Ni loading over the support.

Ni is highly favourable for hydrogenation reaction, which involves model compounds or other triglycerides (TGA) containing vegetable oils. It is a popular choice of catalyst for conversion of TGA to hydrocarbon fuels. In recent years, Santillan-Jimenez et al. [98] investigated the FFA and TGA conversion to hydrocarbon fuels over Ni-Al layered double hydroxide catalysts compared with 20% Ni/Al₂O₃. Their investigation revealed that the catalytic activity are highly depended on the partial pressure of hydrogen. The flexibility of the used catalysts for regeneration was also investigated. They studied the regenerated catalysts for the conversion of FFA to HC fuels. It was concluded that these catalysts had the ability to form strong basic sites, which are favourable to catalyze the deoxygenation of lipids over regeneration [98]. Thus, it can be concluded here that the nickel based catalysts is an interesting catalyst from the HDO industrial point of view as they are inexpensive, capable of producing good hydrocarbon yield and high re-usability.

As Ni-based catalyst becomes more common in hydrogenation process, coupling it with noble metal such as Re gives better catalytic activity in aqueous-phase hydrodeoxygenation. Feng et al. [99] investigated one of the lignin model compound, 4-propylphenol for hydrodeoxygenation using Ni-Re catalysts supported with ZrO₂. The catalyst activity is enhanced in the conversion of the model compound to 4-propylcyclohexanol due to smaller size of the Ni particle in addition with Re. They successfully achieved 54% yield using this combination of the catalyst under the H₂ pressure of 40 bar at 573 K [99].

The effect of precursor and promoter play important roles in any catalytic reaction, especially in their reaction mechanisms. There are various types of promoters and active metals, which are being used in the petroleum industry for refining, HDS, and HDO. To study the effect of promoters, Horacek et al. [100] investigated the deoxygenation of rapeseed oil at 523 K and 543 K by varying the flow rates (W/F = 0.25, 0.50, 1.00 h). Ni and Co-promoted catalysts were tested, and the Ni promoted catalysts give better activity than the Co-promoted catalyst. Among these three catalysts: NiMo, CoW and NiMo, NiMo type was found to be more active as compared to CoW. It is also reported by Horacek et al. [100] that CoMo shows high selectivity for HDO reaction pathways. It is also noted that the addition of Co in NiMo type catalysts decreased the conversion without affecting the selectivity. Among the supports used: Al₂O₃, SBA-15 and SiO₂, the alumina supported NiMo was observed as the most active catalysts,

while SBA-15 supported catalysts changed the product selectivity towards more HDO product formation as compared to the ordinary SiO₂ supported catalysts [100].

Kukushikin et al. [101] studied the effects of Mo loading on the activity of the Ni-based catalyst for hydrodeoxygenation of methyl palmitate and ethyl caprate. A homologue series of catalysts like Ni-Cu/Al₂O₃, Cu-Mo/Al₂O₃, Ni-Mo/Al₂O₃, Ni-Cu-Mo/Al₂O₃ and Mo/Al₂O₃ with different ratios Ni and Mo were synthesized. The activity of these catalysts were tested at 10 bars and 573 K. It was illustrated that with the increase of Mo loading in Ni-Cu-Mo/Al₂O₃ catalysts, the *n*-alkane productivity is enhanced gradually. This increase of *n*-alkane yield was further supported by the findings made from the XPS data exhibited, which suggests the change in the ratio between variable oxidation states of Mo (0, +4 and +6) on the surface of Ni-Cu-Mo/Al₂O₃ catalysts [101].

3.4. Effect of support

Among the available supports, it has been reported that in comparison of Al₂O₃, SiO₂ and TiO₂ supports, the highest dispersion can be obtained by using Al₂O₃ [102]. In another study of HDO, Nava et al. [75] carried out HDO using olive oil over bimetallic catalysts with two different supports i.e. Co-Mo/SBA-15, Co-Mo/SBA-16, and Co-Mo/DMS-1 at 30 bar and 523 K in a down-flow fixed-bed catalytic reactor. The Co-Mo/SBA-16, Co-Mo/SBA-15 and Co-Mo/DMS-1 catalysts are more selective in removing the oxygen from the fatty acids of olive oil. It was observed that the morphology of the catalyst support affected the product distribution and the catalyst deactivation via coke formation is relatively low (1.5–2.4%). The selectivity for the hydrocarbon products is also found to decrease following this sequence: Co-Mo/SBA-15 > Co-Mo/HMS > Co-Mo/SBA-16 > Co-Mo/DMS-1. The SBA-15, SBA-16 and DMS-1 based catalysts are reported to be more significant and more efficient in deoxygenation than the HMS-supported catalyst [75]. This is further enhanced with the used of ultra mesoporous silica foam with Pd nano-particle deposition, to give highly active site on the surface of catalyst for high HDO product from the vegetable oil.

Duan et al. [48] treated sunflower oil with 5 wt% Pd/Al-SBA-15 by varying the molar ratio of Si/Al and Pd/HZSM-5. It was found that the reaction temperature and the acidity of catalysts affected the activity of the catalysts. Among these catalysts, the Pd/A-SBA-15 gives a higher catalytic activity in comparison to Si/Al. The hydrocarbon products in the range of C₁₅–C₁₈ were obtained with 72.9% yield at 523.15 K. With the increase of the temperature, no additional effect is observed and the C–C bond cracking increases due to the catalytic acidity [65]. The research was carried out using conventional alumina as active support component or carrier [48]. Similarly, another study was performed using eugenol as the model compound. The hydrocarbon conversion study was carried out over Pd/C supported with zeolite (HZSM-5). More specific studies were conducted to investigate the pattern of acidity of zeolite with varied ratio of Si/Al ratio. Zhang et al. [88] successfully determined that as the Si/Al ratio decreases, the acidity of zeolite increases and the deoxygenation of eugenol increases based on the catalytic activity during the hydrodeoxygenation process. The 2-methoxyl-4-propylphenol conversion reaches 86.5% and the hydrocarbon selectivity attained is 73.4% over the Pd/C/HZSM-5 (Si/Al = 12.5). This reaction is carried out at 50 bars and 513 K with the ratio of Si to Al in HZSM-5 (Si/Al = 50). Furthermore, the outer surface of zeolite is enlarged with pore treatment using alkali solution. The alkali treatment with zeolite enhances more acid sites for possible availability of the oxygenated compounds. Zhang et al. [88] concluded that the selectivity of hydrocarbons can be enhanced using zeolite catalysts by applying alkaline treatment and varying the Si/Al ratio [88].

The best selectivity and activity for the desired products depends on the catalysts active sites. For the synthesis of the catalysts, the support should have active metal sites for the hydrogenation and deoxygenation

reactions. Similarly, the researchers had recently focused on studying the effect of changing the support with different metal composition in order to synthesize the most active catalysts for the hydrodeoxygenation of vegetable oil. Kaewpengkrow et al. [103] studied the effect of various support with different metal compositions for the catalytic upgrading of bio-oil from jatropha wastes using Py-GCMS. The supports including Al₂O₃, ZrO₂, TiO₂ (rutile, T1) and TiO₂ (anatase, T2) in doping with transition metals (Pd, Ru or Ni) by impregnation method. The hydrocarbon yield was observed to decrease as T2 > Al₂O₃ > CA > NiCA > RuCA catalysts. It was concluded that in Al₂O₃ based catalysts, the carboxylic acids contents were reduced from 0.76% to 19.61% whereas, hydrocarbon yield increases from 42% to 64%. Among all four supports, Al₂O₃ and T₂ supports were found to be the most effective for the improvement of hydrocarbon yield with 15% decline of oxygenated components. The catalytic activities for all four catalysts suggested that high surface area enhances a better catalyst activity with adversely enhanced the nitrogenous compounds. Therefore, it is highly recommended by Kaewpengkrow et al. [103] to use these catalysts for better activity in hydrocracking and pyrolytic activity of various hydroprocessing feedstocks.

The SAPO types support also play an important role in selectivity of hydroconversion more specifically on cracking the long chain hydrocarbon into branched alkanes. Liu et al. [104] studied hydrodeoxygenation of palm oil using SAPO-11 type catalysts. The Ni/SAPO-11 catalysts were synthesized via incipient wet impregnation method with different metal loading of Ni as active metal. SAPO-11 was synthesized via hydrothermal method with large surface area and mesoporosity. The HDO of palm oil was performed to study the reaction pathways between HDO and decarbonylation via carboxylic acid as the intermediate formation. The moderate acidity of synthesized Ni/SAPO-11 catalysts shows a gradual decrease in cracking of primary long alkane chain and produced 70% yield of liquid alkanes. Similarly, the isomerization and selectivity of products were found to be less than 80% [104].

Sustainable and clean fuel production become the most desirable product of biorefineries. To produce environmentally friendly fuel, the researchers are motivated to develop the catalysts' synthetic methods for effective activity and selectivity to remove the oxygenated contents from oxygenates containing in biomass-derived feedstocks, cellulose and triglycerides. The HDS catalysts are commercially available and used in petroleum refineries. These catalysts play an important role in biorefineries too. The catalysts are also investigated for the co-hydroprocessing of heavy vacuum gas oil and waste cooking oil. The most common industrial catalysts supports such as SiO₂, Al₂O₃ and TiO₂ are commonly used for hydrodeoxygenation and hydrodesulphurization of various petroleum distillate fractions. Kubicka et al. [45] reported the hydrodeoxygenation of rapeseed oil by using these three most common catalysts support to study the effect of support for the selectivity and production of green diesel. Ni-Mo was used at 35 bars, between 533 and 573 K with LHSV in the range of 2–8 h^{−1}. From the findings of their comparative studies, it was found that the dispersion of active phase is in decreasing order of SiO₂ > Al₂O₃ > TiO₂. The SiO₂ supported catalysts achieve to an extent of HDO reaction and favouring towards decarboxylation. Furthermore, the TiO₂ supported catalysts exhibit high selectivity towards HDO products, probably due to high active phase and cluster size, widely pore size distribution. Kubicka et al. [45] additionally reported that the conventional HDO catalysts inactive phase is more selective since the catalysts are fine-tuned by the selection of support and modification of the active metals loading [45]. Hence, it is essential to select the right support for high selectivity and high yield of diesel.

It is well known that the acidity of support plays an important role for the deoxygenation of the oxygenated compounds. In addition, the acidity of catalysts can be improved with the addition of some mineral or organic acids as the additives. This increment of acidity also intensifies the active sites and ultimately affects the conversion with

high selectivity. Ayodele et al. [105] studied the effect of the addition of oxalic acid in NiO supported with alumina for HDO using model compound oleic acid. Ayodele and the team prepared the nickel II oxalate (NiO_x) complex incorporated with alumina support to synthesize the nickel oxalate ($\text{NiO}_x/\text{Al}_2\text{O}_3$) catalysts. The catalytic activity was studied at 633 K, 20 bars, and with the catalyst wt% of 30 mg loading and H_2 flow rate 100 mL/min. It was found that a mixture of 21% *iso*-octadecane and 72% *n*-octadecane can be produced. The presence of isomerized product like *i*- C_{18} was attributed to the oxalic acid functionalization, which ultimately increases the acidity of the synthesized $\text{NiO}_x/\text{Al}_2\text{O}_3$ catalysts. The research team also studied the reusability and regeneration of synthesized catalyst that showed a consistent conversion of oleic acid's HDO after 5 runs and it was further suggested that these catalysts are promising and need further investigation for future commercialization [105].

Zeolites are the minerals mostly of hydrated aluminosilicate, chemically composed of aluminum tetrahydrate and silica. In the result of sedimentation of volcanic material, zeolite forms a variety of crystalline structures with wide cavities, regular shapes and arrangement of the same size of small molecules. There are about 40 natural occurring zeolites in the world. According to the US geological survey report, the most common types of zeolite are clinoptilolite, and chabazite. Moreover, the researchers are now able to synthesize a variety of zeolites artificially. About 150 zeolites had been artificially synthesized for different purposes such as zeolite A, Zeolite X and Y, and Zeolite ZSM-5. Among these type of zeolites, Zeolite X and Y are commonly used in catalytic cracking and ZSM-5 is used in petroleum industry. In the petroleum industry, zeolites crack the long chain hydrocarbons into gasoline, kerosene, diesel and waxes and all other types of by-products of petroleum distillate. The porous structure of zeolites is more important due to high reactivity for hydrocracking reactions. Many pores in a zeolite structure are like millions of tiny test tubes. These pores provide the surface to the reacting molecules to allow for the reaction to take place. However, since the pores in zeolite are of fixed sized and shape, these particular zeolites can work selectively for certain reactions and reusable again and again.

Nowadays, the zeolite is also highly used in biorefineries for conversion of triglycerides into hydrocarbons. Three types of zeolites support (Meso-Y, SAPO-34, and HY) had been investigated by Li et al. [106] to convert the waste cooking oil (WCO) into gasoline products. The high jet range alkanes selectivity of 53% and jet fuel range aromatic hydrocarbon selectivity of 13.4% were obtained during the experiment using mesoporous Y zeolite. Li et al. optimized the reaction temperature at 673 K to test the jet fuel quality, and meso Y zeolite exhibits a high gasoline range of alkane with the production yield of 40.5% and low gasoline range aromatic hydrocarbons with the production of 11.3% from WCO. The reaction mechanism proposed by Li et al. suggested that the reaction pathway for WCO to heptadecane undergoes deoxygenation route, and pentadecane via decarbonylation for the first 3 h. It was further reported that the long chain hydrocarbon cracked into gasoline products ($\text{C}_8\text{--C}_{16}$), while cycloalkanes and aromatic compounds are produced via hydrogenation and cyclization routes [106].

As the hydrodeoxygenation process for vegetable oil has been well developed, research nowadays also focuses towards gasoline production to reduce the cost of jet fuel. The gasoline range hydrocarbons can be produced by the hydrocracking of vegetable oils in the presence of hydrocracking catalysts like zeolites. As zeolites range are wide, Verma et al. [55] introduced the hydroprocessing of jatropha oil using bimetallic NiMo and NiW supported on hierarchical mesoporous SAPO-11. The HDO was conducted at optimal conditions (648–723 K, 60–80 bars and WHSV 1 h^{-1}) in a fixed bed reactor. Under these conditions, Verma and team reported the yield to be 84 wt% of liquid hydrocarbon while 40 wt% is kerosene and 20 wt% lighter gasoline. It is illustrated from their work that with the variation of silica contents in support SAPO-11, there is no any significance change

among the catalysts on HDO of jatropha oil. In addition, the catalysts did not show any noticeable deactivation for continuous 6 days. The diesel fractions are obtained with desirable viscosity, density as well as sulphur contents. One of the interesting phenomena that was reported is that production of the aromatic compounds up to 8%. This formation of aromatic contents is due to the unexpected aromatization reaction over hydrocracking catalysts. The aromatization reaction reduced the hydrogen consumption for up to 10%, which is a significant reaction route for HDO process [55].

Correspondingly, a series of Pt/SAPO-31 catalysts were tested for HDO of sunflower by Simrnova et al. [107] recently. The catalysts were synthesized via wet impregnation method with variation in calcination temperature from 523 to 923 K. It was identified that the calcination temperature also affects the product distribution. The high yield of *iso*-alkane can be produced over the catalysts which are calcined at 723–823 K. It was also noticed that the decrease in calcination temperature reduce the *iso*-alkane production [107].

The reduction temperature for various catalysts also plays an important role in producing desirable products in various applications. Likewise in hydrodeoxygenation, the reduction temperature affects the product distribution as well as high yield of hydrocarbons. Recently, Chen et al. [108] developed commercial metal and non-sulphided catalysts to study the effect of reduction temperature on the deoxygenation process. They prepared the Ni and Mo-based bimetallic catalysts supported with SAPO-11. The catalysts' activity was studied after reducing them at various temperatures (673–823 K). The same study was also performed with sulphided catalysts NiMo/SAPO-11, NiO/SAPO-11 and $\text{MoO}_3/\text{SAPO-11}$. It was demonstrated by Chen et al. [108] that the reduction temperature has a great influence on isomerization and deoxygenation activity, as well as the reaction pathways. The catalysts which are reduced at lower temperature exhibit lower deoxygenation activity but has high isomerization selectivity. The catalysts which are reduced at higher temperature give high activity than the sulphided catalysts, which are also reduced at similar temperature. It was further reported that by increasing the reduction temperature, it will lower down the isomerization selectivity. This high isomerization selectivity and high activity can be ascribed due to the increase in the density of Mo^{4+} and Mo^{5+} on the surface of catalysts. In addition to the reaction pathways, the catalysts which are reduced at 673 K give a high decarbonylation selectivity. From their studies, a synergetic effect of Ni and Mo species is responsible for high selectivity in HDO over the reduced catalysts at high temperature [108].

SAPO-11 type of catalysts usually show relatively low hydrothermal stability in HDO of vegetable oils due to the water vapors produced during the process. Rabaev et al. [109] investigated the reason for this low hydrothermal stability of Pt/SAPO-11– Al_2O_3 catalysts during HDO process. The instability was investigated with various physicochemical characterization results such as XRD, NH_3 TPD, TPO, H_2 -TPR HRTEM, and chemisorption and MAS and NMR. It was found that the hydrothermal deactivation of SAPO-11 is resulted partially from the reversible desilication of the SAPO-11 framework, which causes the gradual loss of catalytic activity and loss of acidity in deoxygenation of paraffin products. The addition of additives enhances the hydrothermal stability of supports as reported by Rabaev et al. [109]. They added the amines of surfactant hexadecyl amine to SAPO-11 crystallization gel at HAD/ Al_2O_3 with the ratio of 0.6 that significantly increases the hydrothermal stability of SAPO-11 [109].

The solvent used in HDO as the carrier is also found to be responsible for the deactivation of catalysts, and hence the researchers are focusing to develop highly active catalysts that can be used for hydrodeoxygenation of various feedstock without any utilization of solvents. Hengst et al. [110] reported on the gaseous phase deoxygenation of oleic acid over 1% Pd/ Al_2O_3 in solvent-free conditions. Three different types of aluminum oxides were prepared in aluminum oxide phases. Hengst et al. [110] tested all the catalysts using the best composition for deoxygenation of oleic acid. Among the all types of

alumina, boehmites were found to be the best suitable precursor. In addition, zeolites were also added to enhance the acidity of the catalysts. Under the optimized reaction conditions, all the composites of zeolite catalysts were screened [110]. It is a general trend of using vegetable oil for hydroprocessing without the solvent in a batch reactor. However, the viscosity of vegetable oil is too high such that it resists to flow in a continuous flow reactor. Therefore, the choice of solvent depends on the polarity and boiling point of solvent that should be easily separated from the end products.

4. Model compounds

Furthermost the research works for hydrodeoxygenation were carried out using model compounds to develop certain approaches to understand the kinetics of single step reaction in a reactor [111]. The model compounds such as decanoic acid [112], oleic acid [105,113–119], palmitic acid [120], stearic acid [121], and linoleic acid [122] have been tested for hydrodeoxygenation. However, the detail mechanism study of model compounds helps researchers to understand the reaction kinetics. Snare et al. [123] used oleic acid, linoleic acid (unsaturated fatty acid) and the monounsaturated fatty acid ester, methyl oleate as the model compounds of vegetable oil for HDO using Pd/C 5 wt% catalyst between 15 and 27 bars and 573–633 K for 6 h in a semi-batch reactor. They observed a high selectivity and high yield towards the hydrocarbon conversion. The pure fatty acids such as methyl palmitate and methyl heptanoate were also used as the model compound for hydrodeoxygenation by Deliy et al. [124]. These feedstock were tested over Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ at 35 bars, and 573 K for 6 h in a fixed bed catalytic reactor. The Ni-Mo/ γ -Al₂O₃ demonstrates the highest conversion and selectivity for C₁₆ hydrocarbons. Another study using model compound was performed by Santillan et al. [98], who reported an average achievement of hydrocarbon conversion [98]. The components of vegetable oil were used as the model compounds, such as stearic acid (97%) and tristearins (95%) in the presence of 20% Ni/Al₂O₃. The experiments were carried out between 10 to 40 bar and 623.15 K in a stainless steel auto-clave operated reactor using a semi-batch mode. The conversion of model compounds to diesel range hydrocarbons was intermediated by fatty acids, aldehyde and/or fatty acid ester were observed as reaction intermediates. These intermediates helps to propose the reaction mechanism of complete deoxygenation pathway. The carboxylic acid is a major functional group of fatty acids, this functional group consequently undergoes hydrogenolysis, decarbonylation/decarboxylation and deoxygenation reaction paths. Badari and his co-workers [125] studied the effect of catalytic hydrodeoxygenation on acetic acid and propylamine. They used Acetic Acid (AA) and Propylamine (PA) as model compounds in the presence of catalysts such as Ni₂P/Silica, Ni/SiO₂ and Ni₂In/Silica for HDO. The pressure was kept at 21 bar within the temperature range of 473.15–673.15 K in a microreactor. It was found that the maximum conversion reached 99% [125]. Table 3 summarized the HDO reaction of some model compounds tested over the commercial and synthesized catalysts.

Madsen et al. [126] treated oleic acid (free fatty acid) and tripalmitin (triglyceride) with the molar ratio of 1:3 over 5 wt% Pt/ γ -Al₂O₃ at the temperature range of 523.15–598.15 K. The deoxygenation is followed by the decarboxylation. By comparing two catalysts, Pd/ γ -Al₂O₃, and Ni/ γ -Al₂O₃, the Pd/ γ -Al₂O₃ is found to be more active than Ni/ γ -Al₂O₃. The hydrocarbon conversion depends on the reaction temperature, of which C₁₅–C₁₈ can be obtained at 598.15 K. Almost 80% of overall products formed is C₁₈ at 10 bar H₂ pressure. The conversion of tripalmitin is hindered by the formation of palmitic acid as the intermediates. The main difference that affects the catalytic activity of both reactants is resulted from the difference in molecular sizes and diffusivity of reactants [126]. Simakova et al. [127] conducted the deoxygenation of stearic, linoleic and oleic acids over mesoporous Pd supported on carbide (Pd/C) at 573.15 K. The deoxygenation step is

followed by decarboxylation rather than HDO. The products obtained are found to be of diesel range hydrocarbon fuel (C₁₅–C₁₈). The hydrocarbons obtained from the stearic acid are in the range of C₁₇, while in the case of oleic and linoleic acids, C₁₇ with aromatic hydrocarbons are favoured. The difference of product distribution in the different model compound indicated that the catalytic activity depends upon the degree of unsaturation in the feedstock. The catalysts deactivation occurred, as a results of aromatic compounds formation in the product stream. Meanwhile, *n*-heptadecane is the major product from the HDO reaction using a mixture of stearic acid, C₁₈ isomers and fatty acids [127]. Lestari et al. [128] performed the deoxygenation of palmitic acid and stearic acid using 4 wt% Pd/mesoporous carbide catalysts at 573.15 K and 17 bar H₂ pressure. C₁₅ and C₁₇ are the dominant products for palmitic acid and stearic acid, respectively. The product formation follows the decarboxylation route and it is independent of the carbon chain of model compounds or feedstock [128]. Rozmysłowicz et al. [129] extended their research for the deoxygenation of tall oil with the same catalysts. Straight chain hydrocarbon was produced with C₁₇ with high selectivity approaching 95% [129]. They further extended their work for different support i.e. SBA-15 supported by Pd and tested its activity for the deoxygenation of stearic acids at the same reaction conditions. The large surface area and highly ordered structure of SBA-15 favoured for the hydrocarbon conversion. At different wt%, the Pd shows high activity with 3 wt% Pd/SBA-15 with 90% C₁₇ selectivity [130]. The deoxygenation of methyl oleate to diesel range hydrocarbon over Pd/SBA-15 was performed by Lee et al. [131]. Several parameters including temperature, hydrogen pressure and reaction time were manipulated in a stirred batch reactor over Pd/SBA-15 catalysts. Two different Pd/SBA-15 morphologies i.e. sphere-like and necklacelike structures were tested. It was found that the Pd dispersion on necklacelike SBA-15 gives better activity than that of spherelike SBA-15. Notably, higher Pd dispersion on necklacelike SBA-15 provides significant deoxygenation efficiency as compared to Pd/SBA-15-spherelike. The results showed that H₂ pressures greatly determine the total ester conversion and selectivity to C₁₅–C₁₈ aliphatic hydrocarbons. Total ester conversions with 55% selectivity to *n*-heptadecane is achieved using Pd/SBA-15-necklace like at 543 K, 60 bar H₂ pressure and 6 h reaction time. The gas phase analysis reveals that the formation of C₁₇ is generated via indirect decarbonylation when the reaction time is prolonged. Pd/SBA-15-necklacelike catalyst exhibits good catalytic activity with high selectivity towards diesel like aliphatic hydrocarbons (C₁₅–C₁₈). The physicochemical properties of the Pd supported on different SBA-15 morphologies influence the deoxygenation activity of the catalysts [131].

5. Co-hydroprocessing of triglycerides

The co-processing of crude vegetable oils or their derivatives with a range of gas oils, which are considered as co-hydroprocessing of vegetable oil is shown in Table 4. One of the major problems that was observed by many researchers [11] is, when only pure vegetable oils are fed to the catalytic reactors at high LHSV, waxes are formed by the heat distortion temperature (HDT) effect, and hence, these oils and fats caused reactor plugging. Thus, it is imperative to introduce another type of oil from straight chain hydrocarbon that can reduce this effect. Another reason to use the co-hydroprocessing technology is to make the possible use of existing infrastructure in refineries for the simultaneous hydrodesulphurization (HDS) and hydrodeoxygenation (HDO) [132,133]. The hydro co-processing is a method that is used to improve the yield of hydrocarbon and it was introduced by Mikulec et al. [134]. They carried out various experiments on vegetable oil and gas oil. Mikulec et al. used 6.5% (vol.) vegetable oil and atmospheric gas oil containing (5–5.5%) of biocomponents in the presence of Ni-Mo/Al₂O₃ and Ni-W/Al₂O₃ at 35–55 bars and 593–633 K in a flow tubular reactor. The reaction showed an increase in the selectivity for the hydrodeoxygenation products. Similar experiment was also carried out

Table 3
Few examples on studies of hydrodeoxygenation of different model compounds.

S. No.	Feed	Catalyst	Press. (bars)	Temp. (K)	Time (h)	Reactor	Remarks	Ref
1.	6.5% TAG	Commercial NiMo, NiW	35–55	593.15–633.15	*LHSV = 1 h ⁻¹	autoclave	good yields of fuel-like hydrocarbons	[134]
2.	Triglycerides and fatty acids	Ni–Al double layered hydroxide catalyst and over 20% Ni/Al ₂ O ₃	40	628.15 ± 278.15	6 h			[124]
3.	Propylamine (PA) and acetic acid (AA),	Ni ₂ P/silica, Ni/SiO ₂ , Ni ₂ In/silica	21	573.15–673.15	**WHSV = 1.0 h ⁻¹	microreactor.	99% conversion	[98]
4.	Methyl palmitate and methyl heptanoate	CoMo/Al ₂ O ₃ and NiMo/Al ₂ O ₃	35	573	6	Fixed bed reactor	Highest conversion with selectivity C ₁₆	[125]
5.	Stearic acid and palmitic acid	Pd/Mesoporous C	10	633	**WHSV = 0.45 h ⁻¹			[123]
6.	Stearic and palmitic acid	4% Pd/C mesoporous	17, 5% H ₂ in Ar	573	573			[128]
7.	Guaiacol and woody tar	Ni/SiO ₂ , Co/SiO ₂ , Pt/SiO ₂ , Pd/SiO ₂ , conventional sulphided CoMo/Al ₂ O ₃	10–50 bar	573.15–623.15		batch reactor	65.5% conversion	[129]
8.	Phenol	Reduced and sulfide Co–Mo, Ni–Mo, Ni–W/γ-Al ₂ O ₃ and TiO ₂	15	623	2.5 h ⁻¹			[57]
9.	Methyl palmitate and ethyl caprate	Ni–Cu/Al ₂ O ₃ , Ni–Mo/Al ₂ O ₃ , Cu–Mo/Al ₂ O ₃ , Mo/Al ₂ O ₃ , Ni–Cu–Mo/Al ₂ O ₃ , Ni/Mo	10	573.15	*LHSV 3 h ⁻¹	fixed-bed reactor	Ni–Cu showed 90% conversion	[101]
10.	Furfuryl alcohol	HZSM-5 (Si/Al = 25) Raney Ni	40	373.15		Autoclave	58.9% selectivity of (MFE) and 44.8% selectivity of (EPE)	[53]
11.	Guaiacol	Ni ₂ P/SiO ₂	1–8	523–573	*LHSV of 2.0 h ⁻¹	continuous flow fixed-bed	90% conversion product	[88]
12.	Anisole	Ni–Cu–SiO ₂	60	553.15		batch reactor		[97]
13.	4-propylphenol	Re–Ni/ZrO ₂	40	573.15		Batch reactor	<i>n</i> -propylbenzene reached 54%	[99]
14.	Atmospheric guaiacol	Ni ₂ P/SiO ₂ , Ni _{1.2} P ₅ /SiO ₂	Atmospheric Pressure	573.15		continuous fixed-bed	Guaiacol conversion (78%)	[89]
15.	Methyl laurate	Ni ₂ P on SiO ₂ , CeO ₂ , TiO ₂ and SAPO-11, Ni ₃ P and Ni _{1.2} P ₅ were formed on γ-Al ₂ O ₃ , Ni _{1.2} P ₅ , Ni ₂ P on HY.	30	573–613	*WHSV 10 h ⁻¹	fixed-bed reactor	Ni ₂ P/SiO ₂ showed highest conversion and selectivity	[90]
16.	Phenol	Titania-supported molybdenum carbide, nitride, phosphide and oxide	25	623.15		fixed-bed reactor	highest activity, 15 wt% Mo ₂ C/TiO ₂	[92]
17.	<i>n</i> -butanal, acetic acid and phenol	(Ru/C, Pt/C, SO ₄ ZrO ₂ /SBA-15	40	423.15		batch reactor	100% conversion	[108]
18.	Oleic acid	fluoride ion functionalized nickel oxalate supported on molybdenum modified zeolite (NiMoFOX/Zeolite)	20	633.15			75% and 23% <i>n</i> -C ₁₈ and <i>i</i> -C ₁₈ respectively	[95]
19.	Decanoic acid	Mo/Al ₂ O ₃ CoMo/Al ₂ O ₃ and NiMo/Al ₂ O ₃ sulfided	40	613.15		fixed-bed reactor	Conversion (%) 46.2	[112]

* LHSV: Liquid Hour Space Velocity.

** WHSV: Weight Hour Space Velocity.

Table 4
Few examples on studies of co-hydroprocess of various sources of triglycerides and vacuumed gas oil.

S. No.	Feed	Catalyst	Press. (bars)	Temp. (K)	Time (h)	Reactor	Remarks	Ref
1.	Cotton seed oil in petroleum diesel	Sulphidized Co-Mo/Al ₂ O ₃	30	578–618 K	*WHSV = 5–25 h ⁻¹	Trickle bed reactor	Catalysts deactivation was followed for a period of 450 h in operation	[135]
2.	heavy atmospheric gas oil (HAGO) and waste cooking oil (WCO).	Co-Mo/Al ₂ O ₃ , Ni-Mo/Al ₂ O ₃	56	603.15–623.15, 643.15	*LHSV=1 h ⁻¹	fixed-bed continuous flow reactor	High selectivity with high hydrocarbon conversion	[139]
3.	6.5 wt% vegetable oil + gas oil	Ni-Mo/Al ₂ O ₃ , NiW/Al ₂ O ₃	35–55	593.15–633.15	*LHSV = 1 h ⁻¹	tubular reactor	The catalysts stable for long time.	[143]
4.	Mixtures of sunflower oil and a straight gas oil	sulphidized NiO(3%)MoO ₃ (1.2%)–γ-Al ₂ O ₃ incorporating 0, 15 or 30 wt% zeolite beta	30–60	593.15–623.15	*WHSV=1–4 h ⁻¹	fixed bed reactor	100% conversion VGO oil into hydrocarbons	[78]
5.	gas oil (1.0%) and vegetable oil Different oil contents (0, 5, 15, 25% and 100%).	Ni-Mo/Al ₂ O ₃	60–80	573.15–653.15	*LHSV = 1.0 h ⁻¹	Fixed bed reactor	an increased <i>n</i> - and <i>i</i> -paraffin content	[141]
6.	Waste cooking oil, trapped grease	Ni-Mo, NiW, Co-Mo/Al ₂ O ₃	70	576.15–896.15	*LHSV=3 h ⁻¹	batch reactor and a fixed bed flow reactor	NiW catalyst showed decarboxylation or decarbonylation activity than NiMo and CoMo catalysts	[57]

* LHSV: Liquid Hour Space Velocity.

** WHSV: Weight Hour Space Velocity.

by Sebos et al. [135], of which the research group performed HDO using co-processing of cotton seed oil in petroleum diesel. They treated the mixture for sulphided Co-Mo/Al₂O₃ at 30 bars between 578 and 618 K with WHSV=5–25 h⁻¹ in an isothermal, laboratory bench-scale trickle-bed reactor. They observed the conversion of triglycerides reaches nearly 100%. Another study was performed by Walendziewski et al. [136] by using 10 and 20 wt% rapeseed oil in diesel oil for HDO via co-processing in the presence of Ni-Mo/Al₂O₃ at 30 and 50 bars between 573 and 653 K with LHSV=2 h⁻¹ in a fixed bed reactor. A low yield of gaseous products can also be observed.

Similarly, Huber et al. [18,137,138] experimented HDO by co-processing of sunflower oil and heavy vacuum oil (HVO) mixtures. The reaction was carried out in the presence of Ni-Mo/Al₂O₃ at 50 bars and 573–723 K in a tubular reactor. They observed the selectivity for hydrodeoxygenation products increases under certain reaction conditions. Another co-processing experiment was carried out by Bezergianni et al. [139]. They conducted HDO by using heavy atmospheric gas oil (HAGO) and waste cooking oil (WCO). The active catalysts like Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ were used at 56 bars, at three different temperatures (603 K, 623 K and 643 K) in a fixed bed continuous flow reactor. It was extensively studied that Ni-Mo type catalysts were found to be more suitable for HDO under suitable reaction conditions [139].

Berzergianni et al. [139] investigated the activity of HDS catalysts such as CoMo and NiMo supported with Alumina. The researchers compared the selectivity and effectiveness of commercial catalysts CoMo/Al₂O₃ and NiMo/Al₂O₃ for clean diesel fuel quality. The catalysts were tested for different concentration of HAGO and WCO mixtures ranging from (0–30% v/v) at three different temperature (603, 623 and 643 K) and 81.2 bar, 1 h⁻¹ LHSV with 505.9 mL/L H₂/Oil ratio. Their findings suggested that HDS productivity can be different for both catalysts and primarily depends on the reaction temperature as well as WCO and HAGO ratio. The addition of WCO does not affect the HDS efficiency for NiMo/γ-Al₂O₃ but it is not the case for CoMo/γ-Al₂O₃. The co-hydroprocessing of WCO with HAGO shows favourable compatibility for diesel range hydrocarbon and saturation of feedstocks for both HDS catalysts. In comparison to NiMo/γ-Al₂O₃, an addition of HAGO affects strongly the deactivation rate of CoMo/γ-Al₂O₃. Conclusively, it is evident that NiMo type catalysts are more suitable for co-hydroprocessing of HAGO and vegetable oils containing lipids and triglycerides [139].

Toth et al. [140] aimed to produce the hydrocarbon fuel in diesel range by the hydrodeoxygenation of mixture of gas oil and sunflower oil. It was observed that the product with less aromatic and fewer sulphur contents are producible at 80 bars and 634.15 K, with LHSV of 1.0 h⁻¹ and hydrogen/feedstock ratio = 600 Nm³/m³ on varied vegetable oil contents (0–15 wt%). The 15 wt% vegetable oil gives the highest cetane number. Similarly, the isomerization properties of the products are enhanced at low temperature [140]. The research group extended its investigation to the co-hydrogenation of sunflower with different oil contents and the mixture of gas oil with high sulphur contents [141]. The co-hydrogenation process was performed over sulphided Ni-Mo/Al₂O₃ between 573.15 and 653.15 K and the pressure 60–80 bar. Ni-Mo/Al₂O₃ was found to be an effective catalyst for the conversion of vegetable oil and upgrading of gas oil to diesel range hydrocarbon. About 95% of the hydrocarbon yield was obtained with low sulphur and aromatic contents at the temperature of 633.15–653.15 K, 80 bars pressure with 1.0 h⁻¹ LHSV and feed ratio of (H₂/gas oil) 600 Nm³/m³ with up to 15% vegetable oil [141]. Nonetheless, the upgraded gas oil showed poor low-temperature properties but this can be improved by using additives. As the amount of vegetable oil increases up to 41.5%, the desulphurization decreases. The product shows good ignition and emission properties due to the increasing of *n*-alkane and *iso*-alkane ratio [141]. Overall investigation for hydroprocessing and co-hydroprocessing of vegetable oil blended with vacuum gas oil (VGO) to date had showed many significant results for the

hydroconversion studies. Nevertheless, there are still various parameters, which can be studied to optimize the process of co-hydroprocessing and the effect of blended form of VGO and vegetable oil.

5.1. Merits and demerits

Nowadays, worldwide researchers aimed to produce environmentally friendly and green fuel application in transportation sector specifically. In conjunction to that, the biofuels industry becomes an emerging fuel technology and many researches had focused on several types of biofuel such as biodiesel, bioethanol, biogas, and biohydrogen. Among these biofuels, the biodiesel has been found to be more efficient diesel fuel for the transportation sector. Nonetheless, the paraffin or hydrocarbon produced by the hydrodeoxygenation of biomass feedstock has various advantages over biodiesel for application in transportation industries [142]. Compared to biodiesel, the hydrocarbon fuels are more suitable to be used in transportation sector due to their cold flow properties. Hydrocarbon fuels possess high cetane number as compared to biodiesel and conventional mineral fuels [135]. Additionally, hydrocarbon fuel production via HDO requires low capital cost and low operating costs. The main by-product of HDO is propane, which is a value added product as compared to glycerol formed as the by-product during the production of biodiesel [143]. This petroleum based fuel possess low heating values due to less exothermic ignition of oxygenated compounds [144,145]. The hydrocarbon fuel also has good blending properties due to the deficiency of oxygen contents and unsaturation in its final product [146]. The complete removal of oxygen from oil or other feedstock leads the hydrocarbon towards high lubricity and due to this property, bio-paraffin products have high oxidative stability and good blending properties as compared to biodiesel. The reported work shows that the bio-paraffin is less aromatic and lower sulphur contents than the biodiesel [138,143,147,148]. Furthermore, the bio-paraffin produced from the hydrodeoxygenation of biomass can contribute mainly in aviation industries via hydrocracking of biomass to biogasoline. Nowadays, the hydroprocessing of vegetable oil containing high fatty acids emerges to become prominent technology for hydrocarbon base biofuel. The excessive use of biofuel worldwide is forecasted from 2011 to 2021, suggesting that the biofuel production will be doubled by 2021 [25].

However, from the previous studies on the triglycerides hydroprocessing, considerable analysis must be made with respect to the economic point of view. Regardless of the kinetics and the reaction mechanisms, the dominant results have been found in the formation of *n*-alkanes with saturated hydrocarbons [11,25]. Although *n*-alkanes are attractive desirable products, there are needs for extensive research works that should focus on the mechanism and upgrading fuel properties like cold flow, and cetane properties. This area should be looked into as it is essential to maximize the diesel volume production without any significant compromise on its properties. Additionally, it would be good for the researchers to put their efforts to focus on optimizing the catalytic isomerization and dewaxing of long chain hydrocarbon products obtained during triglycerides hydrodeoxygenation [149]. The main research areas need to focus on improving isomerization catalysts development and the optimization of the process. The dewaxing catalysts should have sufficient acidity to be executed for isomerization activity. However, this should be done by minimizing the cracking activity for high yield of distillate hydrocarbon. From the economic and environmental point of view, there is a need to minimize the hydrogen consumption during the process. It is essential to find alternative ways to minimize the hydrogen consumption for example to use hydrogen donor solvents. This is important as currently, the consumption of hydrogen in HDO route is higher than decarboxylation route. However, the total hydrogen consumption by decarboxylation route could indirectly be higher than the HDO route, since hydrogen is also consumed over secondary reaction for example water gas shift for methanation [150].

The other major problem arises when there is a drop of the desired product pertaining to decarboxylation route. Hydrogen feeding is needed via improved mechanism, process conditions and developed catalysts. More studies needed on expanding the HDO process technology to minimize unnecessary hydrogen feeding [137,150]. Ideally, it is one of the looked forward strategy to co-hydroprocessing the triglycerides with petroleum based fractions in the existing refinery unit. Therefore, a dedicated study must be carried out to understand the effects of triglycerides on the processing of petroleum fraction using the existing refinery unit. Nevertheless, some of the critical analyses revealed that there are no reverse effects for HDS reaction with vacuum gas oil and diesel over solid acid catalysts [18,150]. From this critical review, it would be therefore beneficial to the researchers to expand their studies on understanding the effects of TGA on hydroprocessing of petroleum fractions over solid acid catalysts [11].

6. Recent trends and prospective

It is obvious that the extensive used of edible oil will lead towards food crises. Therefore, alternative sources are required to use non-edible vegetable oils such as castor oil, pongamia oil, nag cham pa oil, jatropha oil and rubber seed oil. Nevertheless, the demand for non-edible oil food crop can lead to the deforestation activity, which ultimately affects the food chain. Interestingly, many non-edible crops can grow in infertile soil with fewer supplies of water and fertilizer [25].

The trend in hydroprocessing mainly hydrodeoxygenation has put forward with many patents applications. Brady et al. [151] treated for soybean oils, rapeseed oil, sewage sludge, fish oil, corn oil and canola oil etc. [151]. Marker et al. [152] studied the used of catalysts system which has the capability to tolerate water and regeneration of hydrogen [152]. Herskowitz et al. [153] experimented for *n*-paraffins (C₁₄–C₁₈) with very less aromatic contents produced from animal fats and vegetable oil [153]. Myllyoja et al. [154–157] produced the hydrocarbon with isomerization in diesel range using different methods. Myllyoja and colleagues acquired many patents in the field of hydroprocessing technology. The demand of total fuel consumption for global jet fuel and diesel fuel has increased up to 5–6 million barrels per day for which ENi.S.P.A and UOPLLC72 had been producing diesel range hydrocarbon from hydrotreating of fatty acids [154–157]. The Neste Oil and NexBTL are in the process of constructing a pilot plant for hydrotreatment of vegetable and waste oil for renewable fuel production with less carbon cycle between 40% and 80% [154]. Moreover, Singapore aimed to produce 800,000 renewable types of diesel per year from edible oil (Palm oil) [25]. In the USA, Valero used the animal fats and waste cooking oil for biofuel generation in collaboration with their partner Darling International [158]. Similarly, Boeing and his colleagues worked on the pilot scale to produce hydrocarbon fuels from Jatropha and camelina oil for the aviation industry [157]. The main concern of renewable fuel production is related to the availability of the vegetable oil. In present circumstances, global vegetable oil production is not enough to utilize the renewable fuel. The sum of global vegetable oils production is about 143.15 million ton, in which the global palm oil production is about 33.6% of the total oil. Presently, the demand for palm oil production has been enhanced due to its better efficiency in renewable fuel production as compared to the soybean oil, which possesses high amount of trans-fatty acids [98,159].

The process of hydrodeoxygenation of vegetable oil is eminent and well developed. However, there are some gaps need to be filled by selecting suitable and the best catalysts, inexpensive feedstock, and studies of detailed reaction mechanism. Researchers are more focused to study the behaviour of catalysts with different vegetable oil as well as model compounds. In addition to that, the reaction mechanisms have only been studied for model compounds, and there is a need to study the detailed intermediates produced, the reaction pathways to develop this process and to bring it up for commercialization.

7. Conclusion

Many interesting information have been dissected, elucidated and put forward from previous studies on hydrotreatment of vegetable oil and model compounds. The investigation on the hydrotreatment in recent years specified the potential suitability of several feedstocks, which are inexpensive with most appropriate catalysts. These studies put a concerted effort to investigate the type of active metals, the catalysts support, the promoters, and the additives to enhance the catalytic activity for the hydrodeoxygenation process. The corresponding catalytic activity, conversion, yield and selectivity for diesel range hydrocarbons with *iso*-paraffins over mostly Ni-Mo based catalysts have been summarized. A numbers of factors and parameters had been identified to improve the overall hydrodeoxygenation process. The physicochemical properties of feedstock is identified as a key factor for certain reaction conditions. The vegetable oil with low unsaturation and more free fatty acids are more suitable for the hydrotreatment. Low H₂ consumption is required in obtaining high yield and selectivity for diesel range hydrocarbons over the deoxygenation of fatty acids. The catalysts with acidic support such as Al₂O₃ and zeolite are highly favoured for the deoxygenation and hydrocracking respectively. Since the beginning of this technology, the hydrodesulphurization catalysts had been modified with different precursors, promoters and additives to enhance the activity as well as the selectivity of the catalysts. However, an extensive consideration is needed to establish in depth the reaction mechanism on the active sites of catalysts. Similarly, the metals incorporated with moderate acidic support with high metal dispersion and small particle size are suggested for deoxygenation of fatty acids and triglycerides to achieve high selectivity. This can be achieved by using noble metal catalysts over mesoporous support. However, the catalyst based on noble metals are expensive and unattractive in comparison to the commercial catalysts. Based on this critical evaluation, the research should focus on the modification of the commercial catalysts to enhance the catalytic activity as a substitute of these expensive noble metals.

Certain gaps had been surfaced out and need to be researched and closed. These research gaps can be divided into two forms (i) optimization of HDO process and (ii) the technology gaps depending on the feedstock and catalysts used for HDO process for the production of renewable fuel. The gaps on feedstock such as triglycerides can be reduced by means of some additional research on dewaxing catalysts, process optimization, and improvement of better considerate of reserve effects of catalysts. The implementation of renewable fuel is another big challenge for commercialization. In addition, the catalytic performances for hydroprocessing from the laboratory scale to pilot scale and to commercial scale need to be further studied. With the economic and environmental benefits that HDO possess, it is crucial to ensure that these aforementioned gaps are closed to ensure its sustainability.

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