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Towards sustainable green diesel fuel production: Advancements and opportunities in acid-base catalyzed H2-free deoxygenation process

N. Asikin-Mijan [a], J.C. Juan [b], Y.H. Taufiq-Yap [c], Hwai Chyuan Ong [d], Yu-Chuan Lin [e], G. AbdulKareem-Alsultan [c], H.V. Lee [b,*]

[a] *Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia.*
[b] *Nanotechnology & Catalysis Research Centre (NANOCAT), Universiti Malaya, 50603 Kuala Lumpur, Malaysia.*
[c] *Catalysis Science and Technology Research Centre (PutraCat), Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.*
[d] *School of Engineering and Technology, Sunway University, Jalan Universiti, Bandar Sunway, 47500 Petaling Jaya, Selangor, Malaysia.*
[e] *Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan.*

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ABSTRACT

This review delves into the potential of renewable biomass for green diesel production. Deoxygenation technology offers a promising method for converting biomass-derived oxygenates oil into high-grade hydrocarbon factions. Hence, various deoxygenation pathways of biomass conversion under free-hydrogen environment were explored. Additionally, the prospects of acid-base bifunctional catalysts to facilitate deoxygenation was discussed, highlighting the correlation between the physicochemical properties of the catalysts and catalytic activity. However, it should be noted that the acid-base characteristics of the catalysts contribute to the breaking of C—O bonds of oxygenated oil via undesirable pathways, which contributed to unfavorable by-product and catalyst deactivation.

1. Introduction

The research interest in identifying a sustainable, environmentally-friendly, and economically viable "green" energy resource is in line with the United Nations' Sustainable Development Goals (SDGs). Particularly, this research is in line with SDG 7, which aims to guarantee access to affordable, reliable, sustainable, and modern energy for all. By identifying and developing green energy sources, we can reduce our reliance on fossil fuels and mitigate the negative impacts associated with their use, thus contributing to SDG 13, which focuses on climate action. Additionally, the development of green energy sources can help to create new job opportunities and stimulate economic growth, supporting SDG 8, which targets sustainable economic development [1].

Among the listed renewable energies, biofuel is counted as an applicable technology that suitable for both under developing and industrialized countries. The term 'biofuels' referred to solid fuels (pellets or briquettes for combustion), liquid fuels (biodiesel, bioethanol, green diesel) or gaseous fuels (syn gas, producer gas) that are renewable and sustainable as it derived from natural biomass. Generally, biomass can be classified into solid biomass and liquid biomass.

Solid biomass includes materials such as agricultural crops and residue; forestry crops; animal residues; industrial residues; and municipal solid wastes. While liquid biomass refers to biomass in a liquid state that involves vegetable oils, animal fats, waste oil from cooking activity, food processing or oil refinery. Both solid and liquid forms of biomass have the potential to be used as renewable energy sources, reducing reliance on fossil fuels and contributing to sustainable energy systems [2]. However, researchers have shown considerable interest in utilizing simple triglyceride forms of liquid biomass (e.g., vegetable oils and animal fats), due to the challenges and undesired byproducts associated with challenges of direct converting solid biomass. This approach avoids the complexities and selective product, making it an appealing option for further exploration [3].

Conventionally, biodiesel has emerged as a promising liquid biofuel that derived from triglycerides/fatty acid, which gained attraction in the market for blended fuels with established technologies. However, biodiesel does have limitations with its high oxygen content, which results in low oxidation stability at high heating environment, and lower calorific values compared to petroleum-based fuels [4]. To overcome these challenges, researchers have been actively working on enhancing

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the quality and performance of biodiesel. On the other hand, triglyceride-derived green diesel offers an alternative solution. It consists of hydrocarbons that encompass both n-alkanes and alkenes fractions, closely resembling petroleum-based diesel fuel [5]. Thus, green diesel serves as a more direct substitute for conventional diesel, effectively addressing some of the drawbacks associated with biodiesel. Various types of conversion technologies have been developed to convert highly oxygenated natural liquid biomass such as triglycerides and fatty acid derivatives into diesel-like hydrocarbons. These technologies include catalytic cracking [6,7], hydrotreating [8], and catalytic deoxygenation [9–11].

In terms of both economic viability and process efficiency, the deoxygenation process offers viable imperative pre-treatment process for production of diesel-like hydrocarbon (green diesel). Deoxygenation (DO) process can take place ideally under H_2 flow (namely hydrodeoxygenation, HDO) or alternative free-hydrogen (H_2) environment. The use of an H_2 atmosphere promotes the thermodynamically favored hydrogenation pathway [12]. Although H_2 may facilitate reduction of catalyst deactivation rates compared to an inert atmosphere, its practical and economic viability is limited in many industrial applications due to its substantial consumption. The overall cost of DO processes is primarily influenced by the high cost of H_2, as well as energy-intensive nature of H_2 production. Moreover, the highly flammable nature of H_2 gas necessitates special precautions and additional infrastructure for safe handling, leading to increased workflow complexity and cost considerations. Additionally, the scaling up of H_2 production from renewable sources is still in its early stages and may encounter challenges related to availability and cost-effectiveness [12].

The techno-economic analysis of HDO of Karanja oil was provided in Table 1. The HDO process was conducted at the temperature of 400 °C

Table 1
Estimation production cost of green diesel for HDO and DO of Karanja oil (cost in million USD).

HDO[*]	Price of chemicals, raw materials, and utilities	DO[**]
H_2 atmosphere	Condition	Free-H_2 atmosphere
0.3	Karanja oil cost (USD/kg)	0.3
1.479	Hydrogen, USD/kg	N/A
0.0189	Catalyst, USD/kg of green diesel produced	0.0189
0.075	Electricity, USD/kWh	<0.075
0.118	Cooling water, USD/1000 gal	<0.118
0.025	Steam, USD/kg	<0.025
0.0005	Water, USD/kg	<0.0005
	Production cost for green diesel (cost in million USD)	
5.506	Operating labours and maintenance	5.506
0.659	Utilities cost (electricity, cooling water, steam)	<0.659
25.000	Karanja oil	25.000
1.130	Hydrogen	N/A
–	Water	–
0.766	Catalyst	0.766
0.310	Operating charges	0.310
2.753	Plant overhead charges	2.753
0.201	Insurance & taxes	0.201
1.071	Depreciation	1.071
4.106	Interest	4.106
0.738	General and administration expenses	0.738
42.240	Total operating cost (A)	<42.240
2.823	Co-product credit (B)	2.823
39.418	Net production cost (C = A-B)	<38.287

[*] HDO reaction condition: 400 °C and 100 bar H_2 pressure, plant capacity of 0.05 MMT Karanja oil/annum [13].

[**] Data provided based on assumption and deoxygenation condition: 300–350 °C.

and 100 bar hydrogen pressure, which is 1.5 times the stoichiometric requirement. Based on the data, (i) raw material (Karanja oil) was the leading cost-contributing factor, with ~73.3% of the production cost, followed by (ii) operating labor and maintenance; (iii) chemicals (hydrogen) and catalyst; (iv) operating & plant overhead charges; and (v) utilities (water, electricity, steam, cooling water). The provided data was compared with deoxygenation process under free-H_2 condition with general reaction temperature of 300–350 °C, which is milder without external supply of pressure and H_2 gas. Hence, an assumption on cost estimation was summarized to indicate both chemicals (hydrogen) and utilities were reduced compared to hydrodeoxygenation process [13]. Hence, it's important to note that the benefit of conduct deoxygenation processes without H_2, such as facile process setup without additional purification and recycling steps; high flexibility choice of feedstock selection for DO upgrading; cost-saving; minimized the safety risks associated with flammable H_2; and promote lower carbon footprint that aligning with sustainability goals. Thus, current efforts are focused on finding alternative approaches for deoxygenation that can be conducted in the absence of H_2. While there are numerous studies that have examined the deoxygenation reaction under H_2 flow, research specifically focused on deoxygenation under a free-H_2 atmosphere is relatively scarce.

Fig. 1 illustrates the trend of publications related to biofuel production through the deoxygenation technology. This trend encompasses various types of publications, including research papers, reviews, and book chapters, spanning the period from 2011 to 2022, all of which displayed considerable interest in this subject. Notably, a remarkable total of 584 publications on biofuel production via deoxygenation in 2023. This figure represents a substantial increase of 680% compared to the 43 publications recorded in 2011. These findings strongly support the assertion that the deoxygenation process is highly favored as a prominent route for biofuel production.

Given the considerable interest in the deoxygenation route, the present article offers an extensive review of green diesel production conducted under a free-H_2 atmosphere condition. It also covers major issues associated with biofuel properties, such as potential biomass feedstocks and oil composition profiles, as well as economic assessments. The deoxygenation mechanism in the absence of H_2 and the detailed reaction pathways, including a summary of catalysts, are highlighted. The article further emphasizes the roles of acidity-basicity characteristics of catalysts and factors that can cause catalyst deactivation profiles. Finally, alternative catalyst deactivation inhibitors in the deoxygenation process are discussed in the last part.

2. The comparative fuel properties of biodiesel, green diesel and petroleum

Green diesel, also known as renewable diesel, falls under the category of liquid biofuels. It is composed of short-chain hydrocarbon fractions (similar to gasoline) with carbon chains ranging from C_6 to C_{12}, as well as long-chain hydrocarbon fractions (similar to diesel) with carbon chains ranging from C_{13} to C_{20}. These products are typically devoid of oxygen, sulfur, and aromatic compounds. Green diesel is composed primarily of n-alkanes and n-alkenes, which the chemical structures are mimic to gasoline and diesel fractions that are produced via conventional petroleum refineries. As green diesel is compatible with petro-derived fuel, the fuel properties closely resemble petro-diesel. However, it is important to note that green diesel has a distinct chemical structure that sets it apart from well-established commercialized biodiesel (fatty acid methyl esters (FAMEs)) [14].

As refer to Table 2, the green diesel rendered better of cetane number (70–90) as compared to biodiesel and petro-diesel, which indicate green diesel's competitive characteristic as petro-diesel substitute [15]. The cetane number of a diesel-based fuels determine its auto-ignition characteristics, with higher numbers suggesting shorter ignition delays, better ignition efficiency, and improved combustion properties.
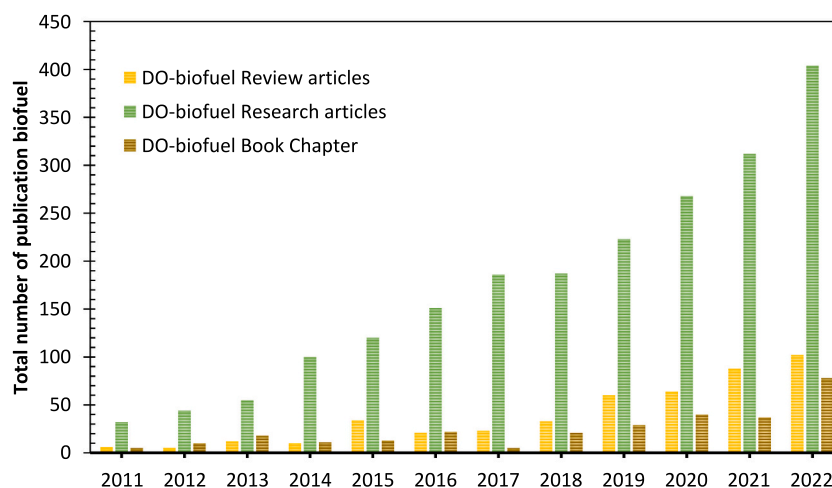
Fig. 1. Deoxygenation of biofuel-related publications according to Indexed Research Journal with "deoxygenation" and "biofuel". Data were retrieved on July 25, 2023.

Table 2
Comparison fuel profile of biodiesel, petro-diesel, syndiesel, and green diesel [15–18].

Fuel Properties	EN-14214	ASTM-D6751	Petro-diesel	FAME Biodiesel	Green Diesel	Syndiesel
Oxygen/%	–	–	0	11	0	0
Density (g/mL)	0.86–0.90	–	0.84	0.88	0.78–0.85	0.77–0.82
Sulfur (ppm)	10	15	<10	<1	<1	<1
Heating Value (MJ/kg)	–	–	43	38	44	44
Cetane Number	51	47	40–55	45–72	70–90	>75
Viscosity (40 °C) CSt	3.5–5.0	1.9–6.0	2.7	3.8–7.9	2.5–4.1	2.1–3.5
CFPP/°C	–	–	−6	(−13)-15	>20	(−22)-0
Cloud Point /°C	–	–	−23 − +4	−6 − +15	−30-(−5)	−18 − +2
Flash Point/°C	120 min	130 min	52–136	96–214	68–120	55–78
Pour Point/°C	–	–	−21	(−15)-16	(−3)-29	–
Acid value mg KOH/g	0.5	0.8	–	–	–	–

However, it is worth noting that if the cetane number is excessively high for a specific engine, it can lead to the formation of black smoke during combustion. The presence of black smoke indicates suboptimal combustion that can be detrimental to engine performance. To ensure optimal combustion and minimize the production of black smoke, it is important to select a fuel with an appropriate cetane number that matches the requirements of the engine (e.g., engine design, fuel injection system, and operating conditions). Thus, green diesel with cetane number range of 70–90 is relatively high and generally considered suitable for diesel engines. Diesel-based fuels within this cetane number range tend to exhibit excellent ignition characteristics, promoting efficient combustion and smoother engine operation [15].

In the case of heating value, the green diesel showed net heating value of 44 MJ/kg, which is comparable to petro-diesel, and higher than biodiesel [16]. Green diesel have the appropriate density (0.78–0.85 g/ml) and viscosity (2.5–4.15 Cst) that meets the diesel standard requirement (EN-14214 and ASTM-D6751) with better properties than biodiesel [17]. The optimum fuel density is important for its ability to enhance both engine performance and exhaust emissions in vehicles, while low viscosity is crucial for minimizing fluid resistance during [17].

Pour point (PP) characteristic is closely related to a fuel's low-temperature properties. This refers to the temperature at which the liquid fuel becomes more viscous and is unable to flow freely or partially solidifies, reducing its flow characteristics. [17]. While cloud point is an important test for the cold weather application by identify the minimum temperature at which the initial visible crystals begin to form as the fuel is cooled, which helps prevent fuel filter plugging [17]. It is relevant to cold filter plugging point (CFPP), which measures the filterability profile of fuel at cold condition [18]. The cloud point test holds significant importance for applications in cold weather conditions as it assists in identifying the temperature at which the initial visible crystals begin to form when a fuel is cooled. This test is crucial as it helps in detecting potential engine problems, such as fuel filter plugging. Generally, biodiesel with high saturated fatty esters will exhibit better cloud point temperature (−6 to +15 °C), while green diesel has a cloud point ranging from −30 to −5 °C. Moreover, the pour point of green diesel (−3 to 29 °C) is higher compared to biodiesel (−15 to 16 °C). Thus, biodiesel is slightly limited in flow characteristics as compared to green diesel with better cold weather. The use of green diesel can effectively prevent issues related to cold climate and enhance performance in cold weather conditions [17,18].

Furthermore, green diesel and petro-diesel have lower flash points compared to biodiesel. This is because the branched fatty acid chain and lower molecular weight components in green diesel and petro-diesel result in lower boiling points, leading to a lower flash point. For instance, hydrocarbon fractions like hexadecane have a boiling point of 287 °C, and decane has a boiling point of 174 °C. In contrast, biodiesels such as methyl palmitate have a higher boiling point at 417 °C, while methyl decanoate has a boiling point of 224 °C [17]. Additionally, green diesel derived from natural biomass resources through hydroprocessing technology results in a low sulfur content (<1 ppm/wt) compared to petro-diesel. This indicates that green diesel is a fuel with low greenhouse gas (GHG) emissions [17]. Considering the points discussed above, it can be concluded that green diesel represents a more advanced liquid fuel option when compared to biodiesel.

3. Green diesel from biomass-derived feedstocks

As an alternative to petro-based crude oil, the solid biomass-derived oil (pyrolysis oil) and liquid biomass-derived triglycerides (present in form of fats and vegetable oils) can be technically deoxygenated into hydrocarbon-graded fuel at petroleum refineries. The potential feedstocks for green diesel production can be categorized into the following: pyrolysis oil (bio-oil), edible oil, non-edible oil, animal fats and yellow grease.

3.1. Pyrolysis oil (bio-oil)

Bio-oil had increased considerable interest as potential feedstock for renewable cyclic hydrocarbons production via biorefinery process. Generally, bio-oil is generated through pyrolysis reaction of solid biomass (e.g. wood, crop residues, or organic wastes) in the absence/limited oxygen supply [19]. During the pyrolysis process, the solid biomass undergoes rapid thermal decomposition, resulting in the formation of various products, including gases, liquids, and char. The liquid fraction is pyrolysis oil (bio-oil), which is a viscous and corrosive dark brown liquid. Bio-oil composes of unstable mixture of oxygenated compounds (oxygen content of 35–40%) that attributed majorly of phenols, furans, acids, alcohols, ketones, aldehydes, ethers, esters, sugars, nitrogen compounds, where the composition is vary based on the pyrolysis condition and biomass feedstocks. The presence of these 300 organic compounds limit the fuel quality due to it's homogeneity, polarity, heating value, viscosity and high acidity [20].

Multiple studies have indicated that pyrolyzed bio-oil typically contains a water content ranging from 15% to 30% by weight. The presence of water in the bio-oil can originate from various sources, including the moisture content of the initial wet feedstock, water generated during the pyrolysis process through dehydration reactions, or water absorbed during prolonged storage periods. Several studies have indicated that pyrolyzed bio-oil consisted of 15–30 wt% of water content. The presence of water in the bio-oil can originate from various sources, including the moisture content of the initial wet feedstock; water generated during the pyrolysis process through dehydration pathway; or water absorbed during long term of storage. Therefore, the presence of high-water content will reduce the immiscibility with petro-based crude oil, as well as reduce heating value of oil by 50% lower than petro-based crude oil. In addition, high acidity (pH 2–4) of bio-oil that originated from acetic acid and formic acid resulted of equipment corrosion especially during processing, storage, and transportation [21].

Due to the vast differences of bio-oil and petro-based crude oil as tabulated in Table 3 [21,22], bio-oil showed limitation as the present form do not meet the transportation fuel usage. Although bio-oil usage for biofuel application is limited by its high viscosity, high moisture and ash content, low heating value, chemically unstable, and high corrosiveness. However, bio-oil is considered as carbon neutral product with cleaner and lower emission of NO_x and SO_x. In addition, the presence of substantial amount of phenolic compounds in bio-oil act as precursors,

that potentially upgraded into cyclic hydrocarbons. The upgraded bio-based cyclic hydrocarbons (e.g., benzene) possess favorable fuel characteristics such as higher energy density, improved combustion efficiency, and enhanced lubricity of biofuel. By converting the phenolic compounds present in bio-oil into cyclic hydrocarbons, the resulting green diesel can exhibit improved fuel properties, making it a more suitable and efficient alternative to conventional diesel fuel [22]. Thus, further treatment of bio-oil is essential to improve the quality of liquid biofuel. Owing to the high content of oxygenates from different organic groups, the upgrading process becomes challenging as it involves complex reaction network. Numerous studies have investigated the thermal upgrading of bio-oil through cracking, deoxygenation, and hydrodeoxygenation reactions. These processes aim to improve the negative properties of bio-oil through reduction of oxygen content, increase the selectivity of hydrocarbon fractions, and reduce the content of undesirable compounds (acids, aldehydes, and ketones). The quality of upgraded bio-oil can vary across studies: Surachai's group reported on in situ deoxygenation of bio-oil that derived from the fast pyrolysis of biomass (cedar wood) by using Cu/MCM-41-CD and Cu/KIT-6-CD catalysts. Result indicated that the rich-phenol bio-oil was successfully converted into monocyclic aromatic hydrocarbons (e.g., benzene, toluene, and xylene) with high content of hydrocarbon (73.2% and 86.1%) [23,24]. In addition, Iliopoulou's group highlighted hydrodeoxygenation of coconut shell-based bio-oil through natural zeolite supported Fe_2O_3, CuO, and ZnO catalysts. The treated bio-oil showed improved quality of physicochemical properties with low H/C (1.59–2.46) and O/C (0.58–1.06), enhanced of heating value (17.7–20.9 MJ/kg) and lower of acid number (118–139 mgNaOH/g oil) as compared to bio-oil (H/C (8.29), O/C (3.98)), low heating value (12.5 MJ/kg), and high acid number (171 mgNaOH/g oil) [24]. While the upgrading process shows positive results in converting complex bio-oil into high-value products, the manufacturing scale of bio-oil upgrading still faces challenges due to the presence of a significant amount of oxygen functionalities and organic acids. As a result, exploring alternative renewable feedstocks that consist of a specific range of compounds becomes essential for effective structural re-engineering.

3.2. Triglycerides- and fatty acid-derived feedstock

By replacing bio-oil upgrading limitations, the utilization of low diversity molecular compounds, such as triglycerides and/or fatty acids derived from non-edible oil, waste oil, and animal fat, offers an alternative to food-based feedstock. The simple chemical structure can significantly enhance the oxygenates species removal via deoxygenation process. Chemically, vegetable-based triglyceride contains three fatty acid chains that attach to single propane unit by ester bond linkage as shown in Fig. 2 (a). Triglyceride is mainly composed of fatty acids, which make up 95% of their total weight. The fatty acids exhibit various of carbon chain lengths and the number of unsaturated chains, which determines the unique characteristics of each type vegetable oil [25]. The chemical structures of some fatty acids that were selected for biofuel studies are summarized in Fig. 2 (b).

3.2.1. Edible plant oil

Numerous types of edible oil are potentially converted to green diesel via deoxygenation reaction (Table 4) [26,27]. Generally, every country has its preferred crop of choice, which is influenced by geographical factors. Therefore, the selection of feedstock for each country is based on regional preferences. Among the various feedstocks, corn, palm, and soybean oil have the lowest prices, with prices per metric ton amounting to 146 USD, 478 USD, and 602 USD, respectively, and the seed or kernel of these crops yielding over 40% oil content. While olive oil offers higher of cost although capable of converting over 70% of the olive to oil, however has limited availability (2.2 metric tons per year), which makes its usage restricted [28]. Additionally, most vegetable-based oils contain

Table 3
Comparison properties of bio-oil and crude oil [21,22].

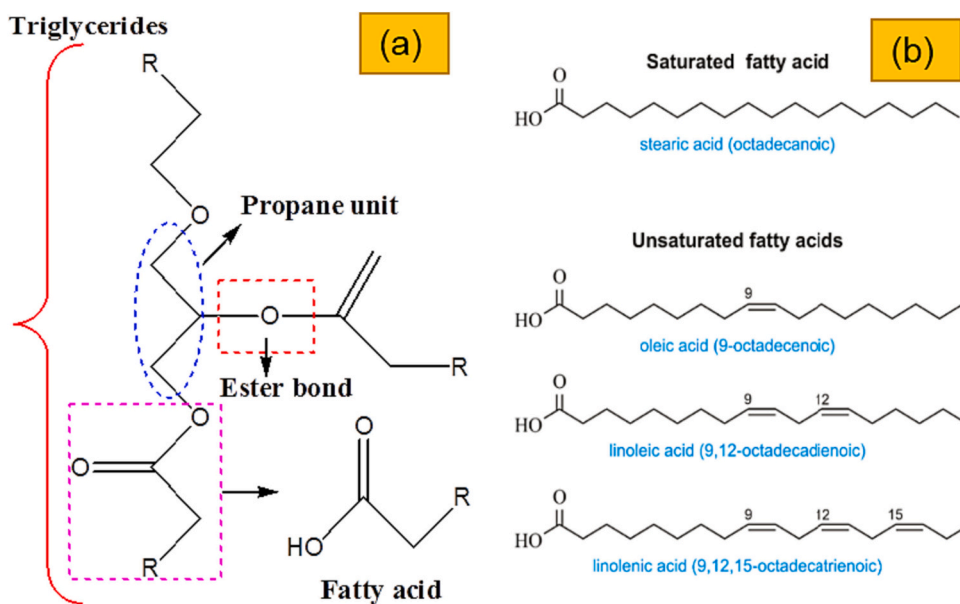| Properties	Bio-oil	Crude-oil
Density at 15 °C (g/mL)	1.05–1.25	0.86
Viscosity at 50 °C (cP)	40–100	180
Water content (wt%)	15–30	0.1
pH	2.8–3.8	–
Heating value (MJ/kg)	16–19	40
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1
N	0–0.2	0.3
Ash	0–0.2	0.1
Solids (wt%)	0.2–1	1

Fig. 2. (a) Basic triglyceride and fatty acid structure in feedstock, (b) Fatty acids' structure.

Table 4
Types of potential vegetable oil for green diesel production [26,27].

Feedstock	Palm	Canola	Soybean	Sunflower	Corn	Peanut	Olive	Coconut
Primary sources	Malaysia & Indonesia	Canada	USA	Europe	USA	China	Spain	Philippine
Availability (mill metric tonnes)	65.5	>16	53.7	16.6	60	29	2.2	61.4
Price (USD)* (April–May 2020) (per metric ton)	478	758	602	732	146	1527	4632	834
Oil in seed or kernel (%)	30–60	44	15–20	25–37	48	45–55	45–70	65–72
Saturated fatty acid	48	6	14	11	16	16	12	90
Unsaturated fatty acid	50	92	81	89	84	79	79	9
Acid value (mgKOHg$_{-1}$)	0.5	0.071	0.6	<1.1	0.223	<4	6.6	<3

* Data collected from http://www.indexmundi.com/commodities.
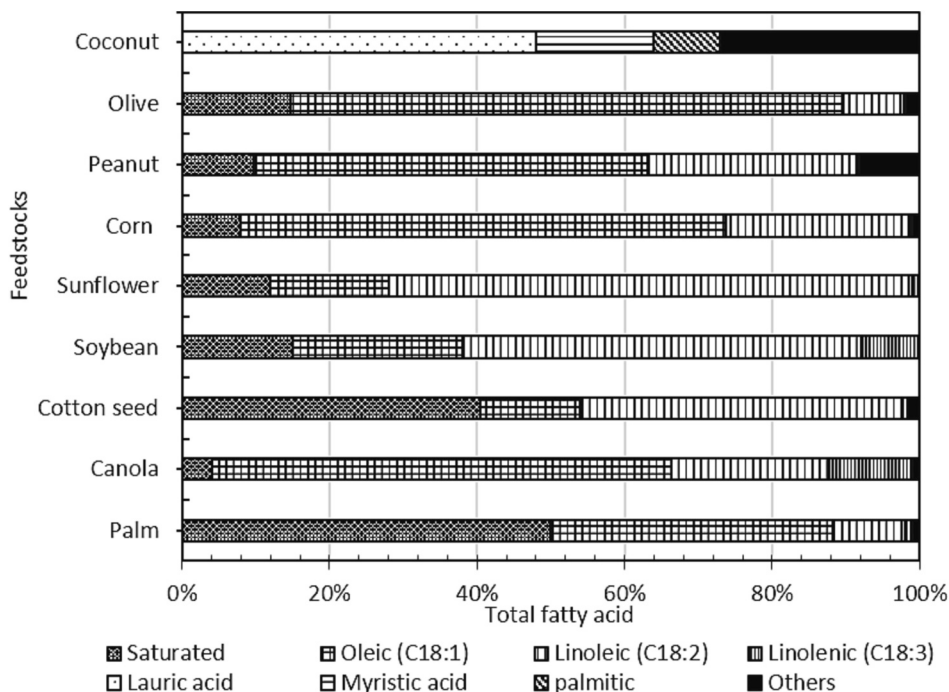

Fig. 3. Fatty acid composition of edible vegetable oils [26,27].

a significant amount of unsaturated fatty acid compounds that non-favorable for stable hydrocarbon production (Fig. 3) [26,27]. It was noticed that canola, corn, peanut, and olive oil primarily consist of unsaturated oleic acid (C18:1). On the other hand, soybean and sunflower seed oils exhibited significantly higher unsaturated levels of linoleic acid (C18:2). Palm oil with major saturated fatty chain, showed a notable concentration of palmitic acid (C16:0) at 46.3%. These feedstocks potentially yield diesel fractions withing n-C_{15} and n-C_{17} fractions through deoxygenation proces. In contrast, coconut oil was predominantly composed of lauric acid (C12:0) (48%) and myristic acid (C14:0) (16%) [26,27]. Hence, the favorable carbon chains derived from coconut oil deoxygenation are n-C_{11} and n-C_{13} paraffinic fractions. Although edible oils hold promise as feedstocks for green fuels production, their continued usage poses challenges of food scarcity and conflicts with green diesel issue [29]. Therefore, employing edible oils as a fuel source for green diesel production may not be economically viable or justifiable.

3.2.2. Non-edible plant oil

Global food or fuel debate towards utilization of edible oil as green diesel feedstock is being seriously reviewed for their long-term impact. The use of non-edible plant oil had gained huge attention as a new generation feedstock due to their high productivity rate with large oil yield, highly available and survival in abandoned land and climatic zones. Their growth is also not reliable with regional weather conditions. Thus, non-edible plants are easily grown with less intensive care and lower cultivation cost. Additionally, several types of the non-edible plant have longer life expectancy as high as 100 years, which is promising in term of continuous feed supply [30]. There are several types of well-known non-edible plant oil used in production of liquid biofuel especially in biodiesel production such as *Jatropha Curcas* oil (JCO) [31], Jojoba oil [32], Karanja oil [33], Linseed oil [34], Cottonseed oil [35], Ceiba oil [36], Sterculia oil [37], Tung oil [38], Castor oil [39], Polanga [40], Tobacco see oil [41], and rubber oil [42] (Table 5). The non-edible plant seeds or kernels render high oil yield productivity, which potentially sustains the transportation fuels market. Among the oils studied, JCO exhibited the highest oil content (50% - 60%) [31], while Tung oil [38] and cotton seed oil [35] had the lowest oil content (16% to 20%), respectively. The Jojoba oil showed lowest free fatty acid (FFA) value at 1 mgKOHg^{-1} [32], whereas rubber oil [42], tobacco seed oil [41], and JCO oil [31] had the highest acid values, measuring 45 mgKOHg^{-1}, >35 mgKOHg^{-1}, and 30.8 mgKOHg^{-1}, respectively. In addition, fatty acid

profile of non-edible oils revealed a higher proportion of unsaturated fatty acids compared to saturated carbon chains, suggesting that the deoxygenation of these feedstocks could lead to the formation of unsaturated hydrocarbon fractions [78]. However, the non-edible oils is highly sustainable due to the lower feedstock cost at < USD500 per ton compared to edible oils [79] (Table 5).

3.2.3. Waste oil and animal fat

Waste oil/waste cooking oil (WCO), is the second most prevalent type of discarded oil resulting from cooking activities, which often discarded without any further utilization. The waste oil can be sourced from restaurants, food processing industries, and fast-food establishments. Thus, utilization of WCO is highly sustainable, as it helps to eliminate debates surrounding food competition, while also providing economic and environmental benefits. WCO is divided into two types of grease: (i) yellow grease (FFA < 15%, acid value <30 mgKOHg^{-1}), and (ii) brown grease (FFA > 15%, acid value >30 mgKOHg^{-1}). It is not suitable to be direct apply for existing motor engines due it's high viscosity and high oxygen content [43]. Thus, further advance upgrading process is required in order to reduce the oil's viscosity and oxygen content, which can improve the atomization and lubricity of WCO-derived fuels. The study focused on upgrading WCO via deoxygenation reaction under free-H_2 environment showed >80% of hydrocarbon fraction yielded with majority of the product fractions composed of unsaturated hydrocarbons [44].

In addition, processed animal tissues can serve as the waste oil that is derived from animal fat. Several types of animal fat had been found such as beef tallow, duck tallow, chicken fat and fish fat. Chicken fat consisted of a high percentage of linoleic acid (17.9–22.8%), while beef tallow shows high content of oleic acid (between 47 and 50%) with ~40% of palmitic and stearic acids. The usage of animal fat for green diesel production is an effective way to reduce the cost of raw materials, which is about 50% lower of the price of edible plant oil [45]. Recent study reported that deoxygenation of waste chicken fat to bio-based diesel over Ni/Al$_2$O$_3$ catalyst at a temperature of 330 °C under the presence of water resulted in a major decarboxylation pathway, whereas hydrodeoxygenation was minor [46]. The major composition of *n*-alkanes in the liquid product consisted of *n*-C_{15} to *n*-C_{17} hydrocarbon fractions. The non-edible feedstock would not compete with food, thus providing more opportunity for green diesel production.

Table 5
Types of non-edible oils and their free fatty acid value [31–42].

Feedstock	JCO	Tung	Cotton seed	Lin seed	Jojoba	Ceiba	Sterculia	Castor	Rubber seed	Polanga	Tobacco seed
Price USD per metric ton	400/t	1800/t	330/t	421/t	2000/t	360/t	250/t	1100/t	329/t	–	500/t
Oil in seed or kernel	50–60	16–18	18–20	35–45	45–50	25–28	34	45–50	40–60	65	30–43
Acid value (mgKOHg^{-1})	30.8	9.5	19.6	4.9	1	5.1	12.0	5	45	44	>35
Lauric (C12:0)	–	–	–	–	–	0.1	0.1	–	–	–	–
Myristic (C14:0)	–	–	1.0	–	–	0.1	0.2	–	–	–	0.2
Palmitic(C16:0)	15.2	5.5	25.8	5.1	1.2	19.2	18.4	1.0	10.2	12.0	8.4
Palmitoleic(C16:1)	0.7	–	0.6	0.3	–	0.3	0.3	–	–	–	–
Stearic(C18:0)	6.8	–	2.5	2.5	–	2.6	7.6	–	8.7	12.9	3.4
Oleic(C18:1)	44.6	4.0	17.2	18.9	10.7	17.4	4.0	3.0	24.6	34.0	11.2
Linoleic(C18:2)	32.2	8.5	51.5	18.1	–	39.6	11.1	5.0	39.6	38.3	75.6
α-Eleosteari (C18:2)	–	89.0	–	–	–	–	–	–	–	–	–
Linolenic(C18:3)	–	–	0.2	55.1	–	1.5	2.3	1.0	16.3	0.3	1.0
Arachidic(C20:0)	0.2	–	0.3	–	9.1	0.56	–	–	–	–	–
Gondoic (C20:1)	–	–	–	–	59.5	–	–	–	–	–	–
Behenic(C22:0)	–	–	0.2	–	–	–	–	–	–	–	–
Erucic(C22:1)	–	–	–	–	12.3	–	–	–	–	–	–
Nervonic	–	–	–	–	1.7	–	–	–	–	–	–
Riconoleic	–	–	–	–	–	–	11.1	89.0	–	–	–
Malvaloyl18:*CE)	–	–	–	–	–	–	44.1	–	–	–	–
Sterculoyl(19:*CE)	–	–	–	–	–	18.5	–	–	–	–	–
Others	–	–	0.70	–	–	–	–	–	–	–	–
Saturated	22.2	5.5	29.8	7.6	10.3	22.6	26.3	1.0	18.9	24.9	12.0
Unsaturated	77.8	94.5	70.2	92.4	89.7	77.4	73.7	99.0	81.1	75.1	88.0

3.3. Basic chemical reaction pathways for green diesel production via free-H_2 deoxygenation

General deoxygenation process of triglycerides and fatty acid derivatives under lower H_2 pressure or free-H_2 atmosphere involves several reaction pathways (Fig. 4). The cracking process has become a viable pathway because it simultaneously removes the oxygenated species present in the fatty acid molecules, as well as reduce the fatty chain through C—C bond cleavage. Generally, cracking involves thermal cleavage or catalytic decomposition of triglycerides. The cracked product possesses lighter alkanes, alkenes, and fatty acid [47,48]. Cracking activity would also result in scission of C – C bonds of intermediate fatty acids, which form shorter fatty acid chain, as well as cracking of C—C bonds of long carbon chain of hydrocarbon fractions (Fig. 4; entry 1–2). Both cracking pathways would yield light hydrocarbon fractions [48].

The literature on various catalytic cracking systems of vegetable oil suggests that solid acid catalysts, such as zeolite-, alumina-, and silica-alumina-based catalysts, promote the cracking pathway [49]. Zeolite is a type of mesoporous acid material that contains both Bronsted and Lewis acid sites. These acid sites facilitate the selective conversion of desired products such as hydrocarbons, cyclic, aliphatic, and aromatic compounds due to the specific structure of zeolite. It has a well-defined network of internal canals that allow for precise control of the reaction conditions, resulting in the formation of the desired product. On the other hand, SiO_2-Al_2O_3 is an amorphous material that exhibits a high surface area of mesoporous catalyst, with a predominance of Lewis acid sites. The catalytic process facilitated by Lewis acid promotes the selective formation of short-chain aliphatic hydrocarbons while minimizing the production of aromatic hydrocarbons [50].

The primary deoxygenation process involves eliminating the oxygen atom from oxygenated biomass feedstocks in the form of H_2O, CO_2, or CO. The deoxygenation pathways are typically carried out through several plausible reaction pathways, including: (1) decarboxylation, which involves removing carboxyl groups to produce n-alkanes and CO_2 (as shown in Fig. 4; entry 3); (2) decarbonylation, which produces n-

alkenes, CO, and water (as shown in Fig. 4; entry 4); and (3) hydrodeoxygenation, which produces n-alkanes and water (as shown in Fig. 4; entry 5).

Both decarboxylation and decarbonylation resulted in deoxygenated n-alkanes and n-alkenes, which exhibit a loss of one carbon atom from the original carbon chain number [48]. Hydrodeoxygenation is a well-suited process for converting bio-oils and vegetable oils into non-oxygen fuels. This process involves the utilization of H_2 gas to hydrogenate C—O, C-O-C, and C—C bonds found in fatty acids or bio-oil compounds. The hydrodeoxygenation pathway leads to the formation of n-alkane molecules with the same number of carbon atoms in the chain, along with water molecules as a by-product [48].

Despite the belief that free-H_2 deoxygenation is not possible through hydrodeoxygenation route, several studies have successfully produced hydrodeoxygenation products (C18 alkanes) from deoxygenation of vegetable oil under a free-H_2 atmosphere. However, it should be noted that the amount of C_{18} produced is relatively small [51]. According to the studies conducted by Zulkepli et al. [52] and Emori et al. [53], the in-situ H_2 was obtained from the water-gas shift reaction (WGS) (CO + $H_2O \rightarrow CO_2 + H_2$) and cracking activity. Emori further noted that the generation of H_2 is enhanced when the cracking activity is carried out under N_2 flow atmospheres. The in-situ H_2 facilitates the transfer of H (hydrogenation, Fig. 4; entry 6), which subsequently hydrogenates the n-alkenes to produce corresponding n-alkanes. It is worth noting that n-alkanes can also be obtained by hydrogenating triglycerides with unsaturated fatty acid chains (C=C double bond) into saturated form [54], followed by the hydrogenolysis pathway to yield fatty acids and propane (Fig. 4; entry 7).

4. Perspective on deoxygenation catalysts

The selective deoxygenation process typically involves the use of heterogeneous catalysts, with those possessing high acid density being preferred due to their ability to remove oxygen via C—O cleavage from fatty acids through a deoxygenation reaction (as depicted in Table 6). It

Entry	Liquid phase	Precusor	End product
1	Cracking		
2	Cracking		
3	Decarboxylation		+ CO_2
4	Decarbonylation		+ CO + H_2O
5	Hydrodeoxygenation		+ H_2O
6	Hydrogenation		+ H_2O
7	Hydrolysis		

Fig. 4. Overview possible for deoxygenation pathways [47–54].

Table 6
Performance of representative catalysts in the deoxygenation of triglycerides and fatty acid derivative via deCOx reaction.

Type catalyst	Catalyst	Feed	Reaction condition	Reactor mode	[a]Con. (%)	Selectivity (%)	Properties	References
Noble metal	5% Ru/C	Stearic acid	6 h; 300 °C; atm; He 6 Mpa	Semi-batch	13.2	65 (C_{17})	High selectivity Expensive	[55]
	5% Pd/C				100	99 (C_{17})		
	5% Pt/C				86	95 (C_{17})		
	1% Rh/C				19.9	85 (C_{17})		
	5% Os/C				6.9	53 (C_{17})		
	1% Pt/C	Tristearin	4 h; 350 °C; atm; N_2 6.8 MPa	Batch	42	83 (C_8–C_{17})		[58]
	5% Pd/C				29	93 (C_8-C_{17})		
	0.5% Pd/Al_2O_3	Stearic acid	3 h; 350 °C; atm; H_2	Batch	100	90.3 (C_{17})		[57]
	5% Pd/Al_2O_3				100	91 (C_{17})		
	5% Pd/C	Oleic acid	6 h, 360, 15% H_2/Ar		98			[56]
Sulfided metal	NiMo/Al_2O_3 Mo/Al_2O_3 Ni/Al_2O_3	Rapeseed oil	4 h^{-1},280 °C, H_2 = 3.5 MPa	Fixed-bed	100 100 100	85 (C_{15}-C_{18}) 78 (C_{15}-C_{18}) 60 (C_{15}-C_{18})	High selectivity Poor quality oil due sulfur leaching	[59]
	CoMo/γ-Al_2O_3	PRO-primary refined rapeseed oil	2 h^{-1}, 310 °C, H_2 = 3.5 Mpa	Fixed-bed	90	80 (C_{17}-C_{18})		[60]
	NiMo/SiO_2 NiMo/Al_2O_3 NiMo/TiO_2	Rapeseed oil	2–8 h^{-1}, 260–300 °C, H_2 = 3.5 MPa	Fixed-bed	100 100 100	80 (C_{17}-C_{18}) 85 (C_{17}-C_{18}) >60 (C_{17}-C_{18})		[61]
Phosphide and Carbide metal	Ni_2P/SiO_2 MoP/SiO_2	Methyl laurate	14 h^{-1}, 340 °C, H_2 = 3.0 MPa	Fixed-bed	~96 ~90	~94 (C_{11}-C_{12}) ~87 (C_{11}-C_{12})	High selectivity Tedious and complex synthesis catalyst method	[62]
	b-Mo_2C/CNF b-W_2C/CNF	Stearic acid	3 h, 350 °C, H_2 = 30 bar	Batch	65 >96	41(C_{17}-C_{18}) 91 (C_{17}-C_{18})		[63]
Zeolite	ZSM-5	Sunflower oil	500 °C; atm; N_2	Fixed-bed	32.2	63 (C_{18}-C_{43})	Expensive Poor product selectivity	[6]
	1% Pt/HZSM-5 (23)	JCO	2 h, 270 °C, 6.5 MPa of H_2/N_2 gas	Batch	100	91 (C_5-C_{21})		[67]
	1% Pt/USY (6.3)				31	88 (C_5-C_{21})		[65]

has been found that catalysts containing promoted noble metals such as Pt, Pd, or Rh are effective reactive metal catalysts for deoxygenation. Snåre's study reported that deoxygenation activity by using different transition metals such as Ni, NiMo, Ru, Pd, Pd/Pt, Pt, Ir, Os and Rh with different catalyst supports (metal oxides and carbon-based materials) [55]. It was found that the Pd/C catalyzed deoxygenation process showed efficient pathway in hydrogenolysis of C-O-C bond of fatty acid [55–58]. Although noble-based catalyst showed high selectivity towards oxygen removal and favor the formation of hydrocarbons, however the high cost and rarity of noble metals limit mass-scale green diesel production.

Due to the limitations of noble-based catalysts, sulphided catalysts have been selected for the deoxygenation process. From the investigation of conventional hydrodesulfurization catalysts such as sulphided CoMo-, sulphided NiMo- and sulphided NiW-supported with alumina, the findings indicated that the catalysts render efficient effect for oxygen removal [59–61]. The elimination of oxygen was mainly achieved by breaking the C—O bond through oxygen adsorption at the vacancy site of a sulphide-metal surface. However, the use of sulphided catalysts resulted in sulfur contamination in the final product, which adversely impacted the quality of the fuel oil. Besides, stringent regulations have been implemented to reduce the sulfur content of diesel fuel to ultra-low levels (10 ppm) to minimize harmful exhaust emissions, as mandated by the US Environmental Protection Agency. Therefore, it is essential to develop alternative and cost-effective free-sulfur catalysts such as metal phosphide [62] and carbide [63]. These catalysts have been the subject of ongoing debate among industrialists and researchers regarding their complex preparation steps and limited reusability.

Apart from noble metal, sulphided-, phosphided and carbided metal-based catalysts, zeolite-based catalysts have emerged as efficient support materials applicable for crude oil refinery. Zeolite possesses superior characteristics, such as high surface area, well-defined micropores with an interconnected network of channels, strong acidity, and high thermal stability, making it ideal for high heat reactions. Zeolite catalysts enable faster reaction rates, higher product yields, and easier heat recovery. However, zeolite-catalyzed reactions are susceptible to unselective cracking reactions, leading to a broad range of hydrocarbon fractions [64].

Previous research has shown that the narrow channels of zeolite structures can result in a high deactivation rate of the catalyst. The low accessibility and diffusion rate of the reactant to the zeolite interior can lead to undesired cyclization and aromatization reactions, ultimately leading to the formation of polyaromatic compounds that block the catalyst's pores and deactivate it [6,65]. Huang's research on the deoxygenation of cyclopentanone using commercial zeolite H—Y with SiO_2/Al_2O_3 ratios of 5.2 and 30 demonstrated that both catalysts exhibited coking due to the formation of poly(aromatics) compounds [66]. Given the catalytic limitations outlined in literature, there is a need for an alternative catalyst that is low-cost, sulfur-free, easily prepared, and capable of producing high-quality fuel oil via a selective deoxygenation reaction.

4.1. Mono- and bimetallic mixed metal oxide

Metal oxide catalysts have been found to achieve high efficiency in oxygen abstraction under a free-H_2 atmosphere. These catalysts are free of sulfur content and exhibit high catalytic activity at relatively mild reaction temperatures. Moreover, they are reasonably priced compared to noble-based catalysts. Transition metal oxides such as Ni, Co, W, Mo, Cu, Fe, and Zn are commonly used in deoxygenation processes, as reported in various studies [68,69]. Among these transition metals, Ni and Co have shown the highest deoxygenation activity. Ni is found to be effective in decarbonylation, while cobalt is capable of promoting both decarboxylation and decarbonylation routes [70]. It is noted that Ni metal oxide was also recognized as potential material that offer comparable promotional effect as noble Pd and Pt catalysts in deoxygenation activity. Study showed high dosage of Ni metal (20 wt% Ni) rendered comparable catalytic activity as 5 wt% Pd and 1 wt% Pt-promoted catalyst [58]. Although NiO-promoted catalyst showed promising deoxygenation profile, but NiO-promoted catalyst was easily deactivated due to metal sintering, metal leaching and coke formation. Thus, several studies have focused on the implementation of coke inhibitor

species that derived from alkaline-earth metal oxide (e.g. beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra)). Among these alkaline earth metals, calcium (Ca) and magnesium (Mg) demonstrated a significant potential for deoxygenation activity [136]. This suggests that the strong basic active sites present in Ca/Mg facilitate the removal of oxygenated species through decarboxylation pathways [71,72].

Although monometallic oxide catalyst is catalytically active, yet the catalyst easily to deactivate due to coke deposition. Thus, more attention has been focused towards the usage of bimetallic mixed metal oxide catalyst, and it was revealed that the catalyst exhibited a substantial amount of bifunction acidic-basicity active sites [73–75] that effective in deoxygenation reaction for production of green diesel. Despite their effectiveness, mixed metal oxide catalysts often have limited surface areas that hinder the adsorption of reactants at the catalyst's active sites. To overcome this limitation, catalyst supports (both non-carbon and carbon-based) are widely explored in deoxygenation reactions.

4.2. Non-carbon-based catalyst support

Aluminum oxide (Al_2O_3) and zeolite are popular choices for catalyst support in the hydro-processing of petroleum fuel. The acidic support plays a crucial role in promoting cracking activity by providing additional reaction sites for H_2 dissociation or adsorption of oxygenated compounds [76]. Zeolite, in particular, contains a significant number of Brønsted acid sites, while Al_2O_3 is primarily dominated by Lewis acid sites. The presence of Brønsted acid support facilitates the hydrogenation-dehydration-hydrogenation route, which is conducive to hydrodeoxygenation reactions. On the other hand, Lewis acid sites are more favorable towards decarboxylation/decarbonylation (deCOx) pathways [77].

It has been observed that the use of an acid support with strong acidic sites catalyst, such as zeolite, results in severe catalyst deactivation due to coke formation and unselective cracking processes. As a result, the use of a moderate acidic support, such as Al_2O_3, is essential to selectively break down the carboxylic group in vegetable-based oil. Although Al_2O_3 exhibits high catalytic activity, it still experiences coking, which is suggested to be due to the acidity of the Al_2O_3 support [76]. For this reason, the focus has been focused on the use of neutral supports such as Silica (SiO_2). SiO_2 has been indicated as a prospective support material for hydrotreating reaction. The SiO_2 has a neutral characteristic in nature, thus possess relatively low affinity towards coking [78]. Moreover, SiO_2 facilitated higher metal dispersion compared to Al_2O_3, and this was identified as one of the factors that influenced the decarboxylation activity. Concerning the limitation of Al_2O_3 support and advantages of SiO_2 support, a mildly acidic silica–alumina support (SiO_2-Al_2O_3) with low Si/Al ratio had gain interest for further study. The SiO_2-Al_2O_3 support with lower acid density promotes a favorable balance between cracking and isomerization, thereby minimizing secondary cracking [79,80].

Other support materials such as CeO_2 and ZrO_2 had gained large interest owing to their high thermal stability, better dispersion of metal, ability to store oxygen and high redox ability [81]. On the other hand, deoxygenation activity can be assisted by support materials with basicity such as CaO and MgO. Although the use of alkaline supported catalysts is appealing due to their resistance to the formation of carbonaceous compounds, they are inefficient in promoting deoxygenation and are prone to cracking [82]. Thus, the catalyst exhibiting significant basicity necessitates in the presence of acid active sites to augment deoxygenation reactivity. A study investigated the role of CaO-MgO as the basicity modifier of Ni/ γ-Al_2O_3 for deoxygenation of palm oil. The presence of basicity modified the acidity density of the catalyst, which suppresses and control the cracking pathway. Thus, the target greed diesel yield (C_{15}-C_{18} paraffins) with longer carbon chain was retained without over-cracking [83].

Metal organic frameworks (MOFs) have garnered significant attention as potential catalyst support for deoxygenation process. The MOF are functional materials with framework structures formed by metal atoms and organic ligands through coordination bonds. These materials possess various unique characteristics, including open metal sites, permanent porosity, and high specific surface area. In addition, MOFs render good chemical tunability for hydrophobicity functionalization, which enhances non-polar oil accessibility to the catalyst surface, as well as to reduce deactivation degree through limiting the water adsorption during process. Due to these characteristics, MOFs serve as excellent starting supporting materials for creating composites with metal nanoparticles and carbon [84]. Zheng and co-workers successfully synthesized M-Co_3O_4 nanoparticles, with a carbon matrix shell, using MOFs as a precursor for deoxygenation of stearic acid [85]. The results demonstrated that M-Co_3O_4 exhibited outstanding deoxygenation performance, achieving a stearic acid conversion rate of 98.7% and selective production of C_8-C_{18} alkanes at 92.2%. Despite their impressive effectiveness, MOFs are generally considered expensive, limiting their practical use for industrial purposes.

4.3. Carbon-based catalyst support

The use of carbon-based supports as an alternative catalyst for deoxygenation has gained significant attention. Carbon considered as good catalyst support due to its diverse porous structure and textural properties, tunable of functional surface (acid-base tunability), high chemical stability, low density, facile synthesis process and heat resistance [86]. The superior adsorption capacity of carbon support is typically attributed to its substantial specific surface area, pore volume, and porosity. Generally, the intricate carbon pore support network can be classified into three categories based on their size: microporous (with pores smaller than 2 nm), mesoporous (with pores ranging from 2 to 50 nm), and macroporous (with pores larger than 50 nm). Both microporous and macroporous carbon support typically not favorable for deoxygenation. Microporous carbon will result in inefficient accessibility and diffusion limitation of the bulky-sized of biomass compounds into the interior pores. Meanwhile, macroporous carbon resulted of high collision rate between biomass compounds and catalyst, thereby, increasing the cracking reaction rates that favor to light olefins product [87]. Although numerous studies have shown that zeolite catalysts with microporous structures exhibit strong selectivity towards green diesel production [11]. However, there is a scarcity of research discussing the relationship between selectivity of green diesel yield with the presence mesoporous carbon support. It is possible that mesoporous carbon support could have a positive impact on the production of diesel-like hydrocarbons, although further research is needed to confirm this.

Other than the desirable mesoporous characteristic of carbon structure, the nanostructures feature of carbon can make a substantial contribution in enhancing the deoxygenation reaction, going beyond considerations solely related to pore size. These materials exhibit exceptional properties, including high dispersion of active metal, a large surface area, tunable pore structure, and excellent stability, all of which render them highly promising catalysts for the deoxygenation process. Specifically, nanostructured supported catalysts offer improved structure-activity characteristics, which play a crucial role in comprehending the behavior of biomass model compounds.

The inclusion of carbon nanotubes (CNTs) with diverse functional groups in the deoxygenation process can effectively mitigate unfavorable side reactions that occur with conventional activated carbon (AC). This selective approach enables a more precise deoxygenation pathway. The presence of CNT with diverse functional groups able to limit the unfavorable side reactions, which provide a more selective deoxygenation pathway as compared to activated carbon (AC) [88]. In addition, the effectiveness of CNT have been proven with high reusability for four to five consecutive cycles in deoxygenation reaction. Although promising deoxygenation activity has been observed over CNT-based catalyst, yet, this nano-catalyst still considered very pricy and consequently

impractical for petrochemical industry [51]. Due to this reason, there has been a recent interest in using biomass-derived carbon as a sustainable carbon-based nano-architectonics catalyst for driving the thermal upgrading process of biomass into biofuels/biochemicals. Biomass-derived carbon is a cost-effective, environmentally friendly, and easily obtainable natural organic resource generated through the thermochemical degradation of biomass (such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization). The presence of varying biomass composition (cellulose, hemicellulose, and lignin) resulted in differences in carbon structure and yield, degradation mechanism and pathway for each component as shown in Fig. 5. During the thermal degradation process, carbon-rich biomass compounds will be upgraded into polymeric-carbon structure through the possible of reaction pathways (e.g., depolymerization, dehydration, decarboxylation, decarbonylation, isomerization, condensation, aromatization, and radical quenching) [89]. These techniques lead to biomass-derived carbon possessing desirable characteristics, such as a high surface area, a porous structure, acid-based characteristic, redox flexibility, and various surface functional groups, making it a versatile catalyst suitable for a wide range of chemical processes [90,91]. Several studies have been reported on the usage of biomass-derived AC (such as walnut shell-derived nano-rode activated carbon and coconut residue-derived activated carbon catalyst) for the deoxygenation process [51,92–94].

Table 7 summarized the deoxygenation of triglycerides and fatty acid derivatives over carbon-supported catalysts under free-H_2 atmospheres. For instance, the renowned noble metals (Pd/C, Pt/C and Ru/C) have been reported for deoxygenation of fatty acid at 300–350 °C under inert condition in a semi-batch reactor. The result showed high selectivity of 95% to hydrocarbon fractions with complete conversion. The studies summarized preferable deoxygenation pathways of carbon-supported noble metal catalysts (Pd, Pt, Ru), where Pd/C catalyst favor for decarboxylation pathway, Pt/C catalyst prone for decarbonylation pathway, while Ru/C catalyzed both decarboxylation and decarbonylation pathway [88,95–98]. Simakova's study reported that synthetic mesoporous carbon (Sibunit) supported Pd (Pd /C) with different metal dispersion within range of 18–72%. They found that all Pd/C catalysts were active for stearic and palmitic acid deoxygenation. The liquid product is mainly composed of heptadecane and pentadecane. Interestingly, low percentage of Pd loading was identified as the most active ratio for deoxygenation reaction and selectively for heptadecane and pentadecane formation [99]. Immer et al. focused on the deoxygenation of C18 fatty acids (stearic, oleic, linoleic acids) over Pd/C [100]. The team discovered that catalytic deoxygenation of C18 fatty acid under helium conditions occurs primarily through decarboxylation and yielded *n*-heptadecane and heptadecenes. Similar study reported by Fu et al. [101] regarding the ability of Pd/C in deoxygenizing fatty acid via hydrothermal decarboxylation process. The prepared catalyst is able to maintain the pentadecane selectivity for >90% without the loss of reactivity. Other than Pd, Pt and Ru have been proven as effective catalyst, where heptedecane selectivity reached 97% during deoxygenation of stearic acid in batch reactor at 330 °C within 1 h with 10 mg catalyst loading [88]. To summarize, Ru, Pd, and Pt are excellent active metal promoters for carbon support in deoxygenation reactions, but their high price limits their industrial use. As a result, researchers have investigated the use of transition metals as promoted metals for deoxygenation catalysts.

Ni has been found to be effective in removing oxygen atoms from oxygenates and producing diesel-like hydrocarbons. For instance, Santillan-Jimenez and co-workers reported on the comparison deoxygenation profile of 20% Ni/C and 5% Pd/C towards tristearin conversion in a semi-batch reactor [98]. Although 5 wt% Pd/C consistently showed higher selectivity to C_{17}, but 20 wt% Ni/C afforded good yield of fuel-like hydrocarbons. Thus, the 20 wt% Ni/C is potential substitute of 5 wt% Pd/C in the deoxygenation of tristearin. This finding also in agreement with Morgan et al.'s study [58], where 20 wt% Ni/C has been found to be particularly effective for deoxygenation of triglycerides

under N_2 atmosphere. The 20 wt% Ni/C showed high conversion of the triglyceride in most studies with high yields of aliphatic hydrocarbons ranging from C_5 to C_{17}. Besides, it was noticed that 20 wt% Ni/C catalyzed deoxygenation affording high production of CO_2/CO gases which concomitant with the occurrence of C—O cleavage in fatty acids through decarboxylation/decarbonylation pathways. Although Ni suffers from coking due to Ni species, this can be addressed by altering Ni through bimetallic phase formation or incorporation of acid-base metals. The coke affinity by the Ni species can be overcome by modification of electronic properties of Ni oxide phase via incorporation of other potential metal oxides such as $NiO-AgO_2$ [92] and Ni—Co oxide [102], $CaO-La_2O_3$ [51], $Co_3O_4-La_2O_3$ [94] and $Ag_2O_3-La_2O_3$ [93]. The mentioned carbon-supported bifunctional acid-base catalysts have focused on catalyzing the deoxygenation of high unsaturated feedstocks in a free-H2 environment. All the tested catalysts gained high hydrocarbon fraction (>80%) with increased green diesel yield.

4.4. Free-H_2 deoxygenation of triglycerides and fatty acid derivatives over base and acid-base catalysts

In the past, extensive research has been conducted on catalytic deoxygenation reactions of various fatty acids and triglycerides. While many studies have proposed reaction mechanisms for catalytic deoxygenation reactions carried out under H_2 environment, less attention has been given to reaction mechanism studies for free-H_2 deoxygenation over base-catalyzed and acid-base catalyzed studies. This section summarizes the important findings related to the proposed mechanism in deoxygenation reactions over base and acid-base catalysts.

Researchers suggested that base-catalyzed deoxygenation favored triglycerides breakdown by forming intermediate fatty acid via C—O cleavage through hydrolysis pathway [44,104]. Formation of by-product (glycerol) was observed during the triglyceride hydrolysis. The context agrees with a study conducted MgO catalyzed deoxygenation in CSTR system, which resulted in the co-production of by-products (water and glycerol). The study further claimed that water would continue to be obtained through the dehydration of glycerol, releasing gaseous hydrocarbons (propane) and free fatty acids that could undergo further oxygenates abstraction via decarboxylation or decarbonylation pathways [104].

In addition, the majority of studies confirmed that base-catalyzed deoxygenation tends to favor decarboxylation activity, which involves the removal of oxygen in the form of CO_2 [48]. These findings are consistent with previous research on the deoxygenation of triolein using nano-sized $Ca(OH)_2$ and micron-sized CaO catalysts, which resulted in the production of over 90% of decarboxylated product (mono-unsaturated n-C17) [105]. Furthermore, the study reported on the dominancy of decarboxylation pathway in deoxygenation of palm oil over MgO-promoted catalyst under free-H2 environment, where large formation of decarboxylated products (n-C_{15} + CO_2) was observed [104]. However, the role of the basic character in promoting the decarboxylation reaction is still controversial since some studies have found that decarboxylation pathways occur during acid-catalyzed processes [106].

In the case of acid-base catalyzed deoxygenation reaction, it was suggested that the initial reaction started with liberation of fatty acid from triglycerides cleavage via ß-elimination at the glycerol backbone. It is possible for the elimination of carboxylic acid from unsaturated diester without the presence of H_2. The fatty acid obtained will further undergoes fast decarboxylation reaction. The observed reaction pathways aligned with the investigation of acid-base $NiO-Fe_2O_3$/MWCNT catalyzed deoxygenation of Jatropha curcus oil (JCO) in the absence of H_2 (Fig. 6) [107]. The study's reaction mechanism involved several pathways, including hydrolysis, decarboxylation, decarbonylation, hydrogenation, dehydrogenation, cracking, ketonization, and polymerization. Initially, JCO underwent self-hydrolysis, resulting in the formation of primary intermediates, namely oleic and palmitic acid (1). These fatty acids subsequently underwent decarboxylation (2) and
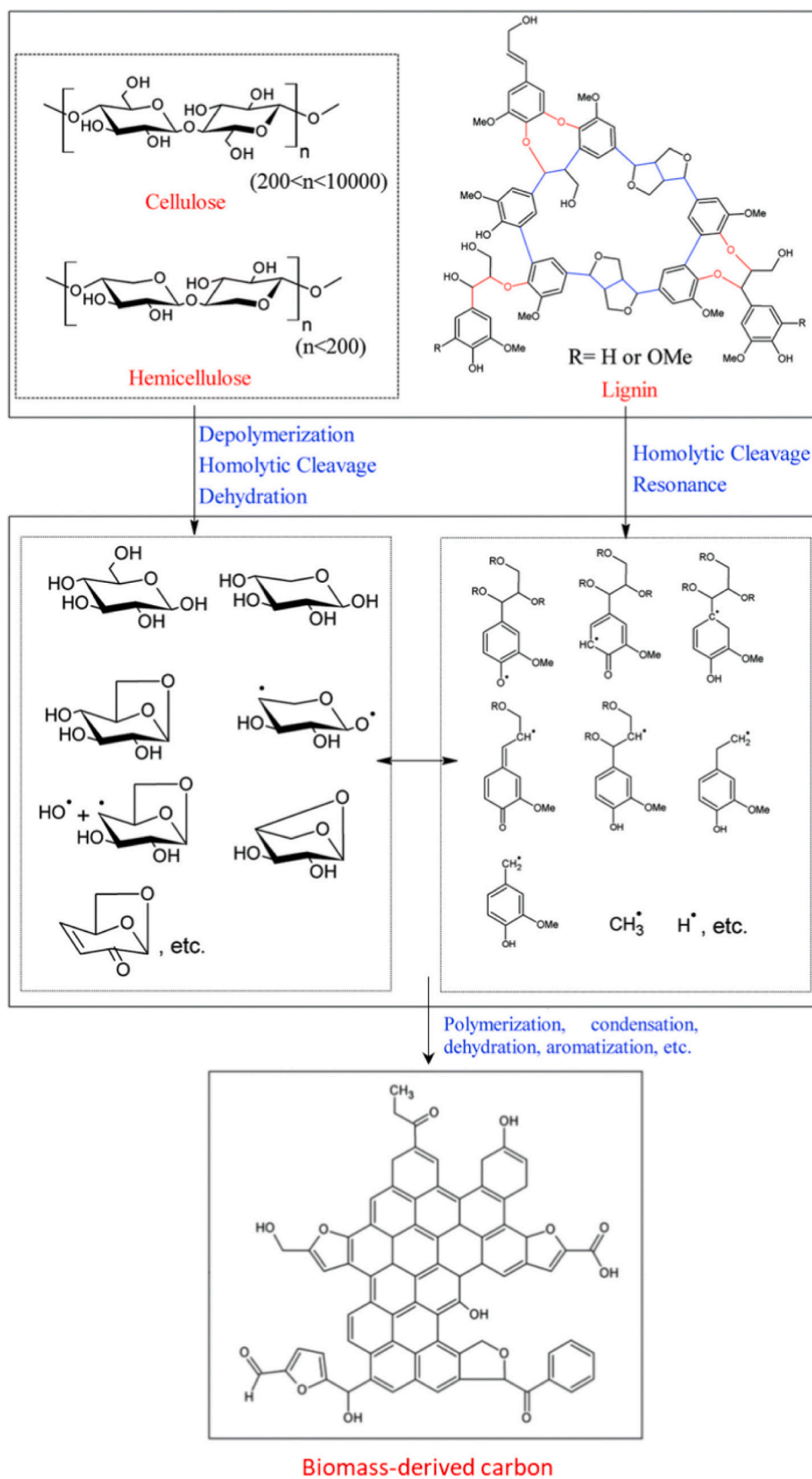
Fig. 5. Thermal upgrading of biomass into biomass-based carbon. Reproduced from Ref. [89] with permission from Royal Society of Chemistry.

Table 7
List of carbon-based catalyst applied in deoxygenation.

| Catalyst	Source of C	Feedstock	Reactor mode	Optimum reaction condition	H/C yield[a]	Sel.[b]	Reference
5% Pd/C	C from commercial activated carbon	Palmitic acid	Batch reactors which	290 °C, 1.5 h, atm pres.	–	35	[95]
		Oleic acid		330 °C, 4 h, atm pres.		16	
5% Pd/C	C from commercial activated carbon	Tristearin	Semi-batch	360 °C, 6 h, N_2 atm,	86	33	[98]
20% Ni/C					75	30	
Pd/C	C from commercial carbon (Sibunit)	Stearic acid, Palmitic acid	Semi-batch	260–300 °C, 5 vol% of H_2 in He/Ar, 17.5 bar	–	54	[99]
Pd/Si-C	C from commercial activated carbon	Oleic acid	Stirred-batch	300 °C, 1 h, Ar atm	–	35	[97]
Pt/C, Pd/C, Ru/C	C from commercial multiwall carbon nanotube	Stearic acid	Micro-batch	330 °C, 1 h	–	97	[88]
Ni/C	C from carbon black	Oleic acid	Fixed-bed micro-reactor	300 °C, 4 h, 10% H	–	98	[93]
1% Pd/C, Pt/C	C from commercial activated carbon	Tristearin, Triolein Soybean oil	Semi-batch	350 °C, 1 h, N_2 atm	–	13–34	[58]
Co_{25}/AC	C from coconut shell	PFAD	Semi-batch	350 °C, 2 h, N_2 atm	90	72	[103]
Ni-Co/MWCNT	C from commercial MWCNT	JCO	Semi-batch	350 °C, 1 h, N_2 atm	80	64	[102]
Ni_5-Ag_5/AC	C from coconut fiber husk	JCO	Semi-batch	350 °C, 1 h, N_2 atm	95	83	[92]
CaO-La_2O_3/AC	C from natural walnut shell	WCO	Semi-batch	330 °C, 3 h, N_2 atm	72	82	[51]
Ag_2O_3-La_2O_3/AC_{nano}	C from natural walnut shell	WCO	Semi-batch	350 °C, 2 h, N_2 atm	89	93	[93]
Co_3O_4-La_2O_3/AC_{nano}	C from natural walnut shell	WCO	Semi-batch	330 °C, 1 h, N_2 atm	96	93	[94]

press = Pressure.
[a] Hydrocarbon yield (%).
[b] Selectivity towards desired deoxygenation product.
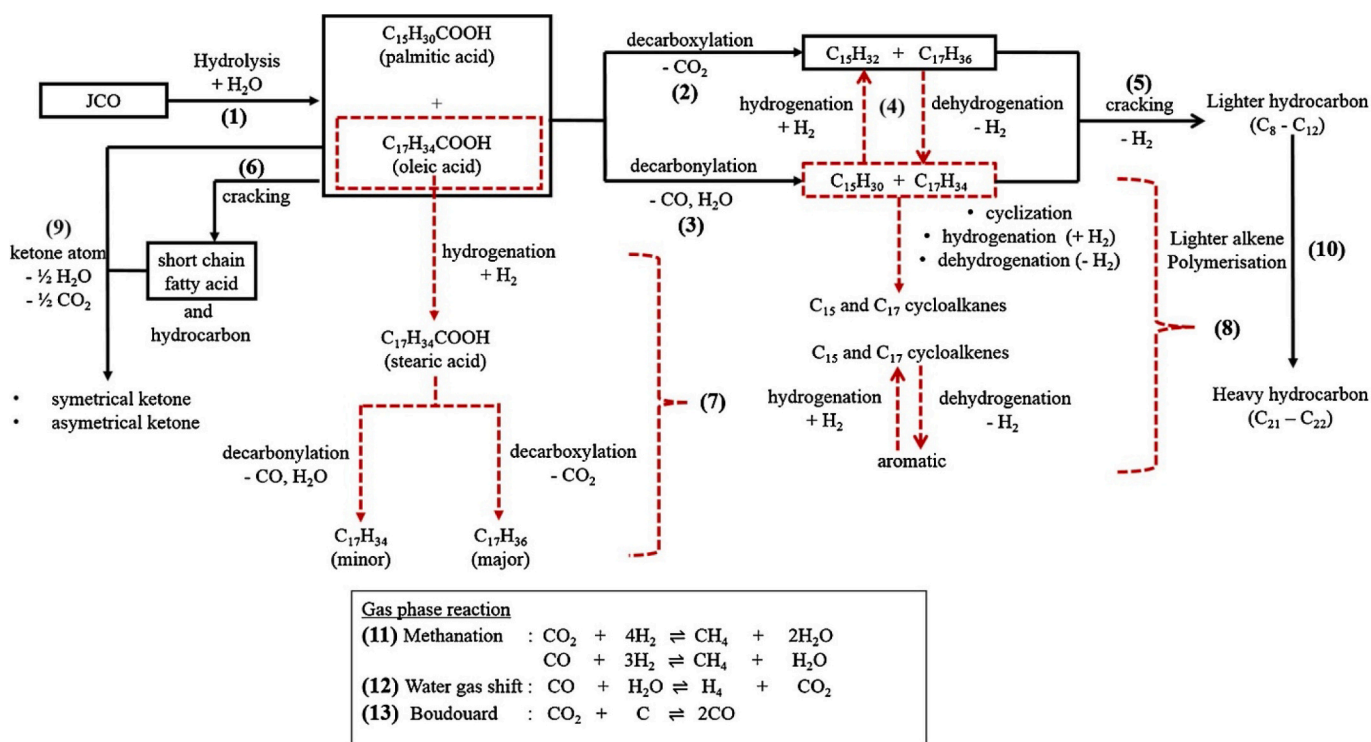
Fig. 6. Proposed reaction mechanism for acid-based catalyzed deoxygenation of tryglyceride. Adapted from Refs. [107] with permission from Elsevier.

decarbonylation (3), leading to hydrocarbon fractions primarily composed of (n-C15, n-C17) and by-products like CO_2, CO, and H_2O. The decarboxylation yielded alkanes ($C_{15}H_{32}$, $C_{17}H_{36}$), while decarbonylation produced alkenes ($C_{15}H_{30}$, $C_{17}H_{34}$) as fuels (4). Some of the $C_{15}H_{30}$ and $C_{17}H_{34}$ also underwent in-situ hydrogenation/dehydrogenation to form $C_{15}H_{32}$ and $C_{17}H_{36}$ (4). It is worth noting that no external H_2 was utilized, and the in-situ hydrogenation was facilitated by cracking and water-gas shift (WGS) reactions. Light hydrocarbons (C_8-C_{12}) were present, indicating the occurrence of cracking reactions where

H_2 was dissociated (5). Concurrently, these light hydrocarbon fractions have a tendency to undergo polymerization (10), leading to the production of heavier hydrocarbons (C_{21}-C_{24}). Other the other hand, the generated palmitic and oleic acid from hydrolysis of JCO could directly undergo cracking, generating shorter fatty acids and light hydrocarbons (6). The study showed high selectivity of C_{15} + C_{17} alkanes (>70%), which attribute to the in-situ hydrogenation of oleic acid into stearic acid. The stearic acid underwent decarboxylation and decarbonylation reactions, resulting in $C_{17}H_{36}$ as the main product with minor amounts

of unsaturated $C_{17}H_{34}$ (7). A small amount of cyclic compounds (e.g., cyclopentadecane) was formed, which suggesting that some $C_{15}H_{30}$ underwent isomerization and/or in-situ hydrogenation/dehydrogenation to generate minor quantities of cyclic alkanes, which further be transformed into aromatics (8). Consequently, the ketone product is directly formed through the ketonization of acid carboxylates to heavier ketone products (9). In addition, the gaseous by-products (e.g., CO_2, CO, H_2, and H_2O) generated during the deoxygenation process underwent gas phase reactions, including methanation of CO_2 and CO (11), water-gas shift (WGS) reactions (12), and Boudouard reactions (13) [107].

Abdulkareem [51,93]] [94] group summarized that the acid-base catalysts (e.g., $CaO-La_2O_3$, $Co_2O_3-La_2O_3$ and $Ag_2O_3-La_2O_3$ supported AC) are effective for deoxygenation of waste cooking oil (WCO) via decarboxylation and decarbonylation reactions It has been observed that acid-base catalyzed deoxygenation may also facilitate mild cracking, which is attributed to the basicity sites on the acid-base catalysts. Comparison studies have shown that base-catalyzed reactions mainly proceed via decarboxylation and mild cracking, while acid-base catalyzed reactions favor both decarboxylation and decarbonylation pathways. Other studies such as deoxygenation of triglycerides over bifunctional acid-base Ni/Al layered double hydroxides (LDHs) catalyst reported the predominantly decarboxylation pathway, which in turn producing large amount CO_2 with high degree of oxygen removal [108]. In addition, deoxygenation of palm fatty acid distillate (PFAD) and WCO over acid-base Co/AC under free-H_2 atmosphere indicated that direct decarboxylation was dominated, where the oxygen is removed in the form of CO_2 as by-product gas with high yield of *n*-pentadecane ($C_{15}H_{32}$) and *n*-heptadecane ($C_{17}H_{36}$) [103]. It was observed the generation of

CO gas but in minor concentration, which suggests decarbonylation occurred with lower extent. Aliana et al. observed an improvement in high decarboxylation and mild decarbonylation reactivity in the deoxygenation of chicken fat oil using bifunctional acid-base Ni-Mg/MWCNT. They suggested that the enhancement of decarboxylation activity was mainly due to the presence of weak and medium acid sites from Ni and MWCNT support, as well as the nature of active basicity from Mg itself, which induced the decarboxylation pathway [109].

5. Catalyst deactivation

While the aforementioned catalysts exhibit a high degree of deoxygenation activity and selectivity towards green diesel, it is important to note that these catalysts may experience reversible or irreversible deactivation over time. Table 8 provides a summary of the catalysts used and the reasons for their deactivation.

5.1. Coking

The primary cause of catalyst deterioration and deactivation is coking, which occurs when coke deposits on the catalyst surface, leading to the blocking or masking of active sites and a reduction in catalyst activity. Several factors contribute to coking, including (i) the presence of acidic or basic sites on the catalyst, (ii) a high degree of unsaturation in the feed or product, and (iii) the presence of oxygen-containing compounds in the deoxygenated product. Recent research indicates that strong acidic sites on the catalyst promote aromatization, polymerization, and polycondensation reactions that result in the formation

Table 8
Deactivation of catalyst in catalytic deoxygenation under free-H_2 atmosphere.

Catalyst	Feed	Product	Reaction condition	Reactor mode	Deactivation				Coke (wt %)	Reference
					Coke	Poisoning	Leaching	Sintering		
Co-CaO	Triolein	C8-C17 hydrocarbon (renewable diesel)	1 h; 350 °C; partial vacuum, 5 wt% catalyst loading	Semi-batch	√	√	–	–	8.2	[114]
NiO-CaO/SiO₂-Al₂O₃	Triolein WCO JCO PFAD	Diesel-like fuel	1 h; 350 °C; partial vacuum & N₂ flow condition 30 ml/min	Semi-batch	√	√	√	–	13.7	[116]
ZSM-5	Rapeseed oil	Biochemicals and biofuels (hydrogen, light olefins, aromatic hydrocarbons and carbon nanotubes)	3 h; 550 °C; atmospheric N₂ condition	fixed-bed (down flow)	√	–	–	–	~15	[111]
Pd/C, Pd/Sebunit	Lauric acid	Renewable diesel (undecane & undecene)	26 h, 300 °C: 0.075 ml/min reactant flow rate (WHSV 0.33 h⁻¹), 15 bar Ag, 10 ml/min argon flow, 4.4 mol/l (solvent-free conditions).	Fixed-bed	√	–	–	√	–	[106]
Pd/C	Lauric acid	Diesel-like products (hydrocarbons)	1 h; 270 °C; Atm pressure	Fixed-bed	√	√	–	–	–	[60]
CsNaX zeolite	Methyl octanoate	Transportation fuel (heptenes, hexenes, olefin)	6 h; 425 °C, 1 atm, W/F = 198 gh/mol, 25 ml/min of He.	Fixed-bed	√	–	–	–	3.5	[123]
MgO/ Silica–alumina; MgO/ sulfated zirconia	Methylglyoxal	Upgraded compounds (e.g. propenal, methyl vinyl ketone)	500 °C under inert He atmospheric condition	Single shot Micropyrolyzer	√	–	–	–	–	[113]
Pd/C, Pt/C	Stearic acid	Diesel-like hydrocarbon (C17 product)	6 h; 300 °C, 6 bar; He 25 ml/min	Semi-batch	√	–	–	–	–	[55]
NiCo/MWCNT	JCO	C15- and C17-hydrocarbon	1 h; 350 °C; partial vacuum condition	Semi-batch	√	–	–	–	4–5	[102]
CaO-La₂O₃/ AC_nano	WCO	Automotive green diesel	3 h; 330 °C; N₂ flow condition	Semi-batch	√	–	–	–	<1.5	[51]

*DO = deoxygenation, WCO = waste cooking oil, JCO = jatropha oil, PFAD = palm fatty acid distillate.

of large polyaromatic species, which serve as coke precursors. This was observed in studies conducted on the deoxygenation of bio-oil over a strong acid catalyst (HZSM-5), which led to the formation of large molecular compounds composed of aromatic substrate and resulted in catalyst deactivation [110]. Other studies have shown that 43 wt% and 22 wt% of coke deposited on nanocrystalline ZSM-5 zeolite and hierarchical zeolite, respectively, during deoxygenation of rapeseed oil at 550 °C for 3 h in a fixed-bed down flow reactor [111]. The coking was resulted from the polymerization/condensation of aromatic hydrocarbons. In addition, the presence of rich oxygenated aromatic compounds on the weak acid sites of NaX can also contribute to coking [112].

To date, implementation of high basicity catalysts either as a support or active metals for deoxygenation process catalyst are still considered ineffective due to noticeable coking effect. Study focus on deoxygenation of methylglyoxal at 500 °C has indicated that the high content of coke deposited formed once the MgO incorporated with mild acidic supports (SiO_2-Al_2O_3, sulphated ZrO_2). This implied that MgO apparently favored coking due to the blockage of basic active sites by heavy oligomeric compounds formed from secondary reaction of deoxygenation (aldol condensation) [113]. However, a study reported that the significant reduction of coke occurred when basicity of the catalyst were increased. This result proves that instead of coking, basicity may have positive effect on improvement of catalyst stability [114].

Coking also high favorable when the deoxygenation reaction was carried out using rich unsaturated feed. The unsaturated species can act as inhibitors by adsorb strongly to the catalyst surface and/or acting as precursors to coke formation which simultaneously reduce deoxygenation activity [115]. Investigation of catalyst coking was conducted on free-H_2 deoxygenation of various non-edible oil such as JCO (FFA: 15%), WCO (FFA: 18%), and PFAD (FFA: 86%) over NiO-CaO/SiO_2-Al_2O_3 catalyst [116]. Based on TGA analysis of spent catalyst from deoxygenation of PFAD, the results showed the highest coke formation (14%) as compared to deoxygenation of WCO (13%) and JCO (12%). Coke precursor (Poly aromatic compound) was produced via fast aromatization process (involved cyclization, dehydrogenation and condensation reactions) of unsaturated fatty acid chain in FFA. In addition, rapid deactivation of activated carbon supported Pd and Pt (Pd/C and Pt/C) catalysts was observed under the presence of rich unsaturated hydrocarbons and acids (unsaturated deoxygenation and cracking products) from the DO of stearic acid [55].

It is worth noting that oxygen-containing compounds generated during deoxygenation can adsorb strongly onto the catalyst surface and cause catalyst deactivation. The presence of non-cyclic trimers (e.g. phorone) derived from aldol condensation of mesityl oxide and acetone are the key intermediate species that lead to coke formation. Similarly, other study observed high coking activity due to the presence of rich phenolic species in the reaction product [117].

5.2. Poisoning

Poisoning is a process that chemically deactivates a catalyst by adsorbing chemical compound on its active sites, instead of thermal degradation and physical structure damage of catalyst. Several common poisons compound that consists of organic functional groups and inorganic anions with strong affinity for adsorption on metal catalyst surfaces. This includes carbon monoxide, halides, cyanides, sulfides, sulfites, phosphates, phosphites, as well as organic molecules like nitriles, nitro compounds, oximes, and nitrogen-containing heterocycles. This process occurs through chemisorption by entails the bonding between unwanted compound to the active sites of catalyst, which modifies the chemical nature and electronic properties of active sites; reduce the available active sites; and affects the selective reaction pathway of feedstock conversion [117]. It's important to note that the susceptibility of a catalyst to poisoning depends on several factors, such as, (i) type of chemical compounds generated in reaction medium during catalytic process (e.g. reactive byproduct, inhibitors, contaminants, corrosive

substance, moisture); (ii) type of catalytic structure that favor of compound chemisorption; and (iii) Severe reaction condition (high temperature and pressure) lead to structural changes and undesirable side reaction [117].

Poisoning can occur in two ways: (1) poisoned by gas and (2) poisoned by water. Gas poisoning, such as absorption of CO_2 and CO gases during deoxygenation reactions, can result in chemical changes on the catalyst surface [118]. Evidently, literature study reported the use of active Co-CaO$_{clamshell}$ catalyst in deoxygenation of triolein under free-H_2 condition had converted to inactive $CaCO_3$ phases after completed the reaction [114]. Similar finding were observed MgO catalyst, where MgO was converted into inactive carbonate phase ($MgCO_3$) after reaction [104]. It was noted that the absorption of the poison gases will be noticeable if the deoxygenation reaction is entirely performed under a close reaction system. Water, which forms during deoxygenation reactions, can also disrupt catalyst effectiveness by strongly adsorbing on catalyst surfaces and disturbing the main reactions occurring on active sites. Thus, both unfavorable gas and water poisoning can significantly impact the efficiency of deoxygenation catalysts, especially when reactions occur in closed systems [119].

5.3. Leaching or lixiviation of metal

Leaching or lixiviation occurs when the active metal in a catalyst partially dissolves from its solid phase into a liquid reaction medium, resulting in the removal of active metal particles and a decrease in catalytic activity. The leaching process can occur due to solubilization in the liquid medium or chemical transformations at high temperatures [113,117]. Several factors that can cause catalyst leaching or lixiviation include, (i) the solubility and leaching of catalyst's active components affecting by the corrosive and incompatible solvents; (ii) severe reaction conditions (e.g., extreme pH condition, elevated temperature, prolong time, and highly oxidative/reductive conditions) can lead to the dissolution of catalyst components; (iii) stability of catalyst can be affected by synthesis method, choice of catalyst support and catalyst structure; and (iv) Small particle sizes of catalyst easily susceptible to leaching due to large of surface area and contact surface [120].

Generally, deoxygenation catalysts in the form of metal oxides, hydroxides, and carbonates are typically slightly soluble in water and can undergo direct solubilization. On the other hand, the elements of the catalyst can react with reactants, intermediates, or products in the reaction mixture, forming a soluble or inactive species, resulting in leaching through chemical modification. For instance, metal oxide catalysts can form metal hydroxides during the hydration process in hydrothermal conditions. Catalysts such as CaO are hydrophilic and tend to form hydroxide phases during the deoxygenation reaction, which requires additional treatment, such as a calcination process, to reactivate the active sites of CaO [121].

5.4. Sintering

Another limitation of the catalytic deoxygenation process is the deactivation of the catalyst resulting from sintering of metal particles (metal particles agglomerate and size growth) during the reaction process. Sintering is unavoidable process as it easily to occurred at high reaction temperature, thus leading to a decrease in surface area and catalytic activity [122]. Several factors can contribute to catalyst sintering, such as, (i) Extreme reaction conditions (e.g., high temperature, over prolonged reaction time, high pressure) facilitates diffusion of catalyst particles (coalescence of metal atoms or ions) into close contact and sintering; and (ii) Type of catalyst structure and stability (e.g., chemical composition and catalyst support interactions) affected the propensity of sintering [120].

Obviously, sintering typically enhanced with the use of Ni in catalyst. The enlargement of the Ni particles resulted in the modest reduction of catalyst surface areas and thus reduced the deoxygenation activity [92].

5.5. Alternative pathways for coke inhibitor

Understanding the underlying causes of deactivation can help to mitigate the effects of coking and prolong catalyst lifetime. In this discussion, we provide an overview of alternative pathways that can be used to reduce coke formation and prevent catalyst deactivation.

One of the alternatives of coke inhibitor is solvent usage such as water, methanol, nonane as sources of H_2. The proper solvent usage able to reduce the coke formation as well as improve the selective reaction pathway. Zhu et al., [124] showed that addition of water with the anisole feed in the presence of acid catalyst (HZSM-5) at 400 °C gave 2.5 times of reactivity as compared with the system without water, which simultaneously suppressed the coke formation. Albeit addition of water showed positive effect on catalytic reactivity, but controllable amount of moisture content should be taking concern. Excess of water not only reduce the deoxygenation activity but also change the chemical properties of the catalyst. Moreover, inappropriate amount of water will reduce the dispersion of active metal and resulted the agglomeration of active sites for intermediate reaction pathways [125]. Instead of water, chemical solvent is effective in promoting the deoxygenation and highly resistant towards coke formation. Evidently, Sooknoi's reported the usage of methanol and nonane as solvents in deoxygenation of methyl octanoate over CsNaX. The deoxygenation activity rapidly increased and coke was found lower (3.5–7.9 wt%) [112].

Acidic-based catalysts have been found to be prone to deactivation, making neutral-type support materials such as carbon and SiO_2 more preferable due to their lower activity towards coke formation. For instance, deoxygenation of *Jatropha Curcas* oil over a carbon-based catalyst (NiCo/MWCNT) showed minimal coke formation, thus allowing for continued reusability [102]. Similarly, modified carbon-based catalysts were found to produce only small amounts of coke (< 4 wt %) during the free-H_2 deoxygenation of WCO, PFAD, and chicken fat oil [51,109].

Incorporating an active metal/promoter with basicity into an acidic support has been suggested to reduce coke affinity. Sooknoi and colleagues [112] found that adding Na active metal to zeolite (NaX1.4) was effective in decreasing coke formation. Danuthai and colleagues [123] reported that increasing the Cs content from 2% to 20% resulted in a 20% reduction in coke formation by increasing the number of Lewis basic sites. Besides, a significant reduction in coke formation by adjusting the acidity-basicity ratio of Co-CaO through varying the cobalt loading from 10% to 40% was observed [114]. However, it should be noted that the effectiveness of this approach is still under debate, as some studies have suggested that adding a basic active metal could actually promote coking [113].

Lowering the reaction temperature is an alternative method to minimize the coking effect during the deoxygenation process. By reducing the temperature, unfavorable side reactions such as dehydrogenation can be avoided, preventing the formation of aromatic compounds and further cyclization processes, which contribute to coking. Noteworthy to mention that high coking degree at early stages of deoxygenation reaction could be prevented by allowing more progressive heating. This could be accomplished using fixed bed reactor. Besides, progressive heating can be achieved by using microwave energy as the heat source [126]. Microwave radiation provides a fast, clean and energy efficient heating process as compared to conventional technologies. The latter method provides a faster, cleaner, and more energy-efficient heating process, resulting in a more efficient heat transfer to the feedstock and reducing the formation of undesirable species that can lead to coke formation.

Furthermore, coking during deoxygenation can be mitigated by conducting the reaction under an inert gas flow condition. It is reported that catalytic deoxygenation under an inert N_2 flow resulted in a more favorable reaction system, with high hydrocarbon yield and excellent diesel selectivity, compared to a vacuum system [116]. The catalyst used in the N_2 flow reaction was also more stable, with less coke formation. A similar case was reported by Bernas et al. [106] during the deoxygenation of dedecanoic acid under an inert Ag flow condition, where the conversion dropped to approximately 30% as the Ag gas flow stopped, and increased to 50% as the Ag flow was switched back on. Based on these findings, it suggested that applying a continuous inert gas flow throughout the reaction system could remove the CO_2 and CO gases produced from the $deCO_x$ reaction, while also promoting the desorption of organic contaminants from the active surface of the catalyst through continuous gas purging. This could help conserve the catalytic activity of the catalyst for a longer period.

6. Conclusion

The term "green diesel," also known as bio-based liquid hydrocarbon carbon, has gained significant attention as an alternative to petro-based transportation fuel due to its compatibility with existing fuel and similar characteristics. This fuel can be produced by the deoxygenation process of biomass that includes oxygenate compounds such as triglyceride-based vegetable oil, fatty acid derivatives, or biomass pyrolyzed bio-oil. Deoxygenation involves the removal of oxygen and can occur through several pathways, including cracking, decarboxylation, decarbonylation, hydrodeoxygenation, or hydrogenation. While most studies focus on hydrodeoxygenation requiring H_2 gas, the deoxygenation process in the absence of H_2 has great potential for green diesel production and will reduce dependence on petro-based H_2 usage.

This review summarizes studies on hydrocarbon-like structure production via deoxygenation in a free-H_2 environment, with a focus on potential deoxygenation catalysts such as promoted metal-based catalysts (monometallic and mixed metal oxides) and catalyst supports suitable for free-H_2 conditions. Unlike hydrodeoxygenation, the criteria for deoxygenation catalysts mainly focuses on the acidity-basicity of active sites, followed by textural properties (surface area and porosity) and nanostructure.

The review indicates that bifunctional acid-base catalysts render selective reaction pathways with reduced coking formation compared to acid or base catalysts. Additionally, the discussion covers catalyst deactivation, which is influenced by coking, poisoning, leaching of metal, and sintering, and effective alternatives to prolong the catalyst lifetime. Finally, the factors that induce the coking, poisoning, leaching and sintering effect, such as acid and basic active sites, nature structure of catalyst, unsaturated feedstock, and severe reaction condition are discussed. All of this information will assist researchers in designing reliable deoxygenation catalysts for green diesel production.

6.1. Summary and future perspectives

Drawing from the preceding sections, the utilization of bifunctional acid-base catalysts derived from metal oxides or biomass-derived carbon has proven effective for green diesel production via the deoxygenation reaction. However, these catalysts still encounter numerous challenges. For instance, certain metallics/metal oxides (e.g., calcium-derived catalysts) tend to be susceptible to catalyst deactivation due to coking, poisoning, leaching, and sintering. Generally, catalysts with oxide, hydroxide, and carbonate phases suffer from direct solubilization, while others are prone to coking activity. Additionally, the reaction medium and environment (type of feedstock, oil rich with unsaturated species, and lack of inert gas flow) contributes to rapid catalyst deactivation during free H_2 deoxygenation process.

To address these issues, considerable progress has been made by controlling the characteristics of acid-basic sites and emerge mesoporous catalyst support for better catalyst stability; introducing solvents to enhance the homogeneous of reaction medium by reduce the undesirable by-product/unsaturated species; lowering reaction condition with shorter process time through adopting microwave systems; and implementing sufficiently of N_2 flow systems. At this current stage, the optimal composition of acid-basic sites that positively impact the

deoxygenation reaction remains unclear and necessitates further research. Particularly, the use of solvents with regulated moisture content requires investigation, where excess of moisture resulted in depleted deoxygenation efficiency. While microwave systems offer progressive heating within a shorter time frame, reducing oxygenated species during deoxygenation and minimizing coke formation at lower temperatures. However, further implementation of microwave system in manufacturing scale is hindered by financial constraints. Consequently, the conventional heating systems that apply in biorefinery still hold significant appeal.

Ethics approval

The authors hereby state that the present work is in compliance with the ethical standards.

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CRediT authorship contribution statement

N. Asikin-Mijan: Conceptualization, Writing – original draft. **J.C. Juan:** Writing – review & editing, Supervision. **Y.H. Taufiq-Yap:** Writing – review & editing. **Hwai Chyuan Ong:** Writing – review & editing. **Yu-Chuan Lin:** Writing – review & editing. **H.V. Lee:** Conceptualization, Writing – review & editing, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Not applicable.

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