

Recent Advances in the Catalytic Deoxygenation of Plant Oils and Prototypical Fatty Acid

Models Compounds: Catalysis, Process, and Kinetics

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Abstract

With the inevitable human innate aspirations for better urban mobility and sustainable economic development, bio-based transportation fuels are projected to play an essential role in the foreseeable automotive transportation sector. Agricultural-based renewable diesel (RD) is the prospective fuel of tomorrow due to its excellent fuel properties and environmentally friendly attributes. This review summarises the evolution of research works related to upgrading of plant oils and fatty acids to diesel-like hydrocarbons via catalytic deoxygenation (CDO) technologies in the past decade. Throughout this review paper, a strong emphasis is put on the fundamental

chemistry, reaction mechanism and kinetic modelling. The influence of the key process parameters that may affect the diesel hydrocarbon product yields/selectivity including the types of feedstock, types of catalyst, and key operating conditions are also explicated. This paper also addresses the technical barriers, challenges, and prospects of CDO technologies that could potentially bridge between the existing research gaps and industrial practices in these areas. In summary, this paper will help scientific researchers and industrial practitioners to explore recent scientific advances and potential strategies in producing sustainable diesel fuel from natural plant oils and fatty acids.

Keywords

Catalytic deoxygenation; plant oil; fatty acids; diesel-like hydrocarbons; renewable diesel

1. Introduction

As civilization is advancing inline with modern industrialization and urbanization, the world is at a juncture in combating alarming climate change and a diminishing petroleum oil reserve crisis. The societal realization of the finiteness of fossil fuels and their potential for adverse ecological impacts have spurred the development of sustainable fuel alternatives to replace the concentrated energy source that fossil fuels provide. Production of renewable fuels from biological origins are a key mitigation strategy in fighting climate change and partially meeting the soaring global energy demands. Agriculture based triglycerides are a promising raw material for the production of sustainable transportation fuels. They are non-toxic, renewable in nature, biodegradable, easily exploitable, eco-friendly, and readily available in an abundant quantity. Triglycerides are chemically simple in structure and have 16 - 18 carbon atoms in length corresponding to that found in transportation fuel except for the additional carboxyl functional groups attached. However, direct incorporation of unmodified plant oil as liquid fuels

into the current fuel engine is undesirable due to its inherently high viscosity, thermal instability, low heating value, and high oxygenate contents [1]. As an alternative, catalytic deoxygenation (CDO) of plant oils and fatty acids is the prospective production route in transforming high boiling point and molecular weights triglyceride compounds into highly valued diesel-like hydrocarbons that are fully compatible with the automotive engine without any modification. CDO generally requires high-pressure molecular hydrogen to remove heteroatom and impurities present in the triglyceride feedstock [2]. It transforms residue material into premium quality biofuel with superior fuel properties including high cetane number, excellent energy density, and better oxidation stability [3, 4]. To facilitate the CDO reaction, both homogeneous and heterogeneous catalysis have been well-investigated and reported by many other researchers [5-8].

Table 1 compares the advantages and disadvantages of heterogeneous and homogeneous catalysts in CDO reaction. For homogeneous catalysis, organometallics are the most common catalyst used for CDO reaction due to its simplicity, economically cheap, and highly active physiochemical properties as presented in Table 1 [6]. On the contrary, heterogeneous catalysts are more susceptible to metal leaching and causing product fouling or sintering of oxide supports such as TiO_2 , Al_2O_3 , PtO_2 due to condensation of the polar-polar substrate and catalyst surface cascades. Despite the homogeneous catalysts are fully exempted from the typical limitations encountered by the heterogeneous catalysts, the separation of homogeneous catalysts from the product stream is rather cumbersome and usually incurs additional operational costs [6, 9, 10]. As a result, little effort has been dedicated to the development of homogeneous CDO systems, especially for both acid and hydrogenating metals precursors in homogeneous molecular

dispersed phase. Hence, this review paper exclusively focuses on the application of novel heterogeneous catalysis in CDO of plants oils and fatty acids.

Table 1: Comparison of heterogeneous and homogeneous catalysts in CDO reaction system.

Type of catalyst	Heterogeneous	Homogeneous
Catalytic activity	Variable	High
Price	High	Low
Severity of reaction condition	Harsh	Mild
Reusability	Yes	No
Longevity	Long	Low
Stability	High	Low
Tuneable physiochemical characteristic	Yes	No
Fouling and coking	Yes	No
Mechanistic understanding	Moderate	Easy
Electronic design	Not possible	Achievable

In summary, this review paper focuses on all types of plant oils and fatty acids compounds as a sustainable feedstock for renewable diesel production. Besides, the paper also elucidates the reaction mechanisms of CDO with the critical factors that affect reaction performance and diesel product selectivity such as types of feedstock, types of catalysts, and the principal process conditions. Furthermore, the technical barriers, challenges, and future direction of CDO technologies are highlighted and discussed in detailed to shed lights on some of the pressing CDO issues and knowledge gaps.

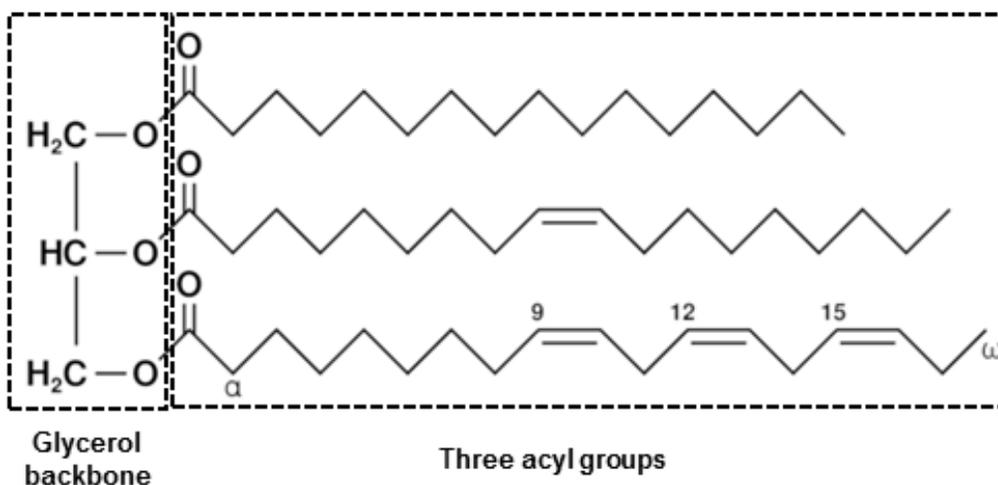
2. Plant oils and fatty acids – Prospective feedstock for renewable diesel (RD) production

Plant oils and fatty acids are the prospective resources for the production of bioenergy due to their inherent renewability, biodegradability, and abundant quantity. However, the suitability of such resources for renewable diesel production depends on several factors including

the local availability of the feedstock, extraction cost, oil yield, and most importantly the fatty acid composition as it will determine the fuel properties of the liquid products [11]. Furthermore, feedstock selection is a major consideration closely associated with the feasibility of commercializing such renewable fuel production as the raw material cost can reach up as high as 75% of the total production cost [12]. Moreover, proper feedstock selection can aid to reduce tariffs and transportation costs which further lower down the overall production expenditures [13, 14].

2.1 Plant oils

Plant oils can be categorized into two types: edible and non-edible plant oils [15]. Plant oils are extracted from a wide range of oil-bearing seed crops via mechanical pressing, supercritical fluid extraction, and solvent extraction [16]. Triglycerides are the main constituent of natural plant oils. Figure 1 illustrates the molecular structure of triglycerides, in which the long-chain fatty acid esters composed of a glycerol backbone with three acyl groups (three fatty acids) bounded. The ester linkage of triglycerides, fatty acids are aliphatic carbon chains connected to a carboxyl group (HO-C=O). They are typically 10 to 22 carbon atoms in length with varying degrees of unsaturation, ranging from zero to three double bonds. The ester molecule usually contains an even number of carbon atoms in a linear unbranched aliphatic hydrocarbon chain with up to three cis oriented double bonds in the position of 9, 12, and 15 [17]. **a**



b

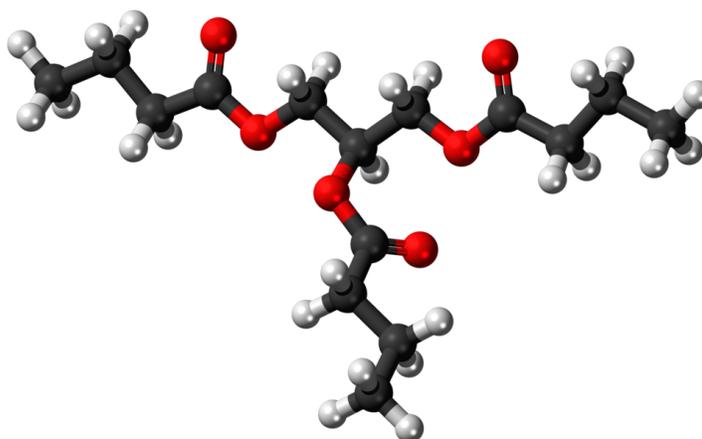


Figure 1: a.) Skeleton structure and b) 3-D ball and stick diagram of a triglyceride

Although plant oils are chemically similar in nature, the nomenclature of triglycerides is usually classified by its chain length and saturation degree of fatty acid side chains. The fatty acid composition profile of some plant-based triglycerides including both edible and non-edible plant oils are summarized in Table 2. Plant oil fatty acids composition varies with the type and quality of its origin source as well as geographical and climate conditions in which the plant grows [18]. The fatty acid rich plant oil commonly contains an even number of carbon atoms up to 22 carbon atoms in total. They seldom have functional groups other than the carboxyl group

and unsaturated center. From Table 2, most plant oils contain palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3). Some of the plant oils also contain other fatty acids like myristic acid (C14:0), palmitoleic acid (C16:1), and arachidic acid (C20:0).

Table 2: Fatty acid composition profiles of edible and non-edible vegetable oils [18, 19].

Types of plant oils		Fatty Acid Composition (wt%)										
		C _{10:0}	C _{12:0}	C _{14:0}	C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}	C _{20:0}	C _{22:1}
Coconut Oil	Edible	5	47	18	9	-	3	6	2	-	-	-
Cottonseed oil	Edible	-	-	1	22	-	3	19	54	1	-	-
Peanut oil	Edible	-	-	-	11	-	2	48	30	2	1	-
Palm oil	Edible	-	-	1	45	-	4	40	10	-	-	-
Sunflower oil	Edible	-	-	-	7	-	5	19	68	1	-	-
Soybean oil	Edible	-	-	-	12	-	3	27	52	6	-	-
Rapeseed oil	Edible	-	-	-	4	-	1	65	22	8	-	-
Almond oil	Edible	-	-	-	7	1	2	67	23	-	-	-
Castor Oil	Non-Edible	-	-	-	1	-	1	3	5	0.6	0.7	-
Jatropha oil	Non-Edible	-	-	0	14	0	6	50	30	0	-	-
Karanja Oil	Non-Edible	-	-	-	11	-	7	53	16	3	-	-
Neen Oil	Non-Edible	-	-	-	16	-	10	50	16	8	-	-
Rubber Seed Oil	Non-Edible	-	-	2	20	-	9	25	30	16	-	-
Carinata Seed Oil	Non-Edible	-	-	-	3	-	1	10	18	19	0	41
Macauba Oil	Non-Edible	-	-	-	28	-	2	61	6	3	-	-

**For the fatty acid composition of C_{a,b}, the subscript a and b indicate the number of carbon atom/carbon chain length and number of double bond (=) within the carbon chain, respectively.*

In the past decade, plant oils have gained considerable attention as a sustainable resource for bioenergy production due to their inherently high energy density and structural similarity to petroleum-based liquid fuels. In the literature, the most common first-generation plant oils that have been used for CDO reaction are those derived from food crops. Among the edible oils, soybean oil [20, 21], palm oil [22-25], sunflower oil [26], and rapeseed oil [27-30] have been used extensively as the feedstock in producing renewable diesel (RD). However, rapeseed, sunflower, and soybean oils are generally unsuitable to be used as feedstock in the Southeast Asia region due to their low crop availability. Thus, many researchers in Southeastern Asia regions, especially Malaysia, Thailand, and Indonesia have incorporated palm oil as the main feedstock for the production of synthetic diesel hydrocarbons due to its abundance and sustainability [31]. In fact, Malaysia is the world's largest producer and exporter of palm oil today followed by Thailand and Indonesia, contributing over 49.5 % of the world production and 64.5% of global exports [31]. Production of diesel hydrocarbons from rapeseed and sunflower oils primarily dominated in Europe include the Czech Republic and Russia. Soybean oil, on the other hand, is the main feedstock for RD production in the United States of America [11, 13]

Figure 2 shows the number of peer-reviewed scholarly articles related to the deoxygenation of plant oils and fatty acids from 2010 to 2020. The increasing scholarly output trend in Figure 2(a) revealed the growing interests of international researchers and industrial practitioners in plant oils and fatty acids deoxygenation. From Figure 2(b), China and the United States of America are the two major publication hubs for such research works, followed by India, the Czech Republic, and Russia. From 2010 to 2015, a number of research works have emphasized on the production of synthetic diesel fuels from a diverse spectrum of edible plant oils including soybean, rapeseed, canola, and sunflower oils. However, like biodiesel production, the main

limitation of using edible oil for fuel production is its affiliation with the “food-versus-fuel” debate, in which the rising food prices is partially related to the increase of energy crop cultivation over food crops [32].

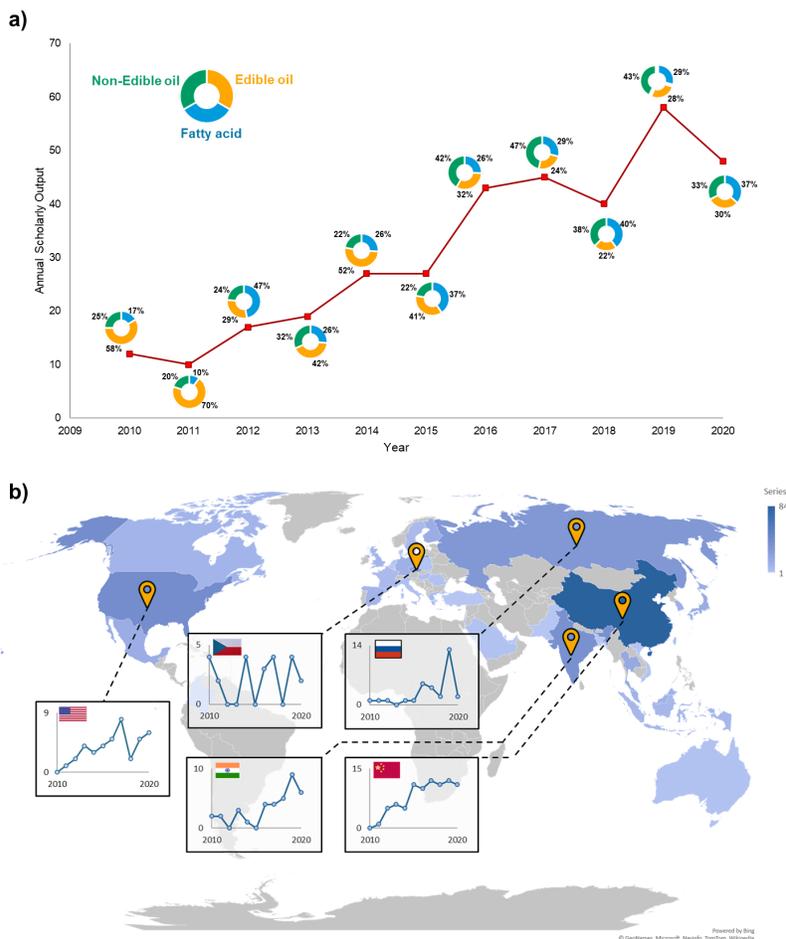


Figure 2: (a) Relevant scholarly output from 2010 to Sept 2020 (Data obtained from Scopus database via keyword search of “deoxygenation”, “plant oil”, “vegetable oil” and “fatty acid”); and (b) World map showing the total number of journal articles published in each country from 2011 to Sept 2020 (note: the line charts present the annual scholarly output of the top five contributors).

From Figure 2(a), one can notice that there is a noteworthy shift in the paradigm of the deoxygenation works from the year 2015, where the “food-versus-fuel” debate that stigmatized edible oils has led the scientists to turn their interests to other non-food-based alternatives. Since then, second-generation non-edible plant oils have been well-considered as the potential low-cost feedstock for synthetic diesel oil production due to its wide availability of resources, liquid nature portability, and inherent renewability origins. Furthermore, non-edible oils are unsuitable for human ingestion due to their toxicity [33]. Most of all, it can be grown in wastelands that are not suitable for food crops and subsequently eliminate the need to compete with food crop plantation sites [34]. These crops can sustain a reasonably high oil yield without intensive care, which subsequently lower the cost of cultivation [33]. In early 2009, various studies were performed to investigate the deoxygenation of non-edible plant oils including jatropha, macauba, rubber seed, castor, and karanja oils into diesel-like hydrocarbon fuels. Among the non-edible plant oils, the conversion of jatropha oil to synthetic diesel oils have been well-investigated due to its high energy density, easy conversion to liquid biofuels, high oil yields at a lower price, ease of establishing and maintaining jatropha plantation [35-41]. With such growing amount of research projects and activities being taken, it has shown the eagerness and readiness of the academic, industry, and public society in tackling the ethical issues of using edible oils in fuel production.

In relation to the debate around the food-versus-fuel dilemma, proper selection of non-edible plant oils feedstock plays an essential factor in determining the practicability and sustainability of the entire deoxygenation process. The fatty acid composition of natural plant oils has been reported to affect the liquid fuel properties, hydrogen (H₂) uptake rate, and degree of exothermic heat releases during hydrogenation reactions. Numerous CDO studies have reported that plant

oil-based feedstock with longer fatty acid carbon chain length and higher unsaturation levels tend to promote oligomerization, dimerization, aromatization, and cyclization of reaction intermediates at low H₂ pressure and low H₂ to oil ratio [42, 43]. Heavy molecular weight species such as cycloalkane and aromatics are readily formed, retard, and inhibit the overall reaction rate, causing catalyst deactivation. Sugami, et al. [29] studied the hydrothermal hydrogenation and decarboxylation of rapeseed oil over Pd/C catalysts under the reaction temperature of 300 °C and H₂ pressure of 1MPa. From the results, a total yield of 91.5 mol% saturated hydrocarbons was obtained after 120 mins. However, it was revealed that a lower diesel hydrocarbon selectivity was mainly found when unsaturated fatty acid moieties underwent deoxygenation. This can be attributed to the co-occurrence of undesirable side reactions include dehydrogenation, cyclization, ketonization, dimerization, cracking under the presence of unstable double bonds. A similar trend in catalyst deactivation and low paraffin hydrocarbon yield was also observed in both deoxygenation studies of Kim et.al. [43] and Asikin-Mijan et.al. [42]. Both studies agreed that the presence of unstable double bonds in triglycerides promoted strong adsorption onto the surface of the catalyst and enhanced the formation of heavy products by oligomerization (mostly dimers) of unsaturated fatty acid derivatives through Diels–Alder reaction and/or radical addition. In terms of molecular hydrogen requirements, hydrogenation of highly unsaturated triglycerides usually requires greater H₂ consumption than that required for less unsaturated triglycerides for the same level of hydroconversion. Furthermore, Jeczmionek & Porzycka-Semczuk [44] investigated the relationship of exothermic heat released associated and the unsaturation level of plant oil in a continuous tubular flow reactor. From the results, it showed that the total thermal heat liberated increased linearly with the unsaturation level of fatty acid contents in plant oil. Highly exothermic olefins saturation reaction can lead to zones of local

overheating and hot spots in the bulk catalyst bed, subsequently resulting in rapid loss of catalytic activity [45]. Thus, the triglyceride feedstock should have the lowest unsaturation level possible to avoid high H₂ consumption requirement and the occurrence of local overheating from a highly exothermic hydrogenation reaction. Furthermore, a high level of free fatty acid in the feedstock is desirable for the production of synthetic diesel hydrocarbon fuels as it could alleviate the severity of deoxygenation conditions considerably by eliminating the triglyceride hydrolysis step. As reported by Cheah et.al [31], the intrinsic viscous property of neat vegetable oil may impose a higher pumping power and energy consumption requirements due to the frictional resistance to flow freely through the pipeline and catalysts bed under room temperature. As a whole, one can conclude that the desired feedstock for RD production must consists of the following criteria: (i.) renewable and local abundance, (ii.) low unsaturation level (less H₂ consumption), (iii) high free fatty acid values, and (iv) low kinematic viscosity.

2.2 Fatty acid model compounds

Prior crude plant oils were presented as a potentially sustainable resource for the synthesis of RD, there has been a plethora of fatty acids deoxygenation works being published in many international scientific journals from 2010 to 2020 as shown in Figure 2. In other words, promising results have been well-acquired for production of paraffinic diesel hydrocarbons from fatty acid model compounds. From Table 2, one can also observe that palmitic acid (hexadecanoic acid, C16:0), stearic acid (octadecanoic acid, C18:0), and oleic acid (cis-9-octadecenoic acid, C18:1) are the dominant constituent of free fatty acids in most plant oils. As expected, saturated and unsaturated fatty acid model compounds such as palmitic acid, stearic acid, and oleic acid have been used extensively as the feedstock in many CDO studies. Among the saturated fatty acids, stearic acid is one of the most widely investigated fatty acid

model compounds in CDO reactions for the synthesis of diesel-like hydrocarbons. To the best of our knowledge, pioneering research work on CDO of a fatty acid model compound was firstly reported in 2006 by Snåre, et al. [46], where his experimental work has successfully demonstrated the production of long-chain paraffinic hydrocarbons via direct HCO₂ of stearic acid over a carbon-supported palladium catalyst (Pd/C) in a semi-batch reactor under a constant temperature of 300 °C and pressure of 0.6 MPa. The precious metal based catalysts demonstrated to be highly active and selective in HCO₂ reaction, which effectively converted the stearic acid completely with over 98% selectivity toward heptadecane products.

Since then, CDO of fatty acids to paraffinic diesel hydrocarbons has gained much attention and many empirical investigations have used saturated fatty acid compounds such as stearic acid and palmitic acid as the feedstock. For instance, Murzin and co-workers have successfully demonstrated direct HCO₂ of stearic acid and oleic acid to linear paraffin hydrocarbons under different reaction atmospheres (15 bar Ar, 15 bar H₂, 15 bar Ar+H₂, and 21 bar Ar+H₂). However, it was revealed that the 5 wt% Pd/C was the most active and selective catalyst towards the HCO₂ reaction under a mixed Ar and H₂ atmosphere [47, 48]. Following studies by Immer et al. [49] and Boda et al. [50] also confirmed that Pd/C is an efficient catalytic material for the direct HCO₂ of stearic acid to heptadecane hydrocarbons under helium-rich atmosphere. Other than stearic acid, Peng et.al. [51] and Liu et.al. [52] employed palmitic acid, a saturated fatty acid model compound with a shorter carbon chain length than stearic acid as their feedstock in their deoxygenation studies. Both of them studied deoxygenation of palmitic acid over a series of sulphur-free supported catalysts (Pd/C, Ni/C, NiP/HZSM-22) under an H₂-free atmosphere. From their results, both studies agreed on the high selectivity performance of Pd and Ni metal species toward diesel-like hydrocarbon formation via HCO₂ and HCO reactions respectively. Despite

such encouraging results obtained from saturated fatty acid model compounds, the individuality of saturated fatty acid as a single representative model compound might not reflect the actual characteristic of a real world, multicomponent feedstock in a deoxygenation reaction. Needless to say, plant oil-based feedstock is far more complex than a single fatty acid model compound. Furthermore, several studies have confirmed that CDO of mono-unsaturated fatty acid over Pd/C is much more difficult to accomplish due to the inhibition of C=C double bonds in the alkyl chain, adsorbing to the catalyst surface, which subsequently results in an elevated H₂ consumption, rapid catalyst deactivation and reduction in catalytic performance due to steric crowding [53, 54].

In recent years, many industrial engineers, academic researchers, and scientists have started to incorporate mono-unsaturated fatty acid for instance oleic acid in their deoxygenation studies. By using mono-unsaturated fatty acids as a feedstock, a much more in-depth investigation can be carried out to provide some practically relevant information for the actual reaction mechanism of real plant oils. Moreover, the fundamental chemistry and reaction mechanism of CDO can be closely elucidated for the real plant oil feedstock. Instead of using plant oils and triglycerides, the main rationale of using surrogate model compounds in many previous deoxygenation works is to reduce, simplify, and possibly eliminate the complexity of the chemical reaction network involved. It is well accepted in the literature that scientific investigation of CDO reaction using real plant oil feedstocks can be challenging due to bulk effects arising from intertwining interactions between the complex mixtures of molecules [55]. Alternatively, deoxygenation studies using a single representative model compound is often preferred to understand the reaction chemistry before evaluating the real plant oil feedstock. The authors acknowledge that studies using single-molecule can lose their characteristics and respective interaction effects

within the complex mixtures such as those found in real plant oils. However, as natural plant oils consist of multiple chemical compounds, it is not practical to simulate such a variation of molecular sizes or chemical species in a single reaction model. On the contrary, a more holistic reaction model can be easily established from a single representative model compound originated from the parent substrate with better precision and accuracy.

3. Reaction pathways of deoxygenation

CDO is a generic term for the removal of a carboxyl functional group from the triglycerides molecule, rendering an oxygen-free-paraffinic hydrocarbon. Under deoxygenation, the reaction mechanisms are generally characterized as hydrogenation (HGN) of the olefinic bond into saturated C-C bonds (R1), followed by scission of C-O ester linkages from the glycerol backbone via hydrogenolysis (R2), leading to the release of saturated monoglycerides, diglycerides and free fatty acids (FFA) [4].

From the thermal decomposition of triglyceride molecules, the FFA formed undergoes three different reaction pathways, namely hydrodeoxygenation (HDO), decarboxylation (HCO_2), and decarbonylation (HCO) as shown in Figure 3. With the C-O cleavage of the carboxyl group in fatty acid, HDO reaction (R3) eliminates H_2O molecules via sequential dehydration and hydrogenations, forming linear alkane hydrocarbon with the same number of carbon as the original carboxylic acid. Meanwhile, direct removal of COOH group from the fatty acid (R4) involves the simultaneous removal of dual oxygen atoms from the carboxylic group by a direct attack on the C-C bond, producing linear alkane and CO_2 [56]. For the removal of COH (R5, 6), the two oxygen atoms are removed sequentially through hydrogenation of the hydroxyl group, producing H_2O at first and followed by CO [56, 57]. Both reaction pathways yield long aliphatic hydrocarbons with one carbon less than that of the corresponding fatty acids.

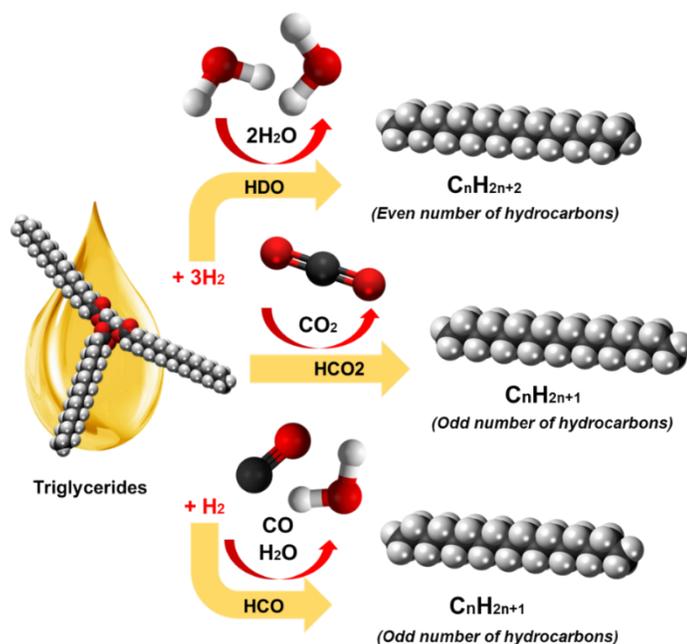


Figure 3: CDO of triglycerides via hydrodeoxygenation (HDO), decarboxylation (HCO_2), and decarbonylation (HCO) pathways.

Under a H_2 -rich atmosphere, the carboxylic acids undergo hydrogenation reaction by forming a partially deoxygenated aldehyde intermediate before yielding pure hydrocarbon and carbon monoxide molecule [58]. Alternatively, the aldehyde can be further hydrogenated to an alcohol compound and indirectly decompose into a hydrocarbon. Other than liquid-phase reactions, the occurrence of undesirable gas phase side reactions such as methanation (MTA) (R7, 8) and the Water-gas shift reaction (WGS) (R9) was reported in many studies. The dynamic interactions between low molecular weight gases species (CO and CO_2) and reduction agent could lead to a higher H_2 consumption rate, forming methane gas at the expense of molecular hydrogen. As a whole, Figure 4 summarises and presents a general reaction mechanism for the catalytic deoxygenation of triglyceride with the dashed red lines indicating the positions of the C-C and C-O bond scission.

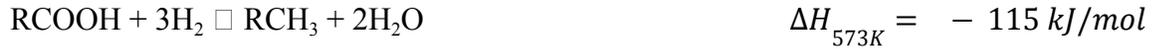
Hydrogenation reaction (HGN)



Hydrogenolysis reaction (HGS)



Hydrodeoxygenation reaction (HDO)

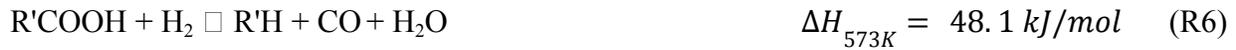


(R3)

Decarboxylation reaction (HCO₂)



Decarbonylation reaction (HCO)



Methanation reaction (MTA)



Water Gas Shift Side reaction (WGS)



Where R is saturated alkyl group and R' is unsaturated alkyl group [59, 60].

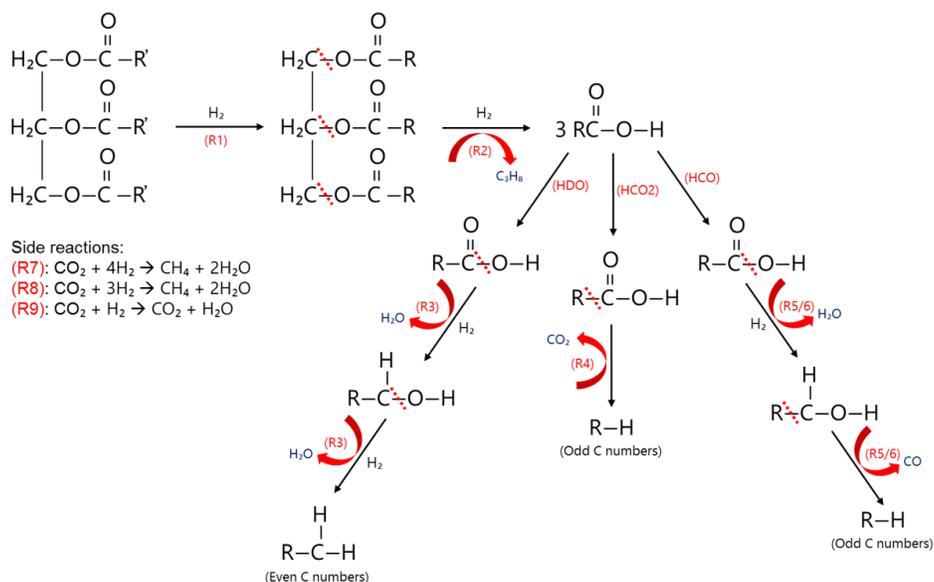


Figure 4: General reaction mechanism of hydrodeoxygenation (HDO), decarboxylation (HCO_2), and decarbonylation (HCO) pathways.

4. Catalysts support

The selection of a catalyst support plays a crucial role in catalyst design as the choice of a support can affect the type of reaction pathway selected (e.g. acid/base characteristics, metal support interactions or structural design), the type of product distribution, and above all, the overall CDO activity. Many previous studies have reported that structural properties of catalyst support can alter the degree of dispersion of the active site on the support surface and influence the interaction bonding between the support and active site. Kubicka et al. [61] impregnated 3.3 wt% of Ni and 15 wt% of Mo onto three different supports (SiO_2 , TiO_2 , and Al_2O_3) to assess their deoxygenation performance of rapeseed oil. These were evaluated in a fixed bed reactor under the temperature range of 260 °C – 300 °C and H_2 pressure of 3.45 MPa. From their work, the results provided clear evidence that textural properties of support material can affect the size, dispersion, and reducibility of active sites, and ultimately steering the product selectivity, significantly. For instance, TiO_2/NiMo and $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts with poor metal dispersion and

large active site cluster size exhibited a higher selectivity toward HDO products, whereas SiO_2/NiMo catalyst with a better dispersion of active phases and a relatively homogenous particle size was favorable towards HCO_2 products. Unexpectedly, the overall deoxygenation performance of both catalysts was only affected to a lesser extent. Similar differences in product selectivity over different support materials was also observed and reported by Chen et. al. [62], Sun et. al. [63], Coumans & Hensen [64], and Wang et. al. [65]. Overall, the differences in product selectivity may not only be originated from the textural properties of the support (specific surface area, pore size, or acid/base characteristic) but also can be plausibly attributed to the synergistic interaction between the support and active site, and strong metal-support interactions.

Figure 5 illustrates the different types of catalyst support materials used for the CDO reaction. In general, a catalyst support can be categorized into four types: oxides/mixed oxides, mesoporous materials, zeolites, and activated carbon. Among the oxide supports reported in the literature, silica (SiO_2) and alumina (Al_2O_3) are two conventional materials that have been widely used by many material scientists for the CDO of fatty acid, mainly due to their excellent thermal and chemical resistance characteristics under severe operating conditions. Polymorphic crystalline aluminium oxides ($\gamma\text{-Al}_2\text{O}_3$) or commonly referred with the generic name of alumina has been used extensively as a catalyst support in the hydrotreatment of petroleum fraction for the removal of heteroatoms such as sulphur (HDS), nitrogen (HDN), and oxygen (HDO) [66]. It is a popular choice for many catalytic applications due to its high specific surface area, good physical strength, and excellent resistance to thermal degradation [67]. However, alumina is well-known to be metastable in the presence of water vapours and very susceptible to structural degradation by partially converting into hydrated boehmite $\text{Al}(\text{OH}_3)$. Under a severe aqueous

environment of near-critical or supercritical water, the high surface area alumina support can undergo hydroxylation to form Al-OH and further dehydrate with an adjacent metal oxide particle to forming Al-O-Al, yielding a low surface area support material as an end product. Thus, poor hydrothermal stability of alumina and its susceptibility to structural change at high-temperature steam-assisted environment has hindered its application in CDO. Similar to the previously mentioned alumina support, the structural change of the silica framework has frequently been reported in many previous studies as other single component metal oxides also tend to suffer from sintering at severe thermal conditions and steam-assisted degradation.

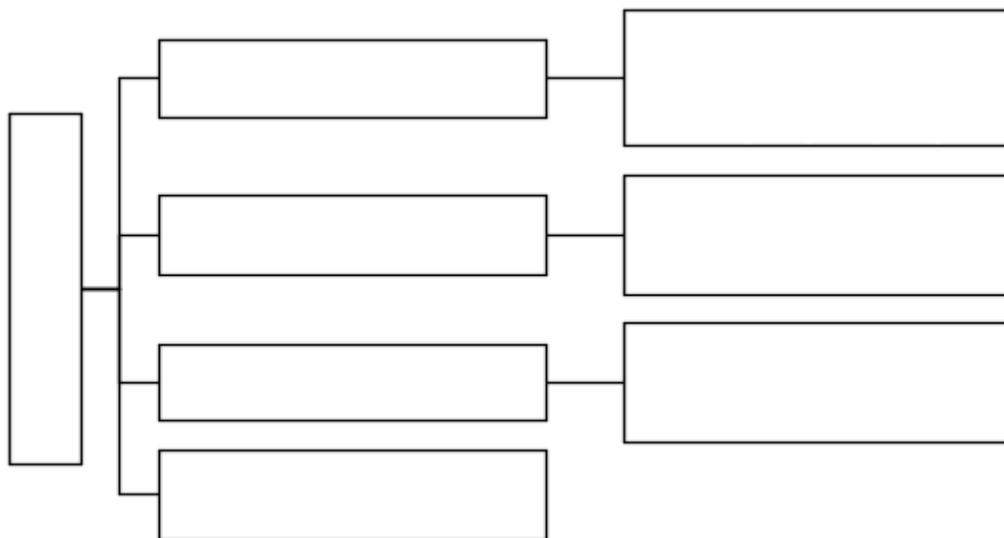


Figure 5: Type of catalyst support materials used previously for the CDO reaction.

Other solid base materials such as ZrO_2 , TiO_2 , CeO_2 , CrO_3 , and hydrotalcites have also been used considerably as support materials for the CDO of triglycerides and fatty acids [69, 70]. The surface of these solid supports consists of a large number of coordinately unsaturated sites or better known as oxygen vacancies. The oxygen vacancies are capable of facilitating the activation of oxygenated compounds like fatty acids, followed by the elimination of the carboxyl

group and thereby promote their catalytic reduction performance. The potential of solid base materials as prospective support for deoxygenation of oleic acid has been well reported in Li et al. [68], Chen et.al. [69], and Asikin-Mijan et al. [70]. In Li et al. [68], several supported Ni/MO-Al₂O₃ catalysts (M = Mg, Ca, Ni, Cu, and Zn) have been prepared for the deoxygenation of oleic acid and the results revealed that Ni/ZnO-Al₂O₃ with its moderate base strength exhibited the best support material for the conversion of mono-unsaturated fatty acids to n-alkanes compared to the other base metal species. The same research team investigated the effect of Zn/Al ratio on the physicochemical properties of the support and deoxygenation activity of the resulting catalyst in converting oleic acid to diesel range alkanes. From their studies, the results revealed that the addition of Zn atoms in moderate amounts improved the dispersion of metallic Ni species, therefore enhancing the number of molecular adsorption site and negating Ni aggregation. As a result stimulating the high conversion of oleic acid and subsequent alkane yields. On the other hand, a catalyst with low concentration of Zn suffered from a strong metal-support which meant that the Ni active site was could not be effectively reduced. At the same time, excessive Zn atoms may limit the dispersion of Ni species and promote the formation of a larger ZnO agglomerates or islands, leading to a decrease in the exposure of metallic Ni sites. From the experimental results, Ni/ZnO-Al₂O₃ catalysts with an optimum Zn/Al ratio of 2 reached a balanced exposure degree of Ni metallic atoms and offered a maximum alkane yield of 95.8% [69].

Furthermore, CeO₂ based materials are well-recognized in the literature for their excellent oxygen storage capacity associated with the intrinsic redox property of cerium species. Many previous studies have reported that the oxygen storage capacity, redox property, reducibility, and thermal resistance of CeO₂ are significantly enhanced by incorporating another cation such as

ZrO₂ into CeO₂ lattice [71, 72]. By exploiting the high affinity of these materials toward oxygenated compounds, Shim and their associates formulated reducible oxide support with a combination of CeO₂ and ZrO₂ for the deoxygenation of oleic acid. From the results, Ce_{0.6}Zr_{0.4}O₂ alone was capable of achieving a fatty acid conversion of 73.8% and is highly selective toward HCO reaction upon treating oleic acid with a mixture of 20% H₂/N₂ at atmospheric pressure [73]. Such superior catalytic performance can be ascribed to the formation of the cubic phase in the Ce_{0.6}Zr_{0.4}O₂ material. The cubic phase of Zr-CeO₂ possesses a higher capability of producing a redox coupling between Ce⁴⁺ and Ce³⁺. However, previous studies have shown that the utilization of basic supports in the CDO reaction usually leads to poor catalytic activity with reaction temperature lower than 350 °C [13].

In recent years, silica-based ordered mesoporous materials such as SBA-15, SBA-16, and MCM-41 have gained importance as they possess moderate acidity, high specific surface area, and large pore diameter required for the larger and longer molecules in real plant oil-based feedstocks. These materials offer several advantages over a conventional alumina support including a higher specific surface area in the range of 600 – 1000 m²/g and homogenous pore size distribution from 1.5 to more than 10 nm [13]. These well-developed mesoporous structured materials allow for a higher dispersion of the active sites throughout the porous network as well as on the support's outer surface. These broad pore size distributions enable the access of larger organic molecules to the active sites located outside the pores [74]. In between SBA-15, SBA-16, and MCM-41, both SBA supports have a better hydrothermal stability property than MCM-41 as the former consist of a uniform hexagonal-structure mesoporous channels in a two-dimensional (2D) array with thicker walls (3-9 nm) than MCM-41 [13]. Furthermore, SBA-16 could be more promising support than SBA-15 due to its body-centered structure in which each mesopore is

connected to eight neighboring mesopores, which making them more desirable to deal with bulky molecules [13, 75]. However, applications of such materials in catalytic HDO reactions are generally unfavorable as they are structurally unstable under extreme hydrothermal stress and often suffer from a gradual loss in surface area after a prolonged reaction, resulting in severe internal pore structure collapse from boiling steam partial pressure.

Another type of hierarchically structured mesoporous support namely crystalline silicoaluminophosphates molecular sieve (SAPOs) including SAPO-11, SAPO-31, and SAPO-41, has been used extensively as selective deoxygenation and isomerization catalyst owing to their high isomerization/cracking ratio characteristic. It has unique chemical functionality and an internal structural framework with a broad distribution of weak protonic acidity sites located at the interface between silica domains and the SAPO phase. The distinct geometry of cavities at the external surface of zeolite crystals allows fast desorption of isomerized carbocations preceding β -scission that yields minimal cracking [20]. Moreover, the mono-branched isomers fit the medium pore size and distances between the neighboring nests at the external crystal surface, which further improves the selectivity of multibranched alkanes. SAPO-11 molecular sieves have 10-membered ring channels with an elliptical pore opening of 0.39 x 0.63 nm, whereas SAPO-31 has circular mono-dimensional channels with pore diameters of 0.54 x 0.54 nm [76, 77]. Unlike SAPO-11 and SAPO-31, SAPO-41 is another type of SAPO molecular sieve with a unidimensional elliptical 10-membered ring pore and a larger pore opening of 0.43 x 0.70 nm. Overall, these mesoporous molecular sieve materials differ from each other by a small margin in the 10-membered cross-section and proton acidity strength. However, due to the difference in pore sizes and shapes, it is envisaged that more or fewer peculiarities in the hydro-conversion of n-alkane would be expected.

The influence of strong acidic supports in altering and modifying the carbon skeleton of the intermediate carbonium ions and linear paraffinic hydrocarbons via isomerization, cracking and cyclization reactions have been well documented and reported in the past literature. The strength, surface density, and pore size of acidic sites on support are known to affect the overall product selectivity, yield, composition, and distribution. A recent study by Ahmadi et.al. [78] has successfully demonstrated the production of diesel range hydrocarbons from oleic acid over Pt/SAPO-11 and Pt-chlorinated alumina. The initially formed paraffin intermediate from HCO_2 undergoes isomerization and cyclization to form branched, cyclic, and alkyl aromatic hydrocarbons in the presence of acidic supports like SAPO-11 or chloride alumina. Furthermore, Pt/SAPO-11 exhibited a better dispersion of active sites on the support, which led to a higher surface area and thereby to better catalytic performance. Encouraged by such optimistic results, this research team extended their works by incorporating the same active sites onto four different supports including SAPO-34, RHO, hydrotalcite, and DNL-6. The four supports were impregnated with two different Pt precursors (potassium hexachloroplatinate and tetraamine Pt nitrate) with the same metal loading of 5 wt%. It was observed that all Pt catalysts derived from the nitrate precursor displayed a higher degree of HCO_2 activity, but Pt-SAPO-34 had the highest selectivity towards linear paraffin hydrocarbons [79]. Similar to previously mentioned SBA and MCM materials, SAPO based materials also suffer from the same drawback of poor hydrothermal stability. Lutz et.al. [80] investigated the hydrothermal stability of the SAPO-11 support in autogenous steam partial pressure as a function of temperature and the results indicated that SAPO-11 exhibited typically lower hydrothermal stability characteristic in pure water above 200 °C and pressure of more than 1.7 MPa. A similar gradual deactivation trend of Pt/SAPO-11 catalysts was also reported in Herskowitz et.al. [81], and Rabaev et al., [20], where

a fraction of SAPO-11 framework structures was found to degrade at a steam partial pressure less than 0.2 MPa when hydrotreating soybean oil. With such low hydrothermal stability property, it is generally unsuitable to be used as a support material for HDO due to the formation of water along during the reaction. Moreover, supports with acidic sites usually promote carbon deposition during the deoxygenation reaction, thereby reducing or even deactivating the catalytic activity. Thus far in the literature, very limited work has focused on the production of branched diesel hydrocarbon isomers via hydroisomerization and aromatization reactions over mild acidic supports.

Other than mesoporous materials, microporous supports such as zeolite-USY, zeolite-beta, zeolite- 5A, H-mordenite, KIT-16, and H-ZSM5 have demonstrated high liquid hydrocarbon yields during the catalytic hydrotreatment of triglycerides and fatty acids. Despite the superior catalytic performance demonstrated by the microporous supports, the selectivity of linear paraffin hydrocarbons has been reported to be poor due to its strong acid strength sites, which promotes catalytic cracking and isomerization reaction [54]. Moreover, these highly acidic zeolite-based supports are prone to deactivate quickly due to the deposition of carbonaceous materials on the catalytic sites and hence retarding the catalytic performance during deoxygenation reactions. Lastly, carbon is a catalytically inert material with a relatively non-acidic characteristics like silica. Activated carbons derived from low-temperature conditions generally possess weak acidic hydrophilic surface, whereas activated carbons generated from a high temperature have basic and hydrophobic surfaces [13]. It has been reported in the literature that enhanced deoxygenation activities were obtained with reactions using carbon-supported metal catalysts, mainly attributed to their amphoteric properties and surface properties [60]. The catalytic activity of activated carbon as support mainly depends on the preparation methods and

hence, tailoring of their activity is highly possible. Up to date now, a few studies have reported that carbon-based support like activated carbon has potentials of enhancing the dispersion of catalytic active metal sulphides due to the weak interaction of the carbon support with a metal sulfide, resulting in a type II character of the active phase. Couman & Hensen [64] compared the effect of activated carbon, mesoporous alumina, and amorphous silica-alumina in the CDO of methyl oleate with sulfide NiMo as the active phase. From the results, the activated carbon-supported NiMo catalyst exhibited the highest MoS₂ dispersion and stacking degree than the oxide supports. The carbon support was able to stabilize the very small MoS₂ slabs efficiently and that active phase exhibited a pronounced type II NiMoS phase character. The catalytic performance of the NiMo sulfides on activated carbon in the HDO reaction was found to be 2x more active than the other oxide supports and remaining active over a prolonged on-stream reaction. In general, activated carbons are easily prepared and cost-effective. They can have high specific surface area, thermal stability, and chemical inertness. They can also consists of a wide range of surface functionality and pore size distribution. In addition, activated carbons have a high deactivation resistance at low temperatures due to their neutral nature [82]. All these unique properties make activated carbon a suitable support material for the CDO of triglycerides and fatty acids. Table 3 lists the strengths and weaknesses of each support material commonly used for CDO reaction.

Table 3: Strengths and weaknesses of support materials used for the CDO of plant oils and fatty acids.

Type of support	Strengths	Weaknesses
Oxides/mixed oxides	<ul style="list-style-type: none"> · Moderately high specific surface area (200 – 500 m²/g) · High physical strength · Excellent resistance to thermal and chemical degradation · Capable of facilitating activation of oxygenated compounds · Excellent oxygen storage capacity with intrinsic redox property 	<ul style="list-style-type: none"> · Poor hydrothermal stability · Metastable in the presence of water vapors · Susceptible to structure degradation · Subject to sintering under steam-assisted conditions
Mesoporous materials	<ul style="list-style-type: none"> · High specific surface area (600 – 1000 m²/g) · Large pore diameter (2 to > 10 nm) · Moderate acidity · A broad distribution of weak protonic acidity sites 	<ul style="list-style-type: none"> · Poor hydrothermal stability · Susceptible to structure degradation · Severe collapse of internal pore structure under steam-assisted conditions
Zeolites	<ul style="list-style-type: none"> · Strong acidity · Promotes isomerization of formed paraffin hydrocarbons · Poor diesel hydrocarbon yields 	<ul style="list-style-type: none"> · Prone to deactivation · Deposition of carbonaceous materials on active sites · Promote catalytic cracking of long-chain hydrocarbons, lower product yields.
Activated carbon	<ul style="list-style-type: none"> · High surface areas (500 – 1500 m²/g) · Excellent thermal stability and chemical inertness · Broad pore size distribution (0.5 to 5 nm) · Amphoteric properties · Good surface functionality · Ease of preparation 	<ul style="list-style-type: none"> · Presence of inorganic impurities (K, Ca, S, etc.) requiring prior pretreatment such as leaching. · Non-homogenous surface and internal structures.

· Cost-effective

5. Active metals

For CDO reactions, the selection of active metal is of utmost importance as it will influence both product yields and quality significantly. Although many studies have dealt with the deoxygenation of fatty acids and plant oils, all these studies are mostly limited to the application of certain catalysts. In general, these catalysts can be classified into two types: monometallic noble metal catalysts, or PGMs (platinum group metals) such as Pd, Pt, Rh, Ru. The second being bimetallic catalysts in sulfide or non-sulfide forms such as NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃, or more recently Pd derived analogue such as PdNi and PdCu supported on carbon [83]. The active metal species mainly consists of a transition metal corresponded to Group 8 to 10 metals in the periodic table, specifically Ni, Co, Cu, and W as shown in Figure 6. Table 4 summarises the primary roles and weaknesses of the typical active metals used for CDO of triglycerides and fatty acids.

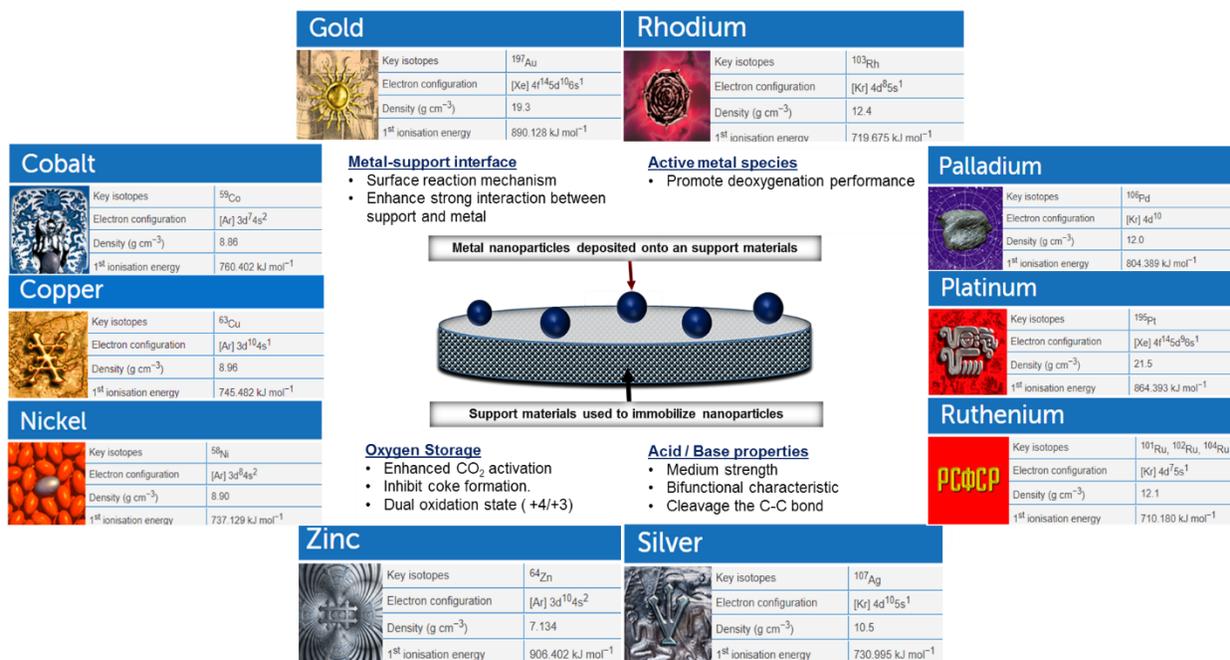


Figure 6: Active metals used in the deoxygenation of triglycerides and fatty acids

Table 4: Primary roles and weaknesses of some active metals used for CDO of plant oils and fatty acids.

Elements	Primary roles	Weaknesses	References
Pt	<ul style="list-style-type: none"> Highly active and effective for hydrogen activation Favour C-C bond cleavage Highly reactive properties toward HCO₂ and HCO reactions 	<ul style="list-style-type: none"> Expensive Rapidly poisoned by CO, S based functional groups and carbon laydown. 	[46, 56, 84, 85]
Pd	<ul style="list-style-type: none"> Highly active and effective for hydrogen activation Favour C-C bond cleavage Highly reactive properties toward HCO₂ and HCO reactions 	<ul style="list-style-type: none"> Expensive Rapidly poisoned by CO, S based functional groups and carbon laydown. 	[56, 86]
Ir	<ul style="list-style-type: none"> Highly selective for producing symmetrical ketones 	<ul style="list-style-type: none"> Expensive Poor selectivity towards deoxygenation 	[46, 87]
Rh	<ul style="list-style-type: none"> Favour HCO reaction 	<ul style="list-style-type: none"> Expensive 	[46, 87]
Ru	<ul style="list-style-type: none"> Favour HDO reaction Highly selective for producing symmetrical ketones 	<ul style="list-style-type: none"> Ru/SiO₂ is very poor for producing deoxygenation products 	[46, 87]
Ni	<ul style="list-style-type: none"> Effective for hydrogen activation High HGS ability Moderate selectivity towards cracking, producing C10-C17 Has chemical properties similar to Pt/Pd for C-C or C-H bond cleavage Cheaper than Pt/Pd 	<ul style="list-style-type: none"> Prone to deactivation from coking Rapidly poisoned by carbon laydown Has been shown to favour hydrogenation over HDO reaction pathways Yield more cracking products than Pd and Pt. 	[83, 88-92]
Co	<ul style="list-style-type: none"> Highly effective towards HCO₂ and HDO reaction pathways High hydrogenolysis ability Favours the production of C18 molecules 	<ul style="list-style-type: none"> Not active for decarbonylation pathways 	[56, 91-93]

Cu	<ul style="list-style-type: none"> ● Low cost compared with PGM ● When alloyed with Pd or Ni, has been found to be very selective towards C17 molecules ● Resistant to CO adsorption, more sustainable ● High HGS ability 	<ul style="list-style-type: none"> ● Selective towards hydrogenation reaction pathways ● Can rapidly oxidise, this means the catalyst must be reduced/regenerated between each cycle 	[83, 92, 94]
Mo	<ul style="list-style-type: none"> ● Favour C-O or C=O bond scission ● Selective toward paraffin production ● Recyclable over 	<ul style="list-style-type: none"> ● Often unselective to hydrocarbons, resulting in a number of side products such as esters and other oxygenates ● Requires sulphurization step to keep the element in active and stable form ● Sulphur leaching causing catalyst deactivation and product contamination. 	[56, 95, 96]
W	<ul style="list-style-type: none"> ● Selective toward olefin production 	<ul style="list-style-type: none"> ● Often unselective to hydrocarbons, resulting in a number of side products such as esters and other oxygenates 	[95]

5.1. Monometallic catalysts

Table 5 summarises the recent deoxygenation studies of plant oils and fatty acid compounds over different types of monometallic catalysts. On the basis of literature, three noble metals (group VIII) with unique d-orbitals electronic configurations, namely Pd, Pt and, Ru have been widely reported as the active metals for the CDO of triglycerides and fatty acid model compounds. On a whole, both Pd and Pt species exhibit highly reactive properties toward HCO₂ and HCO reactions, while Ru species showed excellent HDO activity. In the early years, Snare et

al. [46] screened a series of metal-supported catalysts (Mo, Pd, Pt, Ir, Ru, Rh, and Os) on two different types of supports, metal oxides (including SiO_2 , Al_2O_3 , Cr_2O_3 , and MgO) and activated carbon in a semi-batch deoxygenation system. Among the noble metal candidates, Pd exhibited a high activity and selective in formation of straight chain paraffinic hydrocarbons. In another deoxygenation work by Silva, et al [97], deoxygenation of hydrolyzed macauba and almond oils was successfully catalysed over 5 wt% Pd/C at 10 bar H_2 , 300 °C and 5 h of reaction time. The deoxygenation product obtained from the reaction of hydrolyzed macauba oil has a high diesel range hydrocarbon content with a predominance of forming saturated linear hydrocarbons that correspond to RD.

Apart from that, the application of mesoporous silica materials as a Pd-based catalyst support for the deoxygenation of fatty acids and triglycerides has also been reported extensively due to its broad pore size distribution, allowing bulky molecules passing through the pore mouth without diffusion limitation. Raut, et al [39] evaluated and compared the catalytic performance of two and three dimensional mesoporous silica-supported Pd catalysts, namely Pd/SBA-12 and Pd/SBA-16 in the deoxygenation of oleic acid and stearic acid. Their findings revealed that Pd/SBA-16 had a higher catalytic activity than Pd/SBA-12 due to its higher surface hydrophobicity and metal dispersion. In recent work by Pacheco, J.G. [98], modification of the original mesoporous silica SBA-15 support was made by incorporating mesitylene as an auxiliary swelling molecule in the support synthesis step to enlarge the pore diameter of the pristine silica support and improve its ability to adsorb carboxylic acid molecules within the pores. From the results, the addition of mesitylene as a swelling molecule in the support structure enhanced the specific surface area, pore size, and pore volume, which rendered a disordered structure and amorphous particles with non-uniform pore size and shapes. Such an internal

structure of the SBA-15 promoted a better catalytic property in the materials with lower Pd content (0.5 and 1.5 wt% Pd) for the deoxygenation of stearic acid.

Despite the Pd species exhibiting superior deoxygenation performance and high product selectivity towards diesel hydrocarbons, the vulnerability of Pd-based catalysts and their tendency to rapid deactivate/poison, as well as its low abundance and high production cost have hindered its potential for industrial applications. Alternatively, the exorbitant cost of noble metals has stimulated the use of non-noble metal-based catalysts. Among non-noble metals, Ni has been reported extensively as an excellent active metal in the deoxygenation reaction due to its cost-effectiveness and high availability as compared with noble metals [99, 100]. It is reported in the literature that the cost of Ni is ~ 1000 and ~ 2500 times lower than that of Pd and Pt, respectively [101]. It has been also reported that H_2 molecules can be easily trapped in the defects of the Ni-metal surface, lowering the activation energy of hydrogen dissociation [102]. Besides, Ni also has chemical properties similar to that of precious metals including cleavage of the C–C or C–H bond for hydrocarbon reactions, highly active in radical formation, and electronically stable [89, 90]. The superior deoxygenation activities using Ni-based catalysts have been well-documented in the literature. For instance, Gousi et al. [88] have reported the catalytic activity of co-precipitated monometallic Ni/ Al_2O_3 for the CDO of sunflower oil. The deoxygenation reaction was carried out in a semi-batch reactor under H_2 at 40 bar and a reaction temperature of 310 °C. The final product obtained under such conditions mainly consisted of n- C_{15} to n- C_{18} hydrocarbons [88]. Recently, Baharudin and co-authors used a NiO–ZnO catalyst to convert palm oil refining oil (POFO) to diesel-like hydrocarbons under a H_2 -free atmosphere [100]. This had a high hydrocarbon yield of 83% and a diesel specific hydrocarbon (C_{11} – C_{17}) selectivity of 86% when using 20 wt% NiO–ZnO for 2 hours at 350 °C.

Furthermore, the mechanistic insights of non-noble-based catalysts such as metal carbides, metal nitrides, and metal phosphide supported catalysts in the CDO reaction have also become a “hot-topic” lately [103, 104]. All these emerging catalysts have demonstrated superior catalytic performances and high selectivity in producing hydrocarbons compared to conventional noble metal catalysts. A simple and scalable standard catalyst preparation method like incipient wetness impregnation should be proposed to minimize the processing cost of such catalysts. Given the literature review shown in Table 5, the existing research direction has mainly presented the use of Al₂O₃, SiO₂, TiO₂, or MgO supported noble metals such as Pt, Pd, Cu, or Ru as the catalysis materials for the conversion of fatty acids and their derivatives to linear diesel hydrocarbons.

To the best of the author’s knowledge, only a few studies reported on catalytic HCO₂ or HCO of triglycerides and fatty acids over carbon-based bimetallic catalysts. Owing to the tri-abilities of carbon-based catalysts including a) high dispersion over the support’s surface, b) fine-tuning of chemical physiochemical properties, and c) low affinity towards coke formation, high selectivity towards diesel-range hydrocarbons can be easily attained in the CDO reaction [105, 106]. One of the pioneering works of CDO for triglycerides using a carbon-based catalyst was reported by Taufiq’s group [107]. They have reported the deoxygenation of palm fatty acid distillate over Co and Mn supported on activated carbon (AC). Based on their findings, the Co/AC catalyst displayed a better deoxygenation performance than that of Mn/AC, suggesting a strong acid-base site through the synergistic interaction between Co and the AC support, which favored the deoxygenation pathway. The highest hydrocarbon yield of 90% and C₁₅+C₁₇ selectivity of 72% were achieved in a batch autoclave under the optimum conditions of 3 wt% Co loading, 120 min reaction time, and 350 °C reaction temperature.

Table 5: CDO of plant oils and fatty acids using monometallic catalysts.

Plant oils/Fatty acids	Reactor Type	Reaction Conditions	Catalysts	Conversion (%)	C15 – C18 Yield/ selectivity (%)	References
Stearic acid	Batch autoclave	Temperature: 300 °C Pressure : 1.5 MPa N ₂ Reaction time: 3 h	5% Pd/C	100	98	[49]
Oleic acid	Batch autoclave	Temperature: 300-360 °C Pressure: 15 - 27 MPa Ar, H ₂ , (Ar + H ₂) Reaction time: 4 h	Pd/C	74 - 99	17 - 21	[48]
Oleic acid	Fixed bed	Temperature: 380-450 °C WHSV: 1.6 - 7.9 /h H ₂ flow rate: 5 – 95 ml/min	2%Pd/C	85	28.5	[108]
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure : 1.5 MPa H ₂ Reaction time: 1 h	5% Pd/Si	15	0	[109]
			5% Pd/Si-C-4	87	33.2	
			5% Pd/Si-C-2	74	15.3	
			5% Pd/Si-C-1	42	12.5	
			5% Pd/Si-C-0.5	45	13.9	
Oleic acid	Batch autoclave	Temperature: 350 °C Pressure : 5 MPa H ₂ Reaction time: 5 h	Mo ₂ C/CNF	100	~85	[95]
			W ₂ C/CNF	100	~65	
Oleic acid	Batch autoclave	Temperature: 220-325 °C Pressure : 2 MPa H ₂ Reaction time: 2 h	Pt/SAPO-11	99.1	39.8	[78]
			Pt/chloride Al ₂ O ₃	97.5	62.7	
Oleic acid	Semi-Batch	Temperature: 320-380 °C Pressure: 1 - 4 MPa H ₂ flow rate: 100 mL/min Reaction time: 1.5 h	NiO _x /Al ₂ O ₃	~ 100	72 (C18) 21 (Iso-C18)	[110]
Oleic acid	TGA analyzer	Temperature: 370 °C Pressure: 0.1 MPa	FluoroPalladium Oxalate /Zeolite	-	69 (C18) 18 (Iso-C18)	[111]

		H ₂ flow rate: 100 mL/min Reaction time: 44 mins				
Oleic acid	Batch autoclave	Temperature: 320-380 °C Pressure: 2 MPa H ₂ flow rate: 50 mL/min Reaction time: 1 h	Fluoromolybdenum Oxalate /Zeolite	~ 100	64 (C18) 30 (Iso-C18)	[112]
Oleic acid	Batch autoclave	Temperature: 245 °C, 325 °C Pressure : 2 MPa H ₂ Reaction time: 2 h	Pt/SAPO-34 Pt/DNL-6 Pt/RHO Zeolite Pt/hydrotalcite	~100 ~100 85 ~100	72.2 54.7 38.8 41.7	[79]
Oleic acid	Batch autoclave	Temperature: 320 °C Pressure : 2 MPa H ₂ Reaction time: 2 h	Pt/Zeolite 5A Pt/ZIF-67/Zeolite 5A	98.74 98.70	97.11 96.92	[113]
Oleic acid	Batch autoclave	Temperature: 280 °C Pressure: 3.5 MPa H ₂ Reaction time: 6 h	Ni/MgO-Al ₂ O ₃ Ni/CaO-Al ₂ O ₃ Ni/NiO-Al ₂ O ₃ Ni/CuO-Al ₂ O ₃ Ni/ZnO-Al ₂ O ₃ Ni/γ-Al ₂ O ₃	100 100 100 100 100 100	26.8 10.7 95.9 95.1 100 59.2	[68]
Oleic acid	Semi-Batch	Temperature: 320-380 °C Pressure: 1 - 4 MPa H ₂ flow rate: 50 mL/min Reaction time: 1.5 h	FluoroPlatinum Oxalate/Zeolite	~ 100	68.93 (C18) 28.39 (Iso-C18)	[114]
Oleic acid	Batch autoclave	Temperature: 320-340 °C Pressure : 2.3 MPa H ₂ Reaction time: 4 - 5 h	3%Ni/γ-Al ₂ O ₃ 5%Ni/γ-Al ₂ O ₃ 7%Ni/γ-Al ₂ O ₃	70.1 79.4 84.8	56.95 64.55 68.94	[115]
Oleic acid	Batch autoclave	Temperature: 280 °C Pressure: 2.5 MPa H ₂ Reaction time: 6 h	Ni/ZnO-Al ₂ O ₃	100	93.7 (C17) 2.1 (C18)	[69]
Oleic acid	Batch autoclave	Temperature: 340 °C Pressure: 2 MPa H ₂ Reaction time: 2 h	Ni-BTC/ Zeolite 5A Ni-BM 65 MOF/Zeolite 5A	91.2 92.2 90.3	77.13 83.59 78.42	[116]

		Ni-BM 73 MOF/Zeolite 5A				
Oleic acid	Batch autoclave	Temperature: 290-335 °C Pressure : 1 - 2 MPa H ₂ Reaction time: 0.5 -8 h	Pt/ZIF-67/Zeolite 5A	~ 99	97.6	[117]
Oleic acid	Batch autoclave	Temperature: 250-300 °C Pressure: 2.6 – 4.3 MPa CO ₂ Reaction time: 6 h	Fe/SBA 15	100	> 85	[118]
Oleic acid	Batch autoclave	Temperature: 330-370 °C Reaction time: 5 h	Cu/ZrO ₂ Ni/ZrO ₂	100 100	1.3 22.7	[94]
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure 2 MPa 10% H ₂ /N Reaction time: 3 h	CoMo	88.9	48.1	[119]
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure 2 MPa 10% H ₂ /N Reaction time: 3 h	Pd/Ce _{0.8} Zr _{0.2} O ₂ Pd/Ce _{0.5} Zr _{0.5} O ₂ Pd/Ce _{0.2} Zr _{0.8} O ₂	100 100 100	22 34 7	[120]
Oleic acid	Batch autoclave	Temperature: 320, 360 °C Pressure : 1 - 4 MPa H ₂ Reaction time: 5 h	Ni/HZSM-5	100	67.74	[54]
Oleic acid	Batch autoclave	Temperature: 320 °C Pressure 2 MPa H ₂ Reaction time: 4 h	Co _x P/SiO ₂ Ni _x P/SiO ₂	50.7 78.6	46.3 60.6	[121]
Oleic acid	Batch autoclave	Temperature: 330 °C Pressure 3.0 MPa H ₂ Reaction time: 3 h	Mo ₂ C/CN-700	93.6	89.1	[122]
Oleic acid	Fixed bed	Temperature: 340 °C Pressure: 3.0 MPa WHSV: 2.4 /h H ₂ / oil ratio: 500	Ni/γ-Al ₂ O ₃	100	~95	[123]
Rapeseed oil	Fixed bed	Temperature: 260 - 280 °C Pressure: 3.5 MPa	Ni/γ-Al ₂ O ₃ Co/γ-Al ₂ O ₃ NiMo/γ-Al ₂ O ₃	100 100 100	60 83 98	[124]

		LHSV: 0.25-4 /h H ² /Oil molar ratio: 50 N ³ /m ³				
Rapeseed oil	Batch autoclave	Temperature: 300 °C Pressure : 1 MPa H ² /Oil ratio: Nil Reaction time: 2 h	5wt% Pd/C	100	91.5	[29]
Rapeseed oil	Batch autoclave	Temperature: 220 - 300 °C Pressure : 1.5 - 7 MPa H ² /Oil ratio: Nil Reaction time: 1 – 6 h	66% Ni/SiO ₂ -Al ₂ O ₃	99.13	93.68	[28]
Rapeseed oil	Fixed bed	Temperature: 400 -480 °C Pressure: 5 MPa LHSV: 1.2 /h H ² /Oil ratio: 500-1000N ³ /m ³	1Pt-5Sn/Al ₂ O ₃	100	76.1	[30]
Rapeseed oil	Fixed bed	Temperature: 350 °C Pressure : 5.5 MPa WHSV-1 – 4/h	MoCx/γ-Al ₂ O ₃ MoNx/γ-Al ₂ O ₃ MoPx/γ-Al ₂ O ₃	- - -	80 70 35	[27]
Soybean oil	Fixed bed	Temperature: 380-410 °C Pressure: 7.15 MPa H ₂ LHSV: 0.45 /h H ² /Oil vol. ratio: 810	Mo ₂ N/γ-Al ₂ O ₃ VN/γ-Al ₂ O ₃ WN/γ-Al ₂ O ₃	99.9 97.0 97.1	84.1 85 81.1	[81]
Soybean oil	Batch autoclave	Temperature: 350 °C Pressure: 0.7 MPa N ² H ² /Oil ratio: Nil Reaction time: 4 h	Ni/γ-Al ₂ O ₃ NiAl/LDH MgAl/LDH NiMgAl/LDH	68 74 72 49	46.3 52.9 47.8 29.0	[125]
Soybean oil	Batch autoclave	Temperature: 300 -440 °C Pressure : 2.5 - 15 MPa H ² /Oil ratio: Nil Reaction time: 1 h	Ni/γ-Al ₂ O ₃ CoMo/γ-Al ₂ O ₃	94 84	90 80	[126]
Soybean oil	Fixed bed	Temperature: 300 - 380 °C Pressure: 4 MPa LHSV: 1 - 30 /h H ² /Oil ratio: -	8 wt% Ni/SAPO-11	100	74.8	[127]

Soybean oil	Fixed bed	Temperature: 375 °C Pressure : 3 MPa LHSV: 1 /h H ² /Oil ratio: 300 ³ /m ³	Pt/SAPO-11-Al ₂ O ₃	-	> 99	[20]
Soybean oil	Batch autoclave	Temperature: 370 °C Pressure: 2 MPa Reaction time: 3 h	MoO/Al ₂ O ₃	85.64	59.85	[21]
			Mo ₂ C-AC	100	78.99	
			MoS ₂ /Al ₂ O ₃	83.46	71.57	
			Mo/Al ₂ O ₃	67.99	34.8	
			Ni/Al ₂ O ₃	18.12	18.12	
			Ni ₂ P/Al ₂ O ₃	48.72	45.22	
Soybean oil	Batch autoclave	Temperature: 350 °C Pressure: 1 MPa Reaction time: 5 h	NbOPO ₄	70	97	[128]
Palm oil	Fixed bed	Temperature: 350-370 °C Pressure: 4 MPa LHSV: 1/h H ² /Oil ratio: 1000 mL/mL	2 wt% Ni/SAPO-11		70.0	[129]
			5 wt% Ni/SAPO-11		71.8	
			7 wt% Ni/SAPO-11	-	75.3	
			9 wt% Ni/SAPO-11		49.0	
Palm oil	Trickle bed	Temperature: 330 °C Pressure: 5 MPa LHSV: 1/h H ² /Oil ratio: 1000N ³ /m ³	Ni/γ-Al ₂ O ₃	100	68.6 - 91.5	[93]
			Co/γ-Al ₂ O ₃	100	91.6 - 94.3	
			Pt/C	95-100	40.7 – 88.2	
			Pd/C	99-100	30.3 – 82.5	
Palm oil	Trickle bed	Temperature: 330 °C Pressure: 5 MPa LHSV: 2/h H ² /Oil ratio: 1000N ³ /m ³	Ni/γ-Al ₂ O ₃	99.5 - 100	80.1 - 82.9	[25]
			NiAl ₂ O ₄	100	45.4 - 94.3	
Palm oil	Batch autoclave	Temperature: 370 °C Pressure : 1 MPa Reaction time: 2 h	Fe/zeolite	89	76.3	[24]
Palm kernel oil	Batch autoclave	Temperature: 300-350 °C Pressure : 1 MPa Reaction time: 5-10 h	H Beta Zeolite	96	80	[130]

Palm kernel oil	Trickle bed	Temperature: 270 - 330 °C Pressure : 3 - 5 MPa LHSV: 1 - 5/h H ² /Oil ratio: 1000N ³ /m ³	Ni-MoS ₂ /γ-Al ₂ O ₃	89 - 95	92	[22]
Palm kernel fats	Batch autoclave	Temperature: 300 °C Pressure : 1 MPa Reaction time: 5 h	Pd/C	87-96	98	[131]
Sunflower oil	Fixed bed	Temperature: 310 -360 °C Pressure: 2 MPa LHSV: 0.9 – 1.6/h H ² /Oil ratio: 1000N ³ /m ³	Pd/SAPO-31	100	75 - 80	[132]
Canola oil	Batch autoclave	Temperature: 300 - 400 °C Pressure: 5 - 11 MPa Reaction time: 1 – 6 h	NiMo/ γ- Al ₂ O ₃ Pt/HZSM-5 Pt/HY	- - -	80 35 25	[133]
Canola oil	Batch autoclave	Temperature: 300 °C Pressure: 19 MPa Reaction time: 8h	Pd/C	> 90	98.1	[134]
Canola oil	Batch autoclave	Temperature: 375 °C Pressure: 9 MPa H ² /Oil ratio: Nil Reaction time: 8 h	NiMos CoMos	100 100	90.3 86.0	[91]
Castor oil	Batch autoclave	Temperature: 340 °C Pressure: 2.5 MPa Reaction time: 6 h	Pd/C	100	96	[135]
Jatropha oil	Fixed bed	Temperature: 320 , 360 °C Pressure: 2 - 9 Mpa LHSV: 0.8 – 8.0/h H ² /Oil ratio: 21.1-84.4	CoMo/γ-Al ₂ O ₃	89.9 – 99.9	50 - 80	[136]
Jatropha oil	Fixed bed	Temperature: 350 °C Pressure : 3 Mpa LHSV: 0.25 - 2/h H ² /Oil ratio: 1200	Pt/SAPO-11 (0.1) Pt/SAPO-11 (0.2) Pt/SAPO-11 (0.4) Pt/SAPO-11 (0.8)	100 100 100 98.3	83 82.9 82.8 84.9	[137]

Jatropha oil	Batch autoclave	Temperature: 350, 400 °C Pressure: 10 Mpa Reaction time: 3, 6 h	Hydrotalcite (MG70)	100	81.08	[138]
Jatropha oil	Batch autoclave	Temperature: 350 - 400 °C Pressure: 4-11 MPa H ² /Oil ratio: Nil Reaction time: 3/6 h	Hydrotalcite	100	83	[139]
Jatropha oil	Batch autoclave	Temperature: 325 °C Pressure : 0.5 - 3 MPa Reaction time: 5 h	Pd/SBA-16	83.5	99.9	[39]
Jatropha oil	Batch autoclave	Temperature: 425 °C Pressure: 0.3 MPa Reaction time: 3 h	Mg/γ-Al ₂ O ₃	-	63.3	[40]
Jatropha oil	Fixed bed	Temperature: 330 - 390 °C Pressure: 1.5 -3 Mpa LHSV: 1 - 4/ h H ² /Oil ratio: 200 - 1000	Pd/HTC Ru/HTC	91.2 85.6	78.2 75.8	[140]
Jatropha oil	Fixed bed	Temperature: 360 °C Pressure : 4 MPa LHSV: 1.33/ h	W/Pt/TiO ₂	> 90	90	[36]
Jatropha oil	Trickle bed	Temperature: 330 -390 °C Pressure : 1.5 – 3.0 MPa WHSV: 1 - 4 /h H ² /Oil ratio: 200-800N ³ /m ³	Pd/Al ₂ O ₃ Ru/Al ₂ O ₃	85 79	70.3 43.8	[41]
Karanja oil	Semi batch	Temperature: 380 °C Pressure: 35 MPa H ² /Oil ratio: Nil Reaction time: 5 h	Ni/Al ₂ O ₃	~80	75 - 85	[141]
Macauha oil	Batch autoclave	Temperature: 300 °C Pressure: 1/1.9 MPa Reaction time: 5 h	Pd/C	85	35	[97]

Macauba oil	Batch autoclave	Temperature: 300 °C Pressure: 10/19 MPa H ₂ /Oil ratio: Nil Reaction time: 5 h	Pd/C	85	47	[97]
Coconut oil	Batch autoclave	Temperature: 300 °C Pressure: 1 MPa Reaction time: 3 h	Pd/C	100	30.8	[142]
Coconut oil	Batch autoclave	Temperature: 400 °C Pressure: 4 MPa Reaction time: 1 h	HZSM-5	69.55	72.06	[143]
Cashew nut oil	Batch autoclave	Temperature: 300 °C Pressure: 4 MPa Reaction time: 10 h	Pd/C	98	86	[144]

5.2. Bimetallic catalysts

Although CDO over monometallic-based catalyst exhibited an excellent catalytic activity in yielding long-chain diesel hydrocarbons, however, the high cost of noble metal catalysts remains as a major challenge that hinders its application at an industrial scale. Furthermore, the catalytic performances of non-noble metals in the deoxygenation of fatty acids and triglycerides are still not that promising as compared to that of noble metal catalysts in terms of stability and selectivity towards the long-chain hydrocarbons [145-147]. Particularly, it is well known that Ni-based catalysts are prone to sulphur deactivation and coking postulating that the relatively high sulphur compounds present in the biomass feedstock (0.3-0.8 wt%) would adsorb dissociative on the active sites of the Ni surface, forming a sulphur layer which leads to deactivation [148, 149]. Besides, the production of RD from the CDO of triglycerides requiring catalysts of mild acidity, as strong acidic catalysts are known to promote hydrocracking for lighter molecule fuel production [150].

To surpass these difficulties, substantial efforts have been attempted in designing engineered bimetallic catalysts that are i) sustainable and economically feasible, ii) have an ability to remove sulphur (HDS) and nitrogen (HDN), and iii) the presence of both synergetic interactions between basic and acidic sites, as shown in Figure 6 [47, 151]. Table 6 lists the recent CDO studies of triglycerides and fatty acids using bimetallic catalysts. For the past decade, efforts have been extensively focused on the deoxygenation of fatty acids and plant oils over bimetallic metal sulfide catalysts. One major drawback in using bimetallic sulfide catalysts is the inherent need for an external sulfating agent e.g. carbon disulfide (CS_2) or dimethyl disulfide (DMDS) in the liquid feed to maintain its catalytic activity [152]. Moreover, sulphur leaching from the catalyst surface leads to a loss of active sites, resulting in a gradual decline in

catalytic activity and eventual sulphur contamination of liquid products [153]. Therefore, the strong dependency of sulfide-based catalysts on external sulphur agents has attracted considerable criticism in renewable fuel production as it incurs additional production costs and potentially adverse environment effects [154].

According to present-day views, conventional deoxygenation catalysts are normally configured in such a way that transition metals like Ni and Co species are finely dispersed with MoS₂ particles on the silica-based carrier support. Ni and Co are used as promoters to improve the activity of molybdenum sulfide by donating electrons to Mo and weaken the metal-sulfide bond [155]. It is widely known in the literature that the edge surface area of the MoS phase, where the active phase is located, enhanced with the lateral size of the MoS₂ slab reduced [64]. Due to the positive synergetic interaction between the MoS phase and silica-based materials, alumina (γ - Al₂O₃) is the preferred material in achieving a high degree of dispersion of active Co(Ni)-Mo-S phase. Many studies have reported the use of alumina as a support promotes the formation of type II NiMoS phase, the most active phase, which is usually characterized by its weak metal-support interaction, high reducibility of the active phase, and high sulfidation degree.

Many authors agreed on the positive synergetic effects of CoMo and NiMo pairs, which form the basis of innumerable applications of HDO, hydrodesulphurization, and hydrogenation reactions. In the case of HDO of plant oils and fatty acids, NiMo catalysts have shown, in general, a better performance than CoMo catalysts, but there are also contradictory results depending on the type of oil used and the severity of reaction conditions. Taromi & Kaliaguine [156] synthesized wormhole-like mesostructured alumina support with nano-sized crystalline domains using a polymeric template-assisted sol-gel method via evaporation-induced self-assembly (EISA) process and tested the activity performance in continuous deoxygenation

of canola oil. From the results, NiMo-S/ γ -Al₂O₃ catalyst showed satisfactory catalytic properties with some marginal advantages in reaction rate and n-alkanes selectivity than CoMo-S/ γ -Al₂O₃. Similarly, Kaluza and Kubicka [157] investigated and compared the catalytic activities and selectivities of Al₂O₃ supported Co, Ni, Mo, Co-Mo, and Ni-Mo in the deoxygenation of rapeseed oil. From their work, it evidently indicated that NiMo/ γ -Al₂O₃ exhibited higher activity performance than CoMo/ γ -Al₂O₃ catalysts, in fact, 3.5 fold higher than the other counterparts. Significant differences were also observed in reaction pathway selectivity, manifested by differences in final product n-octadecane/n-heptadecane formation. Mo/ γ -Al₂O₃ was found catalyzed selectively toward the HDO route, giving almost exclusively HDO products, while both Ni/ γ -Al₂O₃ and Co/ γ -Al₂O₃ were found to be more favorable than the formation of HCO₂ products.

Río et al. [37] compared the catalytic performances of two commercial NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts in the deoxygenation of Jatropha oil to diesel hydrocarbons. Their work clearly indicated that the superiority of NiMo/ γ -Al₂O₃ over the CoMo/ γ -Al₂O₃ catalysts due to the synergistic electronic properties between NiS and MoS₂. The Ni particles promote the creation of highly active sites by shifting the morphologic structure of MoS₂, leading to the formation of shorter layers with a higher molecular adhesion degree. On the contrary, CoMo/ γ -Al₂O₃ has a lower catalytic performance due to a more severe inhibition of CO released from the HCO reaction. Horacek et al. [158] also confirmed the high oxygen removal activity performance of NiMo/ γ -Al₂O₃ in the CDO or rapeseed oil at a mild temperature range of 250-270 °C in contrast to CoMo/ γ -Al₂O₃ and NiW/ γ -Al₂O₃. Even at a low H₂ pressure of 0.4 MPa, the superior catalytic performance of NiMo/ γ -Al₂O₃ was unaffected in the hydroconversion of methyl laurate to hydrocarbons performed by Imai et al [159]. The addition of phosphorus as a

promoter to a Mo-based catalyst was reported to form phosphor molydate complexes, which promote better Mo dispersion on the support, increases the packing of MoS₂ crystallites and higher acidity strength with Lewis and Bronsted acid sites on the support surface [155].

Since then, a prominent shift in the paradigm of catalyst development can be observed in recent years where numerous studies have been formulated and developed non-sulfide-based catalysts. Other than sulfide NiMo and CoMo catalysts, supported nickel catalysts were reported to be active in the deoxygenation of fatty acids, however the nickel species appeared to be less selective to long-chain fatty hydrocarbons due to its highly active C-C bond scissoring activities such as methanation and hydrocracking [150]. Such shortcomings lead the researchers to look for new approaches and alternatives which do not require any sulphur agents. For instance, Jeon et al. [160] developed a series of Pt, Pd and Ru promoted Ni-Ce-ZrO₂ catalysts for oleic acid deoxygenation and it was revealed that Pt-based catalysts exhibited the highest oleic acid conversion, C₉-C₁₇ hydrocarbon selectivity, and oxygen removal efficiency. The excellent catalytic performance was mainly ascribed to its intrinsic surface oxygen defects and acid properties of a Pt/CZrO catalyst. Despite the excellent HDO activity of noble metal-based catalysts over the bimetallic sulfided catalyst with no sulphur leaching, industrial applicability of such noble metal-based catalysts in the deoxygenation process have always been limited from the economic perspective since they are usually more expensive to make than conventional bimetallic sulfide catalysts [19, 161]. Furthermore, another well-known issue with catalysts like Pd/C used for the CDO of fatty acids is its vulnerability toward rapid deactivation [162]. Many previous studies have reported that Pd as the active metal site is more susceptible to poisoning due to the occupation of surface sites by adsorbed reaction intermediates such as heavy organic substances and carbonaceous deposits, which result in rapid activity degradation of pure Pd

nanomaterials that further limit its practical application in CDO [19, 163]. The route of fully eliminating molecular hydrogen from the CDO process using a monometallic metal catalyst does not appear to be practical due to severe coking deactivation and poor catalytic activities. From the literature review, it is concluded that noble metal catalysts are more active in the deoxygenation of fatty acids with a H₂ modest system. Herein, the H₂ modest system is defined as having a limited supply of external molecular hydrogen with H₂ partial pressures near atmospheric pressures or well below the typical pressures required for the CDO process. Therefore, H₂ modest reaction environment should be used in order to maintain the high activity of noble metal-based catalysts.

Table 6: CDO of plant oils and fatty acids using bimetallic catalysts

Plant oils/Fatty acids	Reactor Type	Reaction Conditions	Catalysts	Conversion (%)	C15 – C18 Yield/ selectivity (%)	Reference
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure 0.1 MPa 20% H ₂ /N ₂ Reaction time: 3 h	Pt/Ni-Ce _{0.6} Zr _{0.4} O ₂	98.7	7.3	[160]
			Pd/Ni-Ce _{0.6} Zr _{0.4} O ₂	90.8	7.2	
			Ru/Ni-Ce _{0.6} Zr _{0.4} O ₂	88.3	6.6	
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure 0.1 MPa 20% H ₂ /N ₂ Reaction time: 3 h	Ni-Ce _{0.6} Zr _{0.4} O ₂	98.3	33.9	[164]
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure - Reaction time: 3 h	CNiAl	90	83	[165]
			CMgAl	98	71	
			CZnAl	89	75	
			CFeAl	97	77	
Oleic acid	Batch autoclave	Temperature: 300 °C Pressure : 0.1 MPa 20% H ₂ /N ₂ H ₂ /Oil ratio: Nil Reaction time: 3 h	Ce _{0.8} Zr _{0.2} O ₂	69.6	16.7	[73]
			Ce _{0.6} Zr _{0.4} O ₂	73.8	18.1	
			Ce _{0.4} Zr _{0.6} O ₂	53.1	14.5	
			Ce _{0.2} Zr _{0.8} O ₂	45.7	13.8	
Oleic acid	Batch autoclave	Temperature: 320 - 380 °C Pressure: 1 - 4 MPa H ₂ flow rate: 100 mL/min Reaction time: 1.5 h	NiMoFO _x /Zeolite	~ 100	75 (C18) 23 (Iso-C18)	[166]
Oleic acid	Batch autoclave	Temperature: 300 - 350 °C Pressure: 1 – 4 MPa N ₂ Reaction time: 3 - 9 h	NiMo/γ-Al ₂ O ₃	96	57	[153]
			CuMo/γ-Al ₂ O ₃	70	10	
			CoMo/γ-Al ₂ O ₃	75	15	
Oleic acid	Batch autoclave	Temperature: 350 - 410 °C Pressure : 6.5 MPa H ₂ Reaction time: 8 h	NiMoN/γ-Al ₂ O ₃	65 - 80	-	[167]
Oleic acid	Batch autoclave	Temperature: 320 °C Pressure: 4.9 MPa H ₂ Reaction time: 4 h	NiMo/γ-Al ₂ O ₃	~ 100	89.6	[152]

Oleic acid	Fixed bed	Temperature: 350 -370 °C Pressure: 2 – 6 MPa LHSV: 0.5 - 2/h H ² /Oil ratio: 400N ³ /m ³	NiMo/ γ -Al ₂ O ₃	> 90	> 95	[168]
Rapeseed oil	Batch autoclave	Temperature: 260 - 300 °C Pressure: 3.5 MPa LHSV: 2 /hr Reaction time: 1 h	15NiMo/TiO ₂ 15NiMo/SiO ₂ 15NiMo/Al ₂ O ₃	~100 ~100 ~100	60 85 85	[61]
Rapeseed oil	Fixed bed	Temperature: 320 -360 °C Pressure: 3.5 – 5.5 MPa LHSV: 1 /h H ² /Oil ratio: 500-1000N ³ /m ³	NiMo/ γ -Al ₂ O ₃	-	88.03 – 91.64	[169]
Soybean oil	Batch autoclave	Temperature: 400 °C Pressure: 2 MPa H ² /Oil ratio: Nil Reaction time: 1 h	NiMo/Sx CoMo/Sx	94 72 – 89	96 89 – 99	[56]
Soybean oil	Batch autoclave	Temperature: 400 °C Pressure: 9.2 MPa H ² /Oil ratio: Nil Reaction time: 2 h	NiMo/ γ -Al ₂ O ₃ Co/Mo/ γ -Al ₂ O ₃	92.9 78.9	64.45 33.67	[4]
Palm oil	Batch autoclave	Temperature: 350 °C Pressure : 5 MPa Reaction time: -	NiMo/ γ -Al ₂ O ₃ Pt/SAPO11	100 100	82 81	[23]
Palm oil	Fixed bed	Temperature: 360 °C Pressure:5 MPa LHSV: 1 /h H ² /Oil ratio: 1000N ³ /m ³	NiMoW/ γ -Al ₂ O ₃ /ZSM -5	-	82.9	[170]
Sunflower oil	Fixed bed	Temperature: 280 -380 °C Pressure: 2 – 8 MPa LHSV: 0.75 – 3 /h H ² /Oil ratio: 400 – 600 N ³ /m ³	NiMo/ γ -Al ₂ O ₃ /F	> 90	73.2 – 75.6	[171]
Sunflower oil	Fixed bed	Temperature: 380 °C Pressure: 4 MPa	NiMoS/5 wt% MoO ₃ - Al ₂ O ₃	100	79.5	[26]

		WHSV: 1 /h H ² /Oil ratio: 2500 N ³ /m ³	NiMoS/10 wt% P ₂ O ₅ - Al ₂ O ₃	100	78.5	
Castor oil	Fixed bed	Temperature: 300 - 370 °C Pressure : 3.5 – 7.0 Mpa LHSV: 0.45 - 0.9 /h H ² /Oil molar ratio: 35 -105	NiMo/ γ -Al ₂ O ₃	-	81.1	[172]
Karanja oil	Fixed bed	Temperature: 300 - 380 °C Pressure : 1.5 - 3.5 Mpa LHSV: 1.1 - 5 /h H ² /Oil Volume ratio: 400 - 600	NiMo/ γ -Al ₂ O ₃ CoMo/ γ -Al ₂ O ₃	73.1 82.6	67.8 70	[173]
Karanja oil	Batch autoclave	Temperature: 280 - 360 °C Pressure : 3 MPa Reaction time: 5 h	(0.9 wt%) Ni (3.4 wt%) Mo/ γ -Al ₂ O ₃	90	75	[174]
Coconut oil	Batch autoclave	Temperature: 375 °C Pressure : 3 MPa Reaction time: 2 h	Ni-Fe/HZSM-5	100	38.6	[175]
Carinata oil	Batch autoclave	Temperature: 350 °C Pressure: 2 MPa H ² /Oil ratio: Nil Reaction time: 5 h	Mo-Zn(2)/Al ₂ O ₃	-	81.05	[176]
Jatropha oil	Fixed bed	Temperature: 330 - 390 °C Pressure : 3 MPa LHSV: 2 /h H ² /Oil ratio: 600 N ³ /m ³	PtPd/ γ -Al ₂ O ₃	100	97.48	[177]
Jatropha oil	Semi Batch	Temperature: 350 °C Pressure: 0.001 MPa Reaction time: 1 h	NiCo/MWCNT	-	64	[35]
Jatropha oil	Fixed bed	Temperature: 375 - 450 °C Pressure: 6 - 8 Mpa LHSV: 1/h H ² /Oil Volume ratio: 600	NiMo/SAPO-11 (0.4 SiO ₂) NiW/SAPO-11 (0.4 SiO ₂) NiMo/SAPO-11 (0.27 SiO ₂)	-	74.68 86.3 86.4	[178]

			NiW/SAPO-11 (0.27 SiO ₂)		87.87	
Jatropha oil	Batch autoclave	Temperature: 300 °C Pressure: 5 MPa Reaction time: 1 h	NiCe/TNT NiCe/TiO ₂ NiCe/TNS	85 71 54	-	[41]
Jatropha oil	Fixed bed	Temperature: 340 - 400 °C Pressure: 3.0 Mpa LHSV: 2 /h H ² /Oil Volume ratio: 600	Ni-HPW/nHA	100	83.4	[179]
Jatropha oil	Batch autoclave	Temperature: 310 - 390 °C Pressure: 2.8 Mpa LHSV: 176.4 – 35.28 /h H ² /Oil molar ratio: 15	NiMo/ γ -Al ₂ O ₃ CoMo/ γ -Al ₂ O ₃	51.7 46.5	69.8 69.9	[180]
Jatropha oil	Fixed bed	Temperature: 280 - 400 °C Pressure : 3 MPa LHSV: 0.8 /h H ² /Oil ratio: 1000 N ³ /m ³	1wt% NiMo/ γ -Al ₂ O ₃ 5wt% NiMo/ γ -Al ₂ O ₃ 25wt% NiMo/ γ -Al ₂ O ₃	76.1 88.9 81.7	89.3 90.0 91.3	[181]

6. Key process parameters of CDO

6.1. Effect of reaction temperature

Reaction temperature is one of the critical parameters that has a considerable effect on the overall conversion and product selectivity in CDO. It also plays an essential role in ensuring optimum catalyst performance and sintering resistance [182]. On the basis of the literature review, most deoxygenation studies of triglycerides, fatty acids, and fatty acid derivatives to diesel-like hydrocarbons are preferably carried out under the reaction temperature ranging from 250 °C to 360 °C. It has been reported by many authors that mild deoxygenation temperatures are more favorable and suitable for the production of middle distillate range products (kerosene, diesel, and jet fuel) as severe reaction conditions tend to promote thermal cracking of long aliphatic hydrocarbon chain and resulting in low diesel range hydrocarbon selectivity. Many researchers have also pointed out that reaction temperatures less than 250 °C showed a significant effect in HGN reactions, resulting in the dominant formation of corresponding saturated fatty acids and triglycerides [19]. Increasing the reaction temperature beyond 330 °C and above, thermal decomposition, aromatization, and isomerization of hydrocarbon products often start to give rise, resulting in a significant decrease in diesel hydrocarbon yield and an increase of volatile hydrocarbon gas [183]. Generally, HCO and HCO₂ are more dominant over reaction temperatures of 300 °C since both reactions are thermodynamically favoured above 300 °C [184]. On the other hand, the exothermic HDO activity is usually dominated at a lower reaction temperature ranging between 270 - 300 °C. One should take note that HCO₂ and HCO reactions are the less H₂ demanding routes compared to HDO. Thus, this work will solely focus on maximizing the hydrocarbon product derived from HCO₂/HCO reactions, rather than the more

H₂ demanding route, HDO since the former routes have the advantages of reducing the H₂ consumption level or avoiding the use of external H₂ source.

Overall, CDO of triglycerides and fatty acids to diesel-like hydrocarbons requires low-mild reaction temperatures as high deoxygenation temperature tends to promote severe hydrocracking reactions, resulting in poor selectivity to long-chain diesel hydrocarbons. It was pointed out by Yang et al. that the hydrocracking of hydrocarbon products was significantly higher at reaction temperature over 335 °C due to the dominant formation of shorter chain hydrocarbon [117]. Thus, this raises the requirement for an optimum reaction temperature in order to strike a good balance between high conversion performance and good selectivity of reaction products. From a review of the literature, many authors have demonstrated and validated that high deoxygenation performance and good paraffinic hydrocarbon selectivity can be achieved under the optimum reaction temperature of 330 °C. Wu et al. demonstrated excellent catalytic HCO₂ performance of stearic acid over carbon-supported nickel and platinum catalysts at 330 °C [185]. In the same work, they also screened the activity performances of a set of three 20 wt% monometallic (Ni, Co, and Cu) catalysts supported on ZrO₂ for the catalytic HCO₂ of stearic acid to heptadecane at 330 °C under inert N₂ atmosphere. Among the catalysts tested, the nickel materials were the most efficient for the conversion of of stearic acid to n-heptadecane, where it exhibited the highest selectivity of heptadecane (72%), and the least active in this set was the Co derived catalysts. Yang [117] and his co-worker investigated the effect of reaction temperature on the catalytic HCO₂ of oleic acid over Pt/Zeolite catalysts and they found out that the highest yield of heptadecane hydrocarbons (91 %) was achieved under the optimum reaction temperature of 330 °C.

In the same line of work, Edeh et al. [186] performed the catalytic hydrothermal HCO₂ of oleic acid over 5 wt% of activated carbon-supported Pd catalysts. Under the reaction temperature of 330 °C, a maximum oleic acid conversion of 88.1% were obtained after 4 h of reaction. Itthibenchapong et al. [22] synthesized a series of NiMo/ γ -Al₂O₃ catalysts using thiourea as the sulphur dopant under an inert atmosphere and tested the catalytic activities in a continuous fixed bed reactor. An optimum diesel fuel hydrocarbon product yield of 92% was obtained from a refined palm kernel oil feedstock under the reaction temperature of 330 °C. In the light of all the findings mentioned above, a minimum deoxygenation temperature of 330 °C is recommended as the essential reaction condition for future deoxygenation works since many previous CDO transformations of triglycerides and fatty acid model compounds have shown an excellent deoxygenation performance at such a reaction temperature, regardless of the type of catalysts used.

6.2.Effect of H₂ partial pressure

The exact role of a H₂ partial pressure in the CDO of fatty acids remains an actively investigated topic in the literature. As a whole, molecular hydrogen has been reported to promote the reaction by favoring the HGN of unsaturated species that would otherwise remain adsorbed on the catalyst surface and/or give rise to coke formation/deposition. It is not only used as a HGN substrate, but also helps to suppress the formation of carbonaceous deposits or coke on the catalyst surface and prolong the catalyst lifetime. However, there are some researchers who reported that the effect of H₂ partial pressure on catalyst performance and/or the reaction pathway was rather insignificant as the nature of the catalyst being employed has a more eminent role in affecting the reaction performance and reaction pathway [117]. Nevertheless, several studies have also concluded that the beneficial effect of H₂ in the deoxygenation reaction was not

monotonic, which has been attributed to the competition between reactant substrates and H₂ molecules for adsorption sites and/or to a change in the reaction pathway resulting in a substantial difference in hydrocarbon selectivity. A recent review by Pattanaik et al. [60] suggested that an excess of molecular hydrogen on the catalyst surface may retard and slow down the reaction rate of HCO or HCO₂ due to competitive adsorption between the reactant substrates and hydrogen atoms. Work by Kim et al. [56] showed the relative rate of HDO, HCO₂, and HCO were influenced significantly by the magnitude of H₂ partial pressure. At a high H₂ partial pressure, the HDO reaction tends to dominate over another two reaction routes as the H₂-rich atmosphere promotes the removal of two oxygen atoms through the formation of water rather than via HCO/HCO₂ through the release of carbon monoxide and dioxide. In short, the HDO reaction is more dominant at a high H₂ partial pressure, whereas HCO and HCO₂ are more readily occur at a lower H₂ partial pressure. Jenišťová et al. [187] investigated the effect of H₂ partial pressure on the HDO of stearic acid over alumina supported nickel catalysts. The results revealed that high conversion performance (99 %) and high selectivity of heptadecane (97 %) were achieved at 30 bar H₂ after 3 h, whereas an inferior conversion performance was observed at a lower H₂ partial pressure. However, this finding differs from that of Yang et al. [117] who found out that the H₂ partial pressure did not effect the oleic acid conversion significantly. Surprisingly, the same 30 bar of H₂ pressure applied in Yang and co-worker's work in fact promoted the formation of CO via water-gas shift equilibrium, which leads to rapid CO adsorption on the catalyst surface and adversely affecting the heptadecane selectivity drastically. From their work, it was also revealed that a high H₂ concentration at the surface of catalysts will promote a higher yield of short-chain hydrocarbons due to the hydrocracking side reaction.

Regardless of the exact role of H_2 partial pressure in the CDO reaction, a continuous supply of high-pressure molecular hydrogen gas is inevitable. Its consumption must be taken into account in terms of economical evaluation of operating conditions. Each reaction pathway has its own minimum stoichiometric amount of molecular hydrogen. HDO pathway generally requires much more H_2 molecules than HCO and HCO_2 . According to the stoichiometry equations listed in R3, R4, and R6, at least 3 moles of H_2 molecules are required for complete HDO of 1 mole of fatty acid, whereas both HCO and HCO_2 essentially require no H_2 molecules at all. Taking the high production cost of industrial H_2 gas into account, achieving direct conversion of fatty acids to linear hydrocarbons with minimum external H_2 feed input is highly desirable from a process economics point of view. Thus, both HCO and HCO_2 routes seem to be conceptually more cost-effective and energy-efficient than HDO since both routes require less H_2 than HDO. Despite HCO_2 theoretically requires no H_2 demand, many previous works have also reported the poor deactivation resistance of Pd-based catalysts under the H_2 -free atmosphere due to its high susceptibility toward coke formation and deposition. Thus, the presence of molecular hydrogen in the reaction system is still necessary in order to suppress the coke formation and keep the noble metal-based catalysts active throughout the reaction.

6.3. Effect of reaction environment

The reaction environment in the deoxygenation of triglycerides and fatty acid model compounds is one of the process variables appreciably affecting the reaction pathway undertaken, conversion, and subsequent product selectivity. The deoxygenation performance and hydrocarbon product distribution have been reported to be enhanced notably under the H_2 -rich atmosphere despite the usage of high-pressure molecular hydrogen significantly increasing the process cost. On the contrary, a lower deoxygenation performance with poor paraffin

hydrocarbon selectivity is usually carried out in a H₂-free atmosphere or an inert atmosphere such as nitrogen (N₂), helium (He) and argon (Ar). In order to minimize the use of high-pressure molecular hydrogen and improve the overall process sustainability, catalytic decarboxylation (HCO₂) under a diluted-H₂ atmosphere using a mixtures of H₂ and inert gases such as H₂/Ar, H₂/N₂, and H₂/He is another plausible deoxygenation technique, which could potentially help in alleviating the high H₂ consumption of deoxygenation field. This reaction mechanism theoretically offers no H₂ requirement, making it more advantageous than a HDO process. Despite the loss of a CO₂ molecule from the lipid reactant, it does not lower the chemical energy of the molecule and in fact, HCO₂ processes produce a paraffin hydrocarbon chain with an even higher energy density [186]. Although the HCO₂ process does not require molecular hydrogen as a reactant, many previous studies have concluded that a mild-H₂ atmosphere (5–10%) is still desirable to maintain the catalytic turnover and prevent the noble metal catalysts from subsequent deactivation due to carbonaceous deposits [60]. It also benefits the saturation of the unsaturated oil derivatives and then desorption of the organic species from the catalyst surface [188]. Kim et al. [126] investigated the effect of H₂ gas on the product distribution and the results suggested that soybean oil undergoes undesirable polymerization of hydrocarbons, yielding a heavy hydrocarbon with a high boiling point under an H₂-deficient atmosphere. Santillan-Jimenez et al. [188] employed carboxylic acid model compounds namely stearic acid and tristeraine as the feedstock for the catalytic hydrotreatment and the findings validated the presence of H₂ in the reaction atmosphere diminishes the undesired consecutive aromatization reactions. The selectivity of aromatic hydrocarbons under the mixture of H₂ and Ar gases was three times lower than pure helium.

6.4. Effect of hydrogen donor solvent/co-solvent

Table 7 summarises all of the previous deoxygenation studies of triglycerides and fatty acids using different types of hydrogen donor solvents. To fully eliminate the practice of using high-pressure molecular hydrogen in the HDO and HCO_2 processes, many research groups have attempted to substitute molecular hydrogen with hydrogen donor solvents such as water [186, 189], dodecane [190, 191], sodium hydroxide [192], supercritical water [84], methanol [193], limonene [106, 194], formic acid [195, 196], and glycerol [197, 198]. Table 7 summarized recent deoxygenation studies of plant oils and fatty acid compounds using hydrogen donor solvents. Watanabe [192] and co-workers initiated the effort in replacing molecular hydrogen with supercritical water at 400°C . The results showed that the rate of decarboxylation for stearic acid was enhanced by the addition of alkali hydroxides under supercritical water. However, the selectivity of hydrocarbons was very low ($<15\%$). In 2010, Fu et al. [84] exploited the formate technique and proposed a new strategy for the deoxygenation of palmitic acid to pentadecane over Pt/C and Pd/C in near or supercritical water without the addition of H_2 . Surprisingly, a single blank experiment revealed the potential of the bare carbon support in hydrothermal HCO_2 of fatty acids and motivated their interest in extending the studies in converting fatty acids to fuel range hydrocarbons using two different commercial activated carbon materials under the same supercritical conditions [193]. They showed that deoxygenation of saturated and unsaturated fatty acids can be conducted at near supercritical water temperature with a selectivity over 90% towards HCO_2 products, but the molar yield of HCO_2 products obtained was only 6 %. Other than supercritical water, Hossain et al. [189, 199] and Edeh et al. [186] exploited the diffusivity of subcritical water in the deoxygenation of fatty acid derivatives and corn oil into diesel-like hydrocarbons, both demonstrated excellent n-alkanes selectivity and liquid yield. In the same theme, both Vardon et al. [198] and Hollak et al. [200] employed hydrothermal aqueous phase

reforming of glycerol for in-situ hydrogen production and the catalytic HCO₂ of triglycerides. The utilization of organic solvents and sub/supercritical water as in-situ hydrogen carriers in the deoxygenation process generally requires either high temperatures (>400°C), long reaction times (≥20 h), or large solvent volumes (2-4 wt%/wt% ratio of solvent/reactant) for sufficient amount of molecular hydrogen to be produced and also for the reaction to be completed.

Type of reactant	Type of solvent	Reactant and solvent ratio	Type of catalyst	Temperature (°C)	Reaction duration (hrs)	Conversion (%)	Diesel hydrocarbon selectivity	Reference
Palmitic acid	Supercritical water	1 : 2.5 wt%	5 wt% Pt/C	370	1	Nil	76% C15 Paraffin	[84]
Palmitic acid	Supercritical water	1 : 3.3 wt%	5 wt% Pd/C	330	3	92	70% C17 Paraffin	[84]
Stearic acid	Water	1 : 5 wt%	5 wt% Pt/MWCNT	330	2	100	91% C17 Paraffin	[201]
Oleic acid	Glycerol	1 : 4 mol%	5 wt% Pd/C	250	20	86	20% C17 Paraffin 16% C17 Olefin	[200]
Oleic acid	Methanol	1 : 4 mol%	5 wt% Pd/C	250	20	95	34% C17 Paraffin 6% C17 Olefin	[200]
Castor oil FAME	Supercritical hexane	1: 30 wt%	5 wt% Pd/C	340	6	10	96 %	[135]
Oleic acid	Glycerol	4 : 1 wt%	5 wt% Pt/C	300	9	100	37% C17 Paraffin	[198]
Oleic acid	Supercritical water	1 : 4.5 wt%	NiWC/Al-SBA-15	480	4	100	2.1% C17 Paraffin 19.7% C17 Olefin 3.7% C18 Olefin	[104]
Oleic acid	Supercritical water	1 : 4 mol%	Activated carbon	370	0.35	99.4	80.6% C17 Paraffin	[196]
Oleic acid	Mesitylene	1 : 16 wt%	14.8 wt% Pd/C	330	9	100	70.5% C17 Paraffin	[202]
Sunflower oil	Glycerol	1 : 2 wt%	Pt-Ni/ Al ₂ O ₃ + Pd/C	300	4	96	-	[197]
Jatropha oil	Formic acid	-	5 wt% Pd/C	360	7	100	-	[197]
Oleic acid	Subcritical water	1 : 4 wt%	Activated carbon	400	2	97	81% C17 Paraffin	[189]

Oleic acid	Subcritical water	1 : 4 wt%	Activated carbon	400	2	91	89.3% C17 Paraffin	[203]
Corn Distillers Oil	Water	1 : 4 wt%	Activated carbon	400	4	100	48.9% C17 Paraffin	[199]
Oleic acid	Subcritical water	1 : 5 wt%	10 wt% Mo/Al ₂ O ₃	375	4	100	18.3 % C17 Paraffin	[199]
Oleic acid	Water	1 : 150 wt%	5 wt% Pd/C	330	3	88.1	10.23 % C15 & C17 Paraffins	[186]
Oleic acid	Tetralin	1 : 1 wt%	5 wt% Pd/C	330	3	92.4	67.4% C17 & C18 Paraffin	[86]
Oleic acid	Tetralin	1 : 1 wt%	5 wt% Pd ₆₀ Cu ₄₀ /C	330	3	~100 ~100	77.4% C17 & C18 Paraffin	[83]

Table 7: Recent deoxygenation studies of triglycerides and fatty acids using H-donor solvents

7. Reaction kinetics and the deoxygenation mechanism

Kinetic modelling is a useful tool for process design, optimization, and operation of industrial reactors. The knowledge of kinetic parameters not only enables a better understanding of the reaction mechanism but also allows the process to be operated at optimum conditions. Furthermore, catalyst development could benefit from kinetic modelling by studying the overall reaction sequence, rate-controlling step, and structure-activity relationship, as well as reaction conditions affecting the conversion and product selectivity. Recently, kinetic studies associated with the deoxygenation of fatty acid and triglycerides have received significant attention in the literature. However, as indicated by Bota et al. [50], it is very challenging to obtain conclusive kinetic and mechanistic results from the hydroconversion of plant oils because of heat and mass transfer limitations, which is inevitable in a three-phase reaction of liquid oil and gaseous hydrogen on a solid catalyst. Moreover, plant oils, which are composed of triglycerides and fatty acids with different reactivities, further complicates the kinetic and mechanistic studies. Non-glycerides and fatty acid contaminating components could make the interpretation of the kinetics results dubious as well. Despite a considerable number of CDO kinetic works been published in the early years, the reaction schemes reported are generally analogous with little attention to the reaction intermediates formed. Moreover, the CDO schemes proposed in the early studies are only based on the knowledge of final products formed without considering the application of kinetic modeling and feasibility comparison of different plausible schemes. In general, most of the earlier studies reported that the prototypical fatty acid models undergo three different reaction pathways (HDO, HCO₂, and HCO) to remove the carboxyl group (-COOH) before forming the long-chain diesel hydrocarbons [46, 49].

To date, a few CDO studies have reported more comprehensive reaction schemes comprising alcohols and aldehydes as major reaction intermediates. As shown in Figure 7, Kim, et al. [56] proposed a reaction mechanism contradicting to the general known reaction mechanism as it involved the scission of triglycerides from the glycerol backbone without being fully hydrogenated, resulting in the liberation of unsaturated fatty acid molecules. The proposed chemistries of Kim et al. [56] is consistent with the findings reported by Zhang et al. [91] and Rozmysłowicz et al. [58] as both studies suggested a more complex reaction pathway with the possible route of aldehyde intermediates to ketones before the formation of paraffinic hydrocarbons. Under a hydrogen-rich atmosphere, the carboxylic acids undergo hydrogenation reactions by forming partially deoxygenated aldehyde intermediates before yielding pure hydrocarbons and carbon monoxide [58]. Alternatively, the aldehyde can be further hydrogenated to an alcohol compound and indirectly decompose into a hydrocarbon.

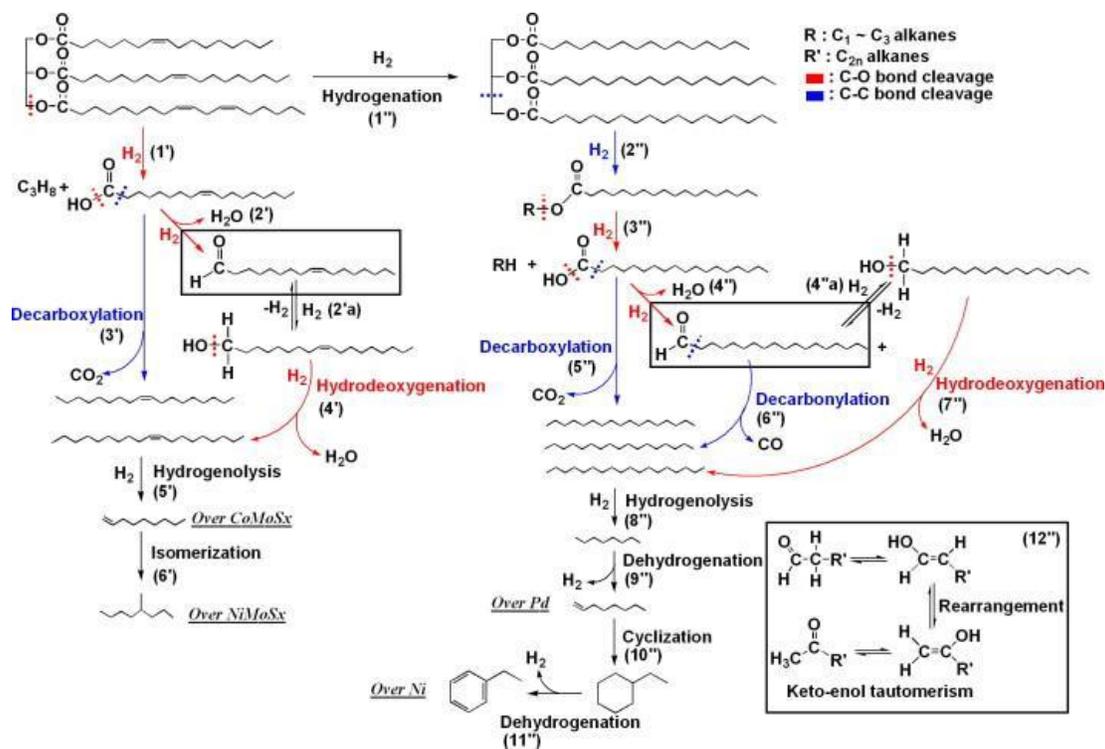


Figure 7: Detailed reaction mechanism in for the CDO of soybean over four types of catalysts
(NiMoSx, CoMoSx, Pd and Ni) [56]

To the best of our knowledge, a search of the literature revealed that most of the kinetic studies reported were first-order power-rate law. For instance, Kumar et al. [204] studied HDO kinetics of stearic acid using n-dodecane as the solvent over Ni/ γ -Al₂O₃. From Figure 8, a comprehensive reaction mechanism was proposed and used to develop a kinetic model based on an empirical first-order power law for a HDO reaction. From a non-linear regression algorithm based on Levenberg-Marquardt, the apparent activation energy of stearic acid, C₁₅, C₁₆, C₁₇, and C₁₈ hydrocarbons were found to be 175.4 kJ/mol, 387.7 kJ/mol, 377.2 kJ/mol, 250.0 kJ/mol and 190.9 kJ/mol, respectively.

$$\frac{dC_{SA}}{dt} = -k_1 C_{SA} \quad (7.1)$$

$$\frac{dC_{HEPD}}{dt} = -k_2 C_{OCTDL} \quad (7.2)$$

$$\frac{dC_{OCTD}}{dt} = -k_3 C_{OCTDL} \quad (7.3)$$

$$\frac{dC_{PEND}}{dt} = -k_4 C_{OCTDL} \quad (7.4)$$

$$\frac{dC_{HEXD}}{dt} = -k_5 C_{OCTDL} \quad (7.5)$$

$$\frac{dC_{OCTDL}}{dt} = -k_1 C_{SA} - (k_2 + k_3 + k_4 + k_5) C_{OCTDL} \quad (7.6)$$

where $\frac{dC_i}{dt}$ is the reaction rate of species i, k is the reaction rate constant, K_1 , K_2 , K_3 , K_4 and K_5 are the reaction rate constants of stearic acid (SA), n-heptadecane (HEPD), n-octadecane (OCTD), n-pentadecane (PEND) and n-hexadecane (HEXD).

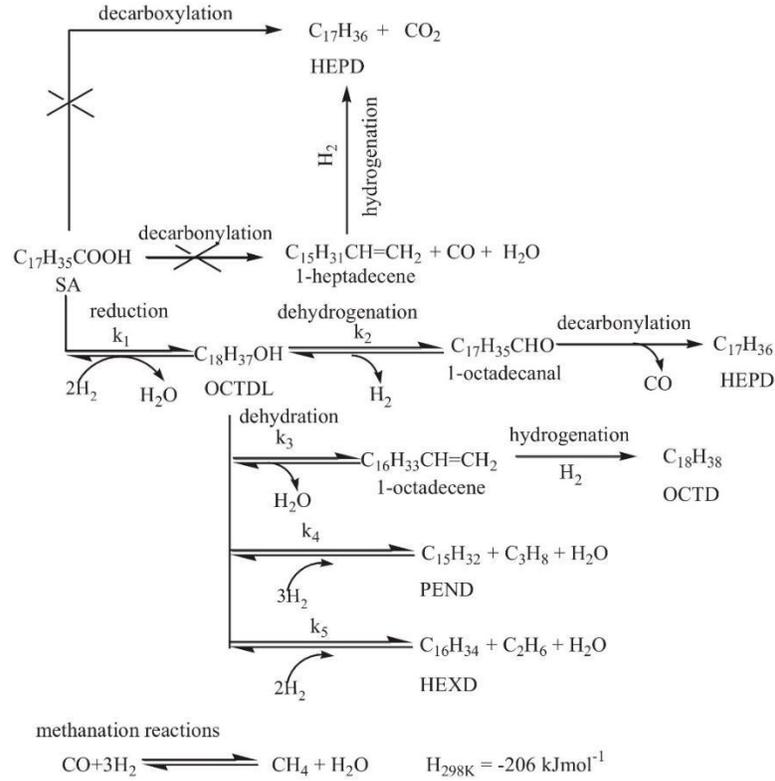


Figure 8: Reaction mechanism of HDO of stearic acid over a Ni/ γ -Al₂O₃ catalyst [204].

In another power-law based kinetic study of Ayodele [112] and their co-workers, a lumped kinetic model based on a simplified reaction mechanism for HDO of oleic acid was proposed as shown in Figure 9. From the results, the apparent activation energy obtained was 130.3 kJ/mol, which is lower than that of Kumar et al. [204]. The differential equations used were as follow:

$$\frac{dC_{OA}}{dt} = -k_2 C_{OA} \quad (7.7)$$

$$\frac{dC_{SA}}{dt} = k_2 C_{OA} - k_3 C_{SA} \quad (7.8)$$

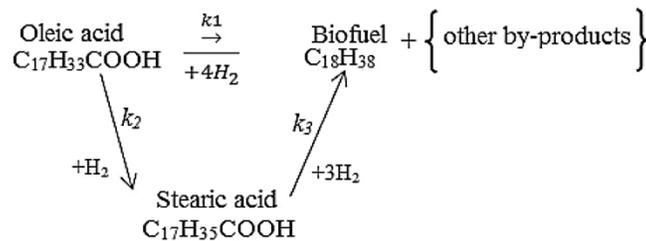


Figure 9: Simplified reaction mechanism for HDO kinetics of oleic acid [112].

From equation (7.7), integration with respect to time gives the following equation:

$$C_{OA} = C_{OA_0} e^{-(k_2)t} \quad (7.9)$$

Substituting equation (7.9) into equation (7.10),

$$\frac{dC_{SA}}{dt} = k_2 C_{OA_0} e^{-(k_2)t} - k_3 C_{SA} \quad (7.10)$$

Upon integration with boundary limits: $t=0$, $C_{OA}=C_{OA_0}$ and $C_{SA}=C_{SA_0}$,

$$C_{SA} = \frac{k_2 C_{OA_0}}{(k_3 - k_2)} \left[e^{-(k_2)t} - e^{-(k_3)t} \right] \quad (7.11)$$

$$\text{As } C_{18} = C_{OA_0} - C_{OA} - C_{SA},$$

$$C_{18} = C_{OA_0} - C_{OA_0} e^{-(k_2)t} - \frac{k_2 C_{OA_0}}{(k_3 - k_2)} \left[e^{-(k_2)t} - e^{-(k_3)t} \right] \quad (7.12)$$

For mechanistic based kinetics models, only a few research groups investigated the surface reaction mechanism for fatty acids deoxygenation, less to say real plant oil deoxygenation due to the complexity of mechanistic models. Until now, several forms of mechanistic kinetic models have been proposed to elucidate the reaction mechanism of the CDO of fatty acids to diesel-like hydrocarbons. These models include Power-rate law, Langmuir Hinshelwood (L-H) model, and the Eley-Rideal (E-R) model. Power-rate is the simplest kinetic expression used to fit experimental data without providing any insights into what is occurring on the catalyst surface, while Langmuir Hinshelwood and Eley-Rideal models are mechanistic based rate expressions used to investigate the sequential elementary steps in the overall reaction and to determine the rate-determining step of the reaction. For example, Bota et.al. [50] investigated the effect of

pressure on the HDO of caprylic acid (CA) over NiMo/ γ -Al₂O₃ and Pd/C using L-H models with competitive and non-dissociative hydrogen molecules as shown in equation (7.13). However, no kinetic parameters were computed for this system.

$$r = \frac{k K_{H_2}^P K_{CA}^P}{\left(1 + K_{H_2}^P + K_{CA}^P\right)^2} \quad (7.13)$$

where r is the reaction rate, k is the reaction rate constant, K_{H_2} and K_{CA} are the equilibrium adsorption coefficients of H₂ and CA.

In a recent kinetics study by Zhou & Lawal [205], both investigated the kinetic HDO of palmitic acid over 1% Pt/ γ -Al₂O₃ using empirical modelling and mechanistic conjectures including power rate law, L-H and E-R models. From the results, rate equations derived from power rate law, L-H mechanism with dual-site non-dissociative H₂ and an E-R model with non-dissociative adsorption of H₂ and non-adsorbed palmitic acid (P.A) were found to fit the experimental data. The calculated activation energies of power-law and E-R were 60.3 kJ/mol and 92.9 kJ/mol for the L-H model.

$$\text{Power-law model: } r_{P.A} = -k_{rxn} C_{P.A}^\alpha P_{H_2}^\beta \quad (7.14)$$

$$\text{E-R model: } r_{P.A} = \frac{-k_{rxn} C_{P.A} P_{H_2}}{\left(1 + K_{H_2} P_{H_2}\right)} \quad (7.15)$$

$$\text{L-H model: } r_{P.A} = \frac{-k_{rxn} K_{P.A} C_{P.A} K_{H_2} P_{H_2}}{\left(1 + K_{P.A} C_{P.A}\right) \left(1 + K_{H_2} P_{H_2}\right)} \quad (7.16)$$

where $r_{P.A}$ is the reaction rate of palmitic acid (P.A.), k_{rxn} is the reaction rate constant, $C_{P.A}$ is the concentration of P.A, P_{H_2} is the partial pressure of hydrogen, K_{H_2} , and $K_{P.A}$ are the equilibrium adsorption coefficients of H_2 and P.A.

As shown in Figure 10, Cheah et al [206] performed a comprehensive mechanistic based kinetic modelling to investigate the surface reaction mechanism of a hydrogen transfer deoxygenation of oleic acid over a bimetallic $Pd_{60}Cu_{40}$ catalyst. To determine the rate limiting step of the proposed tandem reaction system, a series of power-law, L-H and E-R models were developed and derived. From the L-H model assuming single site adsorption of oleic acid with dissociative H_2 adsorption, it was revealed that the rate limiting step of the overall deoxygenation reaction was the hydrogenation of oleic acid with an activation energy of $75.0 \pm 5.1 \text{ kJ mol}^{-1}$, which was evidently lower than that of the dehydrogenation of tetralin ($66.4 \pm 2.7 \text{ kJ mol}^{-1}$) from the Zhou & Lawal [205] study. The findings also demonstrated that the application of tetralin as a hydrogen donor solvent and in-situ H_2 source for the catalytic deoxygenation of oleic acid to diesel hydrocarbons in a novel continuous flow reaction.

$$\text{L-H model: } r_{O.A} = \frac{k_{rxn} k_{O.A} [O.A] k_{H_2} [H_2]}{\left(1 + k_{O.A} [O.A] + \sqrt{k_{H_2} [H_2]}\right)^3} \quad (7.17)$$

Where $r_{O.A}$ is the reaction rate of oleic acid acid (O.A.), k_{rxn} is the reaction rate constant, $[O.A]$ is the concentration of O.A, $[H_2]$ is the concentration of molecular hydrogen, K_{H_2} , and $K_{O.A}$ are the equilibrium adsorption coefficients of H_2 and P.A.

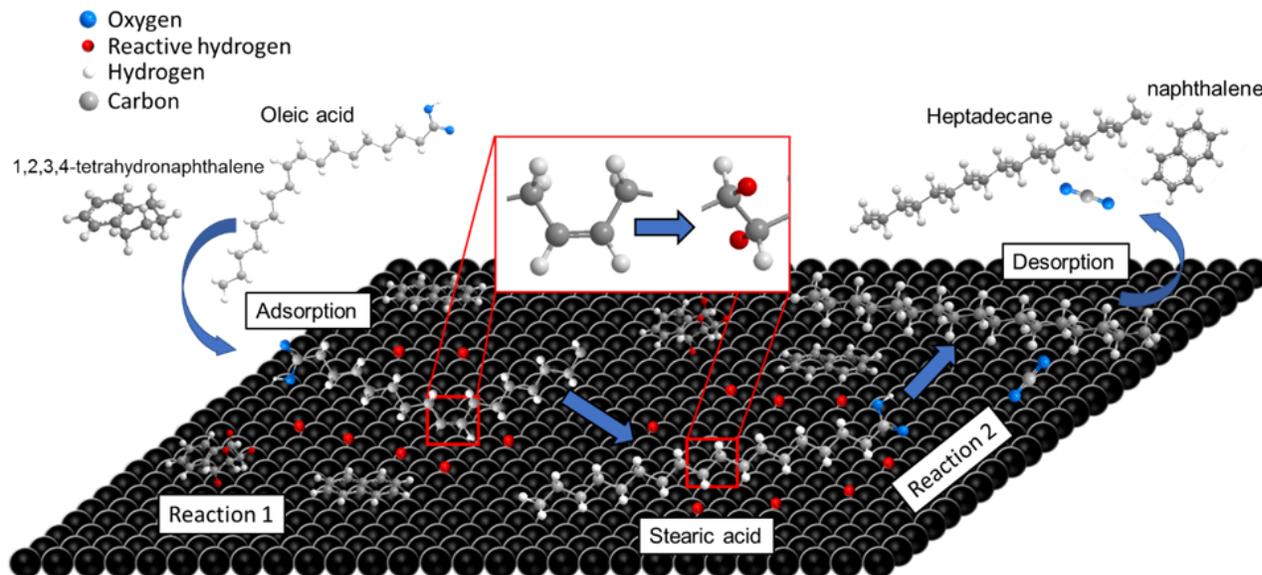


Figure 10: Mechanistic model of deoxygenation of oleic acid with tetralin as a hydrogen donor solvent [206].

8. Future prospective and challenges

8.1 Development of mechanistic kinetic models from real plant oils.

Despite the significance of kinetic mechanisms in industrial reactor scale-up and modelling, far too little attention has been paid in formulating a practical kinetic model for the CDO of crude plant oils. Many previous studies only examined and mapped out the hypothetical reaction pathways of a single model compound based on simple chemical conservation equations. However, the inherent interaction effects between triglycerides molecules, reaction intermediates and hydrocarbon products were remained unclear and yet to be established up to now. As the CDO of real plant oil is a rather complex reaction system in which thousands of organic species participate in multiple parallel reactions, the complexity of such feeds makes it extremely difficult to characterize, less to say describing its kinetic at a molecular level. Thus, it is impossible to establish a kinetic equation for every reaction species by using the conventional methods used in kinetic studies for a single surrogate model compound. More sophisticated and

accurate approaches are required to provide a better understanding and to ensure that the model is a reasonable representation of deoxygenation kinetics. One way of simplifying such a problem is to consider the partition of the species into a few equivalent classes, the so-called lumps or lumping technique, and then assume each class is an independent entity. The middle distillate and naphtha products can be lumped into four discriminated families based on boiling point range, which are diesel, kerosene, heavy and light naphtha. By lumping the kinetic models, the complication and size of the chemical kinetic mechanism can be greatly reduced and simplified. With the intrinsic kinetic data obtained, the deoxygenation mechanism of real plant oils can be expanded and understood in detail. Furthermore, the obtained kinetic parameters will be useful for the designs of the appropriate reactor and prototype development in the future.

8.2 Development of novel single atom catalysts (SACs) for the CDO reaction

In recent years, noble metals supported catalysts such as Pd, Pt, and Ru have demonstrated excellent deoxygenation activities and product selectivity in contrast to the conventional sulfided bimetallic supported catalysts. However, the high production cost of such precious metal-based catalysts is still one of the major industrial concerns and hinders its potential for large scale applications. Furthermore, like most catalysis reactions, it is well known that the deoxygenation reaction occurs exclusively on the surface atoms of the supported metal nanoparticle during the reaction and the core metal atoms are generally inaccessible by the reactant molecules, which consequently leads to poor atom efficiency. Therefore, the key catalytic design strategy for deoxygenation reaction should be maximizing the number of accessible active sites available on the catalyst surface by isolating the atoms individually and exposed it to the reactant substrates atomically. By dispersing the active metals atomically on the support, it is envisaged that the atom-utilization efficiency of the deoxygenation catalysts can be

greatly maximized with enhanced including activity, stability, and product selectivity. With the application of single atom catalysts (SACs) in deoxygenation reactions, the catalyst production cost can be improved significantly as the loading of metal particles in SACs are usually lower than conventional deoxygenation catalysts reported in the literature. Up to date, there is little known about the activity, selectivity and stability of these novel SACs in the deoxygenation of triglycerides and fatty acids. Besides, optimization of metal and support systems with dual deoxygenation and isomerization abilities is also another major challenge in the deoxygenation field. To improve the cold flow properties of the synthetic middle distillate products, bifunctional catalysts with better catalytic stability and coke deactivation resistance should be formulated and developed via a simple, cheap, and easily scalable preparation method. The morphology, structure and acidity level of the support materials can be tailored by using metal-organic framework (MOF) materials with high surface and pore functionalities. Other mild acidity supports can be used to promote high deoxygenation/isomerization performance and low hydrocracking activity.

8.3 In-situ H₂ production from sustainable hydrogen donor solvents

The high H₂ consumption limitation in the CDO of fatty acids to diesel-like hydrocarbons has to date been minimally explored. Only a few research groups have attempted to replace the high-pressure molecular hydrogen with strong H₂ donating solvents such as water, sodium hydroxide, supercritical water, methanol, limonene, formic acid, and glycerol. However, all these solvents generally require either large solvent volumes, high reaction temperatures or long reaction times for sufficient amount of H₂ to be liberated and also for the reaction to be completed. Moreover, the route of fully eliminating H₂ from CDO processing does not appear to be the most practical option due to the severe coking deactivation of the commercial catalysts.

Thus, the high H₂ consumption limitation in CDO requires attention in the pursuit to close such research gaps. Thus, a low-cost and environmentally benign alternative must be explored to replace high-pressure molecular hydrogen transformations of lipids based feedstocks. This will enhance the sustainability of RD production and allow the production to become fully fossil-fuel independent.

To further reduce the external H₂ sources, the development of novel catalysts should not be focused on the sole basis of selective deoxygenation performance and must promote the production of in-situ H₂ from hydrogen donor solvents through dehydrogenation, water-gas-shift and steam-reforming reactions. Furthermore, the economic and environmental aspects of applying hydrogen donor solvents in CDO processes at an industrial scale must be evaluated via a comprehensive techno-economic analysis (TEA) and life cycle assessment (LCA). The simulated results obtained from TEA and LCA can be benchmarked against those of conventional crude middle distillate hydrocarbons production using high-pressure H₂. Despite the CDO of plant oils and prototypical fatty acids using hydrogen donor solvents at laboratory scale, the use of TEA and LCA at such an early stage of development can aid in identifying potential opportunities for cost-effectiveness improvements.

8.4 Optimization of CDO process parameters

Advanced optimization studies should complement the future research and development activities related to the CDO of plant oils and fatty acids. In determining the optimal reaction conditions, the functional relationship and interaction effect of each reaction variable on diesel hydrocarbons selectivity can be further investigated and evaluated using advanced mathematical and statistical tools including artificial neural networks (ANN), Bayesian computational networks, particle swarm optimization, and Monte-Carlo methods. With the optimized process

parameters, the overall process energy requirement and economics can be lowered drastically with the improvement opportunity in diesel hydrocarbon yields/selectivity.

9. Conclusion

CDO of plant oils and fatty acids to renewable diesel fuels is a prominent technology that will continue to grow and develop in the future. For the past decade, the bio-based diesel fuels sector has been anticipating the establishment of a continually expanding industry within a reasonably stable market base. However, conversion of plant-based fatty acids and triglycerides into transportation diesel fuels via CDO technologies still suffer from a few technical operational challenges including low catalyst stability, poor deactivation resistance, and high H₂ consumption requirements. Based on present review, significant progress has been made by many scientific researchers in developing novel monometallic and bimetallic catalysts with superior deoxygenation performance and high deactivation resistance/stability. However, very little work has been done in developing an H₂-free deoxygenation process or at least a deoxygenation system with an H₂-modest atmosphere. To fully eliminate the usage of external H₂ sources in CDO technologies, a novel process with in-situ generation of H₂ from sustainable and renewable hydrogen donor solvents should be developed. Furthermore, from an industrial perspective, an ideal deoxygenation catalyst should have the following characteristics: (i) superior deoxygenation activity, (ii) high resistance towards coke, poisons, water, and other feedstock impurities, (iii) the ability to regenerate under easily scaled up processes, and (iv) cheap and abundant active components. Thus, intensive research efforts should be focused on formulating and developing novel cost-effective bifunctional catalysts with excellent deoxygenation performance and high H₂ generation activity. Lastly, the fundamental mechanistic aspects of plant oil deoxygenation reactions should be explored to allow the researchers to

develop a more efficient and selective deoxygenation catalyst. As a whole, with proper selection of feedstock, supported catalysts, and optimization of reaction conditions, CDO technologies could be one of the promising routes for the production of alternative diesel fuels, globally.

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