Renewable diesel Production: A Review

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Abstract
Biodiesel is considered an alternative to petroleum diesel as it is more environmentally friendly, cleaner, decreases greenhouse gas emissions, non toxic and biodegradagable. Although, low energy density, relatively high cost of production and poor cold flow are some of its demerits. Some of these problems can be reduced by renewable diesel. The demand for renewable diesel is increasing especially due to its high qualities including cetane, cloud point, oxidative stability, cold flow and can be produced and transported using the existing refinery facilities. The current work discusses the feedstocks used in renewable diesel production, catalysts, methods of production, factors affecting the production, reaction pathway/kinetics of renewable diesel production, and analysis of renewable diesel based on existing literature. The review shows that the production of the renewable is increasing globally due to favourable Government policy, and high demand. The utilization of renewable diesel will help to reduce the greenhouse gases by 50%.

Keywords: *Renewable diesel; biodiesel; feedstocks; deoxgenation; catalytic hydro-processing*

Introduction
Increasing prices has been decelerating the growth of biofuel globally [1]. This increase maybe attributed to the high cost of feedstocks such as corn, soybean and other vegetable oils which also double as food for human consumption. At the moment, majority of the biofuels including bioethanol, biodiesel and renewable diesel are produced globally from these feedstocks in Europe and countries such as the United States, Brazil, China, Canada, India, Indonesia, Argentina, Thailand, and Colombia. However, in order to ensure that biofuel is competitive especially due to its role in the reduction of GHG emission, several Governments of the world design policies that influence biofuel growth which may tax credit and subsidy [1]. The effect of this policy is the increasing quantity of biofuel produced globally, as shown by 187 thousand barrels in 2000 and 1.75 million barrels of oil equivalent per day produced in 2021. During this period, the United States produced 41 % of the total biofuel recored globally, making it the largest producer of biofuel in 2021 [1].

Renewable diesel also known as green diesel or advanced biofuel resembles the conventional diesel in chemical composition and are produced through processes such as catalytic hydro-processing and deoxygenation from feedstocks like edible and non-edible oils in the presence of catalysts [2-4]. Commercial-ization of the green diesel is constrained by high cost of raw material and production [5]. This raw material cost is dorminant and consitutes more than 57% of the overall production cost. To ensure competiveness, there is need to source for sustainable, non-expensive and value added feedstock. The waste cooking oil [WCO] is one of them and it is readily available [6]. This will also help to improve the quality of the environment by solving the disposal problem associated with WCO [7].

The current work considers the feedstocks, catalysts, methods, renewable diesel production, factors affecting the production, reaction pathway/kinetics of renewable diesel production and analysis of renewable diesel

Feedstocks for renewable diesel production
Renewable diesel can be produced using the same feedstocks as the biodiesel, which may be edible or non-edible oils. The edible oils include palm oil, and non-edible oils like jatropha, microalgae, waste cooking oil [WCO], chicken fats, activated sludge lipids and crude palm oil. The fatty acid composition of palm fatty acid distillate [PFAD], palm oil and sludge palm oil are presented in Table 1. Fatty acids such as oleic, and palmitic acids have also been investigated for suitability in the production renewable diesel [8-15].

Table 1: Fatty acid composition of some feedstocks

Feed stock	Fatty acid composition (%)							Reference
	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
PFAD	0.46	1.20	46.9	4.30	36.7	9.03	0.31	Taherian et al., 2017
PFAD	0.04	0.42	41.25	7.29	41.58	8.95	ND	Yang et al., 2017
PFAD	ND	1.0	48.0	4.2	37.0	9.4	0.4	Kamaruzaman et al., 2020
PFAD	-	0.27	55.59	6.33	22.76	12.92	-	Gamal, 2020
Palm oil	-	2	45	5	39	9	-	Jin and Choi (2019)
Sludge palm oil	-	-	45.68	-	40.19	-	-	Alsultan, et al.(2022)

ND: Not detected

Catalysts for green diesel production

In the recent time, various researchers have investigated the catalytic deoxygenation of triglyceride including fatty acid bearing feedstock to renewable diesel. The catalysts used include noble metals, metal sulphides, metal phosphides, metal carbides and d-block metal oxides supported on veriaties of oxide substances such as Al_2O_3, SiO_2 and TiO_2 [see Tables 2 and 3] [16,17]. The metal carbides, metal nitrides and phosphides according to researchers have shown. superior catalytic performance and selectivity in deoxygenating natural triglyceride and model compounds over the sulfide-based and platinum group [PGM] based supported catalyst. However, their commercial applications are limited due to complexities in their preparation, often involving uneconomical lengthy synthesis procedures. The noble metals like Pt and Pd are very effective in catalyzing deoxygenation reaction resulting to high yield of hydrocarbons, but, are expensive. The pd catalyst is susceptible to rapid deactivation when used as catalyst for hydroprocessing. Non-nobel based catalyts such as metal carbides, metal nitrides and metal phosphides supported catalysts can help to reduce the problems associated with the application of Pd in the deoxygenation of natural triglycerides and model. The challenge with the use of these catalysts is high cost and complexity in their preparation hindering commercial application [18,19]. The effect of high cost can be minimized by combining the noble metals with cheaper metals leading to the production of an effective and scalable catalyst resulting from the synergistic catalytic effects and decreased nobel metal loading.

Table 2: Catalysts for renewable/ green diesel production

S/N	Catalyts	Purpose	Products/Yield	Reference
1	0.55% Pt/HZSM-22/Al_2O_3	Catalysed the isomerization and cracking of pre-hydrogenated oil	N-paraffin and iso-paraffin compounds	Hancsók et al. (2007)
2	Ni/Co supported on multi-walled carbon nanotubde (MWCNTs), Ni-Co/MWCNT	Deoxygenation of Jatropha curcas oil in a hydrogen free environment	Ni-Co/MWCNT gave the highest selectivity towards C_{15}-C_{17} hydrocarbons. Overall conversion of 76% and more than 60% green biodiesel selectivity	Asikin-Mijan (2016)
3	1% Pt/Al_2O_3, 0.5% Rh/AL2O3 and NiMo/Al_2O_3	Hydro-deoxygenation of microalagae oil to produce green diesel	1% Pt/A_2O_3 gave the highest yield at 310oC and 33 atm. The hydrocarbon range of the product is C15-C17	Zhou and Lawal (2016)
4	Ni/γAl_2O_3	Production of green diesel from waste chicken fats by deoxygenation in a hydrogen free environment	Green diesel	Kaewmeesri et al. (2015)
5	5 wt% Ni/γAl_2O_3	Production of green diesel from stearic acid	A selectivity of 97% and 99% conversion of stearic acid at 300oC and 30 bar was obtained	Jenistova et al. (2017)

6	Ni-Mo/γAl_2O_3	Producing green diesel from canola oil by hydro-deoxygenation at 31 bar and 325-400oC	A complete conversion of canola oil to greeb diesel range hydrocarbons was obtained at 375oC	Taromi and Kaliaguine (2018)
7	16Ni/γ-Al_2O_3, 16Ni/SAPO-11, 8Ni-8Mo/γ-Al_2O_3,8Ni-8Mo/SAPO-11, 12Ni-4Mo/γ-Al_2O_3, 4Ni-12Mo/γ-Al_2O_3	Production of renewable diesel	8Ni-8Mo/γ-Al_2O_3 gave the highest conversion 99.5% and selectivity 98.9% resulting to 73.9 normal alkanes (C15-C18)	Lin et al. (2021)
8	Mn $_{(0.5\%)}$-Mo $_{(0.5\%)}$/AC	Investigated the use of Mn-Mo/AC in the production of diesel range fuel from sludge palm oil	89% liquid hydrocarbons, 93% selectivity favouring n-$(C_{15}+C_{17})$	Alsultan, et al. (2022)

For instance, Pd-Ni and Pd-Cu bimetallic catalyts have been used in many applications including alcohol oxidation, hydrogen separation, nitrate decomposition, electrochemical sensing and production of diesel range hydrocarbons [20]. The metal sulphides catalysts are also very effective in deoxygenation of feedstocks to hydrocarbons but, their usage is restricted due to sulphur leaching which impacts adversely on the quality of the renewable diesel and causes a decline in the catalytic activity. There is also the need for an external sulfiding agents such as carbon disulfide [CS2] or dimethyl disulfide [DMDS] in the liquid feed to ensure catalytic activity. The problems with these agents are increased cost of production and negative environmental impact [22,23].

The acidic catalyst in DO, results to severe deterioration of catalyst sites due to formation of coke. Examples of such acidic catalyst include zeolite-based, MCM-41-based HZSM-5, ZSM-5, SBA-15 and SBA-16 [11,14-17]. The base metal-catalyst gives less coke formation than the acidic metal-catalyst in DO [1,4]. The problem with these kind of catalyst is that they have high cracking activity resulting to poor deCOx producing light hydrocarbon fractions [19,4]. The coke formation and poor deCOx catalyst activity associated with the acidic and base catalysts, respectively can be solved by combining both metals like binary metal oxide. The use of acid-base catalyst is very effective in deCOx reaction selectively favouring the production of diesel range hydrocarbons [C_{13}-C_{20}] [5]. The mixture of CaO and NiO over SiO2-Al2O3 is more stable and can be reused up to fourth cycles without altering the hydrocarbon product, and less impacted by coke formation compared to Ni-Cu/Al_2O_3 and Ni-Sn/Al_2O_3(20). It has been demonstrated by various researchers that transition metal oxides (TMO) involving Mo, Co and Ni are very strong binary metal catalysts due to their strong metal-support interactions and high metal dispersion [21,24-27]. Researchers have also demonstrated that SBA-15 mesoporpus silicas can support the production of green diesel due to their tunable pore size, outstanding thermal stability, ease of surface modification, and high surface area [28]. This shows that modifying the chemical properties of the catalyst can help to reduce the rate of deactivation.

Catalyst Preparation

Prepared a range of activated carbon supported Pd, Cu, Ni, Pdx-$Cu_{(100-x)}$ and $PdxNi_{(100-x)}$ through incipient wetbess impregnation [IWI], and prepared a catalyst using impregnation method, drying and calcination [21].

Catalyst Characterization

Catalysts are usually characterised to determine their physical and chemical properties, and to understand their activity behaviour. The physical properties involves crystallinity, morphology, surface area and thermal stability, and the chemical properties include chemical composition, acid strength and basic strength [29]. Hydrothermal stability can be obtained by determining the loss of surface area and change in morphology. The surface areas and pore sizes could be measured by N2 physisorption on a Quantachrome Nova 4000 instrument [21]. The dispersion state and chemical composition of the catalyst can be identified using X-ray diffraction [XRD]. The specific surface area and pore distribution of the catalysts can be determined by the Brunauer-Emmett-Teller [BET] method using N2 adsorption/desorption analyser. The pore size distributions and pore volumes of the catalyst can be determined using the Baret-Joyner-Halenda [BJH] model on the desorpton branch [39]. The metal concentration can be determined using inductively coupled plasma optical emission spectrometer and the amount of oxygen on carbon surfaces could be quantified by O 1s XPS using Sigma Probe instrument equipped with monochromatic AI K radiation. The N_2 adsorption-desorption isotherms of catalysts could be measured by using a Tristar volumetric analyzer. The H2 and CO chemisorptions could be determined using an ASAP 2020c [8]. The degree of coke formation can be determined by thermogravimetric analysis [TGA] with simultaneous thermal analyzer. The metal leaching in the green diesel can be measured using inductively coupled plasma-atomic emission spectrometer [ICP-AES]. The amount of coke formation in the catalyst can be determined by TGA. The textural properties of the catalyst can be determined by N2 physisorption using an ASAP Micromeritics 2020 instrument. The catalyst surface morphology can be determined using field emission scanning electron microscopy [FESEM]. The elemental composition of the catalyst including C, O, P, Co and Mo can be determined by an X-ray fluorescence [XRF] equipped with a rhodium tube instrument or energy-dis-

persive X-ray [EDX] equipped with Rayny EDX-720 spectrometer. The acidity and basicity of the catalyst can be measured using a temperature-programmed desorption [TPD-NH3 and TPD-CO2] equipped with a thermal conductivity detector [TCD]. The thermal stability of the catalyst could be determined using thermogravimetric analyzer [TGA] [31].

Methods of Renewable Diesel Production

Some of the methods involved in the production of renewable diesel include catalytic hydro-processing, and deoxygenation. These are discussed briefly below:

1. Catalytic hydro-processing of vegetable oils and fats

This process is used to convert vegetable oils to normal paraffin which is high quality diesel similar to the petroluem diesel. The process increases the hydrogen/carbon ratio, and reduces the concentration of heteroatoms and metals, and boiling points of refinery products [3]. Catalytic hydro-processing involves hydrodeoxygenation [HDO] of vegetable oil [triglycerides] or animals fats. This method is also called hydrotreating and it involves a catalytic process with hydrogen leading to the formation of a mixture of straight-chain and branched saturated hydrocarbons with 15-18 carbon atoms per molecules [4]. The oxygen atom in the fatty acids is removed as water. This method is perceived to be expensive as it requires a high pressure [4-9 MPa] hydrogen injection, high temperature of 280-380oC and the use of NiMo/Al$_2$O$_3$ heterogeneous catalyst [4]. The selection of catalyst depends on the activity, stability, and selectivity of metal and catalyst support, surface area and porosity. Thus, an effective catalyst for deoxygenation of vegetable oils must have a high activity, capable to minimize coke formation, water resistant, capacity to regenerate in single processes, have tolerance to chemical poisons and can be scalable for commercial processes [32].

2. Deoxygenation process. This could be decarboxylation leading to the removal of oxygen atom in form of CO2 or decarbonylation removing oxygen atom as CO and H2O [33]. This may not require the addition of hydrogen. used tetralin [1,2,3,4-tetrahydronaphthalene] as a hydrogen donor solvent to avoid operating the reaction at high pressure, for stabilizing hydrocarbon fuels, for its excellent solubility in carboxylic acid and Pd-based catalyst is an effective catalyst for the dehydrogenation of tetralin. The decarbonylation reaction can also take place during hydrotreating [21]. The hydrogenation reaction may precede decarbonylation depending on the fatty acid degree of saturation.

Renewable Diesel Production

Various researchers have investigated the production of renewable hydrocarbon fuels from such feedstocks as vegetable oils, animal fats, or biomass [see Table 2 and 3]. Usually, the required amount of the feed stock and catalyst are fed into the reactor which is purged of air using streams of nitrogen and set to the desired temperature. The mixture is stirred continuously and after the reaction time is attained, the deoxygenated liquid product is condensed using a cooler before it is collected for further purification and analysis [see Figure 1]. The products yield can be calculated using Equations 1-3 [3].
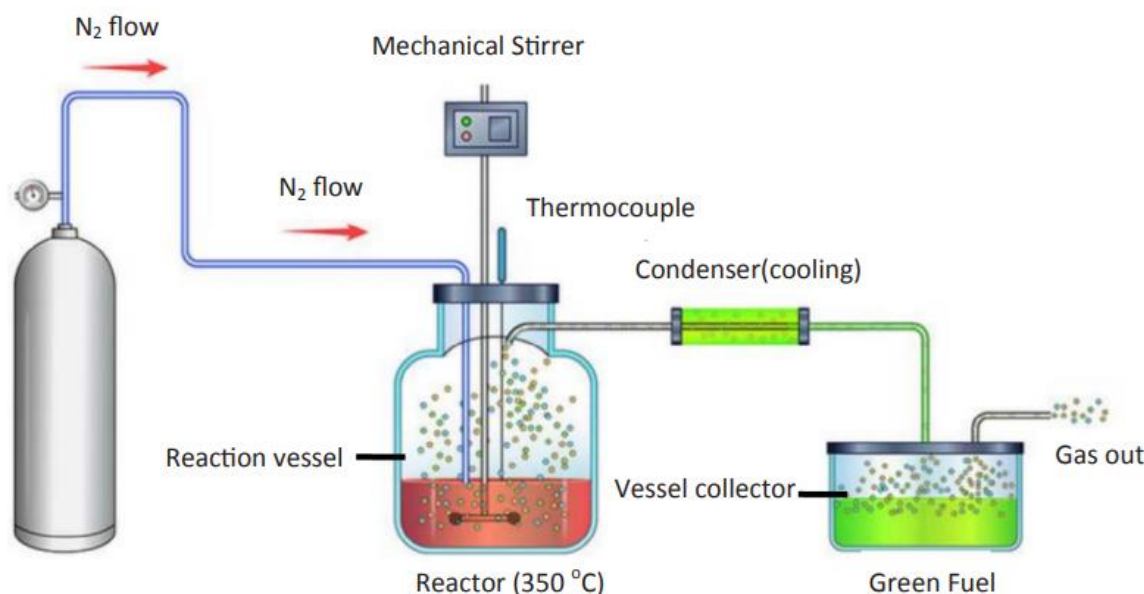

Figure 1: Renewable diesel experimental setup [34]

$$\text{Product yield (\%)} = \frac{\text{Total area of hydrocarbon (C8-C17)}}{\text{Total area of the product}} \times 100\% \quad (1)$$

The product yield can also be calculated using Equation (2)

$$\text{Product} = \frac{\sum n_o + \sum n_i}{\sum n_z} \times 100\,\% \tag{2}$$

$$\text{where } n_o = \text{Area of alkene (C8} - \text{C20)}, n_i = \text{Area of alkane (C8} - \text{C20)}, n_z$$

$$= \text{Area of the product}$$

$$\text{Diesel selectivity (\%)} = \frac{\text{Hydrocarbon fraction (C12}-\text{C17)}}{\text{Total area of hydrocarbon (C8}-\text{C17)}} \times 100\% \tag{3}$$

$$\text{Gasoline selectivity (\%)} = \frac{\text{Hydrocarbon fraction (C8}-\text{C12)}}{\text{Total area of hydrocarbon (C8}-\text{C17)}} \times 100\% \tag{4}$$

The performance of the catalysts can be evaluated by GC-FID in terms of hydrocarbonity (S) for deoxygenated products at optimum condition can be determined by Eq. (2)

$$S = \frac{c_X}{\sum n_x} \times 100\,\% \tag{5}$$

Factors Affecting the Production of Green-Diesel Fuel

Catalyst loading, reaction time, temperature, water and FFA contents of the feedstock have been identified as factors that impact the yield and selectivity of the green-diesel obtained from the deoxygenation of feedstocks [30]. These are discussed below:

Effect of Catalyst Loading

Increasing catalyst loading leads to proportional increase in the hydrocarbon yield until an optimum condition is attained. This is evident from the result obtained by [30]. The authors varied the loading of $Co_{10}Mo_{10}/AC$ catalyst from 0.5 - 7 wt% while maintaining the reaction period and temperature constant. The result obtained showed that increased hydrocarbon [C_8 - C_{20}] yields from 45 - 64 % was observed with catalyst loading 0.5 - 3 wt% and the selectivity of n-[C_{15} + C_{17}] increased from 46 - 63 %. Beyond the calaytst loading of 3 wt%, the yield and selectivity of the hydrocarbons begin to decline owing to the availability of excess active sites which encourages C-C scission through cracking reaction leading to the formation of short chain hydrocarbons [C_8 - C_{14}] [11]. Varied the catalyst loading from 1-6 wt% at 300 °C for 30 min and agitation speed of 500 rpm obtaining predominantly n-C17 hydrocarbon with optimum yield of 47.13 % and selectivity of 72.85 % using 2 wt% catalyst loading. The decline in performance of the catalyst above 2 wt% was attributed to potential overburdening of the catalyst resulting to excess active loci favouring secondary and concurrent reactions [35].

Effect of Temperature

Increase in temperature impact positively on the performance of the deoxygenation reaction in terms of yield and selectivity as demonstrated by [29]. The authors varied the reaction temperature from 300 - 400 °C and the result obtained show that the yield of the C_8 - C_{20} hydrocarbons increased from 52 - 75 % and the selectivity of n-[C_{15} + C_{17}] increased from 46 - 70 % within a temperature range of 300 - 350 oC due to enhanced catalytic activity. At a temperature greater than 350 °C, secondary reactions such as cracking or polymerization occurs favouring the production of short chain hydrocarbons. Comparatively, obtained higher yield of 85.22 - 96 % n-[C_{15} + C_{17}] at lower temperature range of 270-330 oC, and an optimum selectivity of 94.44 % at 350 °C using 2 wt.% catalyst loading, reaction time of 60 min and agitation speed of 500 rpm. However, the deoxygenation performance was observed to decline when the temperature was raised to 350 °C [11].

Effect of Reaction Time

have demonstrated that reaction time impact on the performance of the deoxygenation reaction by varying the time from 60 - 240 min while keeping other parameters constant. It was demonstrated that the performance of the reaction increased from 75 % to 92 % for the yield and 70 - 89 % for the selectivity within 60 - 120 min and beyond which the performance parameters reduce due to the formation of by products [30,11]. Varied the reaction time from 30-240 min at a temperature of 300 °C using catalyst loading of 0.5 wt.% and agitation speed of 500 rpm. It was shown that the yield and selectivity of the n-C_{15}+C_{17} products increased from 29.72 - 64.27 % and 55.93-87 %, respectively owing to sufficient time available for deoxygenation to occur. The decline in the performance of the deoxygenation reaction above 60 min was attributed to the cracking of the oxygenated liquid product to lighter products which may result to the production of product vapour, and potential catalyst deactivated [36].

Table 3: Catalysts for renewable diesel production

S/N	Objective	Condition	Reactor	Catalytst	Product	Reference
1	Synthesize green diesel by catalytic deoxygenation of WCO using bimetallic acid -base catalyst without the addition of hydrogen	10g of WCO, 350°C, 60 min	250 mL semi-batch	5%(wt) CaO-La_2O_3/AC	72% yield of straight chain hydrocarbons (C_8-C_{20})	Alsutan et al., 2017
2	Determining the most effective bimetallic catalyst for deoxygenation of palm fatty acid distillate (PFAD) for green diesel production	10g PFAD, 3 wt% of catalyst, 350oC, time of 60 min, and 50 mL/min N_2	250 mL semi-batch	Co10Mo10/Al_2O_3 and Co-$10Mo_{10}$/Tio$_2$	C_8-C_{20} hydrocarbons	Gamal et al., 2020
3	Deoxygenation of palm fatty acid distillate (PFAD)	10g of PFAD, catalyst loading of 10 wt% at 350oC for 3 h	Semi-batch	Ni/SBA-15, Co/SBA-15 and Ni-Co/SBA-15	Saturated and unsaturated C13-C17 hydrocarbons with 85.8% and 88.1% yields using Ni/SBA-15 and Ni-Co/SBA-15, respectively	Kamaruzaman et al., 2020
4	Determine the most efficient catalyst for green diesel production	2g oleic acid, 30 g heptane, catalyst (10wt% of oleic acid), temperature (180-260), time (1-5h)	100 mL	4Pt/ZrO_2, 4Pt-8MoOx/ZrO_2	Conversion of 75% and C18 selectivity of 94.6 wt%. Octadecane was the major product	Janampelli and Darbha, 2019
5	Investigating the efficacy of PtRe catalyst for hydrothermal deoxygenation of palm oil	Temperature (448-558k), 20g of palm oil, 80g deionized water, 0.92 catalyst and time 24h	200mL autoclave	Pt/CNT, Re/CNT, PtRe/CNT	PtRe/CNT was more effective yielding 72 wt% n-paraffin (theoretical yield:79 wt%)	Jin and Choi, 2019
6	Assess the potential of Pd-Ni and Pd-Cu in deoxygenating oleic acid to diesel like hydrocarbons	Oleic acid (1 mL), tetralin (1 mL), catalyst (0.05g), pressure (10 bar), temperature (330°C) and time (3h)	10 mL mini autoclave	PdxCu$_{(100-x)}$ and PdxNi$_{(100-x)}$		Cheah et al., 2019
7.	Produce green diesel from crude palm oil (CPO) using catalytic hydrogenation method	Pressure of H2 (25psia), temperature 270-330oC),Ni-Mo/Al_2O_3 loading of 0.15g, 300 mL of CPO and resident time of 1 h	-	NiMo/Al_2O_3	68% yield. Main product: paraffin chain C_{15}-C_{18} (range of diesel fuel, 39.63%) obtained at 315oC	Zikri and Aznury (2020)

| 8. | Investigated the use of Mn-Mo/AC in the production of diesel range fuel from sludge palm oil | SPO (10g), 0.1 wt.% of catalyst, temperature (300°C), time (60 min) | 100 mL magnetically agitated batch reactor | Mn (0.5%)-Mo (0.5%)/AC | 89% liquid hydrocarbons, 93% selectivity favouring n-($C_{15}+C_{17}$) | Alsultan, et al. (2022) |

1. Effect of water content and FFA content of the feedstock
According to, the addition of water to the feedstock used in deoxygenation reaction could be beneficial in reducing the acidity of the oxygenated components; ensuring that all the beneficial components that are partially miscible in water are involved in the deoxygenation process; and regulating the catalyst site interaction with the components of the feedstocks, especially when strong catalysts are involved [37].

Reaction Pathway / Kinetics of Renewable Diesel Production

Deoxygenation reaction is used to produce green diesel from feedstocks containing triglycerides free fatty acids by breaking the C-O bond either in an inert environment or by using hydrogen [hydro-deoxygenation]. For instance, WCO can be used as a feedstock for green diesel production as it is composed predominantly of C_{18} and C_{16} fatty acids [Figure 2]. Theoretically, the decarboxylation reaction removes carboxyl and carbonyl groups from these fatty acids to produce hydrocarbon products merely n-heptadecenes [n-C_{17}] and n-pentadecenes [n-$_{15}$] and by-prod-

uct [CO_2, CO and H_2O] [38]. In a semi batch reactor, the cracking of the products formed is possible leading to C-C cleavage of n-C17 fraction producing n-C_{15} by removing ethane [Reaction B] [38]. The cracking occurs as a result of the activities of CaO/AC and La_2O_3/AC components of the catalyst CaO-La_2O_3/AC used. In addition, further C-C cleavage on the products may occur causing the formation of C_{16} fatty acids [reaction C] and this can undergo selective deCOx reaction producing n-C_{15} hydrocarbon products [reaction D] [39]. The cracking reaction is often unavoidable causing the hydrocarbon products to undergo C-C cleavage into short chain hydrocarbon n-[C_8-C_{14}] [reaction E] [40]. Furthermore, using Jatropha curcas oil [JCO] as a feedstock and conducting the reaction in a fixed bed reactor, the reaction pathway shown in Figure [3] is obtained [2]. Jactropha curcas oil is made up of ~20 % C_{16}, ~ 70% C18 [stearic, oleic and linolenic acids] and 15.4% FFA [C_{16} or C_{18}]. The production of the renewable diesel follows two reaction pathways which are decarboxylation and decarbonylation.
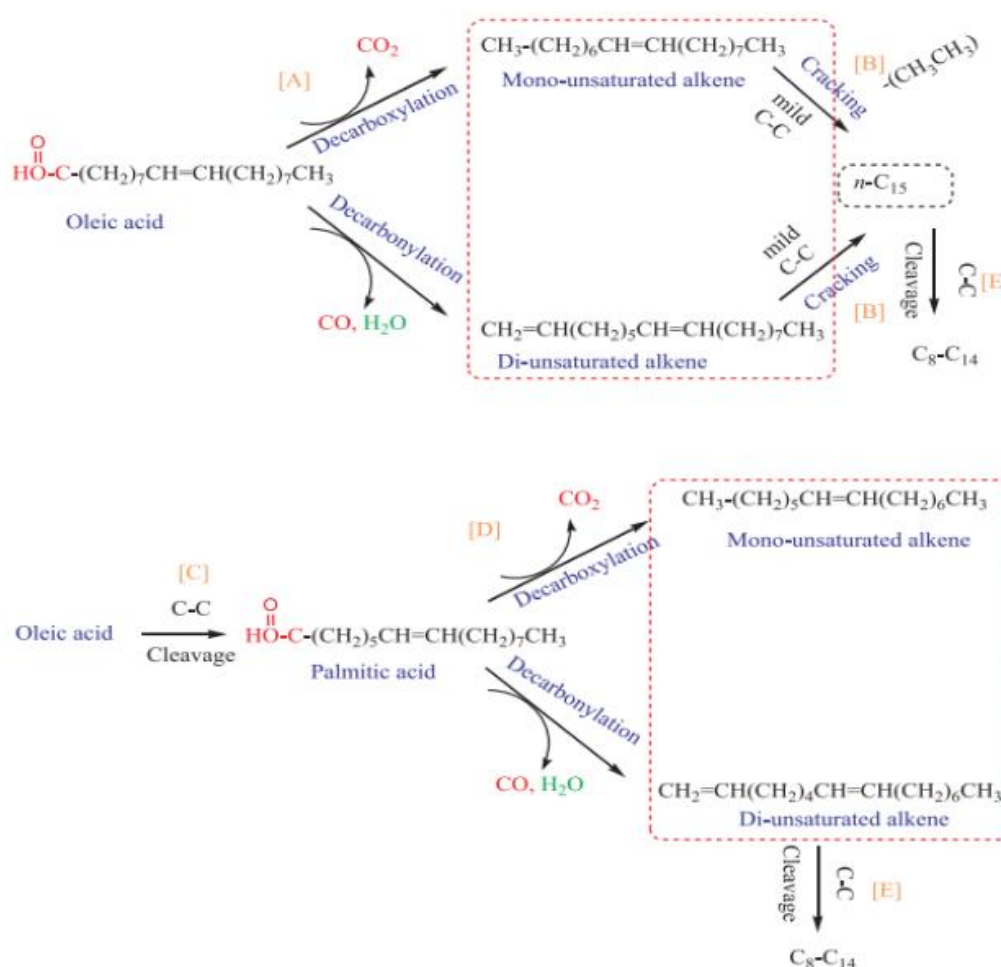

Figure 2: Proposed pathway for the deogenation of WCO to renewable diesel [34]

In decarboxylation pathway, from Figure [3], the triglyceride is hydrolysed to fatty acids by cleavage of C-O bonding [reaction a]. The fatty acid produced are converted to saturated hydrocarbons like n-pentadecane $[C_{15}H_{32}]$ and n-heptadecanes $[C_{17}H_{36}]$ and unsaturated n-heptadenes [mono-unsaturated and di-unsaturated] through decarboxylation reaction by the removal of oxygen from the fatty acids in form of carbon dioxide [reaction b in Figure 3]. In decarbonylation pathway, n-pentadecanes and n-heptadecenes are formed with extra double bond as against mono-unsaturated $[C_{15}H_{30}, C_{17}H_{34}]$, di-unsaturated $[C_{17}H_{32}]$ and poly-unsaturated $[C_{17}H_{28}]$ formed in the carboxylation pathway [reaction c]. The deoxygenation process also results to the formation of light fraction hydrocarbons $[C_8-C_9]$ through C-C scission of product [reaction d] [40]. Cracking of fatty acid intermediates may result to the formation of shorter chain fatty acid and shorter hydrocarbons which further undergoes deoxygenation [carbonoxylation/carbonylation] reaction to produce hydrocarbon products [e-g].
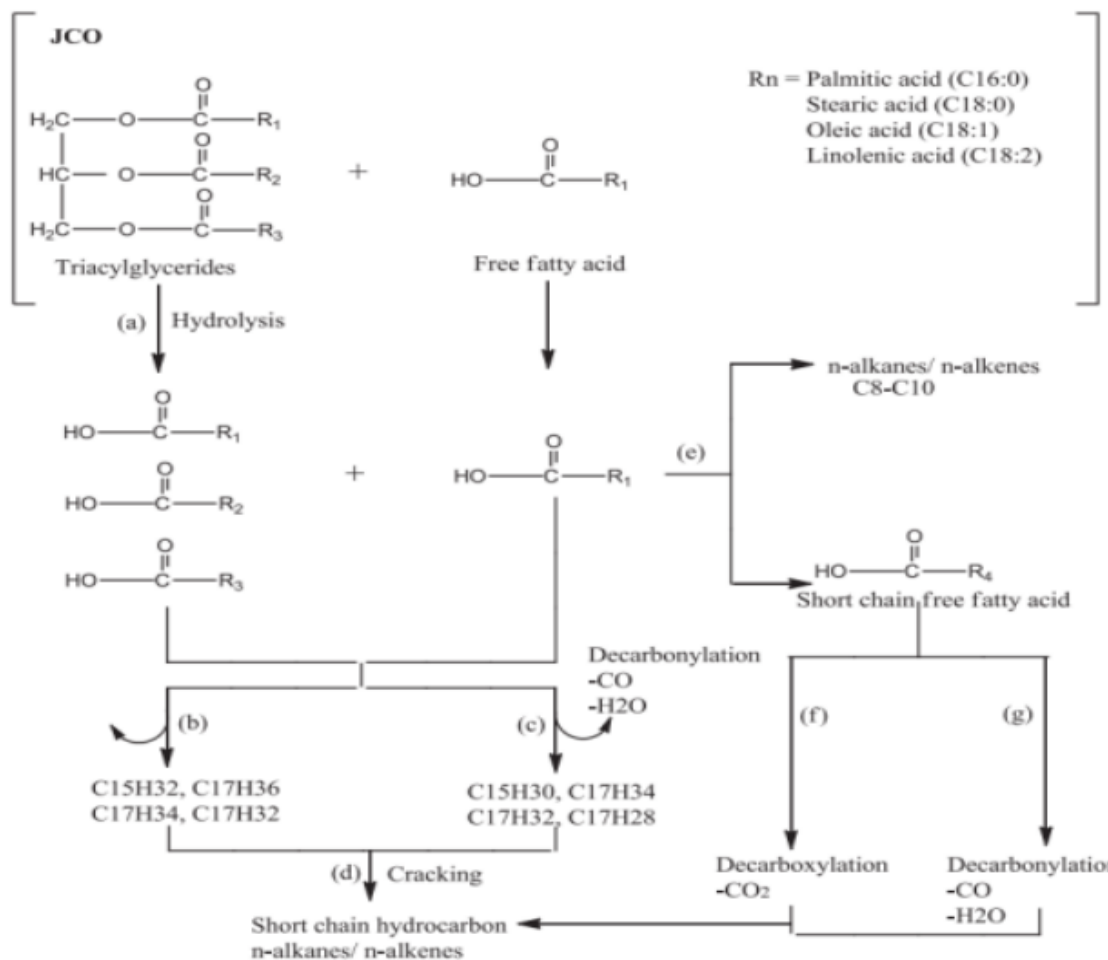

Figure 3: Proposed pathway for the deogenation of WCO to renewable diesel [40]

For the deoxygenation of PFAD over $CO_{10}MO_{10}/AC$ catalyst, the PFAD is composed of saturated C_{16} [~56 %] and a mixture of saturated + unsaturated fatty acids C_{18} [~42 %]. The deoxygenation of PFAD, produced predominantly n-pentadecane and lesser amount of C_{17} with CO_2 [80 %] and CO [20 %] as by-products. The yield of n-pentadecane was 68 % which means that the reaction pathway is suspected to be carboxylation.
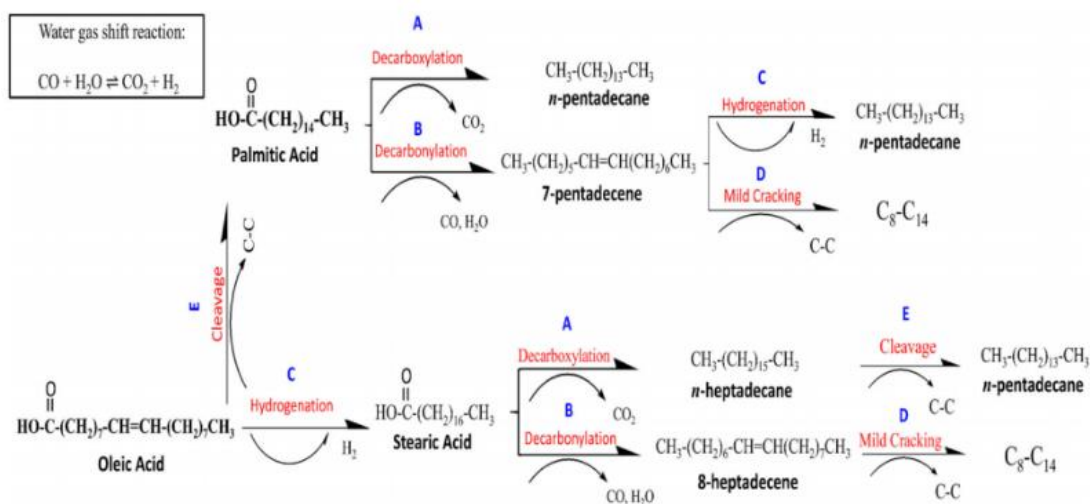
Figure 4: Proposed deoxygnation reaction pathway of PFAD [31]

The use of the Ni/SBA-15, Co/SBA-15 and Ni-Co/SBA-15 to catalyze the deoxygenation of PFAD favoured the carboxylation and carbonylation reaction pathways. The carboxylation pathway produced paraffinic hydrocarbons and carbon dioxide; and carbonylation lead to the production of olefinic hydrocarbons, carbon monoxide and water with some fatty acids undergoing cracking reaction to produce lighter hydrocarbons [30,41]. The reaction pathway for the hydrothermal deoxygenation of palm oil using PtRe/CNT as catalyst was dominated by decarboxylation/decarbonylation as against hydrodeoxygenation. This was suggested as the products of the deoxygenation were predominantly C_{15} and C_{17} n-paraffins showing a loss of one carbon atom from the original C_{16} and C_{18} fatty acids dorminant in the palm oil composition. The reason for this pathway is that the use of water as a solvent during deoxygenation reaction suppresses hydrodeoxygenation pathway producing water in compliance with Le Chatelier's principle [8]. The deoxygenation of SPO under Mn/AC and Mn-Mo/AC catalysts resulted to the production of liquid n-alkanes and alkene [n-C_7-n-C_{20}], oxygenated intermediate substances such as alcohol, aldehyde and ketones, and gaseous products [CO and CO_2]. The reaction pathways favoured the deoxygenation of oxygen in the form of CO_2, CO and H_2O [11].
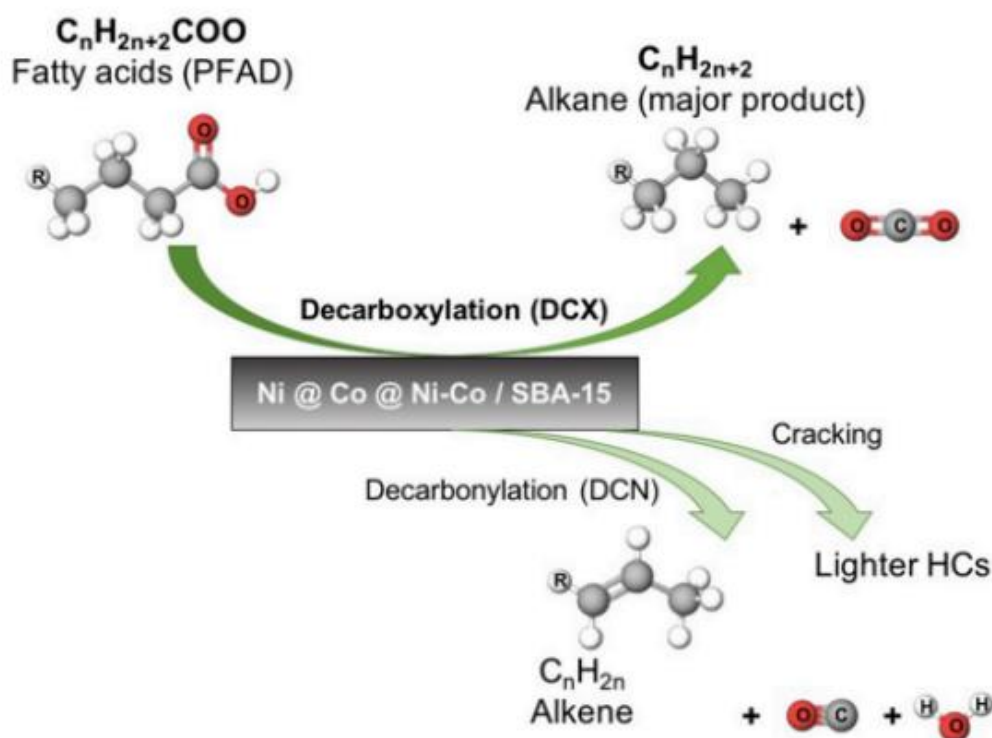

Figure 5: The reaction pathways for deoxygenation of PFAD via decarboxylation, decarbonylation and cracking process [30]

Analysis of Renewable Diesel

The properties of renewable fuel to be considered include visocity, vapor pressure, cloud point, pour point and flash point, heating value, sufur content and other contaminants, octane and cetane number. The properties of the renewable diesel are usually compared with standards ASTM and petroleum USLD. For instance, based on the work by, WCO-green diesel contains some low volatile compound as compared to petroleum USLD standard making it more safer to be handled and use in the diesel engine [Table 4]. Lesser calorific of the WCO-based diesel fuel could lead to higher consumption of this fuel in comparison to the petroleum diesel using the same engine efficiency [34]. The octane number of the green is 70-90 which is higher than 50-65 for biodiesel [42]. Other parameters that are analysed are presented below:

The gas phase composition can be determined using GC-TCD [31. The liquid product can be quantitatively analysed by using gas chromatography equipped with a HP-5 capillary column [length: 30m x inner diameter: 0.32 mm x film thickness: 0.25 μm] with a flame ionization detector [FID] operating at 300 oC]. This can also be determined using CHNOS analyzer [43]. The qualitative analysis of the WCO and the liquid product was carried out using gas chromatography mass spectrometer [GC-MS] equipped with a non-polar DB-5HT column [30 m x 0.25 mm x I.D μm] with split less inlet.

Table 4: Fuel properties of WCO-based green diesel compared to biodiesel and Petroleum ULSD

Fuel properties	Standard for B100 (ASTM D6751[a]/EN 14214[b]	Petroleum ULSD [c]	WCO-based green diesel
Specific gravity @ 15 ºC (kgm^{-3})	860-900	812	810 ± 4
Kinematic viscosity @ 40 ºC (cSt)	1.9-6.0	3.9 ± 0.3	4.6 ± 0.2
Flash point (ºC)	>120	55	64 ± 3
Calorific value (MJkg^{-1})	>37.5	42.5	40.8 ± 0.5
[a]America Society for Testing and Material (ASTM D6751) [b]European standard (EN 14214) [c]Petroleum ULSD: ultra low sulfur diesel			

The chemical functional group of the liquid product can be determined using FTIR. The concentration of the elements in the deoxygenation liquid can be determined using inductively-coupled plasma-atomic emission spectrometer [ICP-AES]. The composition of the CO and CO2 gases can be determined based on standard gas percentages. The atomic ratio of oxygen to carbon (O/C), and hydrogen to carbon (H/C) in the feedstock can be determined using Equations 6 and 7.

$$\text{Atomic ratio of oxygen to carbon (O/C)} = \frac{\text{Number of oxygen atoms}}{\text{Number of carbon atoms}} \qquad (6)$$

$$\text{Atomic ratio of hydrogen to carbon (O/C)} = \frac{\text{Number of hydrogen atoms}}{\text{Number of carbon atoms}} \qquad (7)$$

The acid values of the feedstock and deoxygenated liquid product can be determined using the standard method (AOAS Cd 3d-63) (see Equation 8).

Total acid number (TAN) = $(V_i - V_e) \times N \times (56 / W_{oil})$ (8)

where V_i = solution required for titration of the sample (mL), V_e = solution required for titration of the blank (mL)
N = concentration of KOH sample, 56 = the molecular weight of the KOH solution, and W_{oil} = the mass of sample in grams

Conclusion

Discussions on production of renewable diesel through catalytic hydro-processing and deoxygenation from various feedstocks under different catalysts and operating conditions have been presented based on the existing literature. Due to high cost of the feedstocks involving edible oils, non-edible oils including wastes such as waste cooking oil and activated sludge are being considered. The catalysts used include noble metals, metal sulphides, metal phosphides, metal carbides and d-block metal oxides supported on veriaties of oxide substances. The properties of these catalysts can be modified to help reduce the rate of deactivation. Factors such as catalyst loading, temperature, reaction time, water and FFA contents of the feedstock influence the performance of the reaction leading to the formation of renewable diesel. The renewable diesel is most suitable for buses, waste transport and emergency response vehicles as the have the capacity to reduce particle, hydrogen and nitrogen oxide emissions [44-63].

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