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Synthesis of Green Diesel from Palm Oil Using Nickel-based Catalyst: A Review

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Abstract

Petroleum is the primary energy that is generally used throughout the world. Its non-renewable nature and exhaust gas emissions that can damage the environment are a concern for developing environmentally friendly renewable energy. Green diesel is an alternative energy to replace diesel fuel (diesel) from petroleum which has the potential to be developed. The raw material in palm oil has great potential for development due to its relatively high production. Green diesel synthesis can be carried out using the catalytic deoxygenation method. The type of raw material, catalyst, and process conditions influences this method. The catalyst is the most influential factor in catalytic deoxygenation. Transition metal catalysts like nickel are inexpensive and have good catalytic activity like precious metals. Catalytic activity can be increased by modifying the catalyst components and optimizing the process. Modification of the catalyst can increase the surface area, Lewis and Bronsted sites, and crystal size so that the resulting green diesel can be maximized, such as Ni-Co, Ni-Zn, and Ni-Mo bimetallic catalysts.

Keywords: Green diesel; diesel; catalytic deoxygenation; nickel; palm oil

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1. INTRODUCTION

Petroleum is a primary energy source that is commonly used around the world and contributes to economic growth. Almost all fields, such as industry, electricity companies, and transportation, use fuel from petroleum. This condition can lead to the depletion of petroleum reserves. In Indonesia, crude oil and condensate production fell from 831.06 thousand barrels per day (2016) to only 708.32 thousand barrels per day (2020) (Adriawan et al., 2020). Another concern is the negative environmental impact caused by burning petroleum, such as greenhouse gases (CO_2) (Gurney et al., 2020), nitrogen and sulfur oxides, volatile organic compounds, and other particles produced (Karavalakis et al., 2016). This condition triggers the search for environmentally friendly renewable energies that substitute petroleum.

Biofuel is one of the renewable energies that has the potential to replace petroleum. Biofuel is solid, liquid, and gaseous fuels obtained by processing biomass (Nolfi et al., 2021). Biomass is material of biological origin, such as plants, agricultural and forestry waste and by-products, manure, or microbial biomass (Saladini et al., 2016). The development of plant biomass-based biofuels can significantly reduce greenhouse gas emissions because the CO_2 gas produced from combustion is reused by plants in photosynthesis (Naik et al., 2010). The biofuel produced also does not contain sulfur like petroleum, making it more environmentally friendly. Green diesel is one of the potential biofuels to be developed. Green diesel is a

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second-generation diesel classified as a hydrocarbon compound with the same function as biodiesel, namely as a substitute for diesel fuel (diesel). Biodiesel is produced from the transesterification reaction of vegetable oil and is still classified as an ester compound, so it still contains oxygen (oxygenate biofuel) (Zhang et al., 2022). The presence of oxygen can reduce its qualities, such as thermal stability, low combustion and heating values, and engine compatibility issues (Kordulis et al., 2016). Biodiesel can also increase NO_x gas emissions (Hosseinzadeh-Bandbafha et al., 2018; Murnieks et al., 2016). Green diesel is a biofuel that is predicted to be able to overcome the shortcomings of biodiesel. Green diesel has physical and chemical properties similar to diesel. The absence of oxygen can improve the thermal stability of green diesel; the cetane number is also high (Kamaruzaman et al., 2020). A comparison of physical and chemical properties between diesel (pertamina-dex), biodiesel, and green diesel can be seen in **Table 1**. Pertamina-dex is one type of diesel fuel produced by PT Pertamina (Persero) that has better quality than other types of diesel fuel, such as dexlite and diesel.

Green diesel has a higher cetane number than pertamina-dex. Both biodiesel and green diesel have low sulfur emissions. Biodiesel has better lubricant properties and a higher flash point than green diesel but lower oxidation stability, storage, and cold flow properties (Douvartzides et al., 2019). The high flash point of biodiesel makes this fuel safer than pertamina-dex and green diesel. The difference in chemical composition between biodiesel and diesel fuel means that biodiesel can only be used in blends with diesel fuel. If used purely, engine modifications must be made (Knothe, 2010). Green diesel has the same physical and chemical properties as diesel, so that it can be fully used without engine modification (Khalit et al., 2022).

The most promising feedstock for green diesel production is vegetable oil. These oils consist of triglyceride compounds with long, linear carbon chains and contain less oxygen than starch, cellulose, and other biomasses, making them very attractive for development (Yenumala et al., 2019). In addition, vegetable oils are easy to produce, and their physical and chemical properties are similar to diesel. Palm oil is the most potent vegetable oil to be developed because of its excellent production. In 2021, crude palm oil (CPO) production in Indonesia reached 49.71 million tons, and only about 12 million tons were processed into cooking oil (Sabarella et al., 2021). The rest were processed into various other oleochemical products. Various compounds from palm oil derivatives, such as fatty acids (palmitic, oleic, and linoleic), palm fatty acid distillate (PFAD), and used cooking oil, also have the potential to be converted into green diesel. This condition provides an opportunity to develop palm oil as a green diesel feedstock.

Table 1. Physical and chemical properties of pertamina-dex, biodiesel and green diesel

Parameter	**Pertamina Dex**[1]	**Biodiesel**[2]	***Green Diesel***[3]
Cetane number	53	51	>70
Cetane index	48	-	-
Density , 15^{o}C, kg/m^3	820-860	-	770-790
Density 40^{o}C, kg/m^3	-	850-890	-
Viscocity, 40^{o}C, mm^2/s	2.0-4.5	2.3-6.0	2-4
Sulphur content	0.05%	<10 ppm	<5 ppm
Flash point, ^{o}C	55	130	>59
Pour point, ^{o}C	18	-	-
Residual carbon, %	0.03	0.05-0.3	<0.01
Water content, mg/kg	500	350	-
Oxidation stability	25 g/m^3	-	<25 g/m^3
Ash content, %	0.01	0.02	<0.001
Sediment content, %	0.01	-	-
Water content in sediment (%vol)	-	-	<0.02
Visual appearance	Bright clear	-	-
Color	1	3	-

Note: [1]PT. Pertamina, 2012, [2]Kementrian ESDM, 2019, [3]Douvartzides et al., 2019

The technology of converting vegetable oil and fatty acids into green diesel generally uses the catalytic deoxygenation method, which can produce green diesel equivalent to diesel (Gamal et al., 2020; Nolfi et al., 2021; Hongloi et al., 2021). The type of catalyst and process conditions also influences the use of catalytic deoxygenation in producing green diesel. The catalysts used can be precious metals such as Pd (Mohammed et al., 2022; Trisunaryanti et al., 2018), Pt (Konwar & Mikkkola, 2022; Zhou & Lawal, 2016), Ru (Setyoningsih et al., 2019; Nie et al., 2017), and Au (Abdulkareem-Alsultan et al., 2019). The only problem is that precious metals are expensive and limited availability. Other types of catalysts that can be used are transition metals such as Ni (Papadopoulos et al., 2021; Papanikolaou et al., 2020; Chen et al., 2021; Aziz et al., 2022); Co (Guo et al., 2018; Moreira et al., 2020); Mo (Ameen et al., 2020; Yu et al., 2022); and Fe (Arun et al., 2021; Putra et al., 2018; Pan et al., 2016). Among the transition metal catalysts often used is Ni because it has a catalytic activity that almost matches that of precious metal catalysts, is cheaper, and has considerable availability (Morgan et al., 2010; Ananikov, 2015). In addition, nickel is smaller than other transition metals, making it easier to distribute in the catalyst support.

This article will focus on synthesizing green diesel (catalytic deoxygenation) from palm oil and its derivatives using nickel-based catalysts. Aspects to be discussed include the type of nickel-based catalyst, support, and process conditions.

2. SYNTHESIS OF GREEN DIESEL

Catalytic deoxygenation is the superior method of producing hydrocarbons such as green diesel, where vegetable oils or fatty acids are deoxygenated with thermal and catalytic assistance. This process can be performed using hydrogen gas or without hydrogen. Catalytic deoxygenation without hydrogen is a more convenient, cost-effective, and simple technology (Zhao et al., 2015). Hydrogen gas is not used, so the equipment does not require high pressure like HDO. However, the disadvantage is a lower liquid product yield, a higher light fraction, and coke (Kumar et al., 2019). Catalytic deoxygenation with hydrogen gas has the advantage of a higher liquid product yield and cetane number, so the quality of green diesel increases. The main reaction routes followed in the catalytic deoxygenation process without hydrogen are decarboxylation (DCO_2) and decarbonylation (DCO).

The DCO_2 reaction produces alkane compounds and CO_2 gas, while the DCO reaction produces alkene compounds, CO gas, and H_2O. DCO and DCO_2 reactions produce hydrocarbons (alkanes and alkenes) with fewer carbon atoms than the initial fatty acid. The use of hydrogen in the catalytic deoxygenation process results in the hydrodeoxygenation (HDO) reaction route, so this method is often called hydrodeoxygenation. Besides HDO, there are also DCO and DCO_2 reactions (**Figure 1**). HDO reactions form alkanes and H_2O. In general, the use of hydrogen produces alkane hydrocarbons. A side reaction that can occur is catalytic cracking, where the alkane or alkene produced turns into a lighter fraction. In addition, there is also a catalytic isomerization reaction if zeolite is used as part of the catalyst (Han et al., 2015).

The mechanism of the decarboxylation reaction (**Figure 2a**) occurs when the electrons in the H-O bond (fatty acid) move to the O-C bond, followed by the C-C bond electron transfer to the C atom, causing the O-H bond to break. Furthermore, a pi bond is formed on O-C, and the C-C bond is broken, releasing O=C=O (CO_2). The H+ ions that break the O-H bond will be bound by the negatively charged C, resulting in n-C_nH_{2n+2}. The decarbonylation reaction begins with adding H_2 to the C = O group of the carboxylic acid, followed by the elimination of H_2O to produce an aldehyde group. Furthermore, the free electron pair from O moves to the C = O bond, and the H-C bond electrons are given to the C atom, followed by the transfer of electrons from the C-C bond to the C atom, resulting in the breaking of the H-C and C-C bonds accompanied by the release of CO. Furthermore, the positively charged H is bound by the negatively charged C so that n-C_nH_{2n+2} is formed. The mechanism of the hydrodeoxygenation reaction is almost the same as that of decarbonylation, but excess H_2 is used here. So at stage 1, H_2 addition occurs following the hydrogenation of carboxylic acids into aldehydes, followed by the release of H_2O. Furthermore, the aldehyde is hydrogenated into alcohol with the exact reaction mechanism. The third H_2 addition occurs with the reaction mechanism, where OH uses the electrons in the O-C bond to bond with H so that H_2O is produced. Furthermore, the hydride ion (H^-)

attacks the positively charged C so that CH_3-C_nH_{2n+1} or $C_{n+1}H_{2n+4}$ is formed.

De Oliveira et al. (2021) studied the reaction mechanism of catalytic deoxygenation of palmitic acid contained in PFAD into green diesel without using hydrogen gas. Palmitic acid (C16) is converted to $C_{15}H_{30}$ through the decarbonylation reaction, and the by-products are CO and water. The decarboxylation reaction produces $C_{15}H_{32}$ with a by-product of CO_2. Other possible reactions that can produce hydrogen gas, such as reverse water gas shift ($CO + H_2O \rightarrow CO_2 + H_2$), can occur, so the HDO reaction can occur, which produces $C_{16}H_{34}$ in small concentrations. If the catalyst uses an acidic support, further reactions, such as catalytic cracking of the deoxygenation products to produce light fractions and coke formation, are possible. Ruangudomsakul et al. (2021) also studied the reaction pathway of palm oil conversion into green diesel products using Ni_xP_y catalysts and hydrogen gas (**Figure 3**). First, the double bonds in the triglycerides in palm oil are hydrogenated to form saturated triglycerides. The metal catalyzes this step. Then, the C-O bonds in the saturated triglycerides are broken by hydrogenolysis to produce fatty acids and propane. Next, fatty acids undergo three reaction pathways to form green diesel products. The main route is decarbonylation (DCO), where oxygen atoms in fatty acids are removed in the form of CO and water. The resulting alkane has one less carbon atom (R_{n-1}) than the fatty acid (R_n). The minor route is decarboxylation (DCO_2). The oxygen atom in the fatty acid is removed in the form of carbon dioxide (CO_2). Another route is hydrodeoxygenation (HDO), with only water removed, which forms green diesel with the same carbon atoms as the fatty acid.

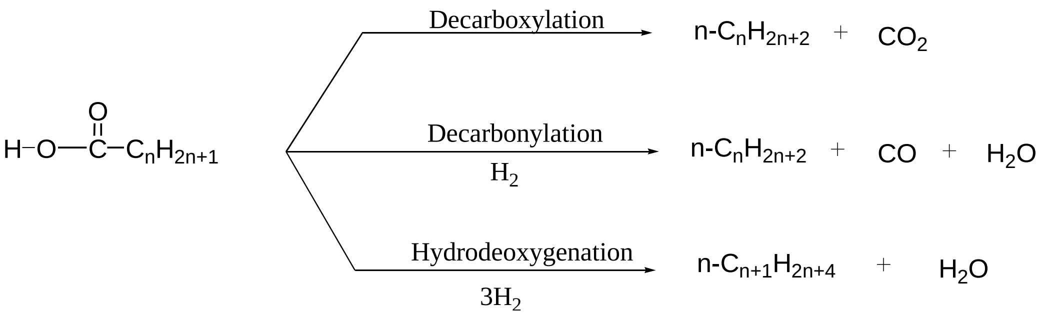
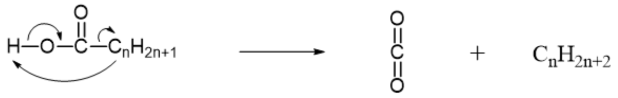
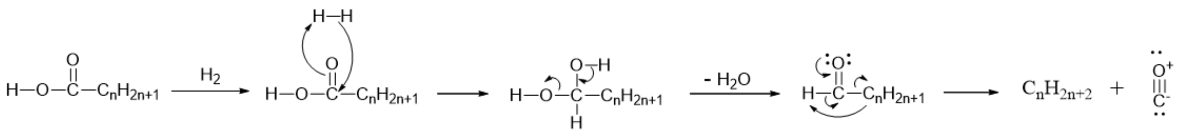


Figure 1. Reaction routes of decarboxylation, decarbonylation and hydrodeoxygenation of fatty acids

a) Decarboxylation



b) Decarbonylation



c) Hydrodeoxygenation

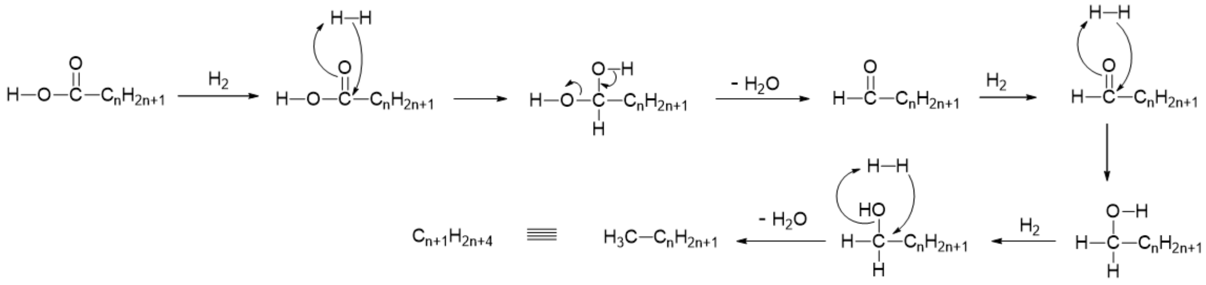


Figure 2. Reaction mechanism: a) decarboxylation, b) decarbonylation and c) hydrodeoxygenation of fatty acids

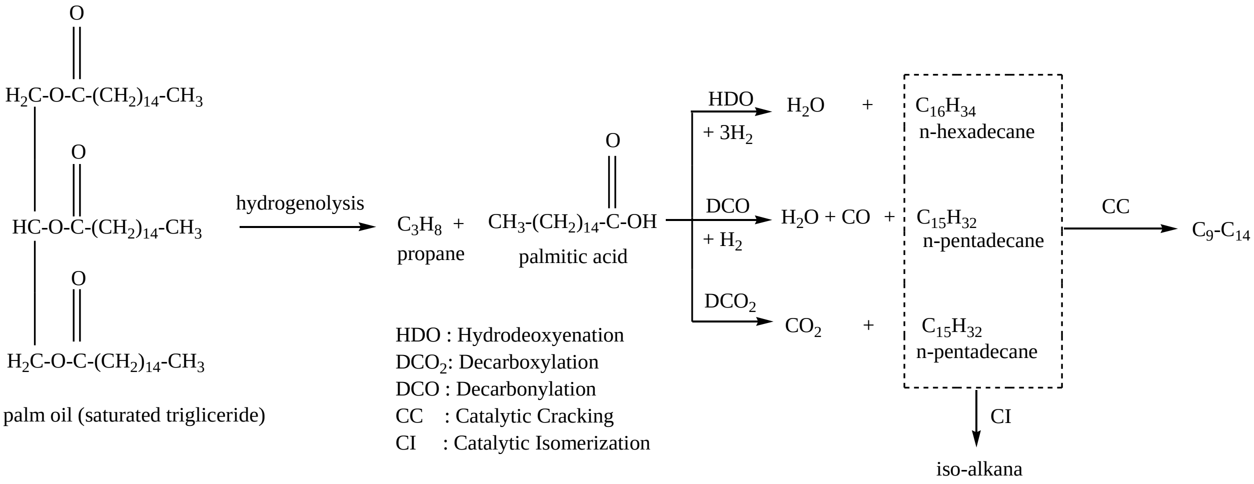


Figure 3. Reaction pathways that occur in the catalytic deoxygenation process of palm oil

3. Crude Palm Oil

Crude palm oil is a type of oil that has excellent potential as a raw material because of its abundant availability, especially in Indonesia. Various derivative products are also produced in refining CPO into cooking oil, as shown in **Figure 4**. The refining process begins with degumming, which aims to remove gom (phospholipids and phosphatides) from CPO through precipitation. This process usually occurs at 90–130 °C using phosphoric acid as a precipitant. Under these conditions, degummed palm oil (DPO) is obtained. The DPO is then bleached to remove unwanted impurities, such as pigments and residual metals, resulting in bleached palm oil (BPO). Next, the BPO is deodorized by removing the free fatty acid content. This step produces refined, bleached, and deodorized palm oil (RBDPO) of about 95% and palm fatty acid distillate (PFAD) as a by-product of about 5%. Finally, RBDPO is fractionated to produce refined palm olein (RPO, 80%) and refined palm stearin (RPS, 20%) (Jumaah et al., 2019).

Changes in chemical compounds contained in CPO, DPO, RPS, RPO, and PFAD can be seen in **Table 2**. In general, the fatty acids contained in CPO and its derivatives are those with a carbon atom number of 12 to 20. The most significant amount is palmitic acid, followed by oleic and linoleic acids. These fatty acids can also be converted into green diesel. RPS has the highest levels of palmitic acid. If all of them are converted to $C_{16}H_{34}$ through the HDO reaction, the quality of the green diesel produced will be high. The content of saturated and unsaturated fatty acids is almost the same. Hydrogen (HDO) can convert unsaturated fatty acids to saturated ones so that the alkane fraction will be produced.

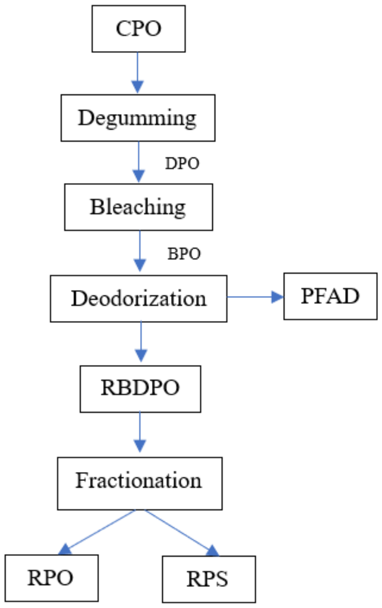


Figure 4. Refining process of crude palm oil (Kiatkittipong et al., 2013)

PFAD is a fatty acid that is non-edible. PFAD has been used as a raw material for soapmaking, oleochemicals, and animal feed. The composition of PFAD consists of free fatty acids (81.7%, glycerides (14.4% and vitamin E, squalene, and sterol (Baharudin et al., 2020). Its fatty acid compounds consist of meristic acid (0.27%), palmitic acid (55.59%), stearic acid (6.33%), oleic acid (22.76%), and linoleic acid (12.92%) (Gamal et al., 2020). Used cooking oil derived from palm oil also has excellent potential for producing green diesel. This oil accounts for about 20% of the new oil used. Its utilization as a green diesel raw material can be a solution to handling used cooking oil waste.

Table 2. Distribution of fatty acid compounds in CPO and its derivatives

Fatty acid	CPO^a (%)	DPO^a (%)	PFAD^a (%)	RPS^b (%)	RPO^c (%)
C 12:0 (lauric acid)	0.8	0.8	-	0.9	0.19-0.49
C 14:0 (myristic acid)	1.2	1.2	1.1	1.7	0.81-1.23
C 16:0 (palmitic acid)	44.5	44.5	49.0	58.8	34.49-38.81
C 16:1 (palmitoleic acid)	0.1	0.1	0.2	-	0.16-0.22
C 18:0 (stearic acid)	3.8	3.8	4.1	4.8	3.52-4.25
C 18:1 (oleic acid)	39.7	39.7	35.8	25.9	42.61-46.03
C 18:2 (linoleic acid)	9.3	9.3	8.3	7.5	11.37-14.07
C 18:3 (linolenic acid)	0.2	0.2	0.3	0.3	0.11-0.23
C 20:0 (arachidic acid)	0.3	0.3	0.3	-	0.2-0.5
C 20:1 (eicosenoic acid)	0.1	0.1	0.2	-	-
C 24:1 (tetracosenoic acid)	-	-	0.6	-	-

Note : $^{a)}$ (Kiatkittipong *et al*., 2013) $^{b)}$ Zou *et al.* 2012 $^{c)}$ Hasibuan 2012

In addition, the price is also low compared to new oil. Rashidi et al. (2022) found that the fatty acids that make up waste cooking oil consist of meristic acid (1.1%), palmitic acid (35.7%), palmitoleic acid (2.7%), stearic acid (4.8%), oleic acid (41.6%), linoleic acid (13.5%), and linolenic acid (0.6%). This condition provides an opportunity to develop palm oil and its derivatives as feedstock for green diesel.

4. NICKEL-BASED CATALYSTS

Nickel is a transition group metal with good catalytic activity in catalytic deoxygenation reactions or other hydrotreating reactions (Yang et al., 2017). Its catalytic activity almost equals that of precious metals. Morgan et al. (2010) found that the use of a nickel catalyst impregnated with carbon (Ni (20%)/C) resulted in greater conversion than Pd (5%)/C and Pt (1%)/C in the deoxygenation of trisetearin, triolein, and soybean oil. When compared to other transition metals, Ni is more reactive or more able to accept free electron pairs, so its acidity is higher (Trisunaryanti, 2018). This acidity is required in cracking reactions. In addition, the bond formed between the reactant or product and Ni is weak, so it is easily desorbed at the end of the reaction. The weakness of Ni is that it is prone to coke formation and sintering during the catalytic deoxygenation reaction (Baharudin et al., 2019). This weakness can be overcome by adding promoters or additives to the catalyst, such as phosphorus, to form nickel phosphide (Li et al., 2011; Dwiratna & Soebagjo, 2015) or other transition metals to form a bimetallic catalyst. Chen et al. (2014) compared the catalytic activity of several transition metals on deoxygenating methyl laurate. The catalytic activity follows the following order: Ni_2P/SiO_2<MoP/SiO_2<CoP/SiO_2<WP/SiO_2<Fe_2P/SiO_2. In addition to good catalytic activity, the price of nickel is also low so it can be a concern for the industrial world (Parlett et al., 2017). Nickel ore reserves in Indonesia are also quite widely available. Based on the executive resume of the Ministry of Energy and Mineral Resources (Anonymous, 2020), nickel ore reserves in Indonesia it has reached 1323 million tons. Conditions also enable the Indonesian people to develop and produce nickel-based catalysts.

The synthesis of green diesel from palm oil and its derivatives can be carried out in batches (Sousa-Aguiar et al., 2021; Jiraroj et al., 2021), semi-batch (Gamal et al., 2020; Oliveira et al., 2021), or continuous (Istadi et al., 2021). The catalytic deoxygenation process conditions without hydrogen generally occur at a reaction temperature ranging from 300–360 °C for 0.5–3.5 h and a catalyst concentration of 5–10% (**Table 3**).

The hydrodeoxygenation process (catalytic deoxygenation with hydrogen) can be carried out using solvents. The addition of solvent is intended to maximize the reaction, but it can increase the cost of the process, and at the end of the process, it must be separated to separate the solvent. The solvents used are dodecane (Chen et al., 2020; Hachemi et al., 2017), n-heptane (Sabarman et al., 2019; Liu et al., 2020), decalin (Li et al., 2019), and other types of organic solvents. This process can also be carried out in batch, semi-continuous, or continuous mode.

Table 3. Synthesis of green diesel via catalytic deoxygenation process without hydrogen

No	Raw Material	Catalyst	Process Condition			Result		Reference
			T (ºC)	T (h)	C (%)	S (%)	Y (%)	
1	PFAD	NiO/SBA-15; NiO.CoO/SBA-15	350	3	10	85.8 88.1	97.2	Kamaruzaman et al., (2020)
2	PFAD	NiO/Al-SBA-15	350	2	10	81-91	81-91	Baharudin et al., (2019)
3	PFAD	NiO/ZnO	350	2	5	70.8-86	77-85.4	Baharudin et al., (2020)
4	PFAD	NiO/Zeo NiO-Co_3O_4/Zeo	350	0,5	5	68.7-78.2	-	De Oliveira et al., (2021)
5	*Waste Palm oil*	Ni raney	350-390	1-6	5-10	5-98	-	Sousa-Aguiar et al., (2021)
6	*Palm oil*	Ni/HY NiCo/HY	450	-	-	28.85 28.54	40.68 40.00	Istadi et al., (2021)
7	Oleic acid	Ni-FSM-16	350	0,5	10	87	85.7	Jiraroj et al., (2021)
	Palmitic acid	Ni-FSM-16				98	67.9	
8	WCO	Zn_{10}/AC Ni_{20}/AC Ni_{20}Znx/AC	350	1	3	65-79	67-86	Khalit et al., (2022)

Notes: T = temperature, t = time, C = catalyst concentration, S = selectivity, Y = yield

In **Table 4**, solvents can generally produce higher product conversion and selectivity than without solvents. The type of catalyst and process conditions used strongly influences the success of green diesel synthesis. The following will describe the effects of these parameters.

4.1. Effect of Nickel Active Phase

Ni catalysts can be monometal (oxide or metal), bimetal, or nickel phosphide (NiP). Kamaruzaman et al. (2020) compared monometallic catalyst (NiO) and bimetal catalyst (NiO.CoO) using SBA-15 support on PFAD deoxygenation. NiO/SBA-15 catalyst (SBA = Santa Barbara Amorphous) produced hydrocarbon yield (85.8%) and diesel fraction selectivity (97.2%). The NiO.CoO/SBA-15 bimetallic catalyst showed a higher hydrocarbon yield than NiO (88.1%). The presence of cobalt helps reduce the particle size of NiO and enhances metal interactions, resulting in improved coke resistance (Mohamedali et al., 2018). The intense interaction between the alloy and the mesoporous support can suppress the thermal sintering of metal particles (Bian et al., 2017). Nevertheless, the resulting diesel fraction selectivity is lower than that of the NiO/SBA-15 catalyst. The presence of CO causes an increase in the gasoline fraction. Khalit et al. (2022) found that $Ni_{20}Zn_x$/AC bimetallic catalysts produced a greater hydrocarbon yield (77-83%) than Ni_{20}/AC and Zn_{10}/AC monometallic catalysts (30–70%). It is attributed to the monometallic catalysts promoting the cracking pathway, resulting in a deficiency of deoxygenation activity, which is reflected in the high production of light hydrocarbons (C8–C14), which reduces the formation of diesel (C15–C18). Ni is a metal that can create large Lewis acid sites. Ni contains empty d orbitals that will act as Lewis acid sites in the catalyst, efficiently accepting electrons from the adsorbate. Incorporating Zn and Ni increases the strong acid and base sites, thus significantly deoxygenating waste cooking oil (WCO). The highest acidity and basicity were found in the $Ni_{20}Zn_{20}$/AC catalyst, with values of 6015 mol/g and 2069 mol/g. It follows the results, which show that most $Ni_{20}Z_{nx}$/AC have bronsted acid sites. Oliveira et al. (2021) found that the hydrocarbon yield and green diesel selectivity produced on the bimetallic catalyst (NiO-Co_3O_4/Zeo) were greater than those produced on the monometallic catalyst (NiO/Zeo). In general, bimetallic catalysts have better catalytic activity than monometallic catalysts.

Table 4. Synthesis of green diesel via hydrodeoxygenation process

Raw Material	**Solvent**	**Catalysts**	**Process condition**			**Results**			**Ref.**
			T (°C)	**t (jam)**	**P (bar)**	**K (%)**	**Y (%)**	**S (%)**	
Stearic acid	Dodecane	Ni/HY80, Ni/y-Al_2O_3, Ni/SiO_2	**300**	6	30	97-100	**-**	37-96(C_{17}) 1-62 (C_{18})	Hachemi et al., (2017)
Stearic acid	heptane	Ni/SAPO-11G Ni/SAPO-11H	290	3	-	97.3 97.6	- -	91.8(C_{15-18}) 92.2(C_{15-18})	Liu et al., (2020)
Oleic acid	Decalin	Ni/Zn-Al_2O_4	280	6	25	-	92,1(C_{17}) 3,9(C_{18})	-	Li et al., (2019)
Oleic acid	Syclohxane	NiLx/SiO_2	260	9	30	75-100	-	35,1-95	Cao et al., (2020)
Palmitic acid	dodecane	Ni/RM	300	4	40	100	-	100	Chen et al., (2022)
		Ni/SiO_2 Ni/ Al_2O_3				100 54,52	-	56,12 57,27	
Palm oil	dodecane	Ni/TPA-HBEA	260	1	40	70	-	-	Ma & Zhao, (2015)
Oleic acid Palmitic acid	-	Ni_2P/HZSM-5	310-360	2.5	-	100 99	- 42.9	- -	Liu et al., (2015)
Palmitic acid	-	NiP/AC	350	2.5	-	86.2-100	-	40.1-74.0	Xin et al., (2016)
Oleic acid	-	Ni/MG70	300	3	20	96.7	-	45.9	Jeon et al., (2022)
Palm oil	-	Ni_2P/SiO_2	380	2	40	100	76.3	-	Jeong et al., (2019)
	-	Ni_2P/ Al_2O_3				100	79.7	-	
Palm oil	-	Ni_2P/NAMOR	425	-	50	100	83.5	-	Rakmae et al., (2020)
Palm oil	-	Ni/Al_2O_3	300	-	50	100	94	-	Srifa et al., (2018)
Palm oil	-	ReNiMoS/Al_2O_3	370	-	40	100	69.5	-	Thongkumkoon et al., (2019)
Palmitic acid	decane	$NiMoS_2$	320	2	70	94,2	65,6(C_{16})	78,5(C_{16})	Yoosuk et al., (2019)
Oleic acid	decane		280	4	60	100	70,3 (C_{18})	78,8 (C_{18})	

Note: T = temperatire, t = time, P = pressure, K = convertion; S = selectivity, Y = yield, Istadi et al. (2021) found that the use of monometal (Ni/HY) and bimetal (Ni-Co/HY) catalysts showed almost the same catalytic activity in the catalytic cracking of palm oil. The conversion and selectivity of diesel produced were about 98% and 40%, respectively.

The concentration of the impregnated metal can also affect the activity of the catalyst. Baharudin et al. (2020) compared the concentrations of NiO impregnated on ZnO support (5, 10, and 20%). A NiO_{20}/ZnO catalyst with 195.84 mol/g acidities produced higher hydrocarbon yield and green diesel selectivity than the other two concentrations. From its characteristics, this catalyst has a larger surface area but a more negligible acidity. The combination of these two characteristics can increase yield and selectivity. When the acidity is high (NiO_{10}/ZnO, 818.19 mol/g), the gasoline fraction increases, so the green diesel selectivity decreases. Chen et al. (2022) also studied the effect of nickel concentration (1–30%) on Ni/RM catalysts. RM (red mud) is a mixture of Fe_2O_3 (40.3%), Al_2O_3 (23.0%), and SiO_2 (15.6%). Nickel concentrations from 1% to 7% caused palmitic acid conversion and alkane selectivity to increase. Concentrations above 7% decreased the conversion. It is due to the Ni(7%)/RM catalyst's large surface area, pore structure, and uniform metal distribution. This condition is also reinforced by the even distribution of Ni particles on the RM surface to maximize the contact between reactants and Ni. Jeon et al. (2022) varied the Ni concentration (5, 10, 15, 20, 30%) with MG70 support (70% MgO in Al_2O_3) on HDO of oleic acid extracted from PFAD. The greater the Ni loading, the greater the resulting conversion. For hydrocarbon (diesel) selectivity, the 20% Ni/MG70 catalyst showed the highest value (45.9%) compared to other catalysts. This result is due to the reducibility, number of Ni active sites, and catalyst acidity. The 20% Ni/MG70 catalyst has more Ni active sites participating in the deoxygenation reaction and is more reducible (Shim et al., 2018). Ni-based catalysts have easier reducibility, resulting in better electron transfer capability and thus enhancing the reaction.

Xin et al. (2016) used a nickel phosphide (NiP) catalyst in palmitic acid HDO by varying the Ni/P ratio. Increasing the Ni/P mole ratio increased the conversion, but the C15 selectivity did not differ. When the Ni/P ratio was increased from 0.5 to 1, the selectivity rose from 54.6% to 74.9%. When further increased to 4, the selectivity dropped to 40.1%. Cao et al. (2020) varied metal oxides (Mo_x, Co_x, Wo_x, Cu_x, and Fe_x) on a NiL_x/SiO_2 catalyst for oleic acid HDO. $NiMoO_x/SiO_2$ and $NiWO_x/SiO_2$ catalysts showed higher diesel selectivity than other oxides. Regarding activity and selectivity towards C18 alkanes, the $NiMoO_x/SiO_2$ catalyst yielded the highest values.

4.2 The Effect of Support Type

Various types of supports have been used in the synthesis of green diesel. Baharudin et al. (2019) compared the Si/Al ratio to the catalytic activity of the NiO/Al-SBA-15 catalyst. The higher the Si/Al ratio, the greater the selectivity of the green diesel produced. The high Si/Al ratio decreases the acidity of the catalyst to encourage the formation of diesel (deoxygenation reaction). However, when the acidity is high (low Si/Al ratio), However, when the acidity is high (low Si/Al ratio), cracking reactions will occur so that the diesel formed is reduced. Hachemi et al. (2017) varied the type of Ni catalyst support in synthesizing green diesel from stearic acid. Y-Al_2O_3 support produced higher conversion and selectivity than HY80 and SiO_2. The selectivity of C17 is greater than that of C18, which indicates the dominant reaction is decarboxylation or decarbonylation compared to HDO. The same thing also happened with the use of SiO_2.

Nevertheless, it is different when HY80 is used; the dominant reaction is HDO, where the selectivity of C18 is more remarkable than C17. Liu et al. (2020) compared silicoaluminophosphate-11 (SAPO-11) support synthesized by different methods on HDO of stearic acid. SAPO-11H was synthesized conventionally, while SAPO-11G was synthesized at a lower temperature and reduced the use of organic fillers to reduce the synthesis cost. Both supports generally produced almost the exact diesel conversion and selectivity of 97% and 92%, respectively. When viewed from the characteristics of the support, SAPO-11G has a higher crystallinity, a smaller particle size distribution, and a lower acidity. However, the catalytic activity produced is almost identical to that of SAPO-11H.

Chen et al. (2020) varied the support type (RM, γ-Al_2O_3, and SiO_2) on palmitic acid deoxygenation. The largest conversion was obtained on Ni/RM and Ni/SiO_2 catalysts which were 100%, while Ni/Al_2O_3 was only 54.52%. The selectivity of alkanes to Ni/γ-Al_2O_3, Ni/RM, and Ni/SiO_2 was 57.27%, 100%, and 56.12%, respectively. The high conversion and selectivity of RM were due to Al_2O_3 and SiO_2. Jeong et al. (2019) used NiP catalyst in HDO palm oil but varied the type of support (SiO_2 and alumina). The use of alumina support resulted in greater selectivity than SiO_2. The same thing was obtained by Srifa et al. (2018), who used alumina support, where the resulting conversion was 100% and green diesel selectivity was 94%. Cao et al. (2020) used a NiMo catalyst with a support: HZSM-5, SiO_2. γ-Al_2O_3, m-CeO_2, and mTiO_2. The NiMo/Al_2O_3 catalyst, which contains many Lewis acid sites, showed 100% conversion and high selectivity toward C17 alkane (69%). The strong Lewis acid is more beneficial in promoting the cracking of the C-C bond. CeO_2 support showed low selectivity, which means the basic support is not favorable for this reaction. NiMo/H-ZSM-5 catalyst, which contains many Brønsted acid sites, showed 95% selectivity towards C18 alkanes at 100% stearic acid conversion. The Brønsted acid sites of the catalyst play an important role in the selective hydrogenation of fatty acids. Therefore, a support with more Brønsted acid sites is more beneficial to improve the selectivity to C18 alkanes of stearic acid conversion.

4.3 The Effect Of Process Conditions

Sousa-Aguiar et al. (2021) optimized the deoxygenation process of waste palm oil using a Raney nickel catalyst. The process conditions varied in reaction temperature (350, 370, and 390 °C), time (1, 3.5, and 6 hours), and catalyst concentration (5, 7.5, and 10%). The best condition was obtained at 390 °C, 10% catalyst concentration, and 3.5 hours with 98% diesel selectivity. Raney nickel catalyst tended to promote decarboxylation reactions and decarbonylation reactions. Chen et al. (2022) studied the effect of temperature on the conversion of palmitic acid and the selectivity of alkanes produced. When the reaction temperature was 180 °C, palmitic acid was difficult to hydrogenate, but when the temperature was increased to 300 °C, the conversion and selectivity immediately reached 100%. The catalytic activity of Ni/RM is almost the same as that of Pd/C noble metal catalysts used to convert palmitic and stearic acid mixtures (Lestari et al., 2009). It indicates that Ni catalysts have comparable activity with noble metals. Pressure also has an impact on palmitic acid conversion. Pressures of 20 Pa and 30 Pa resulted in 70.01% and 84.16% conversions, respectively. When the pressure increased to 40–60 Pa, the conversion rose to 100% (Chen et al., 2022).

Ma & Zhao (2015) studied the effect of reaction time on the HDO of oleic acid and palm oil. The longer the reaction time, the higher the oleic acid conversion and palm oil yield because the longer the time, the greater the number of reactants reacting to produce more products. The highest conversion was obtained at 120 minutes with an oleic acid concentration of 0.065 g/mL (oleic acid/dodecane). The effect of oleic acid concentration was also studied, where the higher the concentration of reactants, the lower the reaction rate. Higher reactant concentrations imply an explicit mass transfer limitation in the gas-liquid-solid three-phase system. Yoosuk et al. (2019) studied the effect of temperature (300–360 °C) and pressure (30–90 bar) on the HDO of palmitic acid. Increasing the reaction temperature caused the conversion and selectivity of C15 to increase, but the selectivity of C16 decreased. It indicates that the higher the temperature, the more dominant the decarboxylation or decarbonylation reaction is than the hydrodeoxygenation (HDO) reaction. Increasing pressure also results in high conversion, increased C16 selectivity, but reduced C15 selectivity. It shows that when the temperature is high, the decarboxylation/decarbonylation reaction pathway is dominant (high C15), but when the pressure is high, the HDO pathway is dominant (high C16).

4.4 The Effect Of Palm Oil-Based Substrate Type

Jiraroj et al. (2021) compared oleic acid and palmitic acid as feedstocks using Ni/FSM-16 catalysts. Oleic acid resulted in a C15-18 selectivity of about 87% and a conversion of 85.7%, while palmitic acid had a C15-18 selectivity of 98% and a conversion of 67.9%. Thongkumkoon et al. (2019) used a ReNiMo catalyst sulfidized on HDO of various substrates. The highest diesel yield was produced by oleic acid (76.5%), followed by PFAD (72.5%), RPS (69.7%), and RPO (69.5%). Liu et al. (2020), who used stearic acid substrates but different solvents, supports, and process conditions, found that the conversion and selectivity obtained were similar. Conversion of 97% and green diesel selectivity of 91%. Li et al. (2019) obtained a greater yield of C17 than C18 in HDO of stearic acid. It also indicates that the dominant reactions are DCO and DCO_2, compared to HDO. HDO processes that do not use solvents produce large conversions but lower selectivity than processes that use solvents. Liu et al. (2015) produced 99.6% conversion but only 42.9% hydrocarbon yield. Yoosuk et al. (2019) also examined the effect of substrate type. Palmitic acid produced optimum HDO conditions at 320 °C, 70 bar pressure, and 2 hours with 94.2% conversion and 78.5% C16 selectivity. Oleic acid produced lower optimum conditions at 280 °C and 60 bar pressure for 4 hours with 100% conversion and 78.8% C18 selectivity. It shows that the type of substrate can affect the optimum process conditions, conversion, and product selectivity.

Based on the study of the two methods above, it is necessary to consider the selection of metal type (monometal, bimetal, sulfide, and phosphide), metal concentration, support type, and process conditions to produce maximum green diesel selectivity. All these parameters are decisive in catalytic deoxygenation without hydrogen or hydrodeoxygenation methods. Compared to the two methods above, HDO can produce higher green diesel (especially alkane group) conversion and selectivity due to the added hydrogen. It has an impact on the quality of the green diesel produced. Side products in the form of CO_2 and CO gas are also less than in the catalytic deoxygenation method without hydrogen. Nevertheless, in terms of cost, HDO requires hydrogen gas and better equipment (high pressure) to increase the cost of the process.

5. GREEN DIESEL DEVELOPMENT OPPORTUNITIES FROM PALM OIL WITH NICKEL-BASED CATALYSTS

Using petroleum fuels triggers environmental pollution such as the greenhouse effect, increased pollutants in the air, and SOx and NOx emissions, so it is an opportunity to start replacing these energy sources with more environmentally friendly fuels. Biofuels such as green diesel have a considerable opportunity to substitute diesel fuel for petroleum. The raw materials, such as vegetable oil, are abundant and easy to produce, which drives their development. Palm oil, the oil with the most significant production in the world, is the primary candidate that can be used as a raw material for green diesel. The by-product of its processing in the form of palm fatty acid distillate also has a tremendous opportunity to be developed because it is non-edible, and the amount is quite large. On the other hand, used cooking oil, which is a waste, has a huge opportunity to be developed. Used cooking oil production is about 20% of new cooking oil production. This amount is quite large and very promising if processed into green diesel.

The catalytic deoxygenation process used in the synthesis of green diesel can produce green diesel maximally by paying attention to catalyst selection, process conditions, and feedstock type. Hydrodeoxygenation is preferred because it produces a higher fraction of green diesel, but hydrogen gas is required. The use of nickel-based catalysts in green diesel synthesis is also auspicious. The low price and catalytic activity that almost equal precious metals, mainly if supported by appropriate supports and optimal process conditions, make nickel catalysts a prospect for development. Nickel is also abundant, especially in Indonesia. If synthesized alone, it will reduce the cost of the green diesel synthesis process. Overall, all raw materials for the production of green diesel are widely available in Indonesia. Starting with palm oil as the primary raw material and nickel as a catalyst, Indonesia has an excellent opportunity to develop renewable energy in the form of green diesel.

6. CONCLUSIONS

The conversion of palm oil and its derivatives using a catalytic deoxygenation process with nickel-based catalysts can produce green diesel with high conversion and selectivity. Some influential factors are the selection of catalyst types (monometal, bimetal, sulfur, and phosphide), support types, and catalytic deoxyenation process conditions. The selection of the right parameters can maximize the production of green diesel.

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REFERENCES

Abdulkareem-Alsultan, G., Asikin-Mijan, N., Mansir, N., Lee, H. V., Zainal, Z., Islam, A., Taufiq-Yap, Y. H. (2019). Pyro-lytic de-oxygenation of waste cooking oil for green diesel production over Ag_2O_3-La_2O_3/AC nano-catalyst. In *Journal of Analytical and Applied Pyrolysis* (Vol. 137). Elsevier B.V. https://doi.org/10.1016/j.jaap.2018.11.023

Adriawan, A. M., Hartanto, R. R., Novizar, A., Aryani, D., Syarifudin, S., Saputra, M. Y. (2020). *Statistik Minyak dan Gas Bumi Oil and Gas Statistics*. Direktorat Jenderal minyak dan gas Bumi, Kemeterian Energi dan sumber daya Mineral.

Ameen, M., Azizan, M. T., Ramli, A., Yusup, S., Abdullah, B. (2020). The effect of metal loading over Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts on reaction routes of hydrodeoxygenation of rubber seed oil for green diesel production. *Catalysis Today*, *355*, 51–64. https://doi.org/10.1016/j.cattod.2019.03.028

Ananikov, V. P. (2015). Nickel: The “spirited horse” of transition metal catalysis. *ACS Catalysis*, *5*(3), 1964–1971. https://doi.org/10.1021/acscatal.5b00072

Anonim. (2020). *Executive Summary pemutakhiran data dan neraca sumber daya mineral status 2020*.

Arun, N., Nanda, S., Hu, Y., Dalai, A. K. (2021). Hydrodeoxygenation of oleic acid using γ-Al_2O_3 supported transition metallic catalyst systems: Insight into the development of novel FeCu/γ-Al_2O_3 catalyst. *Molecular Catalysis*, *December 2020*, 111526. https://doi.org/10.1016/j.mcat.2021.111526

Aziz, I., Adhani, L., Maulana, M. I., Marwono, M. A., Dwiatmoko, A. A., Nurbayti, S. (2022). Conversion of nyamplung oil into green diesel through catalytic deoxygenation using NiAg/ZH Catalyst. *Jurnal Kimia Valensi*, 8(2): 240-250. https://doi.org/10.15408/jkv.v8i2.25943

Baharudin, K. B., Abdullah, N., Taufiq-Yap, Y. H., Derawi, D. (2020). Renewable diesel via solventless and hydrogen-free catalytic deoxygenation of palm fatty acid distillate. *Journal of Cleaner Production*, *274*, 122850. https://doi.org/10.1016/j.jclepro.2020.122850

Baharudin, K. B., Taufiq-Yap, Y. H., Hunns, J., Isaacs, M., Wilson, K., Derawi, D. (2019). Mesoporous NiO/Al-SBA-15 catalysts for solvent-free deoxygenation of palm fatty acid distillate. *Microporous and Mesoporous Materials*, *276*(October), 13–22. https://doi.org/10.1016/j.micromeso.2018.09.014

Bian, Z., Das, S., Wai, M. H., Hongmanorom, P., Kawi, S. (2017). A Review on Bimetallic Nickel-Based Catalysts for CO_2 Reforming of Methane. *ChemPhysChem*, *18*(22), 3117–3134. https://doi.org/10.1002/cphc.201700529

Cao, X., Long, F., Zhai, Q., Liu, P., Xu, J., Jiang, J. (2020). Enhancement of fatty acids hydrodeoxygenation selectivity to diesel-range alkanes over the supported Ni-MoOx catalyst and elucidation of the active phase. *Renewable Energy*, *162*, 2113–2125. https://doi.org/10.1016/j.renene.2020.10.052

Chen, B. S., Zeng, Y. Y., Liu, L., Chen, L., Duan, P., Luque, R., Ge, R., Zhang, W. (2022). Advances in catalytic decarboxylation of bioderived fatty acids to diesel-range alkanes. *Renewable and Sustainable Energy Reviews*, *158*(December 2020), 112178. https://doi.org/10.1016/j.rser.2022.112178

Chen, Jinlei, Wang, D., Luo, F., Yang, X., Li, X., Li, S., Ye, Y., Wang, D., Zheng, Z. (2022). Selective production of alkanes and fatty alcohol via hydrodeoxygenation of palmitic acid over red mud-supported nickel catalysts. *Fuel*, *314*(September 2021), 122780. https://doi.org/10.1016/j.fuel.2021.122780

Chen, Jinlei, Zhu, Y., Li, W., Luo, F., Li, S., Li, X., Huang, Y., Zhang, A., Xiao, Z., Wang, D., Zheng, Z. (2021). Production of diesel-like hydrocarbons via hydrodeoxygenation of palmitic acid over Ni/TS-1 catalyst. *Biomass and Bioenergy*, *149*(January), 106081. https://doi.org/10.1016/j.biombioe.2021.106081

Chen, Jixiang, Shi, H., Li, L., Li, K. (2014). Deoxygenation of methyl laurate as a model compound to hydrocarbons on transition metal phosphide catalysts. *Applied Catalysis B: Environmental*, *144*, 870–884. https://doi.org/10.1016/j.apcatb.2013.08.026

Chen, Y., Li, X., Liu, S., Zhang, W., Wang, Q., Zi, W. (2020). Effects of metal promoters on one-step Pt/SAPO-11 catalytic hydrotreatment of castor oil to C8-C16 alkanes. *Industrial Crops and Products*, *146*(January), 112182. https://doi.org/10.1016/j.indcrop.2020.112182

de Barros, D. M., de Rezende, J. B., Pasa, D. M. D. V. (2020). Deoxygenation of Macauba acid oil over Co-based catalyst supported on activated biochar from Macauba endocarp: A potential and sustainable route for green diesel and biokerosene production. *Fuel*, *269*(January), 117253. https://doi.org/10.1016/j.fuel.2020.117253

De Oliveira, B. F. H., De França, L. F., Corrêa, N. C. F., Da Paixão Ribeiro, N. F., Velasquez, M. (2021). Renewable diesel production from palm fatty acids distillate (Pfad) via deoxygenation reactions. *Catalysts*, *11*(9), 1–16. https://doi.org/10.3390/catal11091088

Di Vito Nolfi, G., Gallucci, K., Rossi, L. (2021). Green diesel production by catalytic hydrodeoxygenation of vegetables oils. *International Journal of Environmental Research and Public Health*, *18*(24). https://doi.org/10.3390/ijerph182413041

Douvartzides, S. L., Charisiou, N. D., Papageridis, K. N., Goula, M. A. (2019). Green diesel: Biomass feedstocks, production technologies, catalytic research, fuel properties and performance in compression ignition internal combustion engines. *Energies*, *12*(5). https://doi.org/10.3390/en12050809

Dwiratna, B., Soebagjo, S. (2015). Pengembangan Katalis Berbasis NiMo Alumina untuk Reaksi HidrodeoksigenasiMinyak nabati menjadi Bioavtur. *Jurnal Energi Dan Lingkungan (Enerlink)*, *11*(2), 75–80. https://doi.org/10.29122/elk.v11i2.1580

Falabella, S., Costa, C., Peixoto Gimenes Couto, M. A., de Almeida Azevedo, D., Filho, J. F. S. de C. (2021). Conversion of residual palm oil into green diesel and biokerosene fuels under sub-and supercritical conditions employing raney nickel as catalyst. *Catalysts*, *11*(8). https://doi.org/10.3390/catal11080995

Gamal, M. S., Asikin-Mijan, N., Khalit, W. N. A. W., Arumugam, M., Izham, S. M., Taufiq-Yap, Y. H. (2020). Effective catalytic deoxygenation of palm fatty acid distillate for green diesel production under hydrogen-free atmosphere over bimetallic catalyst CoMo supported on activated carbon. *Fuel Processing Technology*, *208*(July). https://doi.org/10.1016/j.fuproc.2020.106519

Guo, C., Rao, K. T. V., Yuan, Z., He, S. (Quan), Rohani, S., Xu, C. (Charles). (2018). Hydrodeoxygenation of fast pyrolysis oil with novel activated carbon-supported NiP and CoP catalysts. *Chemical Engineering Science*, *178*, 248–259. https://doi.org/10.1016/j.ces.2017.12.048

Gurney, K. R., Song, Y., Liang, J., Roest, G. (2020). Toward accurate, policy-relevant fossil fuel CO2emission landscapes. *Environmental Science and Technology*, *54*(16), 9896–9907. https://doi.org/10.1021/acs.est.0c01175

Hachemi, I., Kumar, N., Mäki-Arvela, P., Roine, J., Peurla, M., Hemming, J., Salonen, J., Murzin, D. Y. (2017). Sulfur-free Ni catalyst for production of green diesel by hydrodeoxygenation. *Journal of Catalysis*, *347*, 205–221. https://doi.org/10.1016/j.jcat.2016.12.009

Han, F., Guan, Q., Li, W. (2015). Deoxygenation of methyl palmitate over SiO_2-supported nickel phosphide catalysts: effects of pressure and kinetic investigation. *RSC Advances*, *5*(130), 107533–107539. https://doi.org/10.1039/c5ra22973a

Hasibuan, H. A. (2012). Study on Characteristics of Indonesian Palm Kernel Oil and Its Fractionation Products. *Jurnal Standarisasi*, *14*(2), 98–104.

Hongloi, N., Prapainainar, P., Prapainainar, C. (2021). Review of green diesel production from fatty acid deoxygenation over Ni-based catalysts. *Molecular Catalysis*, *January*, 111696. https://doi.org/10.1016/j.mcat.2021.111696

Hosseinzadeh-Bandbafha, H., Tabatabaei, M., Aghbashlo, M., Khanali, M., Demirbas, A. (2018). A comprehensive review on the environmental impacts of diesel/biodiesel additives. *Energy Conversion and Management*, *174*(June), 579–614. https://doi.org/10.1016/j.enconman.2018.08.050

Istadi, I., Riyanto, T., Buchori, L., Anggoro, D. D., Pakpahan, A. W. S., Pakpahan, A. J. (2021). Biofuels production from catalytic cracking of palm oil using modified hy zeolite catalysts over a continuous fixed bed catalytic reactor. *International Journal of Renewable Energy Development*, *10*(1), 149–156. https://doi.org/10.14710/ijred.2021.33281

Jeon, K. W., Park, H. R., Lee, Y. L., Kim, J. E., Jang, W. J., Shim, J. O., Roh, H. S. (2022). Deoxygenation of non-edible fatty acid for green diesel production: Effect of metal loading amount over Ni/MgO–Al_2O_3 on the catalytic performance and reaction pathway. *Fuel*, *311*(July 2021), 122488. https://doi.org/10.1016/j.fuel.2021.122488

Jeong, H., Shin, M., Jeong, B., Jang, J. H., Han, G. B., Suh, Y. W. (2019). Comparison of activity and stability of supported Ni2P and Pt catalysts in the hydroprocessing of palm oil into normal paraffins. *Journal of Industrial and Engineering Chemistry*, *83*, 189–199. https://doi.org/10.1016/j.jiec.2019.11.027

Jiraroj, D., Jirarattanapochai, O., Anutrasakda, W., Samec, J. S. M., Tungasmita, D. N. (2021). Selective decarboxylation of biobased fatty acids using a Ni-FSM-16 catalyst. *Applied Catalysis B: Environmental*, *291*, 120050. https://doi.org/10.1016/j.apcatb.2021.120050

Jumaah, M. A., Mohamad Yusoff, M. F., Salimon, J., Bahadi, M. (2019). Physical Characteristics of Palm Fatty Acid Distillate. *Journal of Chemical and Pharmaceutical Sciences*, *12*(01), 1–5. https://doi.org/10.30558/jchps.20191201001

Kamaruzaman, M. F., Taufiq-Yap, Y. H., Derawi, D. (2020). Green diesel production from palm fatty acid distillate over SBA-15-supported nickel, cobalt, and nickel/cobalt catalysts. *Biomass and Bioenergy*, *134*(January), 105476. https://doi.org/10.1016/j.biombioe.2020.105476

Karavalakis, G., Jiang, Y., Yang, J., Durbin, T., Nuottimäki, J., Lehto, K. (2016). Emissions and Fuel Economy Evaluation from Two Current Technology Heavy-Duty Trucks Operated on HVO and FAME Blends. *SAE International Journal of Fuels and Lubricants*, *9*(1), 177–190. https://doi.org/10.4271/2016-01-0876

Kementrian ESDM. (2019). Standar dan Mutu (Spesifikasi) Bahan Bakar Nabati (Biofuel) Jenis Biodiesel Sebagai Bahan Bakar Lain Yang Dipasarkan Di Dalam Negeri. In *189 K/10/Dje/2019* (p. 5).

Kiatkittipong, W., Phimsen, S., Kiatkittipong, K., Wongsakulphasatch, S., Laosiripojana, N., Assabumrungrat, S. (2013). Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil. *Fuel Processing Technology*, *116*, 16–26. https://doi.org/10.1016/j.fuproc.2013.04.018

Knothe, G. (2010). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, *36*(3), 364–373. https://doi.org/10.1016/j.pecs.2009.11.004

Konwar, L., Mikkkola, J. (2022). Carbon support effects on metal (Pd, Pt and Ru) catalyzed hydrothermal decarboxylation/deoxygenation of triglycerides. *Applied Catalysis A*, *638*, 11861.

Kordulis, C., Bourikas, K., Gousi, M., Kordouli, E., Lycourghiotis, A. (2016). Development of nickel based catalysts for the transformation of natural triglycerides and related compounds into green diesel: A critical review. *Applied Catalysis B: Environmental*, *181*, 156–196. https://doi.org/10.1016/j.apcatb.2015.07.042

Kumar, P., Maity, S. K., Shee, D. (2019). Hydrodeoxygenation of stearic acid using Mo modified Ni and Co/alumina catalysts: Effect of calcination temperature. *Chemical Engineering Communications*, *1630396*. https://doi.org/10.1080/00986445.2019.1630396

Lestari, S., Mäki-Arvela, P., Beltramini, J., Lu, G. Q. M., Murzin, D. Y. (2009). Transforming triglycerides and fatty acids into biofuels. *ChemSusChem*, *2*(12), 1109–1119. https://doi.org/10.1002/cssc.200900107

Li, G., Chen, L., Fan, R., Liu, D., Chen, S., Li, X., Chung, K. H. (2019). Catalytic deoxygenation of C 18 fatty acid over supported metal Ni catalysts promoted by the basic sites of $ZnAl_2O_4$ spinel phase. *Catalysis Science and Technology*, *9*(1), 213–222. https://doi.org/10.1039/c8cy02027b

Li, K., Wang, R., Chen, J. (2011). Hydrodeoxygenation of anisole over silica-supported Ni_2P, MoP, and NiMoP catalysts. *Energy and Fuels*, *25*(3), 854–863. https://doi.org/10.1021/ef101258j

Liu, X., Yang, M., Deng, Z., Dasgupta, A., Guo, Y. (2020). Hydrothermal hydrodeoxygenation of palmitic acid over Pt/C catalysts: mechanism and kinetic modeling. *Chemical Engineering Journal*, *303*(February). https://doi.org/10.1016/j.micromeso.2020.110280

Liu, Yinghua, Yao, L., Xin, H., Wang, G., Li, D., Hu, C. (2015). The production of diesel-like hydrocarbons from palmitic acid over HZSM-22 supported nickel phosphide catalysts. *Applied Catalysis B: Environmental*, *174–175*, 504–514. https://doi.org/10.1016/j.apcatb.2015.03.023

Liu, Yuxiang, Zheng, D., Yu, H., Liu, X., Yu, S., Wang, X., Li, L., Pang, J., Xinmei Liu, Yan, Z. (2020). Rapid and green synthesis of SAPO-11 for deoxygenation of stearic acid to produce bio-diesel fractions. *Microporous and Mesoporous Materials*, *303*.

Ma, B., Zhao, C. (2015). High-grade diesel production by hydrodeoxygenation of palm oil over a hierarchically structured Ni/HBEA catalyst. *Green Chemistry*, *17*(3), 1692–1701. https://doi.org/10.1039/c4gc02339k

Mohamedali, M., Henni, A., Ibrahim, H. (2018). Recent advances in supported metal catalysts for syngas production from methane. *ChemEngineering*, *2*(1), 1–23. https://doi.org/10.3390/chemengineering2010009

Mohammed, S. T., Gheni, S. A., Aqar, D. Y., Hamad, K. I., Ahmed, S. M. R., Mahmood, M. A., Abdullah, G. H., Ali, M. K. (2022). Evaluation and optimal design of a high stability hydrothermal deoxygenation process for production of green diesel fuel via deoxygenation of waste cooking oil. *Process Safety and Environmental Protection*, *159*, 489–499. https://doi.org/10.1016/j.psep.2022.01.006

Morgan, T., Grubb, D., Santillan-Jimenez, E., Crocker, M. (2010). Conversion of triglycerides to hydrocarbons over supported metal catalysts. *Topics in Catalysis*, *53*(11–12), 820–829. https://doi.org/10.1007/s11244-010-9456-1

Murnieks, R., Apseniece, L., Kampars, V., Shustere, Z., Malins, K. (2016). Investigation of Deoxygenation of Rapeseed Oil over Raney Nickel and Ni/SiO_2−Al_2O_3 Catalysts. *Arabian Journal for Science and Engineering*, *41*(6), 2193–2198. https://doi.org/10.1007/s13369-015-1932-2

Naik, S. N., Goud, V. V., Rout, P. K., Dalai, A. K. (2010). Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, *14*(2), 578–597. https://doi.org/10.1016/j.rser.2009.10.003

Nie, Z., Zhang, Z., Chen, J. (2017). Effect of Ni and noble metals (Ru, Pd and Pt) on performance of bifunctional MoP/SiO 2 for hydroconversion of methyl laurate. *Applied Surface Science*, *420*, 511–522. https://doi.org/10.1016/j.apsusc.2017.05.173

Pan, Z., Wang, R., Nie, Z., Chen, J. (2016). Effect of a second metal (Co, Fe, Mo and W) on performance of Ni_2P/SiO_2 for hydrodeoxygenation of methyl laurate. *Journal of Energy Chemistry*, *25*(3), 418–426. https://doi.org/10.1016/j.jechem.2016.02.007

Papadopoulos, C., Kordouli, E., Sygellou, L., Bourikas, K., Kordulis, C., Lycourghiotis, A. (2021). W promoted Ni-Al_2O_3 co-precipitated catalysts for green diesel production. *Fuel Processing Technology*, *217*(February), 106820. https://doi.org/10.1016/j.fuproc.2021.106820

Papanikolaou, G., Lanzafame, P., Giorgianni, G., Abate, S., Perathoner, S., Centi, G. (2020). Highly selective bifunctional Ni zeo-type catalysts for hydroprocessing of methyl palmitate to green diesel. *Catalysis Today*, *345*(November), 14–21. https://doi.org/10.1016/j.cattod.2019.12.009

Parlett, C. M. A., Aydin, A., Durndell, L. J., Frattini, L., Isaacs, M. A., Lee, A. F., Liu, X., Olivi, L., Trofimovaite, R., Wilson, K., Wu, C. (2017). Tailored mesoporous silica supports for Ni catalysed hydrogen production from ethanol steam reforming. *Catalysis Communications*, *91*, 76–79. https://doi.org/10.1016/j.catcom.2016.12.021

PT. PERTAMINA (persero). (2012). *Spesifikasi pertamina dex*. *1*, 6304.

Putra, R., Lestari, W. W., Wibowo, F. R., Susanto, B. H. (2018). Fe/Indonesian natural zeolite as hydrodeoxygenation catalyst in green diesel production from palm oil. *Bulletin of Chemical Reaction Engineering &Amp; Catalysis*, *13*(x), 245–255.

https://doi.org/10.9767/bcrec.13.2.1382.245-255

Rakmae, S., Osakoo, N., Pimsuta, M., Deekamwong, K., Keawkumay, C., Butburee, T., Faungnawakij, K., Geantet, C., Prayoonpokarach, S., Wittayakun, J., Khemthong, P. (2020). Defining nickel phosphides supported on sodium mordenite for hydrodeoxygenation of palm oil. *Fuel Processing Technology*, *198*(May 2019), 106236. https://doi.org/10.1016/j.fuproc.2019.106236

Rashidi, N. A., Mustapha, E., Theng, Y. Y., Razak, N. A. A., Bar, N. A., Baharudin, K. B., Derawi, D. (2022). Advanced biofuels from waste cooking oil via solventless and hydrogen-free catalytic deoxygenation over mesostructured Ni-Co/SBA-15, Ni-Fe/SBA-15, and Co-Fe/SBA-15 catalysts. *Fuel*, *313*(February), 122695. https://doi.org/10.1016/j.fuel.2021.122695

Sabarella, Komalasari, W. B., Manurung, M., Sehusman, Supriyati, Y., Rinawati, Seran, K., Saida, M. D. N. (2019). Buletin Konsumsi Pangan. In *Buletin Konsumsi Pangan* (Vol. 10, Issue 2). http://epublikasi.pertanian.go.id/arsip-buletin/53-buletin-konsumsi/677-buletin-konsumsi-vol-10-no-2-2019

Sabarman, J. S., Legowo, E. H., Widiputri, D. I., Siregar, A. R. (2019). Bioavtur Synthesis from Palm Fatty Acid Distillate through Hydrotreating and Hydrocracking Processes. *Indonesian Journal of Energy*, *2*(2), 99–110. https://doi.org/10.33116/ije.v2i2.40

Saladini, F., Patrizi, N., Pulselli, F. M., Marchettini, N., Bastianoni, S. (2016). Guidelines for emergy evaluation of first, second and third generation biofuels. *Renewable and Sustainable Energy Reviews*, *66*(September 2015), 221–227. https://doi.org/10.1016/j.rser.2016.07.073

Setyoningsih, I. P., Rinaldi, N., Aziz, I., Ridwan, M., Sudiyarmanto, Maryati, Y., Dwiatmoko, A. A., Aulia, F. (2019). Effect of the acid-base properties of the support on the performance of ruthenium catalysts in the hydrodeoxygenation of stearic acid. *AIP Conference Proceedings*, *2175*. https://doi.org/10.1063/1.5134574

Shim, J. O., Jang, W. J., Jeon, K. W., Lee, D. W., Na, H. S., Kim, H. M., Lee, Y. L., Yoo, S. Y., Jeon, B. H., Roh, H. S., Ko, C. H. (2018). Petroleum like biodiesel production by catalytic decarboxylation of oleic acid over Pd/Ce-ZrO_2 under solvent-free condition. *Applied Catalysis A: General*, *563*(March), 163–169. https://doi.org/10.1016/j.apcata.2018.07.005

Srifa, A., Kaewmeesri, R., Fang, C., Itthibenchapong, V., Faungnawakij, K. (2018). $NiAl_2O_4$ spinel-type catalysts for deoxygenation of palm oil to green diesel. *Chemical Engineering Journal*, *345*, 107–113. https://doi.org/10.1016/j.cej.2018.03.118

Thongkumkoon, S., Kiatkittipong, W., Hartley, U. W., Laosiripojana, N., Daorattanachai, P. (2019). Catalytic activity of trimetallic sulfided Re-Ni-Mo/γ-Al_2O_3 toward deoxygenation of palm feedstocks. *Renewable Energy*, *140*, 111–123. https://doi.org/10.1016/j.renene.2019.03.039

Trisunaryanti, W. (2018). *Dari sampah plastik menjadi bensin dan solar* (1st ed.). UGM Press.

Trisunaryanti, W., Triyono, Armunanto, R., Hastuti, L. P., Ristiana, D. D., Ginting, R. V. (2018). Hydrocracking of α-cellulose using Co, Ni, and Pd supported on mordenite catalysts. *Indonesian Journal of Chemistry*, *18*(1), 166–172. https://doi.org/10.22146/ijc.26491

Wan Khalit, W. N. A., Asikin-Mijan, N., Marliza, T. S., Safa-Gamal, M., Shamsuddin, M. R., Azreena, I. N., Saiman, M. I., Taufiq-Yap, Y. H. (2022). One-pot decarboxylation and decarbonylation reaction of waste cooking oil over activated carbon supported nickel-zinc catalyst into diesel-like fuels. *Journal of Analytical and Applied Pyrolysis*, *164*(February), 105505. https://doi.org/10.1016/j.jaap.2022.105505

Xin, H., Guo, K., Li, D., Yang, H., Hu, C. (2016). Production of high-grade diesel from palmitic acid over activated carbon-supported nickel phosphide catalysts. *Applied Catalysis B: Environmental*, *187*, 375–385. https://doi.org/10.1016/j.apcatb.2016.01.051

Yang, Y., Lv, G., Deng, L., Lu, B., Li, J., Zhang, J., Shi, J., Du, S. (2017). Renewable aromatic production through hydrodeoxygenation of model bio-oil over mesoporous Ni/SBA-15 and Co/SBA-15. *Microporous and Mesoporous Materials*, *250*, 47–54. https://doi.org/10.1016/j.micromeso.2017.05

.022

Yenumala, S. R., Kumar, P., Maity, S. K., Shee, D. (2019). Production of green diesel from karanja oil (Pongamia pinnata) using mesoporous NiMo-alumina composite catalysts. *Bioresource Technology Reports*, *7*(July), 100288. https://doi.org/10.1016/j.biteb.2019.100288

Yoosuk, B., Sanggam, P., Wiengket, S., Prasassarakich, P. (2019). Hydrodeoxygenation of oleic acid and palmitic acid to hydrocarbon-like biofuel over unsupported Ni-Mo and Co-Mo sulfide catalysts. *Renewable Energy*, *139*, 1391–1399. https://doi.org/10.1016/j.renene.2019.03.030

Yu, C., Yu, S., Li, L. (2022). Upgraded methyl oleate to diesel-like hydrocarbons through selective hydrodeoxygenation over Mo-based catalyst. *Fuel*, *308*(September 2021). https://doi.org/10.1016/j.fuel.2021.122038

Zhang, Y., Duan, L., Esmaeili, H. (2022). A review on biodiesel production using various heterogeneous nanocatalysts: Operation mechanisms and performances. *Biomass and Bioenergy*, *158*(September 2021), 106356. https://doi.org/10.1016/j.biombioe.2022.106356

Zhao, X., Wei, L., Julson, J., Gu, Z., Cao, Y. (2015). Catalytic cracking of inedible camelina oils to hydrocarbon fuels over bifunctional Zn/ZSM-5 catalysts. *Korean Journal of Chemical Engineering*, *32*(8), 1528–1541. https://doi.org/10.1007/s11814-015-0028-8

Zhou, L., Lawal, A. (2016). Hydrodeoxygenation of microalgae oil to green diesel over Pt, Rh and presulfided NiMo catalysts. *Catalysis Science and Technology*, *6*(5), 1442–1454. https://doi.org/10.1039/c5cy01307k

Zou, X., Huang, J., Jin, Q., Liu, Y., Song, Z., Wang, X. (2012). Lipase-catalyzed synthesis of human milk fat substitutes from palm stearin in a continuous packed bed reactor. *JAOCS, Journal of the American Oil Chemists' Society*, *89*(8), 1463–1472. https://doi.org/10.1007/s11746-012-2046-6