

Nickel-Based Catalysts for Deoxygenation of Biorefinery Products to Renewable Fuels: A Mini Review

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Abstract

Nickel-based catalysts have shown decent performance in deoxygenation reactions. Although palladium catalyst is very effective for this reaction, its high cost increases the cost of production. This review concerns the deoxygenation reactions of higher fatty acids, vegetable oils, bio-oil and its model compounds to fuels using nickel-based catalysts. The hydrodeoxygenation and decarboxylation of model fatty acids and vegetable oils over nickel-based catalysts have been found to produce appreciable hydrocarbons that can be used directly as fuel in diesel engines. Similarly, bio-oil and its model compounds produce hydrocarbons in the presence of various nickel-based catalysts, but the yield is not as prominent as in vegetable oils. In general, the catalytic performance of nickel in such reactions depends on the co-metal, support and the reaction conditions. Like palladium and platinum, the electronic properties of nickel-metal have been shown to significantly contribute to the cleavage of the C-C or C-H bonds during the reactions. It has been reported that hydrogen molecule is stuck in the defect sites of the nickel-metal surface resulting in a decrease in the activation energy of hydrogen dissociation. Nickel, is, therefore, one of the most promising metals for catalyzing hydrodeoxygenation of bio-oils into hydrocarbons.

Keywords: Nickel, Catalyst, Deoxygenation, Bio-oils, Vegetable Oils.

INTRODUCTION

The Utilization of energy in the transportation sector, as well as energy loss during transit and conversion, are the major issues to be tackled in cleaner and justified energy production (Klemes, 2015). Transportation is the major energy consumption area which requires great amounts of fuel and it is likely to remain the same in the future. The extreme use of non-renewable fuels has caused an increase in CO₂ emissions which has led to a severe environmental issue in the sphere such as greenhouse consequences and global warming (Ameen *et al.*, 2017).

Interest has already been shifted towards non-fossil energy sources which include geothermal, bioenergy, solar and hydropower. However, in terms of economics, sustainability and abundance, the energy resource from biomass (wood, lignocellulosic resources, fats and oil) is at the forefront (Ameen *et al.*, 2017).

Biodiesel is the first-generation biofuel that received earlier attention from researchers. It is produced by the transesterification of fatty acids of vegetable oils and animal fats into long-chain fatty acid mono-alkyl esters (Studentschnig *et al.*, 2016). Its low CO₂ emission and high combustion capacity make it one of the most promising renewable energy sources currently (Kamaruzaman *et al.*, 2020). Nevertheless, the expensive nature of raw materials used, coupled with the use of edible raw materials for the production of biodiesel has raised serious concerns relating to the food chain, especially in developing countries. Fatty acid distillates, waste cooking oil and algal oils are among the non-edible, low-grade feedstocks available for producing second-generation biofuels (Baharudin *et al.*, 2019).

Biodiesel offers certain advantages over petroleum-based fuels, such as better lubricating ability and shorter delay in ignition time of fuel i.e higher cetane number (Ogunkoya *et al.*, 2015). However, fatty acid methyl esters' high oxygen concentration causes several issues, including storage stability problems and cold flow qualities such as cloud point and pour point. As a result, the focus has switched to the development of catalytic techniques for deoxygenating triglycerides and upgrading bio-oils to fuel-like hydrocarbons (Ogunkoya *et al.*, 2015).

Decarboxylation/decarbonylation (deCO_x) and Hydrodeoxygenation (HDO) epitomize the main reaction pathways that have been proposed to eliminate the oxygen present in bio-oils, fats and vegetable oils in the form of water and CO₂/CO, respectively (Kubickova *et al.*, 2005; Donnis *et al.*, 2009). Although effective, the use of sulfide catalysts and high hydrogen pressures makes it less attractive. The majority of HDO catalysts consist of precious metals and transition metal sulfides that are supported by oxides. Precious metals are predominantly effective in HDO of fatty acids and their methyl esters; yet, they are prohibitively costly. Transition metal sulfides appear to be commercially tempting; nevertheless, oxygen included in the feed lowers their catalytic activity, thus more addition of sulfide is necessary, which is troublesome (Golubeva and Maksimov, 2019).

Many previous works on deoxygenation reactions were centered on palladium or platinum catalysts (Leo *et al.*, 2016), and they proved to be excellent with high selectivity and decent conversion for diesel-range hydrocarbons. Nevertheless, the exorbitant price of these noble metals may avert their utilization in mega applications. In converting lipid feedstocks to hydrocarbons, low-cost Nickel-based catalysts have revealed outcomes that are almost similar to palladium and platinum-based compositions (Morgan *et al.*, 2010).

As a result, interest in nickel-based catalysts for the removal of oxygen from higher fatty acids and vegetable oils has increased. These catalysts have demonstrated excellent efficacy in removing oxygen. It has been observed that hydrogen is stuck in the flaws of the surface of the metal, which consequently reduces the hydrogen dissociation activation energy. Furthermore, bond breakage such as C-C or C-H can be influenced by the electrical characteristics of the nickel metal which is analogous to reactions initiated by platinum and palladium (Hongloi *et al.*, 2019).

In comparison with other transition metals, nickel has higher energy density, a larger d electron band and the lowest unoccupied molecular orbital (Znak *et al.*, 2008; Chen *et al.*, 2018). Because of these exceptional features, nickel-based catalysts have significant hydrogen absorption capacity and decent catalytic display (Li *et al.*, 2019). Furthermore, industries upgrading bio-oils are using nickel-based catalysts because it is identified as a promising catalyst. It creates active hydrogen species during the hydrogenation process (Li *et al.*, 2020). This mini review focuses on the role of nickel-based catalysts in the deoxygenation of vegetable oils, fatty acids, bio-oil, and their model compounds to fuel hydrocarbons and green chemicals. It highlights the reaction conditions, pathways, and products involved.

Vegetable oils and fatty acids

The high energy density possessed by vegetable oils makes them a very important source of fuel for transportation. However, their prominent high viscosity forestalls their direct use of fuel because it is unsuitable for today's diesel engines. A variety of plant oils are utilized as feedstock for fuel manufacturing (Ameen *et al.*, 2017). *Jatropha*, a notable non-edible plant, develops on infertile soil due to the presence of phorbol esters (Hari *et al.*, 2015). In comparison with other conventional fuels, oil obtained from *jatropha* has superior petroleum properties such as solidifying, flash and ignition points.

Soybean, rapeseed, sunflower, palm kernel, waste cooking, and algal oils have all been widely examined for their deoxygenation properties (Ameen *et al.*, 2017). The chemical configuration of fats and oils varies greatly depending on their origin. Animal fats and vegetable oils are triglycerides which are carboxylic esters obtained from three saturated and unsaturated fatty acid groups and glycerol. The length of the fatty acids also differs according to their origin. The five most predominant fatty acids are palmitic (C16:0), stearic (C18:0), linoleic (C18:2) oleic (C18:1), linolenic (C18:3) (Atabani *et al.*, 2013).

Considering the technology and economics behind it, it will be very difficult and demanding to design engines that will run on plant oils, that is why it is more economical to provide catalytic processes that will convert the plant oils to fuel hydrocarbons that are comparable to petroleum diesel (Olusola *et al.*, 2010).

Over the years, numerous catalytic pathways have been established to produce green diesel which is compatible with the current technology, and also produce green chemicals from fat and vegetable oil feedstocks. These procedures are divided into three classes, namely, deoxygenation, transesterification and cracking which were all extensively revised by Snare *et al.* (2009). Nickel-based catalysts are effective in the removal of oxygen from plant oils and model fatty acids to green diesel.

Role of nickel-based catalysts in deoxygenation of vegetable oils and fatty acids

Nickel catalysts play a vital role in the hydrogenation pathways. When these catalysts are supported and loaded with other metals, their activity and selectivity are enhanced. Moon *et*

al. (2014) prepared and characterized Ni-Cu-SiO₂ to assess its selectivity and activity, the researchers loaded 90 wt% metal and investigated the hydrodeoxygenation of anisole.

Nickel is also ideal for hydrogenation reactions involving vegetable oils and model compounds. It is utilized as a catalyst for the production of hydrocarbon fuels from triglycerides. Recently, Santillan-Jimenez *et al.* (2014) investigated the production of hydrocarbons from fatty acids and triglycerides using a double hydroxide Ni-Al catalyst with 20% metal loading. According to their investigation, the activity of the catalyst is highly dependent on the partial pressure of hydrogen. They further investigated the use of regenerated catalysts for the conversion. It was then concluded that the ability of the catalyst to form strong basic sites makes it favourable to perform deoxygenation reactions (Santillan-Jimenez *et al.*, 2014).

Promoters affect the activity of catalysts, which is why Horacek *et al.* (2014) examine the deoxygenation of rapeseed oil at 250 °C with varied flow rates. Nickel and cobalt promoted catalysts were investigated, and the nickel promoted catalyst gave a higher activity than the cobalt promoted catalyst.

Sulphidation of catalysts is efficient in the conversion of bio-refinery feedstocks to hydrocarbon because it creates active sites on the surface of the catalysts. However, the products often get contaminated with sulphur. This act makes it less attractive for hydrodeoxygenation reactions (Senol *et al.*, 2007). Having that in mind, researchers are now concerned about the production of sulphur-free metal catalysts. When sulphur free Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ were used by Krar *et al.* (2010), it was found that the catalysts have good activity in the deoxygenation of sunflower oil to green diesel.

Hongloi *et al.* (2019) also reported the effective preparation of a nickel-based catalyst for fuel hydrocarbon production from palmitic acid following the deoxygenation pathway at low pressure. 10 bars of monitored hydrogen were passed into the semi-batch reactor. Nickel gave the best conversion (98.33 %) and is attributed to the high acidity of the ZrO₂ surface while the selectivity of n-pentadecane is around 76%. The work of Kukushkin *et al.* (2019) revealed that hydrodeoxygenation of model compounds of triglycerides using Ni/Al₂O₃ and Ni-Cu/Al₂O₃ catalysts was successful with the formation of alkanes.

Rakmae *et al.* (2020) developed a novel bifunctional catalyst called Ni-P/NaMOR (MOR = Mordenite), which is made up of nickel phosphide and sodium zeolite mordenite. The hydrodeoxygenation of palm oil was investigated in a bed reactor with a trickling downflow made up of stainless steel and hydrogen as the environment. Palm oil conversion was completed at an optimal temperature of 425 °C and a pressure of 50 bar. The highest conversion and selectivity for C15-C18 alkanes were also achieved. Green diesel and HDO yields reduced Ni-P/NaMOR were higher than those from pure Ni₂P or mixed Ni₂P-Ni₁₂P₅. Remarkably, a modest quantity of isoparaffins was detected, most probable as a result of NaMOR support.

Golubeva *et al.* (2019) employed unsupported phosphide catalysts composed of Ni₂P and CoP to hydrodeoxygenate palmitic and stearic acids. After 6 hours of hydrodeoxygenation reactions, palmitic acid conversion achieves 93 and 92 percent, while stearic acid conversion reaches 94 and 91 percent in the presence of nickel and cobalt phosphides, respectively. It has been demonstrated that the catalyst generated *in situ* may be separated and recycled.

Kamaruzaman *et al.* (2020) reported that a low-grade by-product of refining palm oil known as palm fatty acid distillate was deoxygenated to green diesel in the absence of hydrogen and solvent. Ni/SBA-15 and Ni-Co/SBA-15 (SBA = Santa Barbara Amorphous, a mesoporous silica) with 5 wt% metal loading were used as a catalyst for the process. The reaction was conducted in a batch reactor at 350 °C, for 3 h and 10 wt% catalyst loading. Both catalysts were able to afford a high yield of liquid hydrocarbons and a conversion of 85.8% and 88.1%, respectively. 85 % was achieved as selectivity for diesel-range hydrocarbons.

Iron, copper and cobalt were incorporated into nickel catalysts supported on silica-alumina (SiAl) for the HDO of stearic acid in a batch reactor in the presence of a solvent. The metals were able to increase the acidity, surface area and particle size of Ni/SiAl catalysts which in return increased the hydrocarbon yield (Rafiani *et al.*, 2020). Stearic acid was also converted to alkanes in a Batch reactor using Ni/HBEA (HBEA = Zeolite Beta) (5 wt% Ni, Si/Al = 75) at 260 °C, 4.0 MPa for 8 hrs and the yield was 78.7%. (Kim *et al.*, 2019).

Hydrodeoxygenation of oleic acid was accomplished by Bhattacharjee *et al.*, (2019). To provide a green reaction medium, the researchers performed the reaction in hexane pressurized with CO₂, using a mesocellular foam (MCF) supported Fe-Pd-Ni/MCF. At 4 h, a yield of octadecane reached 93% .

Tonya *et al.* (2008) investigated nickel as a more economical replacement for platinum and palladium. Their research intended to produce a catalyst for the single-step conversion of plant oils to diesel-range and aviation fuel, with conditions for a potential catalyst as a substitute for noble metals. The findings revealed that Ni catalysts had an adequate capability for triglyceride deoxygenation. Nickel-based catalysts have been observed to be particularly active in upgrading soybean oil and model triglycerides in batch reactors (Morgan *et al.*, 2012). Ameen *et al.* (2017) have conducted a review on the nickel-catalyzed conversions of triglycerides and associated feedstock into fuel hydrocarbons. Cu and Sn have been reported to increase the performance of Ni/Al₂O₃ in the deoxygenation of lipids to fuel-like hydrocarbons, affording greater yield and selectivity than the unpromoted catalyst (Loe *et al.*, 2016).

Catalyst deactivation through coke formation and product dispersion can be affected by the morphology of catalyst supports (Ameen *et al.*, 2017). The acidity of the support is widely understood to play a vital role in deoxygenation reactions. Therefore, selecting the appropriate support is critical for good selectivity and yield of fuel hydrocarbons.

Bio-oil and its model compounds

Bio-oil is also known as bio-crude oil, wood oil and pyrolygneous tar (Demirbas, 2009). It is a dark brown liquid which is acidic and created by treating small-size biomass for relatively brief periods. Its elemental makeup is substantially identical to that of the original biomass, hence it may be considered "liquid wood." Bio-oil is predicted to play a significant part in future energy supplies (Luo *et al.*, 2005).

The bio-oil comprises many chemicals that belong to paraffin, BTX (benzene, toluene, and xylene) derivatives of phenol, and minor amounts of other oxygenates including but not limited to ketones, esters and alcohols with a value >1.5 as the H/C molar ratio (Isahak *et al.*, 2012). The high amount of oxygen in bio-oil causes high viscosity, storage instability, poor calorific value and corrosiveness. Thus, it is not utilized directly as fuel in most applications. Numerous types of biomass and their compositions undergo quick pyrolysis to produce bio-oil containing water and oxygenated chemicals. This complex composition makes raw bio-oil

unsuitable for direct deoxygenation (Carpenter *et al.*, 2014). The water content of bio-oil obtained from different feedstocks differs, for example, bio-oil obtained from agricultural waste is much higher than the one obtained from woody biomass. This is due to water present in the biomass and water obtained by the breakdown of cellulose component of the biomass that is usually stimulated by alkali metals (Czernik and Bridgewater, 2004).

The oxygenated components of bio-oil are classified as 1) hydroxyl-acetaldehydes; 2) hydroxyketones; 3) saccharides; 4) carboxylic acids; and 5) phenolic compounds. A broader categorization was forwarded by Oasmaa *et al.*, 2009.

Bio-oil has the potential characteristics to be utilized as fuel or further refined to value-added chemicals (Furimsky, 2000). Nevertheless, high oxygen concentration has a negative impact on the standard petroleum properties compared to conventional fossil fuels (Shi *et al.*, 2017). To solve these challenges, the catalytic HDO process was developed as the main pathway for efficiently upgrading bio-oil to useful chemicals and hydrocarbon fuels. Typically, in this method, oxygen is removed in the form of H₂O by the use of high-pressure hydrogen (Robinson *et al.*, 2016).

Hydrodeoxygenation of bio-oil to fuels using nickel-based catalysts

Bifunctional catalysts are the most promising catalysts to hydrodeoxygenate bio-oil and other oxygenates among a wide range array of catalysts. These catalysts are composed of different materials that present active sites for many reaction steps. Acidity and catalyst deactivation are two important properties of a catalyst, therefore, designing an excellent catalyst requires striking a balance between the two. The most important goal is to present a catalyst that eliminates oxygen with little consumption of hydrogen with high resistance to deactivation due to coke deposition.

Noble metals have been found to operate under mild conditions that resulted in reduced coke formation. Low-cost transition metal catalysts and their bimetallic combinations were also found to be effective for the hydrodeoxygenation of bio-oil, which is why they are now attractive to researchers. The nature of supports influences the physicochemical properties of the catalyst, thereby impacting the conversion and selectivity in HDO reactions (Wang *et al.*, 2013).

Zhao *et al.* (2009) designed a green catalytic method for upgrading phenolic compounds to hydrocarbons and methanol, with an excellent yield. The catalysts used were RANEYs nickel and Nafion/SiO₂ to enhance hydrogenation, hydrolysis and dehydration. The cost-effectiveness and activity similar to noble metals have made nickel-based catalysts increasingly attractive for HDO of bio-oils to fuel hydrocarbons and green chemicals.

Jin *et al.* (2019) proposed a new approach that doesn't require the use of external hydrogen pressure to remove oxygen from bio-oil compounds. They used water and bifunctional catalysts that have the properties to activate the water and perform HDO. The reaction was conducted in a batch reactor and guaiacol as the model compound to deoxygenate. Nickel supported on ceria and ceria/carbon was used as the catalyst and the carbon-based catalyst gave the best conversion and selectivity due to the higher dispersion of Ni on the carbon/ceria-based support. Bio-oils derived from lignin can be upgraded efficiently through the catalytic hydrodeoxygenation (HDO) pathway.

An acid-free method was used by Li *et al.* (2020) to synthesize Al-SBA-15. Nickel was impregnated unto the support following the incipient wetness procedure. The prepared

catalyst was comprehensively characterized and used for hydrodeoxygenation of eugenol in the presence of water. The study found a substantial correlation between nickel adsorption and dispersion on Al-SBA-15 and the ratios of Brønsted to Lewis acid sites, as well as weak to strong acid sites.

The researchers conducted HDO studies on the Ni/Al-SBA-15 with various Si/Al ratios. During the hydrodeoxygenation of eugenol, the 16Ni/S2-R catalyst demonstrated strong catalytic activity due to its high number of acid sites and good nickel dispersion.

Guaiacol, a bio-oil model compound with an oxygen content of 25.8 wt% was also studied by Sankaranarayanan *et al.* (2015) for hydrodeoxygenation. Methoxyphenol linkages are responsible for the high water content. Nickel (5 wt%) was supported by different zeolite supports and comprehensively characterized by modern techniques. The prepared catalysts were investigated for the HDO of guaiacol in a batch reactor under 40 bars of hydrogen and decaline as solvent. Many hydrogenolysis and hydrogenation reaction pathways were revealed. At 260°C for 2 hours, Ni/H-ZSM-5 (ZSM = Zeolite Sacony Mobil) has a high deoxygenation activity, yielding roughly 98% HDO. They also found a correlation between the hydrophobic and hydrophilic properties of the catalysts and the HDO findings. This study also shows that the performance of Ni-based catalysts is strongly dependent on support.

In the experiments proposed by Koike *et al.* (2015), it was proven that nickel phosphide is an important catalyst for HDO of compounds that are bio-oil model. This further confirms that bio-oil is a good source of fuel when processed to eliminate excess oxygen. The nickel phosphide catalyst was used to investigate the upgrade of bio-oil obtained from pyrolysis of cedar chips. A model compound 2-methyltetrahydrofuran was subjected to HDO using Ni₂P/SiO₂ at 350 °C and atmospheric hydrogen pressure. The catalyst showed promising HDO and cracking activity. The researchers also conducted pyrolysis and upgrading consecutively using a pyrolyser and catalytic reactor. They concluded that Ni₂P/ZSM-5 eliminated oxygen with a slight reduction in the yield and had a higher deoxygenation ability than the conventional catalysts.

Another unique method for upgrading bio-oil obtained from the hydrothermal liquefaction of cornstalk was initiated by (Shi *et al.*, 2014). Ni/ZrO₂ was used as the catalyst under moderately mild circumstances and cyclohexane. After the reaction, a hydrocarbon yield of 81.6 % and a selectivity of 90% diesel and jet fuel hydrocarbons was achieved. All molecules in the bio-oil were remarkably converted to their corresponding alkanes via different notable chemical reactions. The reusability of the catalyst was tested and the selectivity for diesel and jet fuel hydrocarbons remained unaffected. This method unveiled a critical reaction pathway fit for the conversion of bio-oil to fuel hydrocarbons.

Shafaghat *et al.* (2018) used a batch high-pressure reactor to hydrodeoxygenate crude bio-oil in supercritical methanol using Ni/HBeta catalyst (5-20 wt%, 10-30 bar and 2-6 h). Supercritical fluids are recognized to exhibit remarkable physicochemical features. The supercritical methanol caused a significant reduction in the oxygen content of bio-oil than ethanol and 2-propanol. The researchers also looked at the impact of support materials H-ZSM-5, HBeta and HY (Zeolite Y) as support materials.

Table 1. Nickel-Based Catalysts for Deoxygenation of Vegetable Oils and Bio-oils

Authors	Catalyst	Feedstock	Temp (°C)	Pressure	Time	Major Product	Conversion (%)	Selectivity (%)
(Nikolopoulous et al., 2023)	60%Ni/ Al ₂ O ₃	WCO	350		7h	Hydrocarbons		96
(Nikolopoulous et al., 2023)	60%Ni/ Al ₂ O ₃	Sunflower oil	350		7h	Hydrocarbons		97
(Goh et al., 2023)	NiCo	WCO	350		2h	Hydrocarbons		78.78
(Goh et al., 2023)	NiO	WCO	350		2h	Hydrocarbons		89.03
(Usman et al., 2023)	NiO/ Al-PILC	Jatropha	380		1h	Hydrocarbons		51
(Andrade et al., 2021)	Ni/HY	Soybean ester	340		9h	Hydrocarbons	99	61.90
(Andrade et al., 2021)	Ni/ Al ₂ O ₃	Soybean ester	300		7h	Hydrocarbons		41.20
(Ambursa et al., 2021)	Ni-Cu/ Ti-MCM-41	Guaiacol	260	10 MPa	6h	cyclohexane	90.49	50.09
(Ambursa et al., 2021)	Ni-Cu/ Al ₂ O ₃	O-Cresol	380	30.05 MPa	24h	Saturated Hydrocarbons	100	80
(Ambursa et al., 2021)	Ce-Ni-W-B	Phenol	225	4 MPa	1h	cyclohexane	100	100
(Ambursa et al., 2020)	Ni/SiO ₂	Anisole	300	5 MPa	16h	hydrocarbons	100	79.90
(Ambursa et al., 2020)	Ni/ Al ₂ O ₃	Cresol	300	5 MPa	16h	hydrocarbons	98.80	89.80
(Ambursa et al., 2020)	Ni/MgO	Guaiacol	160	3 MPa	3h	Cyclohexanol	97.70	100

CONCLUSION

Biorefinery products such as vegetable oils, higher fatty acids, bio-oil and its model compounds are the future of renewable fuels. These products cannot be used directly as fuel majorly due to their high oxygen content which gives rise to several problems such as cold flow properties, instability, high viscosity, corrosiveness, and low heating values which render them difficult to use and handle. A strategy was developed to eliminate oxygen and produce fuel with better quality. This approach includes catalytic hydrodeoxygenation and/or decarboxylation. Most of the earlier hydrodeoxygenation catalysts were noble metals and they were found to be highly active. However, they came with limitations due to their scarcity and expensive nature. Nickel-based catalysts were later proposed and they gave comparable results. Over the years, nickel-based catalysts have proven to be the most promising catalyst for the hydrodeoxygenation of biorefinery products to renewable fuels and chemicals due to their outstanding performance and lower cost.

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