



Recent advances in thermochemical conversion of biomass into drop-in fuel: a review



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ABSTRACT

The global evolutionary changes towards the use of renewable energy sources for transportation purposes are on the increase in an attempt to mitigate the environmental hazard and the proposed depletion associated with fossil fuel resources. Pyrolysis and hydrothermal processes of biomass conversion into renewable biofuels are resulted into the production of biocrude with high oxygen content due to the presence of large amount of oxygenates in biomass feedstocks. The presence of oxygen content in bio-oil causes corrosion, low heating value, instability and high viscosity in bio-oil. These challenges have necessitated the application of upgrading techniques such as catalytic hydrodeoxygenation process among others. The presence of several oxygenated compounds made the mechanisms of bio-oil synthesis difficult and model bio-oil were reviewed to understand the effects of process parameters and catalysts on aromatic selectivity and conversion. The selectivity of aromatic hydrocarbons was affected by deactivation of catalysts' active sites. Coke formation has been identified as one of the common and notorious causes of catalysts' deactivation which is dependent on the nature of feedstock, conditions of operation and the nature of catalyst. Therefore, the need to develop, evaluate a structurally and thermally stable catalyst with high catalyst recovery and reusability are of importance in the quest to depict hydrodeoxygenation process as an excellent technique for bio-oil upgrading.

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Introduction

The swift depletion of the worldwide deposit of fossil fuel resources due to the over-dependency of human activities has necessitated the search for efficient and effective alternative for fossil fuels [1]. The consumption of fossil fuel is expected to grow at 1.6% annually in the next two decades and global energy-related CO₂ emissions may rise by 1.7% to 33 Gigatonnes

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(Gt) in 2018 [2]. Therefore, energy and environmental pollution remain the main challenges to human and the ecosystem, respectively in this present decade. These challenges are on the rise due to ever-increasing number of population and urbanization which have extensively increased the dependency on natural resources such as petroleum, natural gas and coal for transportation purpose [3].

The applications of renewable sources of energy have paved way for the remediation of greenhouse gasses (GHG) emission and therefore, an excellent source for transportation fuels. These renewable energy sources are identified as cheap, economical and sustainable [4]. The application of biomass materials as an alternative energy source is gaining enormous interest of researchers in this present era [5,6]. Several biomass materials have been extensively employed as feedstock for bio-fuel production. Such feedstocks include rice husk [7–10], bagasse [7,11,12], maize cub [13,14], Orange peel [15–22] and vanillin [23,24] have been used for the production of advanced fuel. Fast pyrolysis process and hydrothermal liquefaction are the two main conversion routes for biomass to bio-oil. Bio-oils are greenhouse gas and carbon dioxide neutral, capable of generating carbon dioxide credit, no sulfur oxides generation and low release of nitrogen oxides gas than conventional fuel [25]. The listed characteristics have made bio-oil to possess appreciable environmental advantages over conventional fuels as a clean energy source.

The rapid organic compounds' decomposition via thermal technique in the absence of oxygen leading to the formation of products (liquids, gasses and char) is termed the flash pyrolysis. For enhanced quality of bio-oil production during the flash pyrolysis process, dried feedstocks are of importance to reduce the presence of water which has huge tendency in catalyst deactivation. In the other hand, hydrothermal liquefaction technique (HTL) requires the application of water during the conversion of biomass at high pressure and temperature. The operation of HTL process could either require the use of catalyst or not; although the application of catalyst has been reported to aid the conversion of oxygenates into deoxygenated compounds. In recent time, pyrolysis technique has been widely adopted over HTL and employed for bio-oil production where the development of technologies are advancing, the study bio-oil's mechanisms are increasing to better understand the best conditions for high quality of bio-oil production for targeted area of application. The application of pyrolysis techniques favours high yield bio-oil although the presence of high content of oxygenates have hindered it for been used directly for combustion process in automobile engines. Upgraded bio-fuels derived from biomass are expected to reduce the dependency on fossil fuels and further reduce the depletion of the ecosystem. Thermochemical conversion process is a widely employed method of bio-fuels production from biomass materials which consists of several pathways including gasification, pyrolysis, hydrothermal process and hydrolysis [26–29]. The application of fast pyrolysis technique has shown a promising outcome over other techniques by producing bio fuels of improved properties, high yield and ability to scale-up the production process for commercial application [15].

The obtained bio-oil from pyrolysis and hydrothermal techniques possess high contents of oxygenates as a result of high content of oxygen of about 50 wt% [30]. The oxygenates obtained in bio-oil are made up of phenols, aldehydes, alcohols, water, carbohydrates, ketones which hinder its direct application in the internal combustion engine. Hence, high oxygen content and lower energy density (as a result of lower hydrogen content in biomass) compared to fossil fuel are therefore, the main setbacks of bio-oil that requires attention towards upgrading the bio-oil to petroleum fuels standards [31,32]. Furthermore, the high oxygen content further leads to reduced bio-oil stability, immiscibility with conventional fuel during blending, high corrosive properties, lower heating value and high viscosity are inherent setbacks to bio-oil [33]. In addition, the presence of phenols and aldehydes; unsaturated and unstable compounds which are found in bio-oils are characterized with their ability to form large polymers of low fluidity and mobility which causes knocking of vehicle's engine [34,35].

Several techniques of bio-oils upgrading into transportation fuel have been reported by researchers towards the removal of oxygenates from bio-oil and to improve its physiochemical properties [36]. Such techniques include hydrotreating, hydrocracking, supercritical fluids (SCFs), solvent addition/esterification, emulsification (emulsions), steam reforming, electrocatalytic hydrogenation (ECH) and catalytic hydrogenation [37–44]. The application of hydrodeoxygenation process has attracted attention of researchers over other methods due to its ability to convert bio-oils into high grade biofuels having high stability, high hydrogen and lower oxygen content with improved heating value [20]. The conversion of bio-oils into deoxygenated transportation fuels via hydrodeoxygenation (HDO) requires the removal of oxygen in the form of water, carbon (iv) oxide and carbon mono-oxide leading to the formation of an improved physiochemical properties in liquid-fuel product [45]. This conversion processes; upgrading technologies are vital in presenting bio-oil as economic product suitable as fuel in power plants, combustion engines, biochemical fractionation and automobiles. Homogeneous catalysts (organic acids, alkalis, inorganic acids and carbonates) and heterogeneous catalysts (molecular sieves, insoluble inorganic and metals) are classes of catalysts employed for the catalytic conversion of bio-oil into biofuel [46]. Therefore, the performance investigations of the employed catalysts in bio-oil upgrading are paramount importance to an improved biofuel production and their tendency to withstand deactivation varies due to their, respective catalytic properties.

This review article comprehensively presents the state-of-the-art, the use and weaknesses of the processes that are employed as upgrading techniques of bio-oil conversion into drop-in fuel, with an emphasis on catalytic hydrodeoxygenation process. Furthermore, the major hindrance associated with catalyst performance and reusability; catalyst deactivation and the way forwards in combatting this challenge were also discussed in this review article. We also reviewed the mechanisms of bio-oil model compounds to understand the effect of catalyst and process parameters on the selectivity of aromatic compounds and percentage conversion. Furthermore, we recommended the way forward (future research) to enhancing the performance of catalyst materials during the hydrodeoxygenation process in obtaining high quality bio-oil.

Biomass conversion

Pyrolysis of biomass

Extensively, pyrolysis process as a means of biomass conversion into bio-oil has been widely studied by several researchers to producing an eco-friendly and renewable alternative source of energy for transportation use. In this process of thermochemical conversion, biomass feedstocks are heated in an inert environment under atmospheric pressure. Biomass is thermally degraded into useful fuels; biofuels, biochar and uncondensable gasses such as methane, carbon dioxide, hydrogen and other accompanied gaseous hydrocarbons [47].

It was reported by different researchers that the quality and nature of product formations during pyrolysis process depends solely on the operating conditions such as temperature, residence time, catalyst loading and feed ratio [48]. The complex structures exhibited by biomass materials are responsible for the different degradation profile obtained during the thermal degradation process, more obvious, during thermogravimetric analysis and this has a direct influence on the properties of the obtained bio-oil [49]. A low degree of polymerization of hemicellulose is evident due to its amorphous structure hence, hemicellulose degrades in two main stages [50]. The thermal behavior due to hemicellulose structural make-up indicated that it contributes less to bio-oils production through pyrolysis process.

The formations of coke and aromatics tar are linked to the decomposition of lignin content in biomass materials or lignin-modeled compound; this therefore retards the performance of catalyst during the pyrolysis process. The classes of pyrolysis reaction are classified into two main stages: primary and secondary pyrolysis reactions [51]. The primary pyrolysis decomposition of lignin and lignin-modeled compounds takes place over temperature range of 200–400 °C while the peak optimum degradation temperature has been reported to exist at a temperature of about 350 °C [51]. The thermal behavior of lignin derived from biomass materials has been reported to depend on the nature of biomass material [52]. Hence, the percentage conversion and selectivity of aromatics hydrocarbons could be said not only limited to catalysts performance and the conditions of operation but also, the chemical structure or composition of feedstocks. The pyrolysis conversion of biomass could be catalyst enhanced on non-catalytic; though the presence of catalyst has been reported to improve percentage conversion and selectivity to aromatic formation [53–56]. Table 1 shows the review of catalytic and non-catalytic pyrolysis of biomass; the feedstocks, process description, operating conditions and the nature of reactor.

From Table 1, the effects of catalyst materials are obvious in promoting the cracking of large molecular oxygenates into aromatic hydrocarbon having high tendency for direct use in automobiles. Therefore, the observed interesting performance of hierarchical catalysts towards improving bio-oil quality requires a review in understanding the mechanisms of conversion and selectivity to aromatic hydrocarbon production.

Hydrothermal liquefaction of biomass

The application of HTL techniques for the conversion of biomass into renewable fuel is dated back to the early 90's. Unlike the pyrolysis process whose performance in obtaining high yield fuels relies on biomass in dried form, HTL is suitable for wet feedstocks. Following the report of the research carried out by Pittsburgh Energy Research Centre in 1970, several researches have explored and modified techniques towards improving HTL performance in biomass conversion. One of the prominent advantages of HTL techniques is the ability to aid combined production of fuel and the treatment of wastewater in areas of dense population where huge amount of wastes on wet basis are discharged [75,76]. One of the main advantages of HTL over a pyrolysis process is that, it does not require the biomass feed to be dried before being used [76]. The ability to convert wet biomass directly to biocrude has depicted HTL has an appropriate technique for algae biomass [75].

HTL is a technique of bio-oil production from aqueous slurry of biomass or organic materials which takes place at temperature range of 280–370 °C (lower temperature compared to pyrolysis process), elevated pressure of 10–25 MPa and in the presence of water contentment [76]. According to Biller and Ross, [76], the process of biomass conversion into crude bio-oil was linked to the natural pathways of fossil fuels formation at elevated temperature and pressure though, under the earth. In this technique, liquid bio-oil is the major product with accompany solid and gaseous by-products. Operative parameters of HTL substantially influence the property and yield of bio-crude. Hydrothermal liquefaction according to Mishra *et al.* (2022), produced higher viscosity biocrude than pyrolysis, temperature, pressure and biomass to solvent ratio influence the bio-crude yield and the biocrude produced by HTL is more advantageous over pyrolysis except for higher yield and sulfur contents which could contribute to greenhouse gas emission.

This technique is mostly employed for the valorization of algae biomass due to its huge water content. Similarly to a typical pyrolysis process, an HTL technique could either be catalyzed or un-catalyzed. The process route for the development of bio-oil from HTL of lignocellulose biomass is as presented in Fig. 1. The HTL process according to Biller and Ross [76] is divided into three main processes as shown in Table 2.

Several researchers have made efforts in producing bio-oil with high quality using the hydrothermal liquefaction technique. The review of the state-of-the-art advancement in the process is as depicted in Table 3.

Since the viscosities of the produced crude bio-oil are similar to those of natural crude oil, the need to upgrade the physiochemical properties of the bio-oil obtained via the HTL technique is necessary. However, the presence of sulfur (S), nitrogen (N) and oxygen (O) in crude bio-oil are higher than those obtained in petroleum crudes, therefore, the high tendency for metals corrosion during bio-oil refining for improved fuel properties and catalyst poisoning are susceptible [88].

Table 1
Catalytic and non-catalytic pyrolysis of biomass.

S/N	Feedstocks	Temperature (°C)	Catalyst	Process description	Reactor	Observations	Refs
1	Maize stalk	420–580	Sand	Fast pyrolysis of maize stalk	Fluidized bed	Highest yield of 66 wt.% at 500 °C, immiscible in diesel, unstable and mild corrosion in copper and steel	[57]
2	Raw and torrefied pine wood	500 °C	HZSM-5	Effects of Torrefaction pretreatment and catalytic pyrolysis of pine wood were studied	Fixed-bed	Torrefaction process has an important effect on yield and bio-oil energy distribution with a decrease in oxygenated compound. The catalyst aids the formation of aromatic hydrocarbon selectivity	[58]
3	Pine wood	600 °C	Char/Fe	Catalytic pyrolysis of pine wood over char-supported Fe: Bio-oil upgrading and catalyst regeneration by CO ₂ /H ₂ O	Fixed bed	Acids, ketones, furans, etc.) in bio-oil were completely converted to aromatic hydrocarbons over char-supported Fe	[59]
4	maize straw	500 °C	core-shell ZSM-5@SBA-15 composite	Catalytic performance of core-shell catalyst for maize straw pyrolysis	fixed-bed	ZSM-5@SBA-15 catalyst significantly increased the production of phenols and hydrocarbons and suppressed solid (char+coke) formation.	[13]
5	Rice straw	450 °C	Catalytic (dolomite) and non-catalytic	Effect of Dolomite on Pyrolysis of Rice Straw	Fixed bed	The product yields and quality of the resultant bio-oil were significantly affected by the use of dolomite catalyst with high content of carbonyl and oxygenated compound in uncatalyzed bio-oil	[60]
6	Empty fruit bunch	500 °C,	–	Thermal pyrolysis of empty fruit bunch (EFB) in a vertical fixed-bed reactor	Vertical fixed bed	Maximum bio-oil yield of 46.20% was attained with gas and char yield of 21.79% and 32.01%, respectively at nitrogen gas flowrate of 300 cm ³ /min and 30 mins holding time	[61]
7	Sawdust	400–600 °C	–	Sawdust pyrolysis from the furniture industry in an auger pyrolysis reactor system for biochar and bio-oil production	Fixed bed	The bio-oil was found to mostly consist of oxygenated compounds such as organic acid, ketones, and guaiacols which indicated the need for upgrading	[62]
8	Brewer's spent grain	450–650 °C	–	An investigation on the pyrolysis of the main residue of the brewing industry where the effects of process parameter were studied	Fixed bed	The highest liquid yield (60.7%) which are mainly oxygenated were obtained at the pyrolysis temperature of 650 °C with a heating rate of 30 °C/min. High heating rates suppress dehydration reactions and favor bio-oil production.	[63]
9	Palm empty fruit bunch fiber	500 ± 20 °C	CaO, (MgO and ZnO	Effect of oxide catalysts on the properties of bio-oil from in-situ catalytic pyrolysis of palm empty fruit bunch fiber	Fixed bed	CaO showed the most favorable effects in terms of reducing the acidity of the bio-oil and anhydrosugar	[64]
10	wood sawdust	350–650 °C	–	Effects of process parameters on products yield and characterization of products on the pyrolysis of wood sawdust	Fixed bed	Maximum bio-oil yield was found as 44.16 wt% at temperature of 500 °C, heating rate of 50 °C/min and nitrogen flow rate of 100 cm ³ /min which are predominantly oxygenated compounds	[65]
11	Pine needles	350–650 °C	–	Effects of process parameters on products yield and characterization of products on the pyrolysis of pine needles	Fixed bed	Maximum bio-oil yield was found as 43.76 wt% at temperature of 500 °C, heating rate of 50 °C/min and nitrogen flow rate of 100 cm ³ /min which are predominantly oxygenated compounds	[66]
12	Rice straw and wheat straw	400–700 °C	MgO, CaO and ZSM-5	Effects of solid acid and base catalysts on pyrolysis of rice straw and wheat straw biomass for hydrocarbon production	Fixed bed	Carbonyls (oxygenated) were observed as major compounds under the non-catalytic condition. basic metal oxide are encouraged to formation of phenolics and ketones compound, while acidic catalysts enhances the formation of aromatic hydrocarbons	[67]

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Table 1 (continued)

S/N	Feedstocks	Temperature (°C)	Catalyst	Process description	Reactor	Observations	Refs
13	Corn cob, wheat straw, rice straw and rice husk	300–450 °C	–	Investigation of the effects of pyrolysis temperature and biomass type on the yield and composition of pyrolysis products	Fixed bed	Corn cob yielded the highest bio-oil of 47.3%. The nature of biomass materials affects the composition of the bio-oil produced whose contents are predominantly phenolic compounds	[68]
14	Oak	500 °C	HZSM-5 zeolite and a hierarchical zeolite	Characterization of heavy products via catalytic fast pyrolysis of biomass over microporous and hierarchical Zeolites	Microfluidized bed	Hierarchical zeolite catalyst resulted in higher deoxygenation and aromatization as the main modifications of the heavy compounds.	[69]
15	H ₂ SO ₄ modified cedar wood biomass	550 °C	–	Enhancement of bio-oil production via pyrolysis of wood biomass by pretreatment with H ₂ SO ₄	Fixed bed	Moderate acid pretreatment produced shorter chain units of cellulose, hemicellulose, and lignin, thereby facilitating the conversion into oil by pyrolysis with maximum oil yield of 46.8 wt%.	[70]
16	Commercial lignocellulosic biomass from beech wood	500 °C	ZSM-5	Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours	Fixed bed	Addition of Co in ZSM-5 is thus suggested to strongly enhance aromatization reactions that result in selectivity increase towards aromatics in the bio-oil produced.	[71]
17	Oil palm tree residues	500 °C	–	Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis	Fixed bed	Highest yield of bio-oil was obtained to be 43.50 wt%. Relative amounts of cellulose, hemicellulose, lignin, volatiles, fixed carbon, and ash in the samples affects bio-oil yield with highest energy density of 15.41 MJ/kg	[72]
18	Sugarcane Bagasse	300–800 °C	–	Properties of bio-oil and bio-char produced by sugar cane bagasse pyrolysis in a stainless steel tubular reactor	Tubular	The amount of liquid product (bio-oil) from pyrolysis of sugar cane bagasse increases with increasing the final temperature and decreases with increasing the heating rate. Highest product yield of 32.80 wt% was achieved at 550 °C and at the heating rate of 5 °C/min.	[73]
19	sugarcane bagasse	500 °C	Metals modified ZSM-5/Al-SBA-15	Pyrolysis of sugarcane bagasse for bio-chemicals production catalyzed by micro-mesoporous composite molecular sieves	Fixed bed	Ni-ZSM-5/Al-SBA-15 catalysts yielded a higher amount of liquid. The chemical compounds of liquid products contained furans, aliphatics, organic acids, phenols, aromatics and esters.	[73]
20	Woody biomass	450 °C	ZSM-5	Effect of different metal cations on the bio-oil final properties in a catalytic upgrading of biomass derived pyrolysis vapors over metal-loaded ZSM-5 zeolites	Fixed bed	Ni-ZSM-5 and Sn-ZSM-5 demonstrated significant improvement of the liquid in terms of lower viscosity and oxygen content, higher high heating value, a decrease of the acidic compounds and an increase in the aromatic fraction	[74]

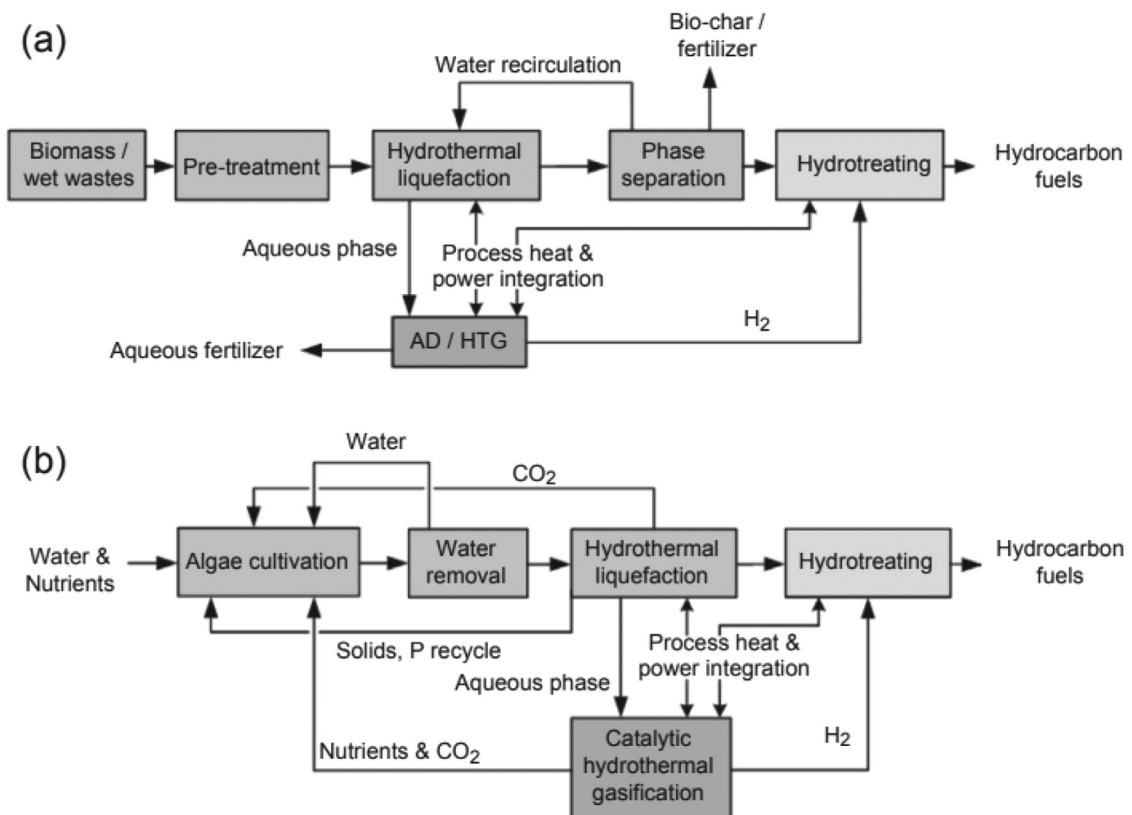


Fig. 1. HTL process flow diagram for (a) lignocellulose and (b) microalgae biomass [76] with permission.

Table 2

Classification of hydrothermal process according to conversion temperature [76].

Processes	Operating Conditions	Main product	Nature of Feed stock	Product's properties
Hydrothermal Carbonization (HTC)	180–250 (°C) and long residence times of typically several hours	Hydrochar or biocoal	Wet/dry biomass	Similar properties with low-rank coal. More energy-dense, more easily friable, and more hydrophobic than the starting material
Hydrothermal Liquefaction (HTL)	250–375	Biocrude; liquid fuel	Wet/dry biomass	The biocrude can be upgraded into a distillate range of petroleum-derived products
Hydrothermal gasification (HTG) or supercritical water gasification (SCWG)	Above 375	Syngas	Wet/dry biomass	Typically high in either H ₂ or CH ₄ with the presence of CO ₂

Effects of bio-oil physiochemical properties on biofuel performance

The bio-oil produced during the thermochemical conversion of biomass are associated with numerous compounds derived from both primary pyrolysis as well as the secondary cracking process; a formation of intermediates. The formations of these chemicals are linked to the product of the thermal cracking of the lignocellulose (which comprises of cellulose, lignin and hemicellulose) [94]. Van et al. [94] observed that the presence of different contents found in lignocellulose have resulted to its varied degradation profile, the activation energies, the degradation kinetic and therefore resulted to the formation of bio-fuels with different compositions. These compositions present in bio-oil obtained via pyrolysis process contain oxygen and water which are highly unfavorable for the direct use in automobile engines and hence, depict bio-oil with lower heating value. Bio-oils application as fuel in the internal combustion engine of automobile have been hindered due to its high content of oxygen and water, low calorific value, immiscibility with fossil fuels owing to its high polarity, poor stability and low storage time [95–98]. The formation of bio-oils with high oxygen content has been reported to aids corrosion during crude bio-oil processing and transport through pipeline coupled with microbial growth [98,99]. The increase in bio-oil viscosity during storage has been attributed to aging process [53]. The oxidation instability posed by high oxygen content during storage has hindered the effective storage of bio-oil for a long period of time. Hence, the presence of high oxygen

Table 3
Catalytic and non-catalytic hydrothermal liquefaction of biomass/algae biomass.

S/N	Feed stocks	Process	Conditions	Process	Description	Observations	Refs
		T (°C)	P	Reactor and contact time (min)			
1	natural hay, oak wood and walnut shell	240–320 °C	–	Tubular microreactor	Influence of temperature and biomass composition on the bio-oil production on the hydrothermal liquefaction of biomass	Phenolic compounds are the major constituents, while the other identified compounds were mainly alcohols, ketones and aldehydes. High lignin content favours bio-oil yield.	[77]
2	Barley straw	280–400 °C	350 bar	Fixed bed	Effects of reaction temperature and aqueous phase recirculation on the HTL of barley straw to biocrude oil	Low temperature favors bio-crude yield, with a peak of 34.9 wt% at 300 °C. The products formed were mainly oxygenates comprise of phenolics, carboxylic acids, aldehydes and alcohols. The HHVs of bio-crude oil from HTL with aqueous phase were 28.4–29.4 MJ/kg	[78]
3	<i>Amphiroa fragilissima</i> biomass	340–520 °C	5 MPa	60	Comparative study on oxygen content and storage stability parameters of bio-oil on the Hydrothermal liquefaction and pyrolysis of <i>Amphiroa fragilissima</i> biomass	The maximum bio-oil yield was HTL (28.9 wt%), HHV value increased by 1% HTL bio-oils stored in stainless steel container at 35 °C for time 60 days.	[79]
4	<i>Scenedesmus obliquus</i> biomass	200–340 °C	5 MPa	60	Effects of Process Parameters on Hydrothermal Liquefaction of Microalgae Biomass Grown in Municipal Wastewater	Maximum bio-oil yield of 24.57 wt% at 300 °C, 15 g/200 ml biomass load and 2.5 wt% NaOH at 60 min holding time. HTL bio-oil was upgraded and it resulted in 30.15 wt% yield with higher degree of C ₇ –C ₂₁ range hydrocarbons	[80]
5	Microalgae <i>Nannochloropsis</i>	350 °C	3.5MPa	60	Hydrothermal liquefaction of a microalga with heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO ₂ -Al ₂ O ₃ , CoMo/ γ -Al ₂ O ₃ (sulfided), and zeolite)	All the catalysts enhanced high yield of crude bio-oil from the liquefaction process in the absence of H ₂ but the elemental compositions and heating values of the crude oil (about 38 MJ/kg) were largely insensitive to the catalyst used.	[81]
6	Microalgae <i>Spirulina sp</i>	315–375 °C	10.98–12.03 MPa	20–60 min	Optimization to Hydrothermal Liquefaction of Low Lipid Content Microalgae <i>Spirulina sp.</i> via Response Surface Methodology	Optimum concentration, temperature, and holding time were obtained to be 10.5%, 357 °C, and 37 min, respectively with biocrude yield of 41.6 ± 2.2%	[82]
7	<i>Nannochloropsis gaditana</i> and <i>Chlorella sp.</i>	180–330 °C	1.38 MPa	30 min	Temperature effect on hydrothermal liquefaction of <i>Nannochloropsis gaditana</i> and <i>Chlorella sp.</i>	Maximum yields of 47.5% for <i>Nannochloropsis sp.</i> and 32.5% biocrude oil yields for <i>Chlorella sp.</i> Were obtained at 300 °C with HHV of crude bio-oil ranging from 34 to 39 MJ/kg.	[83]
8	<i>Cyanidioschyzon merolae</i>	180–300 °C	12	30 min	Hydrothermal liquefaction of <i>Cyanidioschyzon merolae</i> and the influence of catalysts on products	Maximum crude bio-oil yield of 16.98% without catalyst at 300 °C. The crude bio-oil yield increased to 22.67% when KOH was injected into the reaction mixture as a catalyst. The algal biocrude has a higher heating values (HHV) of 32.22 MJ /kg	[84]
9	<i>Scenedesmus obliquus</i>	220–370 °C	–	10–90	Application of hybrid-like supported catalyst to improve green fuel production through hydrothermal liquefaction of <i>Scenedesmus obliquus</i> microalgae and the study of HTL optimization parameters	Ni/AC-CeO ₂ hybrid like nanorods, not only the bio-crude yield would be improved by more than 9% but also the bio-crude could be upgraded to a green bio-based fuel.	[85]

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Table 3 (continued)

S/N	Feed stocks	Process	Conditions	Process	Description	Observations	Refs
10	<i>Nannochloropsis</i> sp and <i>Chlorella</i> sp.	220–300	0.6	30–90	Conversion efficiency and oil quality of low-lipid high-protein and high-lipid low-protein microalgae via hydrothermal liquefaction	Maximum higher heating values (HHV) of biocrude oil from both algae were ~37 MJ/kg and are majorly oxygenated compounds. The highest biocrude yield for <i>Nannochloropsis</i> sp. was 55% at 260. °C, 60. min and 25%. wt, and for <i>Chlorella</i> sp. was 82.9% at 220. °C, 90. min and 25%. Wt.	[86]
11	<i>Nannochloropsis</i>	240–360 °C	6 ~ 8 MPa	30 min	Hydrothermal liquefaction of microalgae over transition metal supported TiO ₂ catalyst	Hydrothermal liquefaction technique of <i>Nannochloropsis</i> over Ni doped TiO ₂ suggested that temperature of 300 °C led to a maximum biocrude yield of 48.23% with highest liquefaction conversion of 89.28%. The doping of Ni on TiO ₂ catalyst reduced the viscosity and yielded more light-fraction in biocrude and enhances total acid number (TAN)	
12	<i>Ulva prolifera</i>	260–300 °C	5.5–12 mPa	15–45 min	Products distribution and characterization from crude bio-oil obtained via HTL of macroalgae over various solids, basic or acidic oxides and metal salt catalyst	Maximum oxygenated biocrude yield of 35.1 wt.% was achieved with metal MgO catalyst in water solvent compared to the acidic (Al ₂ O ₃ , ZrO ₂ , and CeO ₂), salt (MgCl ₂ , FeCl ₃ , and CuCl ₂) and other basic (CaO and CaCO ₃) catalyst. Also, an appreciable HHV of 30.2–34.2 MJ/kg was achieved in catalytic	[87]
13	human feces	250–350 °C	30 MPa	0–720 min	Catalytic liquefaction of human feces over Ni-Tm/TiO ₂ catalyst and the influence of operating conditions on products	The addition of Tm/TiO ₂ catalyst increases biocrude yield from 53.16% with a reaction temperature of 330 °C, a holding time of 30 min to 89.61% and 36.64 MJ/kg HHV similar to those of conventional heavy crude oil.	[88]
∞	<i>Spirulina</i> (<i>Arthrospira</i>)	270 to 310 °C	10–18 MPa	30 min	Effects of reaction parameters on catalytic hydrothermal liquefaction of microalgae into hydrocarbon rich bio-oil in the presence of carbon nanotubes, CNTs based catalyst	Improved quality of crude bio-oil upon ethanol enhanced Co/CNT and Ni/CNT catalyst addition with maximum product yield of 43.6 wt% on Co/CNT due to the higher surface area possessed by the Co/CNT. Addition of catalyst materials enhanced the advanced deoxygenation and hydrogenation activities.	[89]
15	<i>Sargassum tenerrimum</i> (ST) macroalgae	260–300 °C	4.5–12 MPa	15 min	Effects of process parameter on product yield and characterization of macroalgae over solid base catalysts (CaO supported on CeO ₂ , Al ₂ O ₃ , and ZrO ₂)	The presence of water-ethanol co-solvent in non-catalytic HTL yielded high biocrude of 32.02 wt% at 280 °C. Also, the highest crude bio-oil yield of 33.0 wt% was obtained with higher conversion of 70.5% over CaO/ZrO ₂ of 10.0 wt% loading under water-ethanol co-solvent.	[90]
16	Red alga <i>Gracilaria corticata</i>	260–300 °C	4–15.5 MPa	15 min	Product yield improvement by optimization of process parameters via valorization of the red macroalga <i>Gracilaria corticata</i> by hydrothermal liquefaction	under a residence time of 15 min of HTL and 350 °C, 15.7 wt% yield of biocrude was obtained, with an HHV of 36.01 MJ/kg while the presence of organic solvent improved the product formation with high content of oxygenated compounds	[91]
17	Chlorella	350 and 405 °C	20.6 MPa	1.4 - 5.8 min	Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae	Over CoMo and CoNi catalyst, the HTL process resulted in nitrogen and oxygen content reduction of 60% and 85% at 405 °C, respectively. The upgrading of the biocrude result in approximately 25% gasoline, 50% diesel and 25% heavy fuel oil fractions.	[92]
18	<i>Azolla filiculoides</i>	260–300 °C		15–60 min	Role of temperatures and solvents on hydrothermal liquefaction of <i>Azolla filiculoides</i>	Introduction of ethanol increased the bio-oil product yield to 28.8 wt% at 280 °C and 60 min residence time majorly composed of nitrogenated, aromatics and oxygenated compounds.	[93]

Table 4
Physiochemical characteristics of bio-oil derived from varieties of biomass feedstocks.

Sample	Conversion Process	Physiochemical parameters									Refs
		C	H	O	N	S	pH	H/C*	O/C*	HHV (MJ/kg)	
yellow poplar	Pyrolysis	47.80	6.30	45.80	0.20	–	NR	1.57	0.72	NR	[104]
Maize Stalk	Pyrolysis	44.30	6.30	47.50	0.60	0.30	3.20	1.69	0.81	19.60	[57]
Sawdust	Pyrolysis	45.38±0.02	5.12±0.02	48.78±0.02	0.73±0.03	NR	NR	1.34	0.81	22.38±0.53	[105]
Pine wood	Pyrolysis	48.13	6.32	44.63	0.35	0.18	NR	1.56	0.70	18.57	[58]
Wheat husk	Pyrolysis	56.30	7.80	29.70	4.80	1.40	NR	1.65	0.40	26.00	[106]
Rapeseed cake	Pyrolysis	63.56	8.89	23.74	3.60	0.11	NR	1.67	0.28	26.70	[107]
Red Oak	Pyrolysis	59.40	5.20	35.30	NR	NR	NR	1.04	0.45	NR	[108]
Natural hay	HTL	80.70	4.30	15.00	NR	NR	NR	0.63	0.14	31.5	[77]
Oak	HTL	69.40	6.30	24.20	NR	NR	NR	1.08	0.26	27.5	[77]
Walnut shell	HTL	71.20	6.30	22.50	NR	NR	NR	1.06	0.24	28.50	[77]
Cellulose	HTL	67.40	5.30	27.30	NR	NR	NR	0.94	0.30	24.60	[77]

* =estimated from the reported O, C and H of the respected results using;

$$\frac{H}{C} = \frac{(\text{Weight percent of hydrogen})}{(\text{Atomic weight of hydrogen})} \div \frac{(\text{Weight percent of carbon})}{(\text{Atomic weight percent of carbon})} \quad (1)$$

$$\frac{H}{C} = \frac{(\text{Weight percent of oxygen})}{(\text{Atomic weight of oxygen})} \div \frac{(\text{Weight percent of carbon})}{(\text{Atomic weight percent of carbon})} \quad (2)$$

content in bio-oils decreases the fuel quality and its performance as transportation fuel which therefore retards its economic worth. Labeckas et al. [100] has reported the effects of physiochemical properties such as oxygen content of bio-oil on the combustion characteristics, ignition delay and cyclic variation. It was reported that oxygen should be kept at an appreciable level in bio-oil to improve low cyclic variation and ensure complete combustion. Therefore, there is need to upgrade the crude bio-oils into an economically viable fuel for use in the internal combustion engine of automobiles through effective and efficient method such as hydrodeoxygenation. Through bio-oil upgrading, several lignocellulose constituents such as cyclic ketones, phenolics compounds and primary aromatic hydrocarbons are converted to transportation fuels [26]. Due to the complex structural nature of biomass materials, different compositions of bio-oil are obtained such as sugar and furan which are products of depolymerization of cellulose and hemicellulose while lignin decomposition gives rise to the production of phenolics compound [101,102]. The nature of repolymerization reaction occurring in the cellulose and hemicellulose resulted in an increase viscosity, molecular content and water content in the produced bio-oil [103].

The effect of biomass feedstocks on the physiochemical properties of bio-oil was reviewed and it was observed that not only the operation conditions of pyrolysis process affects the bio-oil properties but also, the nature of biomass feedstocks. Table 4 and Table 5 show the physiochemical properties of bio-oil derived from varieties of agricultural biomass materials and algae feedstocks and their respective high heating value (HHV), respectively.

The high oxygen content (high organic acid) in bio-oil derived from biomass materials causes corrosion during storage and low heating value [109]. From the reviewed bio-oil as depicted in Table 1, the variation in physiochemical compositions are apparent; this variation could be as a result of the nature of biomass and the condition of pyrolysis process. Hence, the systematic selection of feedstock is an important factor for enhanced bio-oil production [109]. The large oxygen containing compounds found in bio-oil have been reported to contribute to the low thermal, low calorific value and chemical stability in bio-oil as compared to the conventional fossil fuels [110]. Therefore, the conversion of oxygenated compounds in bio-oil is of importance towards depicting bio-oil as an economic product for transportation industry.

The presence of small amount of acids such as acetic and formic acid in bio-oil have resulted in bio-oil being acidic in nature with pH between 1.85 and 6.1 [38]. The acidic pH is responsible for the corrosive behavior of bio-oil with surfaces such as aluminum and carbon still. Dehydration reaction which occurs during the pyrolysis reaction in biomass feedstocks is responsible for the presence of moisture in bio-oil. The presence of moisture in bio-oil has been reported by Gollakota et al. [38] to possess negative and positive impacts on fuel properties during combustion process. Adversely, the presence of moisture content lowers the flame temperature, increases ignition delay, decreases in combustion rate and lowers the heating properties of bio-oil while it benefits include the lowering of viscosity, enhances temperature uniformity in combustion engine, and retards the formation of NO_x emission; making it environmentally friendly. It is also important to determine the ash content of bio-oil; it is an important parameter which determines the degree of wears and also resulted to corrosion behavior [38].

The effects of bio-oil compositions on engine performance and emissions was studied by Yuan et al. [111] in a direct ignition diesel engine (DIDE). During the study, the bio-oil fractions were divided into three main compounds; sugars, hydroxyl compounds and aldehydes and the bio-oil fractions-based emulsion and the as-produced bio-oil were evaluated in diesel engine. The researchers reported that the presence of sugars enhances the formation of NO_x emission in as-produced bio-oil while a reduction was observed in emulsion derived from aldehydes and hydroxyl based bio-oil fraction. The presence of OH radicals are possible attribute to largest reduction of emissions during combustion process, hence, the presence of aldehydes and hydroxyl compounds are desirable for improved bio-oil quality for environmental friendly fuel [111].

Bio-oil or biocrude upgrading is carried out to improve the hydrogen/carbon ratio (H/C). Several techniques have been adopted by various researchers towards biocrude refining. Examples of such techniques include hydrotreating, hydrocracking,

Table 5
Physiochemical characteristics of biocrude oil derived from algae feedstocks.

Feedstocks	Conversion Process	Physiochemical parameters							Nature of sample	Refs	
		C	O	H	N	S	H/C*	O/C*			HHV
<i>Sargassum tenerrimum</i>	NC- HTL	53.7	33.3	6.3	5.6	0.4	1.40	0.47	22.4	Dry basis	[90]
<i>Sargassum tenerrimum</i>	C-HTL	58.7	26.6	8.1	3.1	0.3	1.64	0.34	27.9	Dry basis	[90]
<i>Azolla filiculoides</i>	C-HTL	–	–	–	–	–	–	–	–	Dry basis	[93]
<i>Ulva prolifera</i>	MgO-ethanol-HTL	66.2	18.6	7.4	6.2	–	1.33	0.21	34.2	–	[87]
<i>Ulva prolifera</i>	MgO-HTL	64.2	19.2	7.5	6.8	–	1.39	0.22	33.6	–	[87]
<i>Ulva prolifera</i>	Al ₂ O ₃ -HTL	60.8	23.8	7.1	6.5	–	1.39	0.29	30.8	–	[87]
<i>Ulva prolifera</i>	MgCl ₂ -HTL	62.5	24.8	7.2	7.0	–	1.37	0.30	30.2	–	[87]
<i>Nannochloropsis</i> sp.	NC-HTL	43.0	22.8	5.97	6.32	0.58	1.65	0.40	18.5	Dry basis	[81]
<i>Nannochloropsis</i> sp.	Pt/C-HTL	75.9	8.48	10.8	4.04	0.72	1.70	0.08	39.6	Dry basis	[81]
<i>Nannochloropsis</i> sp.	H-Pt/C-HTL	76.1	8.34	11.1	3.92	0.62	1.74	0.08	40.1	Dry basis	[81]
<i>Nannochloropsis</i> sp.	Zeolite-HTL	69.6	9.46	9.44	4.33	0.74	1.62	0.10	35.4	Dry basis	[81]
<i>Nannochloropsis</i> sp.	NC-HTL	74.0	9.5	10.2	5.4	–	1.64	0.10	31.5	Dry basis	[86]
<i>Chlorella</i> sp.	NC-HTL	75.6	11.5	12.0	0.3	–	1.89	0.11	34.2	Dry basis	[86]
<i>Scenedesmus obliquus</i>	Ni/AC-CeO ₂ - HTL	72.62	9.77	10.4	6.66	<0.5	1.71	0.10	37.86	Dry basis	[85]
<i>Spirulina microalgae</i>	Co/CNT-HTL	64.2	19.7	7.36	5.8	–	1.37	0.23	33.6	Dry basis	[89]
<i>Spirulina microalgae</i>	Fe/CNT-HTL	58.5	27.8	6.90	5.6	–	1.41	0.36	29.8	Dry basis	[89]
<i>Spirulina microalgae</i>	Ni/CNT-HTL	56.5	28.8	7.12	6.5	–	1.50	0.38	29.2	Dry basis	[89]
<i>Cyanidioschyzon Merolae</i>	NC-HTL	74.53	12.41	4.65	7.37	1.04	0.74	0.13	32.22	Dry basis	[84]
<i>Cyanidioschyzon Merolae</i>	CH ₃ COOH-HTL	74.0	9.27	8.37	6.26	2.10	1.35	0.09	33.36	Dry basis	[84]
<i>Cyanidioschyzon Merolae</i>	H ₂ SO ₄ -HTL	70.75	19.06	4.0	3.72	2.47	0.67	0.20	33.76	Dry basis	[84]
<i>Cyanidioschyzon Merolae</i>	KOH-HTL	76.80	11.46	5.11	5.74	0.86	0.79	0.11	33.66	Dry basis	[84]
<i>Cyanidioschyzon Merolae</i>	NaOH-HTL	74.03	12.91	6.97	5.07	1.02	1.12	0.13	32.89	Dry basis	[84]
<i>Spirulina</i> sp	CCM-HTL	72.37	10.64	9.28	7.16	0.56	1.53	0.11	36.0	Dry basis	[82]
<i>Chlorella</i>	CoMo-HTL [duration of 5.8 min]	72.8	11.1	9.4	6.0	0.8	1.54	0.11	36.1	Dry basis	[92]
<i>Chlorella</i>	CoMo-HTL (duration of 1.4 min)	68.0	16.2	8.9	6.1	0.8	1.56	0.23	32.9	Dry basis	[92]

CCM = Complex catalyst mix.

NC = No catalysts.

NR = Not reported.

* =estimated from the reported O, C and H of the respected results.

thermal cracking (coking i.e. carbon rejection processes) and FCC. The high heating value of bio-oil is important parameter which determines fuel performance. The HHV obtained from Tables 4, 5 were found to range between 18.57–37.86 MJ/Kg while the highest H/C ratio of 0.15 was obtained via the catalytic HTL of *Nannochloropsis* sp. under the influence of H-Pt/C catalyst [81]. It was observed that the adoption of HTL process promotes high HHC over pyrolysis techniques. Interestingly, the use of carbon nanotubes support material as catalyst support favours the achievement of high HHV when HTL technique is used. Comparatively, petroleum crude oil possesses a HHV between 41 and 48 MJ/kg and therefore, efficient refining techniques are required to upgrade crude bio-oil into an acceptable specification [112]. Therefore, the need for upgrade of biocrude into renewable biofuel is of importance to meet the increasing energy demand.

Upgrading of bio-oil

The presence of large oxygenated compounds, high viscosity, high density, high water content, low calorific values, low H/C ratio, instability and corrosion properties of bio-oil derived from pyrolysis and HTL processes have necessitated the need for conversion process to meet energy requirement and to further project bio-oil as an economic product capable of mitigating greenhouse gas effects. Several techniques have been widely reported in literature and under this chapter, insights into the various methods are presented and emphasis is placed on hydrodeoxygenation process due to its efficiency and performance [26,32,113–115]. The presence of low content of H/C ratio in bio-oil as compared to conventional fuel (petroleum) is due to the presence of high content of oxygen molecules found in biomass feedstocks. Removing or reducing the oxygen content is a very important task to promoting biofuel as efficient fuel with excellent properties and performance [38,75].

Hydrodeoxygenation technique

Upgrading of bio-oils and model compounds into transportation fuels via catalytic hydrodeoxygenation (HDO) requires the application of catalyst in the presence of hydrogen towards the removal/reduction of oxygen content to meet the drop-in fuel requirements [115]. Details of several hydrodeoxygenation processes of lignin and model compounds are presented in

this review. The application of catalytic hydrodeoxygenation techniques has attracted interest of researchers due to its effectiveness and efficiency to obtaining high grade biofuel. During the catalytic HDO process, between the reaction temperatures of 100–300 °C, alcohols are formed from the conversion of carboxyl and reactive carbonyl functional groups and cracking at elevated temperature. On this basis, several optimization techniques have been adopted for the improved optimized process of operation such as reaction temperature, residence time, catalyst loading, hydrogen pressure, solvent to feed ratio.

The effects of temperature on the conversion and selectivity of bio-oil/lignin model compounds and deoxygenated bio-fuel have been widely investigated. Mukherjee [116] investigated the effects of temperature (100–160 °C) over the bimetallic (Cu-Ni/CeO₂-SiO₂) towards the conversion of vanillin, a model bio-oil compound to vanillyl alcohol and 2-methoxy-4-methylphenol. It was reported that lower reaction temperature yielded vanillin conversion below 50% and higher selectivity of vanillyl alcohol than 2-methoxy-4-methylphenol at 12 h residence time and 25 bar H₂ pressure. At these constant operating pressure and reaction time, an increase in temperature resulted to a corresponding increase in percentage conversion until a steady state condition was observed at 150 °C. Although equal selectivities of vanillyl alcohol and 2-methoxy-4-methylphenol were observed at a temperature of 115 °C while increase in temperature above 115 °C resulted to an improved selectivity of 2-methoxy-4-methylphenol over vanillyl alcohols [116]. The possibility of converting the obtained 2-methoxy-4-methylphenol compound was conducted by Dang [117] who carried out the effect of temperature on the HDO of 2-methoxy phenol towards the production of “drop-in” fuel cyclohexane within 200–300 °C reaction temperature as compared to the report by Mukherjee [116]. It could be inferred from the report of Mukherjee [116] that lower temperature range resulted to production of oxygenated compound, a phenolic fraction contained in bio-oils derived from lignin which requires further treatment to produce a cyclohexane, a candidate for transportation fuel. Dang [117] reported that an increase in temperature at H₂ pressure ranges from 0.1 to 2.5 MPa over several catalyst mix were observed to increase the selectivity of cyclohexane and also increases the conversion of 2-methoxy phenol conversion from 85 to 100% at a temperature between 200 and 250 °C. Furthermore, the formation of reduced selectivity was observed at higher temperature between 250 °C to 300 °C while coke formation which retards catalyst performance was observed at temperature above 350 °C as observed by the report of Zhang et al. (2019). Also, Hu et al. [21] reported the selective organic phase hydrodeoxygenation of typical phenolic monomers and two lignin oils over highly active Pd/H β catalyst for high-grade bio-fuel production where the effects of operating temperature was investigated. Hu et al. [118] reported the HDO process over Pd/H β catalyst where an increase in temperature from 160 to 220 °C favoured an appreciable increase in guaiacol conversion and selectivity of cyclohexane formation. 100% conversion of guaiacol was observed at HDO temperature of 220 °C and cyclohexane was identified as the major product. This products include [1,1',4',1'']Tercyclohexance, 1,1' -bicyclohexyl, and (cyclopentylmethyl)cyclohexane, unlike the formation of cyclohexane as the main product during the treatment at low reaction temperature.

The mechanism of HDO leading to the removal of water molecule is as presented in equation [1].



The presence of $-(\text{CH}_2\text{O})-$ represents the carbohydrate content in bio-oil, H₂ represents the introduced hydrogen gas (this could be introduced via co-pyrolysis with polymeric materials as co-feed).

Polymerization reaction is the main identified conversion route for obtaining biofuels and phenolic compounds from lignin containing feedstocks. During the pyrolysis process of bio-oil production, several oxygenated products as contained in Fig. 2 are obtained. The compositions of the obtained bio-oils are found to depend on either the lignin source.

During the catalytic hydrodeoxygenation process, dehydration, water separation, decarboxylation (removal O₂), hydrogenation (saturation of unsaturated components of carbohydrates), hydrogenolysis reaction (C–O bonds breakage for oxygen release to form water) and hydrocracking reaction (formation of smaller molecules due to the breakage of high molecular components in the crude bio-oil) take place [119]. From these chains of reactions occurring during the hydrodeoxygenation process, oxygen molecules are removed from the carbohydrate components of the crude bio-oil through the formation of water molecules (Fig. 3). The quality and the yield of the obtained bio-fuels obtained via catalytic HDO process depends on residence time, temperature, solvent, reactor's configurations, pressure and the nature of catalyst. Of all the factors itemized, the need to develop an effective catalyst material for effective HDO of bio-oils is of paramount importance to material researchers.

Techniques of catalyst mix for the hydrodeoxygenation of bio-oil into transportation fuel

Hydrodeoxygenation is the process by which oxygen from oxygenated bio-oil obtained from pyrolysis process are removed in the form of H₂O, CO and CO₂ to obtained an economical biofuels which are capable of being used as transportation fuel. The presence of several components of compounds in bio-oil (Fig. 2) has made its modeling difficult towards understanding the mechanisms of aromatics and alkenes formation.

Mono-metallic catalyst

Globally, the application of several transition metals and noble metals as active part of catalysts has received tremendous attention from researcher. This tremendous interest could be due to the active properties possessed by transition metals

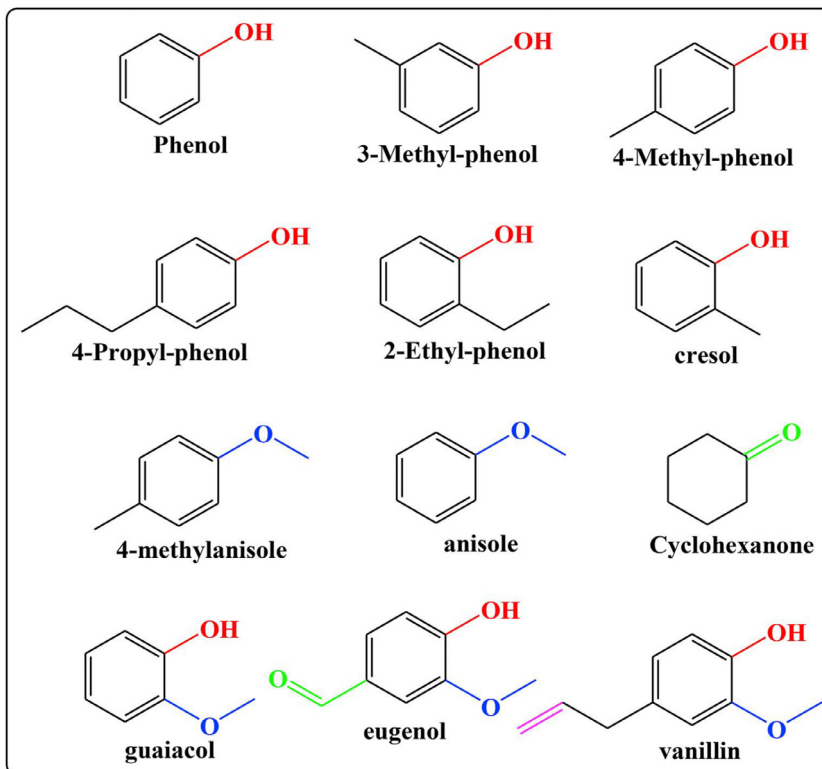


Fig. 2. Compositions of lignin derived bio-oils [119].

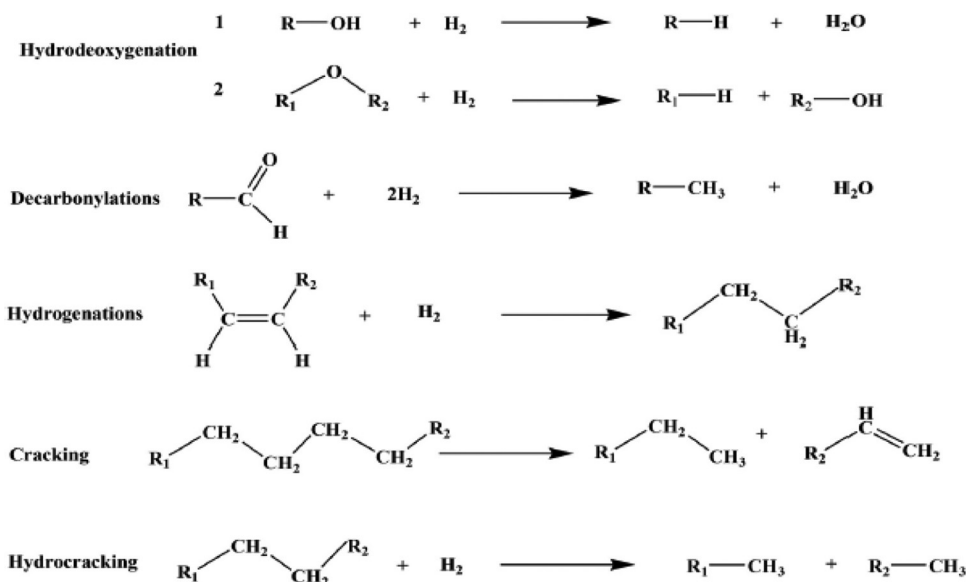


Fig. 3. Possible reaction routes of HDO process [120].

owing to their variable oxidation states and their ability to for a synergy with support materials in areas of catalysts' applications. Such metals that are mostly used as active part of catalyst materials include Fe, Co, Mo, Pt, Pd, and Ni. Basically, the application of metallic catalyst requires the incorporation of noble support materials (such as CaO, Al₂O₃, TiO₂, MgO, SiO₂) that serve as an anchor upon which the active part of the catalyst is being spread. It is interested to state that the application of metals as active part of catalyst resulted in the formation of oxides or complexes during the synthesis stage.

Zhao et al. [17] employed the use of iron (Fe) in several homogeneous and heterogeneous catalyst such as NaOH, Na₂CO₃, FeS and MgO in a mixed additive towards thermal liquefaction of bio-oil. The yield of the hydrothermal liquefaction of woody biomass sample was reported to appreciate at a temperature of 300 °C for a period of 30 min with biomass/water ratio of 1:10. It was reported that the introduction of Fe during the hydrodeoxygenation reaction of the bio-oil promotes the yield of the bio-oil product. It was further obtained that the synergistic effects of mixed additives of iron (Fe) with base catalyst of FeS and Na₂CO₃/NaOH improved the yield of bio-oil. It could be inferred that the activity of catalyst performance of metallic catalyst increases with doping with support materials which could be either a homogenous or heterogeneous mix formation [17]. The findings depicted about 12.02% bio-oil yield increment while loading the HTL with 10 wt% Fe loading (24.81 to 36.82 wt% for non-catalytic feedstock and the one catalyzed with 10 wt% of Fe, respectively).

Zitouni et al. [121] reported the production of bio-jet fuel range hydrocarbon from catalytic hydrodeoxygenation of biobased materials over Ni/SiO₂-ZrO₂ catalyst. The influence of Ni catalyst on the formation of biojet fuel range HC from the feedstocks was investigated and 65% of C₁₃-C₁₆ HC was obtained. This was observed during the hydrodeoxygenation process at 280 °C operating temperature over 0.2 g Ni/SiO₂-ZrO₂ (Si/Zr = 1, 3, 5) as catalyst, 2 MPa of H₂ pressure at 800 rpm for a residence time of 24 h. The product selectivity was evaluated using Eq. (1) where Cp indicates the product content obtained from the HDO reaction.

$$Cp = \frac{nCp}{\sum nCp} \times 100 \quad (2)$$

The application of Ni based bifunctional catalyst was further investigated towards bio-aviation fuel production from hydroprocessing of castor oil [44]. Several catalyst formulations were prepared via impregnation method by varying different ratio of Si/Al over Ni catalyst. Hydrodeoxygenation reaction condition adopted for the castor oil conversion was carried out at 300 °C, 3 MPa of H₂ pressure at flowrate of 160 mL/min for a period of 2 h Liu et al. [44] observed a little low density from the blending of the produced biojet fuel with conventional aviation fuel. This reduction in density following the blending ratio was linked to the absence of cycloalkanes hydrocarbons. The report further revealed that the obtained HDO biojet fuel shows no oxygen content. The reported methodology for hydrodeoxygenation (single-point and 2-step processes) of the obtained biojet fuel is stressful, time consuming and could be expensive due to the series of adopted technique. In addition, the feedstock used was first-generation bio-oil having tendency to compete with agricultural land use for arable crops.

Bi-metallic catalyst for HDO of bio-oil

Combining two transition metals in a matrix to form an active part of catalyst material have been found to improve catalyst activities by combining-effect approach. The adoption of this technique has been widely employed by several researchers to catalytically hydrodeoxygenate bio-oil into a more useful and economical product such as phenol, furfural and bio-jet.

Itthibenchapong et al. [122] have reported the efficiency of Ni-MoS₂/gamma alumina catalyst toward the deoxygenation of palm kernel oil to jet fuel range hydrocarbons. Using thiourea solution for the synthesis of the catalyst, a semi-amorphous material with size ranging from 5 to 10 nm was obtained. The researchers reported 58% selectivity of C₁₀-C₁₂ biojet fuel HC when the palm kernel oil was deoxygenated at a temperature of 200 °C at H₂ pressure of 30–50 bar. The efficiency of the catalyst was linked to the sulfided introduction into the catalyst matrix. Similar observation of catalyst improvement was observed by Eller et al. [123] who worked on the advanced production process of biojet fuel components from graded oil derived from coconut. Hydrodeoxygenation process was adopted for the conversion of bio-oil to biojet fuel under the application of sulfided NiMo supported aluminum oxide catalyst at a temperature range of 280–380 °C, 30 bar hydrogen pressure and residence time ranging from 1 to 3 h. Eller et al. [123] observed the most favourable conditions that produced a biojet fuel containing saturated-straight chain HC, free of aromatic and olefin at 360 °C, 30 bar H₂ pressure residence time of 1 h. Also, the product yield was observed to increase from 0.5 to 2.0% when dimethyl-disulfide was injected. The main disadvantage accompanied this technique of sulfide injection was that, about ≤ 2 mg/kg and 7–9 mg/kg sulfur was reported to be present when H₂S and dimethyl-disulfide were injected into the hydrodeoxygenation process, respectively. Therefore, the introduction of dimethyl-disulfide during the upgrade process reasonably improves the product yield but adversely impacted the biojet fuel's properties/quality as regards its environmental acceptability due to the presence of sulfur which is capable of contributing to greenhouse gas emission.

Metal oxides nano-catalyst

The areas of application of metal oxides such as MgO, ZrO₂, TiO₂, ZnO, CeO, Fe₂O₃, SiO₂, NiO and SnO are well known in areas of physical, chemistry and majorly, materials science. This is due to their ability to form novel structural geometry having electronic structures capable of exhibiting properties such as semi-conductor, insulators, as well as metal. The application of metal oxides as catalyst materials in several areas of applications are well documented in literature. These novel properties exhibited by metal oxide catalyst are mainly due to their high density and nanosized level [124,125]. Several methods have been reported for the synthesis of metal oxides catalyst in literature such as chemical/solution approach, physical vapor deposition, milling and lithography.

In the view of the excellent properties of metal oxide nano-catalyst, researchers in the field of renewable energies development have synthesized and utilized several metallic oxides to improve the thermochemical conversion efficiencies of bio-oils into a more useful fuel for transportation purposes. The application of Al₂O₃ - TiO₂ oxides mixed has been investigated by Ooi et al. [95] towards catalytic deoxygenation of bio-oils to produce biofuel. According to Ooi et al. [95], the

Table 6

Shows the review of some catalyst support used for the hydrodeoxygenation of bio-oil to fuel.

S/N	Feedstock	Conditions of HDO process	Catalyst used	Findings/observations	Refs
1	Rape seed oil	300 °C operating temperature, 3.5 MPa H ₂ pressure for a period of 4 h	NiMo/TiO ₂ (Ni=3.3% and Mo=15%)	100% conversion of rape seed oil during HDO over NiMo/TiO ₂	Kubička et al. (2014)
2	Palm Olein oil	340–420 °C operating temperature, 50 bar H ₂ pressure for a period of 1 h	CoP/porous carbon	100% conversion of the bio-oil to HC fuel mainly a mixture of bio-jet fuel and green diesel with biojet fuel selectivity of 26.9% and 58.0% selectivity to green diesel formation	Kaewtrakulchai et al. (2020)
3	Palm oil	300 °C operating temperature, 5 MPa H ₂ pressure	Co _y /Al ₂ O ₃	Catalytic activities resulted to more than 90% HC yield at 10% Co loading	Srifa et al. (2015)
4	Rape seed oil	300 °C operating temperature, 3.5 MPa H ₂ pressure for a period of 4 h	NiMoS/SiO ₂ (Ni=3.3% and Mo=15%)	100% conversion of rape seed oil with little selectivity to HC	Kubička et al. (2014)
5	Pipe sawdust bio-oil	300 °C operating temperature, 3.45 MPa H ₂ pressure for a period of 5 h	FeCo/SiO ₂	22.4% HC selectivity with an improvement in the acidic medium following the incorporation of FeCo into the SiO ₂ matrix	[105]

choice of support materials during the upgrade of bio-oil enhances the maximum acid strength to promote the C–O bonds hydrogenolysis. It was noted that the use of Al₂O₃ as catalyst supported has attracted attention owing to its high acidic content. The presence of high acidic content in Al₂O₃ favours the formation of coke deposition then renders it unstable and therefore, promotes the deactivation of the catalyst (Table 6).

Dispersion of supported catalyst

Several studies have reported the use of wet impregnation method (this is a technique where excess metal solutions are in contacts with the pores of porous supports materials through diffusion) as an effective methods of catalyst synthesis over other methods to enhance the distribution and dispersion of supported catalyst for hydrodeoxygenation process. This technique of catalyst support via transition metals or noble metals using impregnation method helps in promoting not only the effective distribution of the part(s) of the catalyst on the support materials but catalyst stability, homogeneity, products selectivity and catalyst activity in a typical hydrodeoxygenation process [1]. Active catalyst materials such as transition, noble and non-noble metals have been widely employed for the development of catalyst towards hydrodeoxygenation process of bio-oils conversion into an economical transportation fuels. Several factors such as activation time, calcination temperature and calcination time affects the distribution of active catalyst parts on the porous supports during the wet impregnation method via improved diffusivity. The calcination process and doping technique are one of the most important factors that aid the dispersion, formation of oxides and the removal of nitrogenous gaseous compounds from the bulk of the catalyst materials during catalyst preparation stage [126].

Mechanism of bio-oil formation

The understanding of the mechanisms of hydrocarbon formation through the application of HDO process requires the study of bio-oil model compounds due to the presence of numerous compounds in biomass materials. The presence of several oxygenates present in biomass materials have necessitated the study of model bio-oil to understand the mechanisms in order to effectively define the best process route and parameters which favours high selectivity to aromatics formation. Under this chapter, guaiacol and vanillin model bio-oil reviewed for mechanistic study.

Guaiacol compound

Guaiacol, a composition having the highest percentage in lignin compounds, a representation of lignin, is a model lignin compound which comes from coniferyl alcohol and its used to understand the composition of biomass materials during a pyrolysis or gasification process [127].

The application of several bio-oil model compounds has attracted attention of researchers towards producing high quality transportation fuel. Such model bio-oil include guaiacol, anisole, phenol, cresol, eugenol, vanillin, methyl-guaiacol, o-cresol, and syringol. The hydrodeoxygenation of guaiacol as a model bio-oil over zirconia-supported Rh and NiMoPs catalysts have been studied by He et al. [128,129]. The guaiacol bio-oil model compound possesses a similar compound having large compounds with that of molecular structure of a typical phenyl ring. The phenyl ring was reported to compose of oxygenated functional groups. The process of catalytic hydrodeoxygenation of guaiacol was conducted at a temperature range of 150–350 °C, pressure of 3–7 MPa of hydrogen flow in Rh/ZrO₂ catalyst. The conditions of HDO process such as hydrogen pressure, reaction time, temperature and reactant concentration were optimized. At optimum conditions of 5 wt% of guaiacol, 300 °C temperature, a pressure of 7 MPa of hydrogen and 1 h reaction time yielded a cyclohexane, a deoxygenated compound with 87.7 mol% having an improved O/C and H/C ratio suitable for transportation fuel was reported. The findings reported

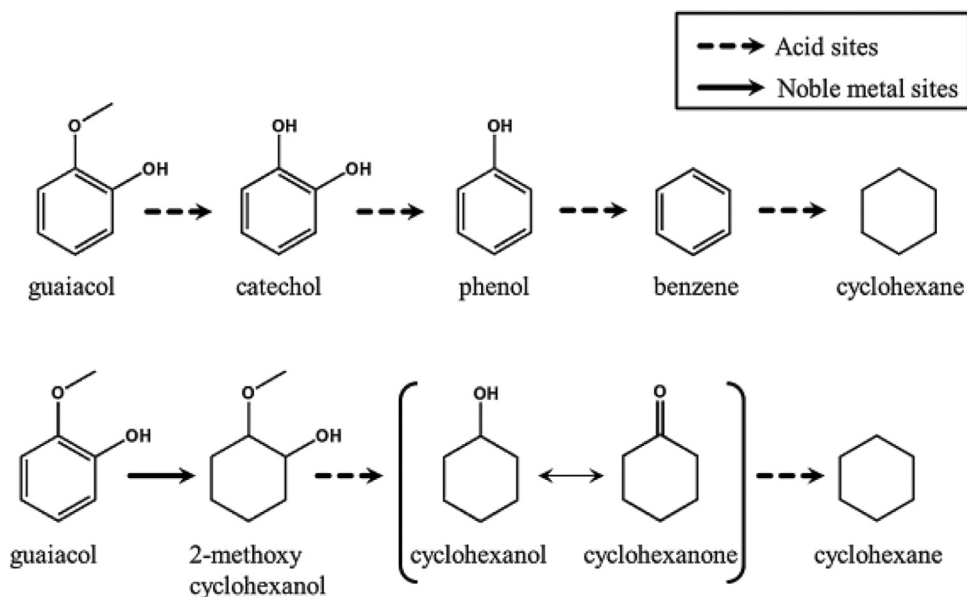


Fig. 4. Hydrodeoxygenation pathway on (a) acid catalyst (b) noble metal catalyst with acid support [22].

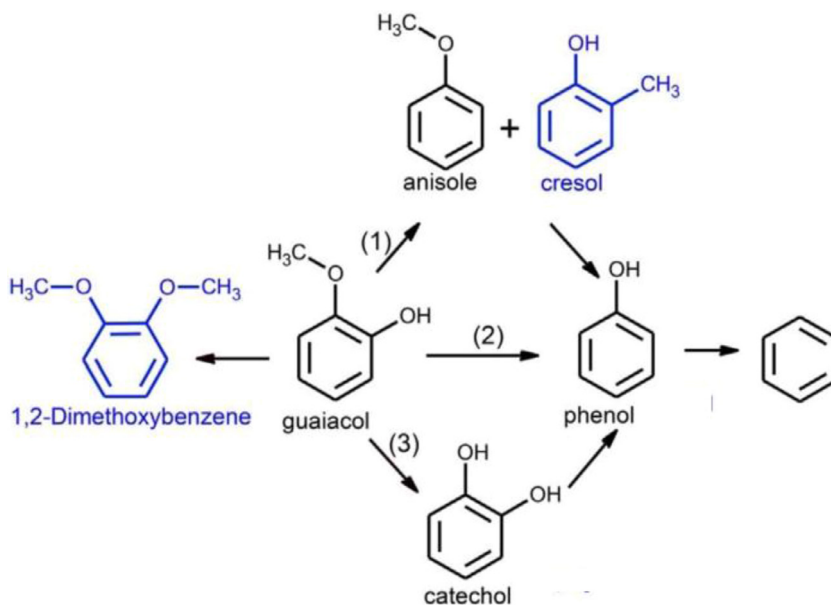


Fig. 5. Mechanisms of catalytic conversion of guaiacol into value added products for transportation [131,132].

3.33% pore volume reduction after the reused of Rh/ZrO₂ catalyst at 5 wt% guaiacol, at 350 °C, 7 MPa and 4 h operating condition. Furthermore, He et al. [128] presented the transformation of guaiacol to 1-methyl-1,2-cyclohexanediol and then cyclohexanone and cyclohexanol (Fig. 6a-b), a completely deoxygenated compound (Fig. 4).

Explicitly, the possible conversion of guaiacol to various aromatic hydrocarbons has been summarized by the report of [130] depending on the nature of the employed catalyst as shown in Fig. 5.

From Fig. 5, three major reaction pathways of guaiacol conversion to cyclohexane have been proposed. The first route [1] indicated the possible conversion of guaiacol into anisole and cresol which is further converted into phenol through successive demethylation and dihydroxylation process [132]. It's worth mentioning that the formation of cresol via reaction route [1] is termed an intermediate through transalkylation of anisole in Brønsted acid sites of the catalyst particles (P-OH). This observation was not obtained from the report of [130] through the hydrogenation conversion of guaiacol over Ni₂P/SiO₂ catalyst. Therefore, the mechanisms of guaiacol conversion into cyclohexene could be said to be catalyst dependence and the conditions of operation [109].

Roldugina et al. [133] reported the hydrodeoxygenation of guaiacol as a model compound of bio-oil in methanol over mesoporous noble metal catalysts. Several catalyst-mixes were developed; PtPd and Ru of bimetallic and monometallic catalysts, respectively supported on mesoporous aluminosilicate and mesoporous zirconia-silica and were tested for their ability to convert guaiacol into a useful biofuel for transportation use. The report further investigated the effect of temperature, catalyst loading, contact time, solvent/guaiacol ratio on the catalytic performance of HDO process. A decrease in Si/Al ratio was found to improve the catalyst acidity which further corresponds to an appreciable increase in the performance conversion of guaiacol. As regards the catalyst loading effect towards the conversion of oxygenated guaiacol into deoxygenated cyclohexane and methylcyclohexane, an increase in catalyst loading favours the selectivity for cyclohexane. Also, the conversion of guaiacol with high selectivity for cyclohexanes (78%) was reported for Ru/Al-HMS(10) in methanol solution at HDO condition of 200 °C reaction temperature and H₂ pressure of 5 MPa. The findings reported that acidic site, catalysts loading and metal sites play important role in deoxygenation of guaiacol into a useful biofuel. Table 7 depicts the HDO of guaiacol model compound for enhanced bio-fuel production.

From Table 4, Activity and selectivity of Ni supported catalysts (serial no10–13) as reported by Griffin et al. [137] indicated that the selectivity and conversion of guaiacol to cyclohexane product are not favourable as compared to phenol. The catalysts were evaluated in a typical packed bed reactor at the temperature of 350 °C, reaction time of 3 h and hydrogen pressure of 0.44 MPa. It was observed that the conversion of guaiacol is support dependent. From the findings, it could be inferred that the high conversion is favoured with support materials having acidic properties i.e. Al₂O₃ and TiO₂. Hence, the below deductions are made from the report of [137] on the dependency of acid site density of the conversion of guaiacol and selectivity of phenol and cyclohexane under a packed bed reactor;

Conversion of guaiacol: Al₂O₃ and TiO₂ > Carbon > MgO
 Selectivity for phenol: MgO > Carbon > TiO₂ > Al₂O₃

Vanillin compound

Vanillin is one of the compounds found in a typical biomass lignin molecule and a source of phenolic compound formation with a molecular formula of C₈H₈O₃ which aid the formation of high-quality biofuel for possible application in transportation sector. The functional groups embedded in the phenolic aldehyde which accompanied vanillin include hydroxyl, aldehyde and ether. Vanillin, an aromatic aldehyde compound contains a carbonyl group that is responsible for the thermodynamic instability of bio-oil [131].

Mild-temperature hydrodeoxygenation of vanillin, a typical bio-oil model compound to creosol, a potential future bio-fuel has been reported by Aliu et al. [138]. The findings investigated the HDO of oxygenated vanillin compound, a phenolic based compound over various metallic catalyst such as Pd/C, PdRh/Al₂O₃, Pd/Al₂O₃, Pt/C, Pt/SiO₂ and Rh/Al₂O₃. The process conditions for the HDO of vanillin was optimized by varying the hydrotreating temperature, H₂ gas pressure, catalyst loading and agitation speed of 318 K–338 K, 1 MPa– 3 MPa, 0.1 kg/m³ – 0.5 kg/m³ and 500 rpm – 900 rpm, respectively via Taguchi approach. Aliu et al. [138] reported that monometallic catalyst, Pd/C has the highest performance of about 71% creosol selectivity with about 9 mmol of H₂/mol of vanillin conversion while bimetallic PdRh/Al₂O₃ catalyst 99% selectivity of creosol selectivity with a lower hydrogen consumption; 8 mmol of H₂/mol of vanillin conversion was obtained to that of monometallic catalyst reported. The optimized conditions that give the highest performance for the deoxygenation of vanillin to potential future biofuel were obtained to be 338 K, 3.0 MPa, 0.5 kg/m³ and 500 rpm for temperature, hydrogen gas pressure, catalyst loading and agitation speed, respectively. The high performance depicted by the catalyst materials was associated with its reduced particle sizes, excellent surface area and larger metal dispersion on the surface of the support materials. The observable increase in percentage selectivity to creosol was attributed to the synergetic effect between the Rh and Pd over Al₂O₃ in the bimetallic catalyst mix. Adversely, Pt/SiO₂ depicted a reduction in creosol selectivity although no coke formation was reported in this catalyst but the possibility of leaching of Pt during the conversion process, agitation process and also the reduction in the Pt strength were attributed to this performance. Mild temperature (318–338 K) favours the catalysts performance by reducing the formation of coke on the micropores of the support materials and also minimizes the formation of gaseous products while increase in temperature increases the percentage conversion [138]. Table 8 shows the HDO of vanillin model compound for the production of biofuel in a batch reactor system while Fig. 6 depicts the proposed reaction path for the production of biofuel range aromatics from vanillin.

Ni-supported catalyst for catalytic HDO process

Nickel containing catalyst are excellent dopants for deoxygenation of large molecular compounds found in bio-oil to obtain an economic product having reduced oxygen content for possible application in the transportation sector [140,141]. The application of Sulfur-free Ni supported on H-Y zeolites has been reported by Hachemi et al. [142] to exhibit excellent catalytic properties. Li et al. [143] worked on the Coke formation on the surface of Ni/HZSM-5 and Ni-Cu/HZSM-5 catalysts during bio-oil hydrodeoxygenation process and reported that the introduction of Nickel on the HZSM-5 catalyst promotes the catalytic hydrodeoxygenation process by through bi-functional acidity formation. During the process of HDO process, nickel has the tendency to inhibit the formation of hydrocarbon polymerization by activating the hydrogen formation during the process. The research further reported the ability of the Cu as co-dopants on HZSM-5 catalyst to enhance the degree

Table 7
Hydrodeoxygenation of Guaiacol bio-oil model compound for advanced biofuel production.

S/N	Catalyst	feedstock	HDO Condition					Product with highest percentage	Percentage		Refs.
			Temperature (K)	Residence time (h)	H ₂ Pres. (MPa)	Stirring speed (rpm)	Reactor Type		conversion	Selectivity	
1	Al-HMS(10)	Guaiacol	473	3	5	1000	Batch	Cyclohexanoles	4	69	[133]
2	PtPd/ Al-HMS[100]	Guaiacol	473	6	5	1000	Batch	Cyclohexane	100	72	[133]
3	Ru/Al-HMS(10)	Guaiacol	523	3	5	1000	Batch	Cyclohexane	97	69	[133]
4	Ru/m-ZrO ₂ -SiO ₂	Guaiacol	523	3	5	1000	Batch	Cyclohexane	95	54	[133]
5	Pd/WO _x /γ-Al ₂ O ₃	Guaiacol	573	1	7	300	Batch	Cyclohexane	100	88	[22]
6	Ni/SiO ₂	Guaiacol	593	1	17	2000	Batch	Cyclohexane	97.3	63.9	[134]
7	Pd/Hβ	Guaiacol	493	4	3	-	Batch	Cyclohexane	100	39.79	[21]
8	Ni-ZrO ₂	Guaiacol	573	8	5	600	Batch	Cyclohexane	93	71.6	[135]
9	Ni/Beta	Guaiacol	573	3.33	2.9	-	Batch	Cyclohexane	100	82.4	[136]
10	Ni/TiO ₂	Guaiacol	623	3	0.44	-	packed bed	Phenol	50	66	[137]
11	Ni/Al ₂ O ₃	Guaiacol	623	3	0.44	-	packed bed	Phenol	56	33	[137]
12	Ni/MgO	Guaiacol	623	3	0.44	-	packed bed	Phenol	24	78	[137]
13	Ni/C	Guaiacol	623	3	0.44	-	packed bed	Phenol	36	67	[137]

Table 8
Hydrodeoxygenation of vanillin lignin model compound for advanced biofuel production.

S/N	Catalyst mixed		feedstock	HDO Condition				Reactor Type	Main Product	Percentage		Refs.
	Name	Catalyst properties		Temperature (K)	Residence time (h)	H ₂ Pres. (MPa)	Stirring speed (rpm)			conversion	Selectivity	
1	Pd/C	835(m ² /g), 0.337(cm ³ /g), 2.7(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	338	1	1	1000	Batch	Creosol	99	71	[138]
2	Pt/C	1344(m ² /g), 0.370(cm ³ /g), 2.3(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	338	1	1	1000	Batch	Vanilly alcohol	42	97	[138]
3	Pt/SiO ₂	272(m ² /g), 0.717(cm ³ /g), 11.4(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	338	1	1	1000	Batch	Vanilly alcohol	37	92	[138]
4	Pd/Al ₂ O ₃	108(m ² /g), 0.125(cm ³ /g), 4.9(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	338	1	1	1000	Batch	Vanilly alcohol	99	99	[138]
5	Rh/Al ₂ O ₃	164(m ² /g), 0.296(cm ³ /g), 7.5(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	338	1	1	1000	Batch	Vanilly alcohol	21	76	[138]
6	PdRh/Al ₂ O ₃	146(m ² /g), 0.272(cm ³ /g), 7.6(nm) for surface area, specific pore volume, average pore size, respectively	vanillin	338	1	1	1000	Batch	creosol	98	99	[138]
7	(Cu-Ni/CeO ₂ -SiO ₂)	142 (m ² /g) surface area	Vanillin	433	12	25	1000	Batch	vanillyl alcohol	96	100	[116]
8	Pd/PRGO/Ce-MOF		Vanillin	373	4	1	900	Batch	2-methoxy-4-methylphenol	100	100	
9	Mo ₂ C/AC	794 (m ² /g), 0.22 (cm ³ /g), 2.6(nm) for surface area, specific pore volume, average pore size, respectively	Vanillin	373	3	2	—	Batch	p-creosol	99.6	57.4	[23]

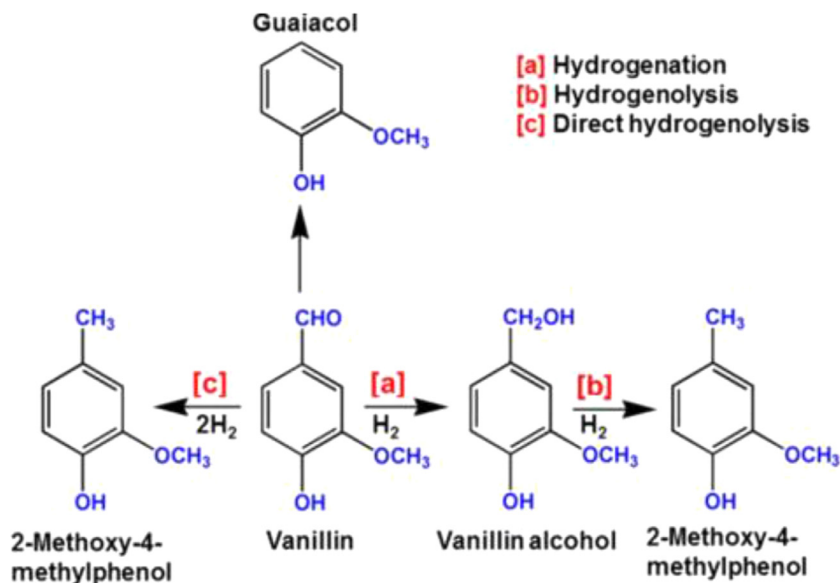


Fig. 6. Proposed reaction pathway for the formation of aromatic hydrocarbons from vanillin [139].

of nickel dispersion, an interesting quality in catalysis that enhances high performance of catalyst. The incorporation of Cu with Ni helps to further improve the rate of hydrogen dissociation through the synergistic effects of introduced by Cu sites. Interestingly, the TEM images of the spent catalyst indicated that the formation of filamentous carbon was observed to be HZSM-5>Ni/HZSM-5>Ni-Cu/HZSM-5. It could be inferred from the findings that surface properties of catalyst materials could have an appreciable effect over the surface area of HDO catalyst because the initial catalyst before doping was observed to possess the highest surface area compared to Ni and Ni-Cu doped HZSM-5 catalyst. Therefore, the selective application of dopants is a quite important to ensuring a tailored surface modification of zeolite catalyst; a required for shape selectivity for high aromatics hydrocarbons formation.

The application of Ni/hierarchical ZSM-5 catalyst has been applied for the deoxygenation of phenolic bio-oil upgrading in a stainless steel autoclave [144]. The commercially obtained ZSM-5 catalyst was converted into a hierarchical ZSM-5 (HZSM-5) via two step seeding approach while incipient impregnation approach was adopted for Ni doping on the parent ZSM-5 catalyst. Several Ni/HZSM-5 catalysts were developed by varying the weight ratio of nickel of the surfaces of the HZSM-5 catalyst. The textural characterization of the catalysts depicted that the catalyst with the 1.5 wt% of Ni gives a catalyst with the highest surface area of 418 m²/g compared to 0.5 and 1 wt% Ni loading. The authors reported a nearly uniformly formed catalyst with NiO dispersion on the surface. The formation of NiO could be attributed to the formation of oxide during the calcination stage of the catalyst preparation. Also, the conversion of guaiacol was found to be hindered with reduced surface areas and the micropores properties exhibited with some catalyst which made the materials diffusion difficult. The introduction of hierarchical structure on the external surfaces of the ZSM-5 catalyst improves the guaiacol conversion and transport properties from the surface pores (micropores) in to the mesopores (inside the acid sites). Interestingly, the Bronsted and Lewis acid sites, and Si/Al ratio were found to have an appreciable effect on the conversion and selectivity of guaiacol and cyclohexane, respectively over surface area. It could be inferred that conversion efficiency and selectivity are more of Si/Al and the acid sites than the specific surface area of the HDO catalysts. According to Li et al. [144], highest conversion and selectivity of cyclohexane of 74.8 and 87.1% were observed when Ni/H-Z5(0.5) was subjected for the HDO process as compared to Ni/H-Z5(1.0) and Ni/H-Z5(1.5) although the highest selectivity of cyclohexane of 89.4% was obtained at the 1.5 wt% Ni doping was applied. This behavior could be associated with the reduction of acid sites. Furthermore, the effective hydrogenation sites possessed by the catalyst was observed to be dependent on the crystals size; larger crystals' catalyst were observed to yield a lower hydrogenation process where low deoxygenated oil are obtained due to diffusion limitation on the surfaces. Hence, improving the surface diffusivity potential through hierarchical pore formation could enhance catalyst performance and therefore aids deoxygenation process.

Also, the catalytic activity of hierarchical mesoporous ZSM-5 supported nickel catalyst has been studied for the HDO of anisole to cyclohexane production [145]. Using a high pressure-batch reactor operating at a temperature between 120 and 200 °C and 6.8 MPa pressure, the HDO of a model lignin molecule; anisole was converted into cyclohexane towards improved fuel properties. Different Ni catalyst loading was developed via incipient wet impregnation methods and steam assisted crystallization (SAC) treatment at varied temperatures and residence time to obtain several catalysts mix. The authors then characterized for pore structure and acid properties after determined the effects of the SAC conditions and the catalyst with 200 °C SAC process condition gave the highest catalyst with mesoporous volumes and highest total acid sites. The catalytic HDO of anisole conversion into cyclohexane was studied in the presence of n-decane solvent at 200 °C and

6.8 MPa for 140 min process condition and highest conversion was obtained on the catalyst having the highest mesopores and selectivity of 98% and 84.2%, respectively. The effects of reaction time on the percentage conversion of anisole and selectivity were determined to understand the mechanisms of the HDO of anisole to fuel products. The authors observed a linear relation between reaction time and anisole conversion and cyclohexane selectivity. Higher conversions with lower selectivity were further observed at lower reaction time with a drastic increase in conversion and slower rate of selectivity as residence time increases. The effect of temperature was found to be linear with anisole conversion and cyclohexane selectivity; as the temperature increases from 120 to 200 °C, the percentage conversion and cyclohexane selectivity also increases. The increase in selectivity and conversion as temperature increases could be linked to the formation of active pores at elevated temperature giving room for effective migration of large molecular oxygenates into the acid sites for efficient cracking and deoxygenation process. Therefore, the introduction of mesopores on the pore structure of ZSM-5 catalyst towards the enhancement of zeolite pore structure is a require approach to achieving higher conversion of bio-oil into a liquid fuel's properties for use in the internal combustion engines. The effect of metal and support properties on the hydrodeoxygenation of anisole as bio-oil model compound over supported Ni and Co catalyst were studied by Sankaranarayanan et al. [146]. Ni and Co in the form of γ -NiO and Co_3O_4 were observed on the surfaces of the h-ZSM-5 support materials following the doping process. The HDO process of anisole conversion at 220 °C and 50 bar of hydrogen pressure for a period of 2 h over the catalyst materials indicated highest selectivity of cyclohexane of 99.8 and 69% on Ni/h-ZSM-5 and Co/ZSM-5 catalyst, respectively (metal loading of 5%). The highest observable selectivity in Ni/h-ZSM-5 catalyst was linked to the presence of effective acid sites in the inside of the catalyst materials which aid high selectivity to aromatic hydrocarbon due to it improved shape selectivity. Catalyst deactivation has been one of the major setbacks to the catalyst performance towards enhanced feedstock conversion and product selectivity [43,143]. Therefore, details understanding of the causes of catalyst deactivation would help towards proffering a lasting solution in enhancing catalyst performance in an HDO process of bio-oil.

Catalyst deactivation

In a typical hydrodeoxygenation technique, catalysts deactivation is resulted from loss of active surface area of metals catalysts due to sintering or leaching, coke deposit on the catalysts active sites in the form of carbonaceous materials and catalysts' site poisoning due to the deposition of phosphorous and nitrogen-containing compounds from the constituents of bio-oil feedstock. Catalyst deactivation has been reported to influence the rates of hydrodeoxygenation of bio-oil and accompanying transalkylation reactions. The effects of catalyst deactivation is mostly pronounced on catalyst's components such as acidic support and metal particles [147].

In liquid enhanced catalytic HDO process of bio-oil or lignin model compounds, catalyst instability are more pronounced due to the high tendency of oxides of catalyst to undergo sintering at elevated temperature of reaction [119,130,148,149]. The fast deactivation process of catalyst performance in biofuel production has created a bottleneck for catalysts stability, reusability and become difficult for their commercial application [150]. The deactivation process of catalysts during HDO process adversely affect the performance of catalyst by reducing the coefficient of hydrogen sticking, reduction in bond strength which exists between metal-oxygen and also, depletion of activation energies of oxygen containing compounds and hydrogen, and reduction facile scission bond in C-O [151].

The determination of catalyst deactivation is basically studied through the comparison of the physiochemical characteristics of as-synthesized and spent catalyst for the HDO processes of bio-oil conversion. These physiochemical properties to be monitored include the surface area/pore size, crystallinity, particle size distribution, acidity and thermal behavior via the application of Brunauer, Emmett, and Teller (BET) surface area technique, X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), temperature programmed desorption and thermogravimetric analysis (TGA/DTG), respectively [109].

Catalyst deactivation due to sintering

The performance of catalyst materials towards an appreciable value is not limited only to the thermal stability and surface area of the catalyst but also to the presence of active sites where catalytic activities take place. At the active pores of catalyst materials, reactants, intermediates compounds formed during the catalytic process and products compete for adsorption. At this phenomenon, the affinity of the pores presents in the catalyst materials to enable the adsorption the chemical species becomes lowered and hence, its efficiency for improved conversion of reactants and enhanced products formation becomes retarded. This phenomenon is generally observed on catalyst active sites including HDO processes most especially, at elevated reaction time.

According to Ambursa et al. [152], the formation of water which is produced during the HDO process has a very high tendency of adsorption competition with reactants on the catalyst active sites which therefore hindered catalyst activities via poisoning. Furthermore, the poisoning of active catalysts' sites has been attributed to reaction conditions of the HDO process which could aid the adsorption of poisons on both Brønsted and Lewis sites; reaction sites at which conversion takes place [153]. The formations of oxygen-containing compounds and waters have been reported to inhibit the activities of acidic support such as Al_2O_3 in NiMo/ Al_2O_3 bimetallic catalyst. Metal supported catalysts have been reportedly deactivated via thermally induced approach at elevated temperature of reaction [154]. Yin et al. [154] has demonstrated the effects

of particle distance which depends on the interaction between metal-support of catalyst materials for mitigating against catalyst sintering. The researchers reported the control of sintering by studying the effects of platinum loading on carbon black; a neutral support material.

Mechanisms of catalyst sintering

To fully understand and proffer solutions to catalyst deactivation through sintering approach, the review of existing literature on the mechanisms of its formation is of interest. Ostwald ripening (OR) and particle migration and coalescence (PMC) are two main mechanisms proposed for the sintering of catalyst during the deactivation process [155]. In migration and coalescence (PMC), Brownian-like particle motion of surface catalyst materials are observed which leads to particle growth via coalescence while OR could be identified as adatoms migration which depends on the local adatom concentration and free energy that exists on the surfaces of support materials. The application of advanced instrument such as in situ transmission electron microscope (TEM) allows for direct observation of catalyst behaviours at high reaction temperature. Rapid sintering (OR is responsible for the loss with disappearance of minutes particles), low sintering (due to disappearance of particles where the contribution of OR and PMC occur) and points of stable performance (Larger particles are formed and temperature-induced surface modification) are the three main phases of thermal catalyst sintering during a reaction process. It was reported that no stable state of active sites were observed on the surface of catalyst support at high temperature [155]. Therefore, to synthesize sinter-resistance catalysts which could be applied for the hydrodeoxygenation of bio-oil to biofuel in a batch reactor, the development of stable structured catalyst support is of importance.

Catalyst deactivation due to coke formation

Coke formation has been identified as the most pronounced form of catalyst deactivation in HDO processes as reported by several researchers [30,114,156]. The formed cokes through polycondensation and polymerization are been deposited on catalyst active sites which causes blockage of active pores. This deposit of cokes are dependent on several parameters such as the conditions of HDO process, nature of catalyst, feedstock [119]. Coke formation has high tendency to lower the efficiency of carbon conversion of bio-oil, clog on the wall of reactor's chamber, and promote catalyst deactivate [143,157]. The presence of unsaturated compounds found in bio-oil such as furans and phenol; oxygen-densed molecules have been identified as the main precursors for coke formation during the HDO conversion of bio-oil [158]. From the report of [153], it could be inferred that the tendency of coke formation on double-oxygen containing molecules > single-oxygen containing molecules during the HDO processes. The formation of coke on the surface of Ni/HZSM-5 and Ni-Cu/HZSM-5 catalysts during bio-oil hydrodeoxygenation has been reported by Li et al. [143]. The report indicated that coke formation is the principal cause of catalyst deactivation in bio-oil HDO, the amount and nature of coke on used catalysts determine the possibility of catalyst reusability, the presence of graphitic carbon and oxygenated compounds in coke promote catalysts deactivation. The introduction of Cu was found to retard the formation of coke on the active pores of the catalyst materials.

During the course of the study, the mechanisms of catalyst deactivation were divided into three main stages; (1) the swift encapsulation of Lewis acid sites by oxygenated HCs in the HZSM-5 which enhances the formation of carbonations (precursors of soluble coke on the catalyst surfaces) via donation of protons from the Brønsted acid sites of HZSM-5 to oxygenates, (2) the formation of filamentous-like strands of carbon termed the soluble coke with similar structure with those of carbon-nanotubes and (3) evolution of filament-like carbon into a graphite carbon. The formation of the three species of (soft coke, hard coke, and graphite) are dependent on the condition of HDO process of bio-oil conversion through either dehydrogenation, alkylation, hydrogen transfer or aromatization reaction [43]. The removal of coke formed during the HDO process is highly necessary to enhance the reusability of the catalyst materials in commercial scale. The presence of soft coke with lower degradation temperature of 250 °C is capable of been dissolve with the introduction organic solvents, hard coke which is formed at a degradation temperature before 300 °C [43]. The deactivation due to coke formation on Ni-Cu/HZSM-5 catalyst is linked to the formation of oxygenated hydrocarbons on the catalyst surface while the swift deactivation of Ni/HZSM-5 is attributed to the formation of graphitic carbon [143]. Therefore, to reduce the formation of coke during HDO process of bio-oil, reduction in reaction temperature, lowering of reactant-catalyst residence time and enhancing the partial pressure of hydrogen gas could be of immense advantages [119].

The role of hydrotreatment catalyst in coke formation during the hydrotreatment of bio-oil using pre-sulphided NiMo and CoMo catalysts were studied at low temperature by Kadarwat et al. [37]. The introduction of levoglucosan into the feedstock resulted in an appreciable depletion of the amount of coke formed during the HDO process with 150–300 °C reaction temperature. The addition of levoglucosan induced the formation of coke could possibly imply its cross-link potentials with other compounds found in bio-oil in the absence of a catalyst. Higher temperature of 300 °C resulted to an increase in coke formation which causes catalyst deactivation through blockage of active sites of the catalyst materials [37].

Catalyst deactivation due to poisoning

Catalysts deactivation through catalyst poisoning during the HDO process is another form of challenges which hinder the effective performance of catalysts during bio-oil upgrade. Unlike the catalyst deactivation by sintering which is thermal

enhanced, the deactivation of catalyst via poisoning is referred to as chemisorption in nature. Chemical impurities are adsorbed on to the active sites of catalysts materials and therefore hinder its performance by preventing reactants from active sites for conversion process. Through electronic modification and chemical structure reconstruction, active parts of catalysts materials are altered thereby, enhancing the dissociation and adsorption of external species on catalysts active surfaces. During this process, the chemically produced poison therefore compete for the active catalyst sites with the main reactant thereby, retards the reactants conversion rate and the corresponding catalyst performance [151]. Catalysts poisoning could be classified as either reversible (this is a situation where the removal of poisons from the catalysts' active parts fully restored the catalysts performance), irreversible (in this case, the poisons permanently poison the catalysts active sites which ultimately reduces the number of effective active parts of the catalyst and hence, retards its performance) and quasi-irreversible poisons (observable slow rate of desorption of poison from catalyst active sites during the removal process though, the performance of the catalyst would to be restored fully) [153].

According to Senol et al. [159], the poisonous characteristics of HDO catalysts could be as a result of intermediate water produced during the hydrogenation process with high tendency of impair or modify the structural make-up of support material. Such observation of structural modification due to the formation of water, a by-product of hydrodeoxygenation process has been reported by Senol et al. [159] during the HDO of methyl esters on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. In the report of [159], an hydrated boehmite (Al(OH)) phase material was formed via the reaction between water and the alumina support materials.

The poison of active parts of catalyst materials was also reported by Mortensen et al. [160] to involve the chemical conversion of Mo₂C to MoO₂ during the hydrodeoxygenation of 1-octanol and phenol into aromatic hydrocarbon. Mortensen et al. [160] reported a decrease in the conversion of phenol and 1-octanol from 37% to 19% and 70% to 37%, respectively, over 76 h of operation. Furthermore, a complete deactivation of catalyst active parts was observed at the 12 h of process operation while co-feeding with 30% water. The deactivation of nickel-based catalyst leading to the formation of Ni-S (irreversible poison) and Ni-Cl (reversible poison; chlorine removal restores the catalyst performance by enhancing the active parts) during the introduction of sulfur and chlorine in the HDO process, respectively was reported [161]. The observations were made while the author was studying the Stability and resistance of nickel catalysts for hydrodeoxygenation as regards carbon deposition and effects of sulfur, potassium, and chlorine in the feed. Therefore, the control of catalysts deactivation during HDO processes is of immense importance towards maintaining catalysts performances and stability.

Future perspectives

Biofuel obtained from pyrolysis of biomass is hydrogen deficient and this has resulted to it low energy content and not energy efficient when compared to HTL. In an attempt to upgrade bio-oil to transportation fuel, the adoption of HDO process which depends on the injection of hydrogen at high pressure has been widely reported in various literatures. Since bio-oil obtained from polymer materials are hydrogen dense, the future research towards bio-oil upgrading is therefore suggested to involve the co-feeding of oil obtained from polymers to aid hydrodeoxygenation in the presence of catalyst without the introduction of hydrogen. The application of catalyst materials has been extensively studied and catalysts having high acidic properties have been applauded for its high conversion efficiency and selectivity to aromatic hydrocarbon formation during HDO process. Catalyst deactivation has been identified as one of the major challenges in the area of research. To combat the challenge of catalyst deactivation either through coke formation, sintering and catalyst poisoning, the development of structurally and thermally stable catalyst are highly recommended. Further studies should be established on the catalyst stability and its regeneration potential to meet commercial application. Also, the need to study, understand and evaluate catalyst lifespan for the HDO process is needed. Therefore, control of catalyst deactivation via structural modification of catalyst active sites on support materials should be researched.

Conclusions

The conversion of biomass feedstock into biofuel helps in limiting the accompanied environmental effects when burns indiscriminately. The obtained bio-oil from biomass materials has been characterized with high content of oxygen which hindered the direct application in the internal combustion engine. This high oxygen content is related to the presence of large and complex compounds found in biomass feedstock which yields oxygenated compounds during thermochemical conversion processes. HTL has been observed to yield biocrude of higher HHV and H/C ratio over pyrolysis process. The presence of large oxygenates present in bio-oil derived from biomass has made the understanding of the mechanism of aromatic carbon formation difficult during the catalytic HDO process. Hence, the application of bio-oil model compounds such as vanillin and guaiacol have aided the understanding of catalytic HDO's mechanisms easy towards effective design of catalyst and operation condition for improved product and selectivity. Although catalysts promote the rate of chemical reaction and enhance the selectivity of aromatic hydrocarbon during HDO process, the deactivation of catalysts' active parts have posed a serious setback to most catalysts including the most sourced catalyst; zeolite. Coke formation has been identified as one of the common and notorious type of catalyst deactivation during HDO process and it was observed to be dependent on the nature of feedstock, condition of operation and the nature of catalyst. Deactivation of catalyst' active sites hinder catalyst performance for enhanced conversion and selectivity to aromatic hydrocarbon formation. Therefore, the need to de-

velop, evaluate a structurally and thermally stable catalyst with high catalyst recovery and reusability are of importance in the present researches in the HDO of bio-oil.

Declaration of Competing Interest

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

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