

Review

Advancements in the Conversion of Lipid-Rich Biowastes and Lignocellulosic Residues into High-Quality Road and Jet Biofuels Using Nanomaterials as Catalysts

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Abstract: At present, the majority of available road and jet biofuels are produced from oleochemical feedstocks that include vegetable oils and biowastes such as waste cooking oils and animal fats. Additionally, one of the most promising ways to achieve long-term environmental goals is to sustainably use lignocellulosic residues. These resources must be treated through a deoxygenation process and subsequent upgrading processes to obtain high-quality road and jet biofuels. Accordingly, in this review, we explore recent advancements in the deoxygenation of oleochemical and lignocellulosic feedstocks in the absence of hydrogen to produce high-quality road and jet biofuels, mainly focusing on the use of nanomaterials as catalysts and the valorization of lipid-rich biowastes and lignocellulosic residues. As a result, we found that regardless of the catalyst particle size, the coexistence of basic sites and weak/medium acid sites is highly important in catalytic systems. Basic sites can enhance the removal of oxygenates via decarboxylation and decarbonylation reactions and inhibit coke formation, while weak/medium acid sites can enhance the cracking reaction. Additionally, the extraction of value-added derivatives from lignocellulosic residues and their subsequent upgrade require the use of advanced methods such as the lignin-first approach and condensation reactions.

Keywords: biowaste; lignocellulosic residue; deoxygenation; nanomaterial; biofuel; lignin-first approach



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1. Introduction

At present, different economic sectors produce considerable amounts of biowastes and lignocellulosic residues that are not fully exploited or properly disposed of, but it is estimated that, by 2050, renewable sources will be the main resources used in energy production, and among these, biomass will play a significant role in the production of zero emission fuels [1]. The biofuel sector is making a significant contribution in improving the capability to transform biowastes into high-quality road and jet biofuels, which is highly advantageous for the development of a more sustainable global economy. In fact, the majority of available road and jet biofuels are produced from oleochemical feedstocks that include vegetable oils and biowastes such as waste cooking oils (WCOs), animal fats, and tallow. However, these resources are characterized by having a high content of oxygen, unlike fossil fuels which are oxygen free. Consequently, biowastes and lignocellulosic residues must be treated through a deoxygenation process and subsequent upgrading processes to obtain high-quality road and jet biofuels [2,3].

Hydrodeoxygenation is the most widely used process for producing renewable hydrocarbons, while isomerization and cracking are used to upgrade them into road and jet biofuels. Current hydrotreating facilities include Neste (Netherlands, Singapore and Finland), ENI (Italy), Diamond Green Diesel (USA), UPM (Finland), World Energy (USA), Renewable Energy Group (USA), and Total (France). However, most facilities produce only road biofuels because it is economically more convenient as compared with jet biofuel. In fact, the production of jet biofuel is limited to less than 0.1% of the global total consumption

of all types of jet fuels and the only facilities that produced jet biofuel in 2019 were Neste and World Energy [4]. The low production of road and jet biofuels is mainly due to the high costs of oleochemical feedstocks and the use of hydrogen and catalysts in the hydrodeoxygenation process, which can represent 50% and 40% of the total production cost, respectively. For civil aviation, reducing the costs of feedstocks and production is a major challenge because airlines generally have low profit margins and fuel accounts for about 30% of the total expense of operating costs [5]. Consequently, in the last decade, enormous efforts have been focused on avoiding the use of hydrogen during the deoxygenation process, and among these, the use of different materials as catalysts to promote reactions such as decarboxylation and decarbonylation.

Despite the wide variety of oleochemical feedstocks, their availability will not be enough to satisfy the future demand for feedstock; therefore, one of the most promising ways to achieve long-term environmental goals in the development of biofuels is to sustainably use lignocellulosic biomass. Because the precursors of the lignocellulosic biomass fractions are short chain oxygenated molecules that typically have low-grade fuel properties, recently, it has been proposed to use innovative catalytic approaches to synthesize long-chain oxygenates via various C–C coupling reactions such as aldol condensation, alkylation, oligomerization, ketonization, Diels–Alder, Guerbet, and acylation reactions [6–8]. Then, long-chain oxygenates can be upgraded into high-quality road and jet biofuels using processes such as hydrodeoxygenation, isomerization, and catalytic cracking. Overall, although encouraging results have been obtained, it is obvious that there is still a long way to go in the study of the nature of the conversion of biomass into renewable hydrocarbons involving the discovery and understanding of reaction pathways, reaction kinetics or mechanisms, and product compositions. Likewise, the study of different materials that can be used as a catalyst, including the analyses of the catalytic effects such as yield, conversion, and selectivity [9].

Considering these premises, the development of highly active and stable nanocatalytic systems seems to be a promising strategy for optimizing the transformation processes of biomass platform molecules and increasing the selectivity towards hydrocarbon biofuels with a high-energy content. In fact, at a nanoscale, many materials display novel properties and, consequently, different behaviors than those of a larger size. Some materials become stronger, lighter, increase in stability, or are better at conducting electricity or heat, while others display different magnetic properties or become chemically active under special conditions. Therefore, the application of nanomaterials can be extended to many fields such as the agricultural, food, cosmetic, pharmaceutical, electronic, environmental, and energy industries [10]. In the biofuel sector, the use of nanostructured materials is still in an early stage and is not a simple task due to the complex chemical nature of biomass feedstocks [11–13]. However, the rational control of several parameters such as size, shape, composition, and surface of nanoparticles, can be manipulated to finely tune the active sites both electronically and geometrically, resulting in high chemical reactivity [14]. Accordingly, in this review, we explore the recent advancements in the deoxygenation of oleochemical and lignocellulosic feedstocks in the absence of hydrogen to produce high-quality road and jet biofuels, mainly focusing on the use of nanomaterials as catalysts and the valorization of lipid-rich biowastes and lignocellulosic residues.

2. Oleochemical and Lignocellulosic Feedstocks

2.1. Vegetable Oils and Lipid-Rich Biowastes

Recently, vegetable oils have been widely used as feedstocks to produce biofuels as an alternative to petroleum, mainly due to their wide availability (more than 350 edible and inedible oilseed crops identified around the world), capacity to store energy (HHV between 37 MJ/Kg and 41 MJ/Kg), low water content (from 0.03 wt.% to 0.47 wt.%), and relative low oxygen content (from 10.50 wt.% to 14.50 wt.%) [15–20]. Vegetable oils are composed of lipids, mostly triglycerides (~98%), diglycerides, and monoglycerides. Triglycerides consist of one glycerol molecule and three fatty acids with carbon chains

usually comprising between 8 to 24 carbon atoms connected to the glycerol backbone via a carboxyl group. The fatty acids can be saturated (no double bond), monounsaturated (one double bond), or polyunsaturated (more than one double bond). For example, palm oil has the highest palmitic acid (saturated) content, while rapeseed and soybean oils have the highest oleic acid content (monounsaturated), and sunflower oil has the highest linoleic acid (polyunsaturated) component (68 wt.%). The composition of fatty acids in vegetable oils directly affects their properties, such as viscosity, density, melting point, and boiling point. Moreover, the composition of fatty acids in vegetable oils can also significantly influence the yield and quality of biofuels. To avoid competition with the use of resources such as land and water dedicated to the food industry, the use of non-edible vegetable oils of second-generation feedstocks such as *Jatropha curcas* oil and algae oil has been encouraged, mainly due to their wide cultivation versatility and high lipid content [21–28].

Additionally, the use of biowastes to produce road and jet biofuels has received more attention due to their wide availability and because the improvement of waste management in the industries is essential to develop a sustainable global economy. Biowastes include biodegradable garden and park wastes; food and kitchen wastes from households, restaurants, caterers and malls; and wastes from food processing plants [29,30]. Biowastes are an important fraction of municipal solid waste (MSW). For example, in the OECD countries which generate 44% of the total MSW of the world, in 2013, the fraction of MSW varied significantly from 14% to 56%, with a yearly generation rate of approximately 177 million tons, and only a limited part of this amount (37%) was directed to biological treatments [31]. Because biowastes from MSW have a high content of lipids (~30 wt.%), these can be extracted directly using different methods such as Soxhlet extraction and supercritical fluids extraction. Other lipid-rich sources such as WCOs and animal fats are also widely available in food industries such as fish processing and food-service establishments such as restaurants, food markets, hotels, cafeterias, caterings, or even cruise ships [32–35]. Additionally, pulp and paper industries produce large amounts of crude tall oil, which can be distilled in different fractions such as tall oil fatty acids (TOFAs) (~30%), tall oil resin (~35%), distilled tall oil (~10%), light oil (~12%), and pitch (~30%) [36]. Table 1 shows the properties and compositions of various non-edible oils and lipid-rich biowastes.

Table 1. Properties and compositions of various non-edible oils and lipid-rich biowastes.

Properties and Composition	<i>Jatropha curcas</i> Oil [37]	<i>Microalgae Chlorella sp.</i> [38]	WCO [39]	Swine Fatty Wastes [40]	Crude Tall Oil [41]	Wood Bio-Oil [42]	Waste Fish Oil [43]
Density (g/cm ³)	0.94	-	0.91	-	-	-	0.89
Viscosity	33.90 cSt at 40 °C	-	38.15 cSt at 40 °C	-	55.00 cSt at 70 °C	40–100 cP at 50 °C	27.00 cSt
HHV (MJ/kg)	38.65	19.44	38.91	-	39.75	16–19	39.00
Moisture content (wt.%)	-	4.13	0.08	-	5.20	15–30	<0.05
Acid value (mg KOH g ⁻¹)	-	-	263.00	-	157.70	-	-
Fatty acid (%)							
Myristic acid (C14:0)	0.50–1.40	1.62	0.40	-	-	-	1.05
Palmitic acid (C16:0)	12.00–17.00	16.46	15.11	16.00	-	-	16.00
Palmitoleic acid (C16:1)	-	-	-	-	-	-	5.00
Stearic acid (C18:0)	5.00–9.50	3.27	3.96	11.00	2.10	-	10.50
Oleic acid (C18:1)	37.00–63.00	14.64	43.43	18.00	52.70	-	45.60
Linoleic acid (C18:2)	19.00–41.00	20.61	33.93	-	38.30	-	20.60
Linolenic acid (C18:3)	-	15.35	0.34	-	6.90	-	-
Behenic acid (C22:0)	-	-	-	10.00	-	-	-
Others	-	7.41	3.24	45.00	-	-	-
Element (wt.%)							
C	-	44.93	76.30	65.38	-	54.00–58.00	-
H	-	6.42	11.70	11.32	-	5.50–7.00	-
O	-	40.67	11.98	21.99	-	35.00–40.00	-
N	-	6.41	0.02	0.58	-	0.00–0.20	-

2.2. Lignocellulosic Residues

Residual biomass is not classified as waste and typically includes lignocellulosic residues generated by the agricultural, forest, and agro-industrial sectors such as sugar cane bagasse, corn stover, rice hulls and straw, nutshells, grasses, maize cobs, wheat chaff, banana stalks and sawdust, bark, and shavings of hardwood and softwood [44,45]. In Europe, maize cob and wheat chaff alone could provide an annual biomass potential availability of 9.60 Mt and 54.80 Mt, respectively [46]. Large amounts of residues are also produced in the cultivation of vineyards and olive groves. In fact, it has been estimated that the production of vineyard residues in Europe is 2.67 Mt per year [47,48]. Lignocellulosic biomass mainly comprises three fractions, namely cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%). Cellulose is a polymer composed of glucose monomers linked through β -1,4-glycosidic bonds [49]. Cellulose has a rigid structure due to the cyclic structure of the main polymer chain and the presence of strong intramolecular hydrogen bonds between the hydroxyl groups, which create an orderly crystalline region that blocks access to most organic solvents and water. Hemicellulose is also a polymer composed of glucose monomers linked through β -1,4-glycosidic bonds and occasionally β -1,3-glycosidic bonds. However, unlike cellulose, hemicellulose has an amorphous as well as random structure organized in branched chains. Hemicellulose plays an important role in strengthening the cell walls of plants by forming a network of hydrogen bonds with cellulose fibers and lignin residues, which generates strong stability and stiffness in cell walls [50]. Moreover, lignin is an aromatic polymer composed of primary lignin monomers such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol (C₉–C₁₁ monolignols). Several functional groups conform to these units as aromatic phenolic hydroxyl and methoxyl, carbonyl groups such as aldehydes and ketones, primary and secondary aliphatic hydroxyl, and carboxyl groups [51]. In general, the composition of lignocellulosic biomass highly depends on its source, i.e., whether it is derived from hardwood, softwood, or grasses. For example, softwoods contain the highest lignin content (28–32%), followed by hardwoods (20–25%) and grasses (17–24%). The integrity and resistant ability of lignocellulosic biomass to depolymerization are attributed to cellulose crystallinity, lignin hydrophobicity, and trapping of cellulose polymer in the lignin-hemicellulose network [52,53]. The difficulty in depolymerizing lignocellulosic biomass also increases after it is processed through harsh treatments such as those used to produce kraft pulp [54].

Pyrolysis, which includes various methods such as torrefaction, carbonization, and fast pyrolysis, has been used as a typical thermochemical route for the depolymerization of biomass into biofuels, in particular, a liquid product known as bio-oil [55–58]. Bio-oil contains a wide variety of oxygenates divided into three major groups: small carbonyl compounds (acids, ketones, and aldehydes), sugar-derived compounds (furans and anhydro sugars), and lignin-derived compounds (phenols and aromatic oligomers) [59]. These compounds provide the bio-oil with unwanted chemical and physical characteristics; therefore, it cannot be used directly as a fuel for transportation [60,61]. Figure 1 shows a representation of the chemical structure and composition of the main compounds in lipid-rich biowaste (WCO) and lignocellulosic residues, while Table 2 summarizes the biopolymers distribution in various lignocellulosic residues.

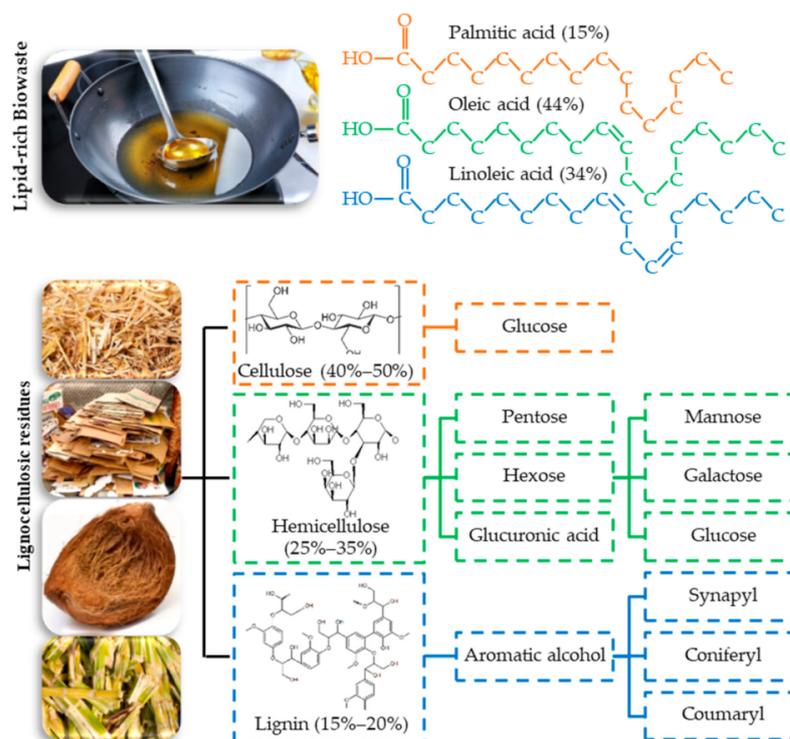


Figure 1. Representation of the chemical structure and composition of the main compounds in lipid-rich biowaste (WCO) and lignocellulosic residues.

Table 2. Biopolymers distribution in various lignocellulosic residues.

Lignocellulosic Residue	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)
Wheat straw [62]	37.80	27.50	34.70
Grass [63]	32.50	19.93	3.10
Willow [63]	45.34	12.78	16.77
Waste cardboard [64]	12.50	45.00	35.00
Rice straw [65]	28.00	32.15	19.64
Sorghum bagasse [65]	31.28	34.80	24.77
Coconut husk [65]	17.33	21.26	46.36
Olive tree pruning [65]	25.70	41.00	21.80
Groundnut shell [65]	27.62	38.31	21.10
Hardwood [65]	40.00–46.00	24.50–36.00	20.00–26.00
Softwood [65]	39.5–42.00	23.00–30.60	24.00–27.50
Corn cobs [66]	33.60	37.20	19.30
Newspaper [66]	40.00–55.00	25.00–40.00	18.00–30.00
Sugarcane bagasse [66]	45.00	20.00	30.00

3. Characteristics of Diesel and Jet Biofuels

Diesel fuel is a complex mixture produced by the distillation of crude oil. It consists of hydrocarbons with carbon numbers predominantly in the range of C₉–C₂₀ and boiling points in the range of ~163–357 °C [67]. Diesel fuel contains approximately 75% aliphatic hydrocarbons, mainly straight- and branched-chain paraffins (alkanes), and about 25% aromatic hydrocarbons (with one or more aromatic rings and alkyl side chains). The typical atomic mass concentrations are about 86% C, 14% H, and a minor fraction of sulfur depending on the crude oil source and cleaning quality [68]. Renewable diesel obtained by hydroprocessing of oleochemical feedstocks also contains straight- and branched-chain paraffins (alkanes), however, it is practically free of aromatics. Due to its paraffinic composition, renewable diesel can be blended with diesel fuel without limitations set by vehicle technology or fuel logistics. Moreover, the presence of isoparaffins obtained by an addi-

tional isomerization step provides renewable diesel with good cold properties. For example, during isomerization, the melting point of n-paraffins, i.e., around 28 °C for C18, can be adjusted down to −40 °C to meet the requirements of fuels used in severely cold climates [69]. In general, for improved low temperature properties, shorter chain, isomerized compounds are more desirable than long-chain alkanes, although an excessive presence of shorter chain, isomerized species provides a lower number of cetane. Hexadecane (cetane) is the high-quality reference compound on the cetane scale, and it is related to the ignition quality of diesel fuel. [70].

Conversely, conventional jet fuels are mainly composed of C8–C16 hydrocarbons, categorized into four principal hydrocarbon groups: n-paraffins (alkanes), iso-paraffins (branched iso-alkanes), cyclo-paraffins (naphthenes), and aromatics, with a content of around 20%, 40%, 20%, and 20%, respectively [71,72]. The content of each of these compounds has a direct effect on the properties of the fuel. For example, the presence of n-paraffins ensures the energy density, while iso-paraffins and cyclo-paraffins are responsible for decreasing the freezing point, since they have a significantly lower freezing point than that of n-paraffins with the same carbon number. Aromatics also help to reduce the freezing point and to enhance the shrinkage of aged elastomer seals, minimizing potential fuel leakage issues, however, excessive use of aromatics can reduce the net heat of combustion and can lead to more soot formation [73–75]. The ASTM D1655 standard classifies jet fuels according to their properties as jet fuels for commercial airplanes (Jet A and Jet A-1) and jet fuels for military aircrafts (JP-5 and JP-8). The only difference between Jet A and Jet A-1 is the freezing point, which is −40 °C and −47 °C, respectively. Jet A fuel is generally used in the United States, while Jet A-1 is adopted in the rest of the world [76]. Although some test flights have operated with 100% bio-synthetic paraffinic kerosene (Bio-SPK), ASTM D7566 has restricted its use in mixture with jet fuel of fossil origin to a maximum of 50% to guarantee effective operation of aircrafts. Additionally, the ASTM D7566 has stated that the final composition of Bio-SPK must be at least 99.5% in carbon and hydrogen. Consequently, the removal of oxygen is highly important to increase biofuel stability, miscibility with conventional fuels and the H/C molar ratio [77–79]. Table 3 presents the typical properties for road and jet biofuels and limits in fuel standards.

Table 3. Specifications and properties of various road and jet biofuels as compared with fuel standards.

Properties	Diesel Fuel (EN 590) [69]	Renewable Diesel [69]	Jet A (ASTM D1655) [76,78]	Bio-SPK (ASTM D7566) [76,78]	Bio-SPK from <i>Jatropha c.</i> [79]
Acidity (mg KOH/g)	-	-	<0.100	<0.015	-
Final BP (°C)	-	-	300.00	25.00	254.90
Flash point (°C)	>55.00	>70.00	>38.00	>38.00	46.50
Density at 15 °C (Kg/m ³)	820.00–845.00	780.00	775.00–840.00	730.00–772.00	749.00
Freezing point (°C)	≤10.00–≤ 34.00	Severe winter grades available	<−40.00	<−40.00	<−54.50
Viscosity (mm ² /s)	1.20–4.50	3.00 (at 40 °C)	<8.00 (at −20 to −35.5 °C)	<8.00	3.66 (at −20 °C)
Net heat of combustion (MJ/kg)	~43.00	~44.00	43.28	42.80	44.30
Smoke point (mm)	-	-	Min 25.00	-	53.00
Distillation (°C), initial boiling point	-	200.00	-	-	164.50
FAME content	≤7.00% (V/V)	0.00% (V/V)	-	Max 5.00 (ppm)	-
Lubricity (mm)	≤46.00	~65.00	Max 0.85	Max 0.85	0.76
Sulphur	≤10.00	<5.00 (mg/kg)	Max 0.30 (total mass %)	-	0.00
Cetane number	>51.00	>70.00	-	-	-
Antioxidants (mg/L)	-	-	Max 24 (not including weight of solvent)	17.00 to 24.00	-
Aromatics	from 15% to 30% but not regulated by EN 590	Below detection limit	18.53 (wt. %)	26.50 (vol%)	-
n-Paraffins (wt.%)	-	-	19.98	-	-
Cycloparaffins (wt.%)	-	-	31.80	-	-
iso-Paraffins (wt.%)	-	-	29.69	-	-

4. Deoxygenation of Oleochemical Feedstocks in a Free-Hydrogen Environment

At present, the most widely used route to produce road and jet biofuels from oleochemical feedstocks uses hydrogen in the process (hydrodeoxygenation). When hydrodeoxygenation is applied to free fatty acids (FFA), it allows the removal of two oxygen atoms involving two sequential C-O cleavage steps by sequential hydrogenations, giving rise to the formation of a linear hydrocarbon and two H₂O molecules. As described earlier, oleochemical feedstocks and the use of hydrogen and catalysts in the hydrodeoxygenation process, can represent 50% and 40% of the total production cost, respectively (Table 4 shows the variable operating cost of a hydrotreating facility). Therefore, from an economic point of view, it is highly desirable to widen the range of feedstocks, use less costly catalysts, and avoid the use of hydrogen in the process. In this regard, the deoxygenation of FFA can occur directly without using hydrogen in the process through reactions such as decarboxylation, decarbonylation, and ketonization. On the one hand, selective decarboxylation applied to FFA involves one C-C cleavage step, which results in the removal of oxygen atoms producing CO₂ and a paraffin hydrocarbon (n-alkane with one less carbon atom than the starting fatty acid); selective decarbonylation involving C-C and C-O cleavage steps leads to the formation of CO, H₂O and an olefinic hydrocarbon (the corresponding alkene) [80,81]. On the other hand, the ketonization reaction converts two molecules of FFA into a ketone releasing CO₂ and H₂O. The ketonization reaction has proven to be highly efficient for the selective removal of oxygen from FFA because three of four oxygen atoms are removed eliminating only one carbon atom, and consequently, a lesser amount of hydrogen is required to remove the last oxygen atom of the ketone and produce linear alkanes [82,83]. Tests performed on CI engines have shown that deoxygenated vegetable oils can provide better engine performance and emissions as compared with diesel fuel. [84]. Figure 2 shows a representation of the four plausible reaction routes for the deoxygenation of stearic acid using hydrogen (hydrodeoxygenation) or in the absence of this gas (decarboxylation, decarbonylation, and ketonization).

Table 4. Variable operating cost of a hydrotreating facility with a capacity of 600 tons/day [5].

Material	Consumption	Unit Cost (USD Per Unit)
Feedstock	25,000.00 kg/hr	0.80/kg
Natural gas	35,527.00 MJ/h	0.39/m ³
Cooling water	345,700.00 kg/hr	0.41/m ³
Electricity	2496.76 kWh	0.07/kWh
Hydrogen	676.84 kg/hr	3.51/kg
Hydroprocessing catalyst	25,000.00 kg/year	3266.10/kg
Hydrocracking catalyst	5991.34 kg/year	5935.39/kg
Wastewater treatment chemicals	21.75 kg/hr	6.81/kg
Propane	1771.55 kg/hr (production)	1.00/kg
Heavy oil	809.10 kg/hr (production)	0.60/kg

The materials that have been used as catalysts in the deoxygenation of oleochemical feedstocks can be divided mainly into four groups: catalysts containing noble metals (e.g., Pd, Pt, and Ru); transition metals (e.g., Ni, Co, and Mo); alkaline earth metals (e.g., Mg and Ca); and zeolites (ZSM-5). Metal catalysts can be used in the form of pure metals (e.g., Mo, Ni, and Co); metallic mixtures (e.g., CoMo and NiMo); metal oxides; metal phosphides; metal nitrides; or metal carbides [85]. Additionally, metal catalysts have typically been used with suitable supports such as metal oxides (TiO₂, Al₂O₃, SiO₂, CeO₂, and ZrO₂); zeolites (ZSM-5, HY, and H-Beta); mesoporous materials (MCM-41, SAPO-11, SBA-15, Al-SBA-15, and Al-MCM-41); and activated carbon (AC). Among these, Al₂O₃ is one of the most common supports, which in combination with metals, has shown excellent deoxygenation properties due to its acidic property; however, the high acidity of Al₂O₃ also causes a high tendency for coke deposition on the catalyst surface that eventually leads to instability and deactivation [86].

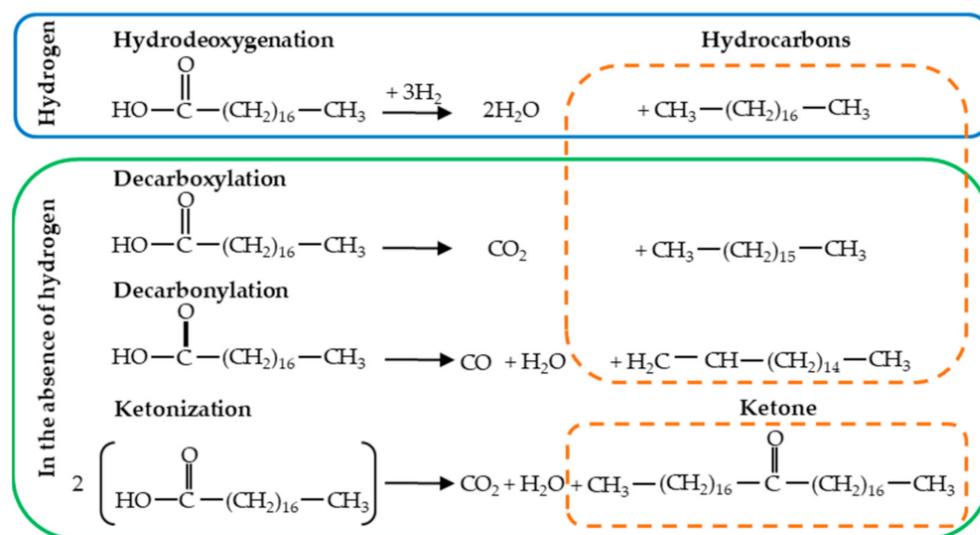


Figure 2. Representation of plausible reaction routes for the deoxygenation of stearic acid using hydrogen (hydrogenation) or in the absence of this gas (decarboxylation, decarbonylation, and ketonization).

Transition metals, such as Pt and Pd, have proven to be excellent catalysts for the deoxygenation process; however, their high cost represents an important drawback from an economic point of view [87]. Consequently, less expensive materials such as Ni, Mg, and Ca have been proposed. In fact, it has been reported that feedstocks such as non-edible oil (*Jatropha curcas* oil) and waste cooking oil (WCO) can be successfully deoxygenated and converted into hydrocarbons in a hydrogen-free atmosphere by promoting decarboxylation and decarbonylation reactions using γ - Al_2O_3 , CaO, and Mg-Al mixed oxides (calcined hydrotalcite) as catalysts. In experiments that were mainly carried out in a batch setup (up to 110 bar), the possibility of obtaining a liquid fuel potentially suitable for use in the transportation sector has been verified, with yields over 80 wt.% and a high proportion of hydrocarbons (i.e., around 83%) of mainly C8–C18; additionally, significant improvements in terms of heating value (44 MJ/kg), viscosity (4 cSt), and sulfur content (below 10 ppmw) were achieved [88–90]. In addition, the performance of Mg-Al mixed oxides has also been compared with other activated hydrotalcite-derived catalysts (FeAl, ZnAl, and NiAl) in the deoxygenation of oleic acid under atmospheric pressure. Mg-Al and Ni-Al mixed oxide catalysts both produced a high yield of hydrocarbons, i.e., 81% and 89%, respectively. Although it was evidenced that Mg-Al mixed oxides provided greater selectivity towards C8–C12 hydrocarbons (30%) as compared with Ni-Al mixed oxides (17%), for which the selectivity towards hydrocarbons in the range of C13–C20 was predominant (30%). These results highlighted that hydrocarbon yield and selectivity of the deoxygenation products were predominantly influenced by the acid-base properties of the catalyst [91].

Although Ni-based catalysts have shown good potential for the deoxygenation process, they have been identified to be prone to undergo coking mainly due to their acidity properties, and subsequently, high activity in cracking reactions [92]. Consequently, to neutralize the acidity properties of Ni-based catalysts, their integration with basic metal materials such as Co and Ca oxides has been proposed. For example, the performance of NiO-CaO/SiO₂-Al₂O₃ (5 wt.% CaO metal content) has been evaluated during the deoxygenation of triolein, WCO, *Jatropha curcas* oil, and palm fatty acid distillate (PFAD). However, although all feedstocks were effectively deoxygenated, producing a high percentage of hydrocarbons (>74%) with a selectivity mainly towards C15–C17 hydrocarbons (>54%), the results also showed that using NiO-CaO/SiO₂-Al₂O₃ as a catalyst, in all cases, resulted in the formation of a significant amount of coke (around 14 wt.%) [93]. In addition, the performance of Co-Ca/SiO₂-Al₂O₃ (10 wt.% of Co) has been evaluated during the deoxygenation of triolein, Ceiba oil, and Sterculia oil. In general, it was possible to obtain a high hydrocarbon yield comprised between 73% and 86% and, when triolein was used

as a raw material, the selectivity of the C15–C17 hydrocarbons reached 48%, however, high production of char was also evidenced (31 wt.%). Furthermore, the results showed the presence of a significant carbon amount (33–63 wt.%) on the reactivated Co-Ca/SiO₂-Al₂O₃ catalyst surfaces implying a slight gradual reduction in deoxygenation activity and coke formation [94]. In addition, a study was conducted on the catalytic performance of mono-functional metals supported on activated carbon derived from coconut shell (Co/AC and Mn/AC) as catalysts in the deoxygenation of PFAD. The results showed that the Co/AC catalyst exhibited high deoxygenation activity, with a hydrocarbon yield of 90% and C15–C17 hydrocarbon selectivity of 72%, however, the mass fractions of the liquid products were relatively low, i.e., between 40 wt.% and 52 wt.%. The low yield of liquid products was mainly attributed to the mild cracking of the deoxygenated products, leading to the formation of significant amounts of volatile materials (38 wt.%), as well as the formation of char (19 wt.%), while the high hydrocarbon yield was attributed to the synergistic effect between the CoO and the active carbon support, which promoted the characteristics of the acid–base sites [95]. Additionally, a study reported the development of mixed metal oxide Ni-Ag supported on activated carbon (AC) derived from coconut fiber residues (CFR) for producing diesel-like hydrocarbons via the deoxygenation of *Jatropha Curcas* oil. Under optimal process conditions it was possible to obtain a hydrocarbon yield of up to 95% with 83% selectivity towards C15 and C17 hydrocarbons, produced predominantly by decarbonylation rather than decarboxylation. Despite the high hydrocarbon yield, the experimental results showed that the mass fraction of liquid product was not greater than 42 wt.%, with the drawback of the formation of char and residue (29 wt.%), which blocked the accessibility to the active sites and diminished the efficiency of the catalyst. Ni-Ag/AC was reused for five consecutive runs without a drastic reduction in hydrocarbon yield, but with inevitable coke formation in the spent catalyst (2.5 wt.%). Interestingly, the study also highlighted that an Ni-rich catalyst facilitated the conversion of triglycerides to fatty acids rather than the conversion of fatty acid to hydrocarbon fractions, suggesting that an Ni-rich catalyst favors cracking and polymerization reactions. Furthermore, it was evidenced that there was no correlation between the catalyst's textural properties and the increment of hydrocarbons, instead, the deoxygenation activity strongly depended on the chemical nature of the catalyst, specifically, in relation to the distribution of strong and weak acidic sites [96].

5. Deoxygenation of Oleochemical Feedstocks Using Nanomaterials as Catalysts

As a strategy to optimize the deoxygenation of oleochemical feedstocks, it has been proposed to test the use of nanocatalysts such as transition metal oxides supported on TiO₂ (WO/Pt/TiO₂), which have been tested during the deoxygenation of stearic acid and FFA from *Jatropha curcas* oil. Tungsten addition to Pt nanoparticles supported on TiO₂ showed remarkably enhanced performance of the catalyst, providing a conversion of 86% and more than 90% for the deoxygenation of stearic acid and FFA, respectively, which was more than two times higher than the conversion degree achieved using a Pt/TiO₂ catalyst. The liquid fuel obtained was composed of saturated hydrocarbons, mainly C17 and C15, meaning that decarboxylation and decarbonylation were the dominant reaction routes. In the study, the effect of environment gases (N₂, 10% H₂/N₂, and H₂) on the degree of deoxygenation of FFA was also measured. When N₂ was used, the degree of deoxygenation was decreased to 55% after 9 h (time on stream), while using hydrogen-contained gases, preferably 100% hydrogen gas, the degree of the deoxygenation was above 90% for more than 20 h (time on stream), demonstrating that the hydrogen supply on the catalyst was favorable for preserving catalytic performance [97]. Moreover, it is noteworthy that carbon could help to reduce the production cost of the deoxygenation process because it is a widely available material typically used as a support for transition metals [98]. It has been proposed to study the deoxygenation of heptanoic acid over Pt nanoparticles supported on three different carbon supports (Pt/Norit activated carbon, Pt/Silicon carbon, and Pt/Vulcan carbon) prepared by an incipient wetness impregnation (IWI) method. It was shown that this

method was unsuccessful for obtaining a high dispersion of Pt on Silicon carbon and Vulcan carbon, however, it was possible to obtain a high Pt dispersion on Norit carbon (31%). Although it was possible to obtain high selectivity towards the formation of olefin hydrocarbons by using Pt/Norit C as the catalyst, through decarbonylation as the primary reaction, the heptanoic acid conversion was low [99]. In a subsequent study, the use of an alcohol reduction method was tested to deposit Pd nanoparticles on Vulcan carbon and Silicon carbon, however, it was verified that the impregnation method did not influence the catalytic performance or stability of the resulting Pd nanoparticles [100]. A further study proposed using multifunctional zeolite (ZSM-5)-based catalysts loaded with heterometallic nano oxides of Fe, Zn, and Cu to produce gasoline fuel (identified by standard reagents, namely iso-octane, n-heptane, cyclohexane, n-hexane, n-pentane, toluene, benzene, phenol, and ethanol) from palm oil. The use of the Fe-Zn-Cu/ZSM-5 nanocatalyst resulted in the production of gasoline with a yield of 59%, however, no further details were given about the mass fraction of liquid products [101].

It has been identified that an alkaline earth metal-based nanocatalyst such as $(\text{Ca}(\text{OH})_2)$ can provide better reactivity and product selectivity as compared with a CaO catalyst, mainly due to its superior textural properties (surface area, pore volume, and pore diameter) and basicity. Therefore, the deoxygenation of triolein using a $\text{Ca}(\text{OH})_2$ nanocatalyst derived from low-cost natural waste shells has been studied. As a result, it was identified that the shape of waste shell-derived CaO, which initially appeared in irregular aggregate forms, changed to cubic-like nanostructures after being treated with surfactants (ethylene glycol (EG) and N-cetyl-N,N,N-trimethylammonium bromide (CTAB) solutions) and wet sonochemical effect. In addition, it was possible to verify that using $\text{Ca}(\text{OH})_2$ -EG and $\text{Ca}(\text{OH})_2$ -CTAB nanocatalysts, the deoxygenation process was carried out successfully and the initial O/C ratio of triolein was strongly reduced from 0.31 to around 0.07–0.08, while the H/C ratio was maintained from 0.180 to around 0.175–0.177. Furthermore, both catalysts produced hydrocarbon yields of around 46%, although no further details were given about the mass fraction of liquid products [102]. In addition, the deoxygenation of WCO using bimetallic $\text{CaO-La}_2\text{O}_3$ on activated carbon nanorods (ACnano) derived from walnut shells has been tested. Interestingly, the study showed that, after being subjected to chemical treatments, walnut shell goes from having a smooth surface of large bulk irregular shape with particle size of about $>1 \mu\text{m}$ to be a nanocrystalline fibrous-like structure along with a thickness of about 15–20 nm. In fact, the acid treatment promoted breakage of hydrogen bonds in the crystalline region of the walnut shell cellulose by resulting in swelling of cellulose wall and further led to the formation of a nanocrystalline fibrous-like structure. The bimetallic $\text{CaO-La}_2\text{O}_3/\text{AC}$ nanocatalyst resulted in noticeable, well-dispersed, small particle scale-like needle (bladed) thin structures with long slabs and diameters between 50 and 165 nm. Additionally, under optimal process conditions, it was possible to obtain ~73% of hydrocarbon yield with a major content of C15 selectivity (82%). The $\text{CaO-La}_2\text{O}_3/\text{AC}$ nanocatalyst also showed negligible coke formation (1.4 wt.%) and high catalytic stability and reusability for up to six cycles, with around 73% of hydrocarbon yield and selectivity to n-C15 of around 82% [103].

Although, at present, multi-walled carbon nanotube (MWCNT) supports are not economical, their use in the deoxygenation of biomass feedstocks is highly promising. Consequently, MWCNT-supported NiO and Co_2O_4 catalysts (Co/MWCNT, Ni/MWCNT, and Ni-Co/MWCNT) have been tested during the deoxygenation of *Jatropha curcas* oil. It was evidenced that the Ni/MWCNT catalyst showed a better catalytic activity providing a hydrocarbon yield of 82%, followed by Ni-Co/MWCNT catalyst (70%) and Co/MWCNT catalyst (60%). However, for the Ni/MWCNT catalyst, the selectivity of C15 (37%) and C11 (23%) hydrocarbons was higher than C17 (11%) fractions, which showed further mild cracking. By incorporating Ni-Co into the MWCNT system, the catalyst preferred the decarboxylation and decarbonylation pathways, producing a high hydrocarbon yield (80%), increasing the selectivity towards C15–C17 hydrocarbons (64%), and producing a negligible amount of coke deposited on the surface of the spent catalyst. However, it

should also be noted that substantial solid char and residue as by-products (19 wt.%) were reported, reducing the mass fraction of liquid product (51 wt.%) [104]. In addition, it has been proposed to compare the use of NiO-Fe₂O₃ supported on MWCNT with the use of NiO-Fe₂O₃ supported on other carbon sources such as commercial activated carbon (ACcommercial) and biomass-derived activated carbon (ACwalnut shell). The results showed that the NiO-Fe₂O₃/MWCNT catalyst produced a higher hydrocarbon yield (89% with a C15–C17 selectivity of 79%) than NiO-Fe₂O₃/ACcommercial (~78%) and NiO-Fe₂O₃/ACwalnut shell (~72%). However, it should also be noted that the mass of the liquid product was not more than 26 wt.%, mainly due to the high production of non-condensable gases (~56 wt.%) and char (~12 wt.%), moreover, although Fe is a strong basic promoter (coke inhibitor), coke deposition on active sites during deoxygenation was inevitable. The study also highlighted that surface area and metal dispersion showed no correlation with improving the catalytic activity, instead, high decarboxylation/decarbonylation activity was correlated with the existence of rich weak + medium acidic and strong basic sites in the NiO-Fe₂O₃/MWCNT catalyst [105]. When the Ag₂O₃-La₂O₃/AC nanocatalyst was tested during the deoxygenation of WCO, it was evidenced that this catalyst resulted in a high yield of liquid fuel (~89%) and selectivity to C15–C17 hydrocarbons (93%), in addition to low coke formation on the spent catalyst surface (1.8 wt.% after six runs). In terms of product yield and C15–C17 selectivity, these results are comparable with the use of Ni-Ag/AC as a catalyst (discussed in the previous section) [106].

Overall, bimetallic acid-based nanocatalysts have been shown to play important roles in the deoxygenation of lipid-rich sources by promoting the development of reactions such as decarboxylation and decarbonylation under a hydrogen-free atmosphere and providing, in many cases, a higher conversion and selectivity of hydrocarbons as compared with mesoporous catalysts. This is due to the superior textural properties (e.g., surface area, pore volume, and pore diameter) of the nanocatalysts as well as due to the coexistence of basic sites and weak/medium acid sites in the catalytic systems. In fact, the type of metal, ratio composition, size, and shape are all essential parameters to achieve desired reactions and products. Additionally, the lower tendency of carbon-based nanocatalysts to form coke allows them to have better catalyst stability, avoiding major negative effects such as the occurrence of side reactions on the deoxygenation process. In addition, the uniform shape of these supports facilitates the diffusion of biomass-derived compounds as compared with conventional catalysts. As highlighted in the next section, nanocatalysts can be used to valorize whole lignocellulosic materials (lignin, cellulose, and hemicellulose), and to more efficiently promote the extraction of their main compounds, as well as the synthesis of long-chain oxygenates via C–C coupling reactions and their subsequent deoxygenation in the absence of hydrogen. Table S1 summarizes the main results of the use of mesoporous/micron size catalysts and nanocatalysts for the deoxygenation of different oleochemicals in the absence of hydrogen.

6. Transformation of Lignocellulosic Feedstocks into Value-Added Products

Historically, the paper and pulp industries and, more recently, second-generation bioethanol processes have focused on obtaining value-added products from cellulose and hemicellulose, whereas the lignin fraction has been considered to be an unwanted low-quality by-product. To improve the economic performance and sustainability of the use of lignocellulosic biomass, a wide range of pretreatment methods have been developed such as steam explosion and organosolv processing. Organosolv pulping is one of the more promising methods and has already been demonstrated at the pilot scale. However, typical monomer yields are low because, during lignin extraction and downstream recovery steps, undesired condensation reactions take place. These reactions lead to recalcitrant C–C bonds, rendering the resulting lignin unreactive towards mild depolymerization [107]. Recently, the lignin-first approach has emerged as a new biorefinery model that proposes to use the entire lignocellulosic biomass to disassemble lignin prior to cellulose and hemicellulose valorization. This approach embodies a tandem strategy that involves three elementary

steps: the solvolytic extraction of lignin from the lignocellulosic matrix, its direct fractionalization/depolymerization, and stabilization of the intermediate compounds to produce a high yield of aromatic monomers (in the form of a crude lignin oil) and holocellulose-rich pulp as residue [108]. The process can be carried out in a one-pot setup using a batch type reactor, in the presence of a solvolytic solvent, which generally is a short-chain alcohol (C1–C4), and under relatively high H₂ pressure (around 30 bar) and temperatures between 180 °C and 250 °C for 2–6 hours. In practice, in the first step, the short-chain alcohol (that can also act as a hydrogen donor) and heat induce the extraction of lignin from the biomass, followed by partial fragmentation through ether bond cleavage. This initial solvolysis generates reactive unsaturated fragments that are prone to undergo repolymerization [109]. The subsequent depolymerization and stabilization steps are driven by redox-active catalysts (e.g., Pd/C and Ru/C). In fact, the activity of redox catalysts is crucial in the reductive stabilization of lignin unstable species, suppressing repolymerization reactions and formation of condensed lignin products, thus, increasing the overall monomer yield [110]. The most appreciated depolymerization products from lignin fraction are high-value aromatic monomers such as BTX (benzene, toluene, and the three xylene isomers) and phenols, which can be used directly as basic fuels (e.g., biomarine fuel) or, similar to holocellulose residue, can be catalytically upgraded to a wide variety of high-quality fuels and chemicals [111–113]. BTX are produced today in large amounts from fossil raw materials and are among the top 15 petrochemicals in terms of market, mainly because they are applied as building blocks for producing many secondary intermediates and final products [114]. The annual demand of BTX exceeds 100 million tons, and the average price for BTX is around 1200 USD per ton. Thus, BTX represents a 100-billion-dollar market. Furthermore, phenol production volumes amount to 8 million tons per year, and the phenol market value is around 1500 USD per ton [115]. Similar to depolymerization products from lignin fraction, holocellulose-rich pulp residue can be upgraded to a wide variety of high-quality fuels and chemicals. For example, holocellulose-rich pulp residue can be used to produce nanocelluloses, a group of materials with nanometric-sized structural dimensions, which has gained increased attention because the materials exhibit some exceptional mechanical, thermal, and biological properties [116,117]. Nanocelluloses are classified as nanofibrillated cellulose (having a fibril width of 10–100 nm), nanocrystalline cellulose (having a fibril width of 1–10 nm), and bacterial nanocellulose. Of these cellulose types, nanofibrillated cellulose has higher mechanical properties as compared with crystalline and bacterial nanocellulose; therefore, it has been used in the production of biopolymers to improve their mechanical, thermal, and physical performance [118,119]. Additionally, nanocellulose has enormous potential for applications in biomedical, food industry, composites and coating, cosmetics, electronics and optoelectronic devices, and water treatments [120].

Considering the lignin-first approach, it has been demonstrated that the use of metal triflates (Yb, Ni, Cu, Al, Sc, La, and Hf) in combination with Pd/C are effective catalysts for the extraction of lignin from a lignocellulosic matrix, and its subsequent depolymerization into aromatic monomers. Metal triflates can catalyze the cleavage of phenyl glycoside, phenyl ether, and ester bonds between lignin and (hemi)cellulose, while the resulting lignin fragments are then disassembled into the aromatic monomers by Pd-catalyzed hydrogenolysis reactions. Typically, the process is carried out under mild process conditions (180 °C, 30 bar H₂, and 2 h) and methanol is used as a solvent. In this way, it is possible to obtain a yield of aromatic monomers of around 50 wt.% (based on lignin content) and cellulose-rich solid residue which is an ideal feedstock for established biorefining processes [121–123]. Furthermore, the depolymerization of lignin into phenolic monomers using a Pt/ γ -Al₂O₃ catalyst with methanol/water and without using an external source of hydrogen has been reported. The use of this catalyst and solvent mixture obtained a delignification of 94% and a high yield of aromatic monomers (49%) from birch sawdust under optimized conditions (230 °C, 30 bar N₂, 3 h, methanol/water molar ratio 1:2), and 98% of the cellulose remained intact in the carbohydrate residue [124]. A catalytic depolymerization process over a Cu₂₀MgAl catalyst in supercritical ethanol has also been

developed and its utility to directly upgrade woody biomass (scotch pine sawdust) has been explored. At 340 °C, it produced a lignin crude oil with high yield of monomers (67 wt.%) and characteristics of a marketable product (biomarine fuel). Additionally, the yield of the monomers obtained by the conversion of holocellulose fraction was 63%, and the major products identified were oxygenates (alcohols, aldehydes, esters, ethers, and ketones) [125–127]. Figure 3 shows a schematic overview of the lignin-first approach and potential value-added products.

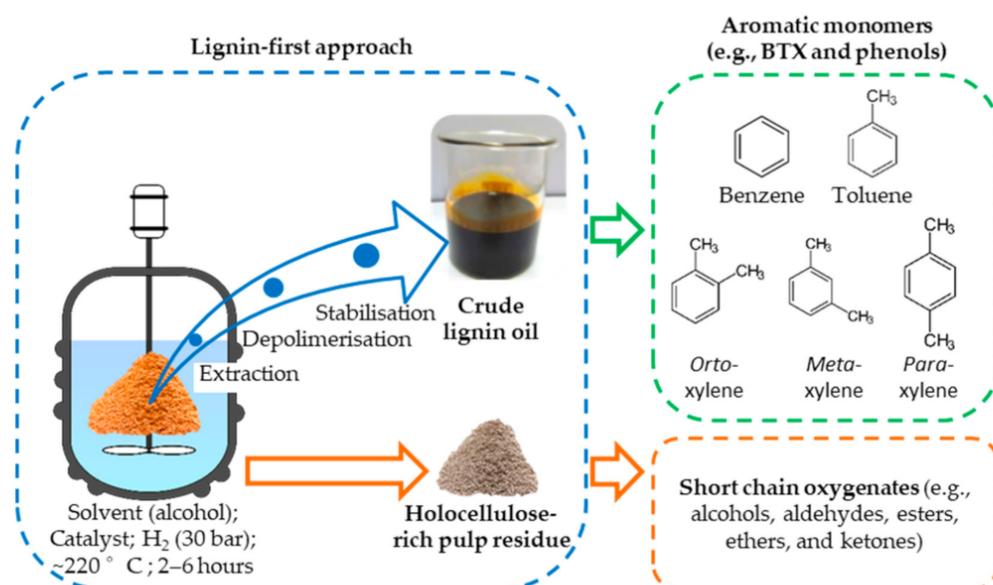


Figure 3. Schematic overview of the lignin-first approach and potential value-added products.

Notably, one drawback of the lignin-first approach is the recovery of heterogeneous catalysts, because they mix with the cellulose pulp residue. A promising solution to avoid this issue is the application of magnetic catalytic nanomaterials (e.g., FeO- and Ni-based nanomaterials). Owing to outstanding paramagnetic properties and inherent insolubility, magnetic catalysts can be efficiently separated from complex reaction mixtures using external magnets without affecting their activity and selectivity [128]. For example, a study reported the use of core-shell Fe₃O₄@C-SO₃H nanoparticles with magnetic Fe₃O₄ cores encapsulated in sulfonated carbon shell as a recyclable catalyst for the hydrolysis of cellulose. The Fe₃O₄@C-SO₃H catalyst showed high cellulose conversion (49%) and selectivity of glucose (52%). Additionally, Fe₃O₄ allowed the catalyst to be easily separated from reaction mixtures by using an externally applied magnetic field [129]. Magnetite Fe₃O₄ nanoparticles have also been used to support Co nanoparticles and construct a nano-Fe₃O₄-Co catalyst that was employed for the synthesis of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF). The experiments showed encouraging results regarding the FDCA yield (69%) after 15 h at a reaction temperature of 80 °C and, in the same way, the catalyst was successfully separated by magnetism [130]. Raney Ni has also been proposed as a catalyst in the depolymerization of wood pellets. As a result, lignin oil was obtained as the main product under mild process conditions (e.g., at 180 °C for 3 h) and Raney Ni was easily removed from the holocellulose residue with a magnet [131]. Furthermore, magnetic nanoparticles of Ni_{0.5}Zn_{0.5}Fe₂O₄ were used as heterogeneous magnetic nanocatalysts in the reactions of biodiesel production. These studies show that magnetic nanocatalysts are economical and environmentally friendly alternatives for practical applications in the biofuel industry [132].

7. Deoxygenation and Upgrade of Lignin Oil and Holocellulose Derivatives into Road and Jet Biofuels

The depolymerization of lignocellulosic biomass has led to a variety of aromatic monomers (e.g., BTX and phenols) and short carbon chain oxygenates (alcohols, aldehydes, esters, ethers, ketones, etc.), which generally have low-grade fuel properties or limited applications in organic synthesis; therefore, it is necessary to develop sustainable approaches that can reduce their oxygen content and upgrade them into value-added fuels and chemicals. In this way, one of the innovative catalytic approaches recently emphasized is the synthesis of long carbon chain oxygenates via various condensation reactions such as ketonization, aldol condensation, alkylation, oligomerization, Diels–Alder, Guerbet, and acylation, which can then be completely deoxygenated by hydrodeoxygenation or an alternative process. For example, the synthesis of long-chain oxygenates through ketonization followed by hydrodeoxygenation using two catalytic reactors in a cascade mode has been reported [133]. In addition, it is possible to use a single-bed catalytic process, however, the development of robust and easily regenerated bifunctional catalysts is needed, because side reaction components could alter the catalyst selectivity and decrease their activity, thus, hampering the catalyst's performance [134]. Additionally, hydrogen could be supplied by the same raw material through a hydrogen redistribution reaction, for example, through the dehydrogenation of fatty acids to unsaturated by products such as di-unsaturated acids, tri-unsaturated acids, or aromatics [135]. Lignin biomass can also be used as a hydrogen donor, as reported in the deoxygenation of triglycerides, fatty esters, and fatty acids to jet fuel-ranged hydrocarbons containing arenes over bimetallic PdNi/HZSM-5 catalysts [136]. A new route has been proposed for the simultaneous production of road or jet fuel range cycloalkanes (C₉–C₁₅) by the hydroxyalkylation/alkylation of 2-methylfuran and cyclopentanone followed by hydrodeoxygenation over Ni-based catalysts. 2-Methylfuran and cyclopentanone are the selective hydrogenation products of furfural, which is a main component of bio-oil obtained from the pyrolysis of lignocellulose biomass. Compared with straight-chain alkanes and branched-chain alkanes, cycloalkanes have higher densities and volumetric heating values due to robust ring strain. These characteristics are highly desired in aviation fuel, because they can extend the flight range of aircrafts, and consequently, reduce operating costs [137]. In addition, a liquid fuel composed mainly of perhydrofluorene with density (0.93 g/mL) and low-temperature properties (freezing point of −40 °C) has been synthesized by alkylation reaction of phenols and benzyl ether, followed with hydrogenation treatment. The authors have claimed that the density of perhydrofluorene is the highest among the bio-fuels reported in the past and even higher than JP-10 high-density jet fuel, however, its viscosity and freezing point are too high for practical application, so it can be used only as an additive for jet fuels [138]. High-performance hydrocarbons with improved cryogenic properties have also been synthesized from the biomass-derived 4-ethylphenol and phenylmethanol through alkylation reaction. The conversion of phenylmethanol achieved 100% with monoalkylated products (2-benzyl-4-ethylphenol and 3-benzyl-4-ethylphenol) and a selectivity of 71% under optimized process conditions (using HPW as catalyst, 110 °C, and 4-ethylphenol/phenylmethanol ratio of 2). After hydrodeoxygenation catalyzed by a mixture catalyst of Pd/C and HZSM-5, the alkylation products were converted into liquid fuel, which showed a high density of 0.873 g/cm³ (20 °C), gravimetric net heat of combustion of 42.7 MJ/kg, and freezing point of −42 °C, and therefore were promising to be used as a blend component for jet fuel application [139]. Furthermore, a multi-step process has been developed to produce jet biofuel range polycycloalkanes from cyclopentanol. This route consists of three consecutive steps that are operated under solvent-free, mild conditions. In the first step, cyclopentanol was dehydrated to cyclopentene over solid acids; in the second step, the cyclopentene was further converted to a mixture of C₁₀ and C₁₅ polycycloalkenes (with 1,2,3,4,5,6,7,8-octahydronaphthalene as the major component) by acid-catalyzed oligomerization/rearrangement; and in the third step, the C₁₀ and C₁₅ polycycloalkenes obtained in the second step were further hydrogenated to a mixture of C₁₀ and C₁₅ polycycloalkanes (with decalin as the major component). The final product

obtained showed high density (0.896 g mL^{-1}), and therefore, could be used as an additive to improve the volumetric calorific values of conventional jet fuels [140]. Additionally, a one-pot process has been reported that could produce jet fuel range spiro-fuel with an overall yield of 71.6% by co-conversion of lignocellulose-derived cyclopentanone via zeolite catalytic Mannich–Diels–Alder reaction. Under optimal conditions, a high Mannich–Diels–Alder product selectivity of 81.6% and yield of 80.9% was achieved with almost complete conversion of cyclopentanone. This product was further hydrodeoxygenated to spiro-cycloalkane by the bifunctional catalyst Pt/HY (with 88.5% yield). The resultant spiro-cycloalkane showed much higher density and volumetric neat heat of combustion (0.952 g/mL , 40.18 MJ/L) than the widely used JP-10 fuel (0.936 g/mL , 39.41 MJ/L), representing a promising route to produce a high-performance jet fuel from biomass [141]. Although the use of the lignin-first approach and the synthesis of long carbon chain oxygenates via various condensation reactions are highly promising strategies to optimize the transformation of lignocellulose residues into high-quality road and jet biofuels, it is necessary to expand the study of their commercial opportunities to identify the best production and distribution alternatives. In fact, only a few contributions have discussed the economic performance of the entire conversion cycles of lignocellulosic residues into jet biofuel, and most of them are based on simulations obtained from experimental data. For example, different scenarios of the economic performance of the production of jet biofuel intermediate from furfural through aldol condensation with acetone has been recently discussed. It was calculated that the yearly unit manufacture cost of 0.716 USD/kg could be the nearest solution to enhance the economic performance of the production of jet biofuel intermediate based on the technology studied [142]. The idea of using furfural as the precursor of jet biofuel intermediate has motivated additional research, in which selling prices for this fuel in the range of 1.00 to 6.75 (USD/gal) have been proposed [143,144]. Figure 4 shows representative C-C coupling reactions for the synthesis of long carbon chain oxygenates: aldol condensation, oligomerization, and hydroxyalkylation/alkylation.

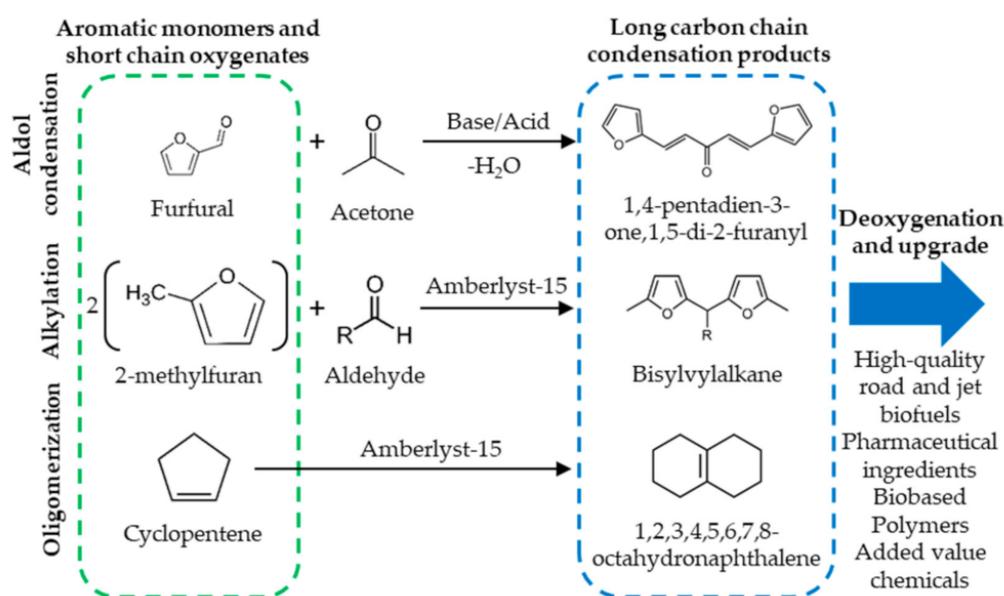


Figure 4. Representative C-C coupling reactions for the synthesis of long carbon chain oxygenates: Aldol condensation [6], oligomerization [140], and hydroxyalkylation/alkylation [145].

8. Conclusions

In this study, we have reviewed the recent advancements in the deoxygenation of oleochemical and lignocellulosic feedstocks in the absence of hydrogen to produce high-quality road and jet biofuels. The review highlighted that lipids can be obtained from biowaste using relatively simple pretreatment methods, however, the extraction of value-added derivatives from lignocellulosic residues such as aromatic monomers and short

chain oxygenates requires more advanced methods such as the lignin-first approach, which proposes to use the entire lignocellulosic biomass to disassemble lignin prior to cellulose and hemicellulose valorization. Although high capital investment costs, weak feedstocks supply chains, and a continuous increase in the prices of oleochemical feedstocks are factors that limit increased production high-quality road and jet biofuels, it is expected that in the medium/long term the use of lignocellulosic residues can contribute to reduce the production costs, as more efficient materials and production technologies are developed and commercialized. In this regard, this review showed that different materials at the micro and nano scale have been tested as catalysts and their supports. The former has included noble, transition, and alkaline earth metals, while the latter has included metal oxides, zeolites, and carbon-based materials. Regardless of the catalyst particle size, the coexistence of basic sites and weak/medium acid sites is highly important in catalytic systems. Basic sites can enhance the removal of oxygenates via decarboxylation and decarbonylation reactions and inhibit coke formation, while weak/medium acid sites can enhance the cracking reaction. Moreover, the use of carbon-based catalysts can avoid the undesirable effect of coke deposition on catalyst surfaces due to their mild acidity properties. Therefore, although nanomaterials still have a high production cost, the development of highly active and stable nanocatalytic systems is highly promising as a strategy to optimize the transformation processes of biomass platform molecules and increase the production of high-quality road and jet biofuels, contributing to the growth of a more sustainable global economy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr10020187/s1>. Table S1: Comparison between the use of mesoporous/micron size catalysts and nanocatalysts in the deoxygenation of different oleochemicals in the absence of hydrogen.

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