Sustainability of the Catalytic Process for Biomass Conversion: Recent Trends and Future Prospects

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Abstract Depleting conventional resources and increasing energy demand have placed immense pressure on the environment and forced mankind to look for alternate and sustainable energy resources. Biomass is a promising resource which is environment friendly as well as sustainable. Lignocellulosic biomass can be fractionated into cellulose, hemicelluloses, and lignin, out of which the structure of lignin makes catalytic processing more challenging. The selection of suitable solvent, catalysts, and reaction conditions for biomass conversion has a vital role in the yield and composition of targeted products. Biomass can be converted into oil, gas, and char using a suitable catalyst and conversion processes. Valuable chemicals and transportation fuel can be generated from oil obtained from sustainable biomass such as agricultural waste, forestry products, inedible plants, etc. The product obtained from most of the conversion processes is a complex mixture of chemicals demanding further separation and upgradation. Catalytic oil upgradation is necessary before being used as a transportation fuel. It is essential to identify the basic/platform components that can be produced from biomass and serve as feedstock for the synthesis of the majority of the chemicals. Catalyst can facilitate the selective transformation of molecules provided it is sustainable in terms of its activity and regeneration. An emerging approach integrates various routes of biomass conversion technologies such as catalytic pyrolysis, hydrolysis, and liquefaction over a suitable solid catalyst to transform biomass into useful chemicals and fuels. This chapter summarizes the technological challenges to selectively convert biomass to oil or basic chemicals and fuels by catalytic processes.

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1 Introduction

Biomass has the potential to produce value-added chemicals and has the potential to become an alternative to fossil fuels. It is a stored solar energy in the form of chemical bonds of carbon-hydrogen by photosynthesis or the metabolic activity of the organism. The reason for the search for an alternate form of energy is the depletion of fossil fuel reserves, as well as the emission of greenhouse gases and its impact on the environment due to the consumption of fossil fuels. The potential of biomass can be gauged from the fact that it is recognized as the fourth largest source of energy. The other sources being crude oil, coal, and natural gas [1].

Utilization of biomass as a fuel source is sustainable that will help to balance out the net emission of CO_2 by the interplay between photosynthesis and biorefinery. Biomass is mainly obtained from lignocellulose, lipid, and starchy crops. There are various methods for conversion of biomass, viz., catalytic processes like biochemical (fermentation and enzymatic hydrolysis) and thermochemical (combustion, pyrolysis, and gasification) processes, transesterification, and isomerization, etc. [2]. These processes make use of both homogeneous and heterogeneous catalysts with relative advantages and disadvantages. The choice of conversion process depends on factors such as type of feedstock, the volume of biomass, targeted chemicals, reactor type, etc.

1.1 Biomass Resources

A complex linkage exists between biomass for energy and materials, biomass for food production, biomass for energy use, water requirement, and their impact on biodiversity and climate change. Figure 1 illustrates the complexity by showing key relationships and assumptions. Biomass feedstock can be classified into three groups, viz., (1) agricultural waste, municipal solid waste, and forest residue, (2) surplus forestry, and (3) biomass produced via cropping system. Altogether, the three categories could produce 500 EJ/year of energy. As far as category one is concerned, the biomass supply is almost inevitable. However, conventional uses of biomass can affect its availability for energy applications. Approximately 100 EJ/year of energy is estimated from this source, i.e., biomass residue [3]. The second source, surplus forestry, indicates the possible growth of surplus forests that can account for 60–100 EJ/year of energy worldwide. The availability depends on sustainable forest management principles [3]. The third category includes the

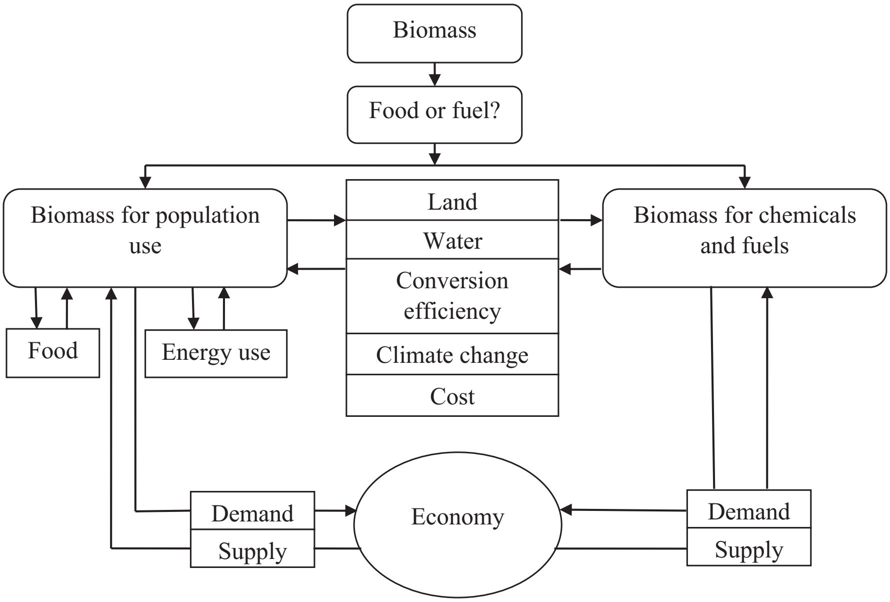

Fig. 1 Key relationships relevant to the assessment of biomass potentials

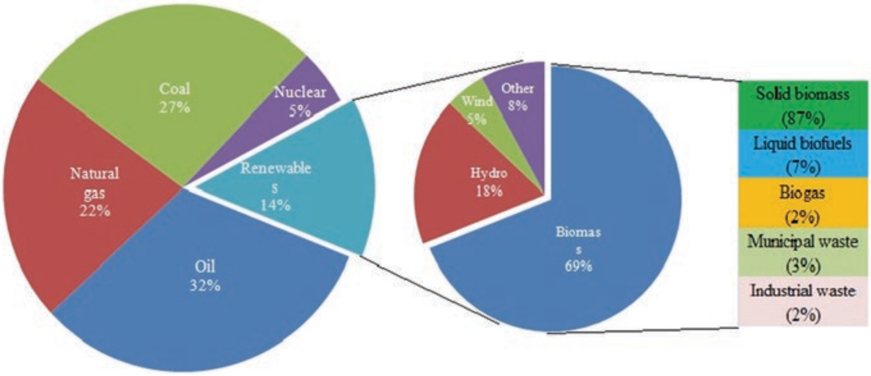

Fig. 2 Bioenergy share in world energy demand in the year 2017

possible surplus land available for energy crops. The better quality land, which is not utilized for main crops and requires less water and fertilizer, can be used for this purpose. The potential contribution from the third source is estimated to be 120 EJ/year. The arid land (water scarce and degraded) can be used for energy crops and can account for 70 EJ/year [3]. The contribution will depend on the choice of energy and planting rate and will be influenced by the water availability, environmental constraints, logistic issues, etc. The share of bioenergy in total energy demand in the year 2017 is shown in Fig. 2 [4]. The bioenergy share is 3% of the agriculture and energy sector, and less than 1% of agriculture land is used for an energy crop.

Another source of biomass is microalgae and macroalgae (seaweed) as a feedstock for bioenergy but is limited due to its relatively low dry matter content. So it is difficult to evaluate the sustainability and economic competitiveness of algal biomass [3].

Even though the potentials of biomass can be evaluated, the question remains as to how effectively this potential can be utilized? Factors like economic and environmental impact have to be taken into account while evaluating the utilization of biomass potential. Typically, USD 3–4/GJ is considered as a threshold value to compare it with fossil fuel price. Higher fossil fuel price and government incentives in favor of bioenergy can certainly make it more sustainable [3].

The land for agriculture and for bioenergy crops will compete with each other, and preference will be given to agriculture in the countries with an agricultural-based economy, like India. Additionally, the land will be constrained by environmental and logistical factors. The modern and efficient methods of agriculture can free part of the land for bioenergy crops. It is apparent that the first generation of food crops will contribute in a major way compared to second-generation energy crops. The selection of conversion technology is chosen on the basis of feedstock availability and suitability. The various available technologies are elaborated in the following sections. A huge estimate of ten billion tons of dry biomass is produced annually, which is equivalent to 10% of the global energy demand. This biomass could generate energy equivalent to two billion tons of standard coal [5].

1.2 Components of Lignocellulosic Biomass

The biomass is available at a low cost, and there are no competing interests between lignocellulosic biomass and food source. The three basic components of lignocellulosic biomass are (1) hemicellulose consisting of five-carbon sugar polymers (20–35%), (2) cellulose consisting of six carbon glucose polymers (35–50%), and (3) lignin consisting of aromatic compound polymers (10–25%). Hemicellulose is easy to hydrolyze and can be converted at mild operating conditions due to the low degree of polymerization. Cellulose is a straight-chain polymer and can be depolymerized into glucose, which is further decomposed into useful chemicals and fuels. The processing of cellulose and hemicelluloses involves similar reactions but yields different products. Lignin is an amorphous polymer and has aromatic functionality. The structure of hemicellulose and lignin varies from biomass to biomass. The decomposition behavior of each of these components is different from each other and depends on temperature, heating rate, and contamination. Hemicellulose and lignin can affect the degradation of cellulose but will not hinder each other's process. As a rule of thumb, cellulose leads to bio-oil formation, and lignin leads to bio-char formation. Also, higher volatile matter leads to bio-oil and syngas formation, and high fixed carbon leads to bio-char formation.

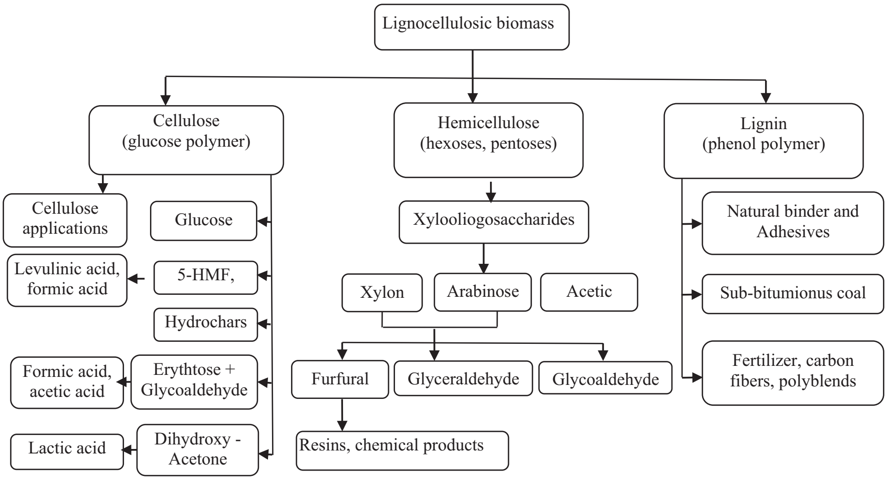

Fig. 3 Representation of products from lignocellulose based biorefinery

Biomass moisture content has a significant influence on the heat transfer process and product distribution. High moisture content helps to increase the bio-oil yield, which is a poor fuel that contains nearly 50% water and highly oxygenated products. The overview of lignocellulosic feedstock-based biorefinery is shown in Fig. 3. As can be seen, the biorefinery is analogous to petroleum refinery and can produce multiple products ranging from chemicals to fuels.

In biomass processing, the three components are separated and processed separately. Typically, pretreatment steps to remove hemicellulose and lignin from biomass. Cellulose is deconstructed into glucose monomer and is the feedstock for useful products, i.e., 5-hydroxymethylfurfural (5-HMF). Xylan is the major component (8–25%) representing hemicelluloses and used to produce furfural and its derivatives [6]. Lignin is a major source of aromatic functionality and consists of *p*-coumaryl alcohol monomer, coniferyl alcohol monomer, and sinapyl alcohol monomer. Lignin is a source for high carbon and contains nearly 40% possible energy of biomass.

1.3 Biomass Conversion Strategies

Biomass as a resource is complex and extremely varied in nature, and one or more conversion steps are needed to convert it into a usable energy form. Biomass can be used without being fractionated, such as combustion, but with low efficiency. For efficient use, each lignocellulosic fraction needs to be isolated for processing, as each one of them has a distinct structure. Typically, the following conversion strategies incorporating various catalysts are adapted for the conversion of lignocellulosic biomass to useful products:

1. Chemical
2. Thermal
3. Microbiological

Chemical catalytic processing is gaining importance as the resultant product exhibits properties similar to petroleum-based products. These processes are conducted at mild operating conditions relative to non-catalytic methods and can be tuned to get the desired product distribution. The various useful chemical processes are catalytic pyrolysis, hydroprocessing, hydrolysis, dehydration, oxidation, isomerization, transesterification, etc. Homogeneous, as well as heterogeneous, catalysts can be used for the catalytic process. Homogeneous catalyst has a high turnover frequency (TOF); however, it poses problems like toxicity, corrosivity, reusability, and complex postprocess separation. Hence, heterogeneous catalysts are a better option compared to their homogeneous counterpart. As shown in Fig. 3, hemicelluloses are used to produce furfural, lignin is used to produce aromatic compounds, and cellulose is used to produce levulinic acid or glucose. All of this can be achieved by using conventional as well as modified catalysts such as zeolites and silica monometallic as well as bimetallic catalysts [6]. During biomass processing, the C-C coupling reactions such as oligomerization, aldol condensation, and ketonization use acid or metal oxide catalysts, whereas reforming, hydrogenolysis, hydrogenation, and oxidation use bimetallic catalysts. Bimetallic catalysts are preferred over monometallic catalysts due to their increased catalytic activity, modified selectivity, and improved catalyst stability. In the case of simple processing, the entire biomass is subjected to thermochemical processes such as gasification, pyrolysis, etc. The biological route utilizes living microorganisms (enzymes, bacteria) to degrade biomass feedstock and produce liquid and gaseous fuels.

The abovementioned technologies can be used independently or in combination, such as thermochemical processing (catalytic pyrolysis/gasification). The choice of conversion route will depend on many factors such as type of feedstock, targeted products, the volume available, and readiness of the technology. In addition, handling, transport, and storage of the biomass are cumbersome and sometimes costlier, making the whole process uneconomical. So all factors needs to be considered while selecting a suitable process for biomass conversion.

2 Catalytic Processes for Biomass Conversion

The catalyst requirement for biomass conversion is different from the petroleum industry. Petroleum feedstocks are oxygen-deficient, whereas biomass is rich in oxygen. Hence, conversion strategy differs as the addition of functional groups, and removal of it is required for petroleum and biomass feedstocks, respectively. Biomass molecules are highly complex and vicious and pose mass transfer limitations whenever heterogeneous catalysts are used. The energy density of biomass can be increased through the removal of oxygen and can be achieved through various conversion processes mentioned earlier. Thermal processes are nonselective, whereas chemical processes are selective such as dehydration, hydrogenolysis, decarboxylation, and decarbonylation. The catalyst then affects the conversion rates and the selectivity of the products but suffers from deactivation. Many catalysts for biomass conversion have been tested, but few found suitable on the basis of stability, selectivity, and reusability. Most of the catalysts are tested with model components, and the problem appears when real feedstocks with impurities are used. Bimetallic catalysts seem to be promising as the catalyst properties can be modified to handle real feedstocks [6].

The porosity of the catalysts plays a vital role in biomass conversion. Porous materials with mixed pores (micro, meso, and macro), compared with single-mode pores, are more suitable for biomass conversion [7]. As an important step in processing, biomass is converted to platform chemicals through various routes. There are five platforms reported in the literature. They are the sugar platform, thermochemical or syngas platform, biogas platform, carbon-rich chain platform, and plant product platform. The sugar platform focuses on the fermentation of sugar extracted from biomass; the thermochemical platform focuses on the gasification/pyrolysis of biomass feedstock; the biogas platform decomposes the biomass through anaerobic digestion with the help of microorganism, carbon-rich platform converts oil and fats via etherification/transesterification; and plant product platform is the biorefinery operations in a plant kingdom itself rather than in an industrial plant. Sometimes, the plant strains are genetically modified to produce more feedstock or chemicals than it does naturally. Presented below is the list of top 12 chemical products that form the building blocks of the biorefinery by evaluating their potential market, their derivatives, and the technical complexity of the synthesis pathways [8]; these are:

- 1,4- Succinic, 1,4-fumaric, and 1,4-malic acids
- 3-Hydroxy propionic acid
- Glucaric acid
- Itaconic acid
- 3-Hydroxybutyrolactone
- Sorbitol
- 2,5-Furandicarboxylic acid
- Aspartic acid
- Glutamic acid
- Levulinic acid
- Glycerol
- Xylitol/arabinitol

2.1 Catalytic Processes for Lignocellulosic Biomass Conversion

In this section, the various catalytic processes for the conversion of biomass into fuels and valuable chemicals are discussed. The chemical processes for biomass conversion are sensitive to reaction conditions and nature of solvents and catalysts and produce a complex mixture of products requiring further separation and upgrading. An integrated processing approach with a multifunctional catalyst will be beneficial for biomass conversion.

2.1.1 Catalytic Hydrolysis-Acid/Alkaline Catalysts

The biomass must be pretreated to improve the product yield in downstream processing. The pretreatment changes the biomass structure that can be achieved either by physical, chemical, and thermal processing or sometimes by a combination of these treatment methods. The aim of pretreatment is to decrystallize cellulose, separate hemicellulose, and break the lignin seal. During hydrolysis, the cellulosic component of lignocellulosic biomass is converted to glucose and xylose as the main products. However, due to its crystalline form and hydrogen bonding, the hydrolysis of cellulose is significantly difficult and requires the use of strong liquid acid as a catalyst [9]. This process yields reducing sugars, which is furthermore converted to useful chemicals. Among the different liquid acids, mineral acids (H_2SO_4 and HCl), as well as organic acids (carboxylic acid, p-toluenesulfonic acid), can be used as a catalyst. Dilute acids are used to avoid corrosion of process equipment and also the degradation of glucose and xylose to products such as 5-HMF. Dilute H_2SO_4 has been used commercially for the production of furfural from cellulosic biomass. It is also used for the hydrolysis of hemicelluloses to sugar products such as xylose. The limited solubility of cellulose in water is a major issue; hence, solvents like ethanol are commonly used. The effect of reaction conditions such as temperature and acid concentration was investigated with four timber species (aspen, balsam fir, basswood, and red maple) and switchgrass. They were subjected to hydrolysis in the presence of dilute H_2SO_4 in an identical reaction condition (temperature, 160–190 °C; H_2SO_4 concentration, 0.25–1% (w/v), particle size (28—10/20 mesh)). The maximum product yield was 94% for xylose and 13.6% for glucose. Both temperature and acid concentration have a strong influence on the reactions [10]. Various solid catalysts used for hydrolysis are discussed in subsequent sections of this chapter.

In alkaline hydrolysis, lower temperatures and pressures are utilized compared to acid hydrolysis, but the treatment time runs in a few hours to a few days as against minutes or seconds for the acid catalyst. The treatment effectiveness largely depends on the lignin content of the biomass material. Sodium, calcium, potassium, and ammonium hydroxides are the commonly used alkaline agents, of which sodium hydroxide is widely used. The enzymatic hydrolysis of cellulose is one of the reactions influenced by alkali pretreatment [10].

2.1.2 Catalytic Solvolysis of Lignocellulosic Biomass

In solvolysis, an organic molecule modifies the chemical and physical properties of cellulose so that it can be in contact with the catalyst for a longer time. The organic molecule acts both as solvent and reactant, and therefore it has a significant effect on the product formation. For example, solvent methanol in the presence of dilute

H_2SO_4 reacts with lignocelluloses to give methyl glycoside. A mixture of methanol in water and ethanol in water was tested to be suitable for liquefaction of lignocelluloses [11]. Comparatively, the solvolysis of cellulose (in water or alcohol or mixture) is difficult than hemicelluloses and lignin due to its chemical structure. The typical solvents used for this solvolysis are acetone, ethylene glycol, toluene, etc. The solvolysis method is also used for lignin extraction along with other pretreatment methods such as acid/alkaline hydrolysis and reductive or oxidative catalytic fractionation. Non-catalytic solvolysis of lignocellulosic biomass is possible but requires longer reaction time and results in low product yield.

2.1.3 Hydrothermal Liquefaction of Lignocellulosic Biomass

The objective of the liquefaction process is to maximize the production of C_1–C_6 compounds over xylose and glucose. Compared with the catalytic hydrolysis process, the hydrothermal process targets the deep degradation of lignocellulosic biomass that involves isomerization and dehydration of glucose. The final distribution of the product depends on the type of catalyst used. An advantage of the hydrothermal treatment is that it does not get affected by the presence of water in biomass, whereas other processes require pre-drying of biomass. Numerous halide, sulfate, and alkaline catalysts are used for the hydrothermal liquefaction process such as $CrCl_3$, $FeCl_3$, $CuCl_3$, $NiSO_4$, $CoSO_4$, KOH, $Ca(OH)_2$, etc. The use of halide/sulfate catalysts promotes the formation of levulinic acid, furans, and formic acid, whereas alkaline catalysts give bio-oil and phenolic compounds as major products. The hydrothermal reaction is typically carried out at ~500 K in order to convert cellulose completely. In the case of bio-oil, higher reaction temperature (>500 K) and longer reaction times lead to the formation of secondary products, thereby decreasing the bio-oil yield. The separation of the products produced from catalytic hydrothermal liquefaction requires multiple extraction steps with different types of solvents due to the complex mixture of liquid, gases, and tar. At present, it is uneconomical to produce bio-oil by hydrothermal liquefaction when compared with petro-diesel and gasoline. Hydrothermal liquefaction is energy-intensive and time-consuming [9]. Therefore, innovative separation methods are required for the separation of products obtained from hydrothermal liquefaction. Comparatively, the fast pyrolysis method discussed in the following section is more promising.

2.1.4 Catalytic Pyrolysis

Pyrolysis is a high-temperature decomposition process carried out in the absence of oxygen and can be used to convert lignocellulosic biomass to bio-oil in the absence of oxygen. Pyrolysis of biomass results in three products, namely, oil, gas, and solid char. Pyrolysis operating parameters such as residence time and heating rate can be tuned to get the maximum of oil or gas or char. Furthermore, pyrolysis can be classified as slow pyrolysis (heating rate <20 °C/min, residence time >15 min), fast pyrolysis (heating rate 10–200 °C/s, residence time 0.5–10 s), and flash pyrolysis (heating rate >1000 °C/s, residence time <0.5 s). Slow pyrolysis is traditionally used for maximizing solid yield, whereas fast, as well as flash, pyrolysis is preferred for bio-oil yield [1]. Pyrolysis reduces the H/C ratio of the products against hydrogenation that improves the H/C ratio. The reactions that take place during pyrolysis are depolymerization, dehydration, decarboxylation, esterification, condensation, cyclization, etc. The bio-oil obtained by biomass pyrolysis is a complex mixture of organic acids, ketones, esters, and aromatic compounds. Pyrolysis oil is acidic in nature and contains aqueous as well as organic phases. Hence, further treatment is necessary to get useful fuel-like products. The major factors that affect the progress of pyrolysis are biomass heating rate, operating temperature, residence time, and the catalyst [9]. The pyrolysis process can be improved by proper selection of heating rate, operating temperature, catalyst, and residence time.

Catalyst helps in enhancing the rate of cracking of higher molecules into the smaller ones. Each catalyst exhibits its own kinetics that results in varied product distribution under a different set of operating parameters. The catalytic pyrolysis process can be classified into three different groups, viz., catalyst pre-added in the feedstock, catalyst added into the primary reactor, and catalyst in the secondary reactor located downstream to the primary reactor. The heterogeneous catalysts used in the pyrolysis process are divided into four catalytic groups, viz., dolomite type, Ni-type, alkali metal, and noble metal catalysts [12]. A bimetallic catalyst is a promising option for biomass upgrading using pyrolysis. Fast pyrolysis is a proven technology to convert renewable feedstocks to an energy-rich liquid product (~17 MJ/kg). Fast pyrolysis utilizes heating of biomass at a high rate and rapid cooling of vapor (residence time <2 s), thereby minimizing the secondary cracking reactions and polymerization. Fast pyrolysis is two to three times more economical than liquefaction and gasification but exhibits a complex reaction mechanism.

Catalytic pyrolysis is preferred as it increases the reaction rate and exhibits selectivity toward the desired product. Acid and base, in homogeneous as well as heterogeneous forms, are used as catalysts. The pretreatment of the biomass also has positive effects on pyrolysis. The widely used catalysts for pretreatment of biomass are H_2SO_4, HCl, H_3PO_4, and Lewis acids. For example, pinewood sawdust was treated with phosphoric acid before being subjected to fast pyrolysis, which increased the formation of levoglucosan content. Levoglucosan was further converted to syngas [13]. In the case of supported heterogeneous catalyst, the activity change with the change of support was evident from the pyrolysis of cellulose to produce 5-methyl furfural at 773–1073 K. The catalyst SO_4^{2-} supported on TiO_2 yield furfural, while SO_4^{2-} supported on ZrO_2 yield furan [9]. The solvent also plays an important role in pyrolysis by dissolving lignocellulosic biomass or reaction intermediates and thereby increases the yield of products. It was observed that the yield of levoglucosenone and furfural is found to increase when pyrolysis of cellulose is carried out at 473 K for 6 min using H_2SO_4 as a catalyst and tetramethyl sulfone ($C_4H_8O_2S$) as a solvent [14]. The acid and alkaline catalysts used in pyrolysis exhibit a corrosive effect and have its effect on the stability of the bio-oil. Hence, the use of phosphates, sulfates, and chlorides is suggested in place of these catalysts [15]. Use of zeolite-based catalysts such as ZSM-5 and MCM-41 has an advantage such that selective pyrolysis can be conducted to obtain bio-oil containing hydrocarbons, much like the gasoline. However, the catalyst activity may decrease as a result of coke formed on the catalyst surface [16]. The lignocellulose biomass, along with catalyst and reaction condition, should be selected carefully to get the desired product.

2.1.5 Catalytic Gasification

Gasification is the process of obtaining gaseous products such as H_2 and syngas by thermochemical conversion of biomass in an oxygen-deficient environment. The product syngas is further converted to hydrocarbon fuel through Fischer-Tropsch synthesis. The gasification followed by Fischer-Tropsch is referred to as indirect liquefaction of lignocellulosic biomass. Another route to make syngas is partial oxidation of lignocellulosic biomass at elevated temperatures (800–900 °C). Air is used as a source of oxygen; hence, separation of nitrogen becomes a problem in biomass gasification. The tar formed during gasification contains polyaromatic hydrocarbons, and its conversion to useful products requires multiple processes. To avoid tar formation, steam gasification is preferred where water at supercritical conditions is used to improve the solubility of biomass in water, thereby reducing the mass transfer limitations. Under supercritical conditions (673 K and 1 MPa), cellulose was converted to methane over Ru/TiO_2 catalyst, and a 44% yield of methane was obtained [17]. The catalyst can deactivate due to coke formation. Also, the tar formation can block and foul the downstream process equipment. The best way is to convert tar into syngas using a multifunctional catalyst and remove bio-char by catalytic combustion. One of the risks associated with biomass gasification is incomplete combustion leading to the emission of toxic gases and particulate matter.

2.1.6 Integrated Processing

In integrated processing, two or more processes are combined together to produce the desired product. For example, in hydroprocessing, hydrogenation follows the hydrolysis, solvolysis, liquefaction, and pyrolysis. In the integrated approach, the depolymerization is followed by an in-situ decomposition to yield commodity chemicals and fuels. On decomposition, the oxygenated molecule is obtained, which is further deoxygenated/hydrogenated to get new C-C bonds. The commonly used catalysts for hydrogenation are Pt, Ru, and Pd and for hydrolysis are liquid acids. When a multifunctional catalyst ($Pt/\gamma\text{-}Al_2O_3$) is used, the process of decomposition and hydrogenation occurs simultaneously. For example, a gasoline-like product is obtained (carbon yield, 57%; octane number, 96.5) when maple wood is hydrolyzed using H_2SO_4 and then hydrogenated over metal Ru and Pt catalyst in an integrated process. The process was carried out at 433 K [18].

2.2 Advanced Heterogeneous Catalysts for Biomass Conversion

Heterogeneous catalysts are characterized by size, shape, and porosity. The nanosize metal catalyst shows improved properties such as selectivity, durability, reusability, and other such properties compared to their bulk counterparts [19]. This is beneficial for biomass conversion as it results in improved interaction between active sites and reacting molecules. The porosity of the solid catalyst is an important tunable property that can influence the product selectivity. The widely used porous catalysts for biomass processing are zeolites and silica. Multipore catalysts (micro, meso, and macro) are preferred over monopore catalyst to overcome certain drawbacks of monopore catalyst such as mass transfer limitation resulting in poor selectivity, catalyst deactivation, and low conversion.

2.2.1 Zeolites, Silica, and Metal Oxides

Porous materials are classified as micropore (diameter up to 2 nm), mesopore (diameter between 2 and 50 nm), and macropore (diameter above 50 nm). Zeolites are microporous materials with tunable Brønsted and Lewis acidity that makes them suitable candidates for biomass conversion. For example, sugarcane bagasse has been fast pyrolyzed to aromatics (yield 12.4%) and olefins (yield 10.9%) using zeolite catalysts. Also, HZSM zeolites are used for catalytic hydrolysis of furfuryl alcohol to levulinic acid with a 70% yield. Zeolites are also used for various conversion processes such as upgrading glycerol to valuable chemicals, aromatic hydrocarbons from furans, phenolic components from lignin, etc. [2]. Zeolites as support can accommodate various metals, and their oxides and can be used in application such as biomass pyrolysis (Fe/HZSM-5), glycerol upgradation (Sn/HZSM-5), and production of other biomass-derived components (Pt/(NH_4-USY).

Zeolite suffers from mass transfer limitations due to its microporous nature. This can be overcome by the use of silica that has a mesoporous structure. Silica can accommodate different functional groups and has a high BET surface area (400–1400 m^2/g), tunable pore diameters, and optimized acid sites [20]. Therefore, the mesoporous silica catalysts are ideal candidates for the conversion of bulky biomass molecules. For example, glucose is converted to 5-hydroxymethylfurfural (5-HMF) over SiO_2-Al_2O_3 catalyst. Similarly, lignin can be converted to aromatic hydrocarbon using silica-based catalysts [21]. Aluminum-doped silica catalyst with varying silica-alumina ratio was used for the conversion of lignin to aromatics. For example, Al-SBA-15 (Si/Al = 50) was used for pyrolysis of corncob to selectively get 2-methoxy phenylacetate [22]. Also, the MCM-41 catalyst was found to be useful for converting ethanol to ethylene at temperatures above 350 °C [23]. For the conversion of cellulose to hydrogen, a higher hydrogen yield was obtained with Ni/KIT6 and Ni/SBA15 [24]. The better performance of the silica-supported catalyst is attributed to higher BET surface area and reduced diffusional resistance due to large pore diameter. The bimetallic catalyst can also be supported on silica (CoCu/SBA-15) and used for hydrogenation reactions such as furfural to furan. In a similar reaction, about 99% conversion of furfural can be achieved with 80% selectivity to furfuryl alcohol. The high conversion is due to the synergistic effect of metal-metal and metal-support interactions [25].

Metal, metal oxides, and their combinations are the commonly used catalysts for oxidation and hydrogenation reactions. In general, the metals present on the left side of the transition metal series in the periodic table exhibit good activity for oxidation reactions in their bulk form. At the same time, many materials (like Au for oxidation) that do not exhibit any activity in their bulk form become active catalysts at the nanoscale (1–100 nm) due to improved surface and electronics properties [26]. Hence, careful selection of metal catalysts for the oxidation process requires information of their position in the periodic table as well as their properties at the nanoscale. Mixed metal oxides exhibit attractive catalytic activity due to their enriched acid-base, redox, and surface area properties. However, their oxidizing ability for biomass oxidation can reduce due to excess basicity. As biomass conversion is conducted at harsh hydrothermal conditions, the hydrothermal stability of the catalyst is of paramount importance. Importantly, metal oxides such as TiO_2, ZrO_2, CeO_2, and ZrO_2 exhibit higher hydrothermal stability [27]. Despite all these advantages, the control over the aggregation of metal nanoparticles during synthesis and reaction remains a great challenge. This can be tackled by depositing the nanoparticles on high surface area metal oxide support. Metal-support interaction enhances the properties of nanoparticles [28]. For example, PtSn/γ-Al_2O_3 was able to convert mono- and polysaccharides with higher yield compared to PtSn/C [29]. A well-dispersed Ni nanoparticle on SiO_2 was used in the levulinic acid hydrogenation to γ-valerolactone and performed well due to the presence of optimum porosity and highly dispersed nanoparticles [30].

2.2.2 Micro- and Mesoporous Catalysts for Catalytic Processing of Edible/Non-edible Biomass

The edible biomass comprises lipids and starch, whereas non-edible biomass includes lignocellulosic materials. Among the edible biomass feedstocks, sugarcane or corn is converted to bioethanol via the fermentation route, whereas edible oils (sunflower, soybean, safflower, and palm), as well as non-edible oils (jatropha, karanja), are converted to biodiesel via catalytic transesterification with alcohols (methanol or ethanol). Both homogeneous (methanolic NaOH and KOH) and heterogeneous catalysts (ZnO/HZMS-5, PbO/HZSM-5) are used for transesterification reactions [31–33]. Homogeneous transesterification reactions are carried out at mild reaction conditions (temperature 60–70 °C, atmospheric pressure), whereas heterogeneous catalyst reactions are performed at higher temperatures (100–180 °C) and pressures (20–40 bar).

The non-edible biomass, i.e., all plant-based residues, are converted to syngas or bio-oil through thermochemical routes. The biodiesel synthesis from non-edible and waste cooking oils is gaining momentum as these oils are available at a cheaper rate and do not have competing usage. Vegetable oil and bio-oil can also be converted to biogasoline via catalytic cracking but require proper catalyst and reactor setup. The product of cracking comprises an organic liquid, gas, coke, and some amount of water. The organic liquid is a mixture of hydrocarbons having properties similar to gasoline, kerosene, and diesel fractions. The catalysts used for catalytic cracking of oil include alumina, silica (SBA-15), zeolites (HZSM-5), and silica-alumina [34]. For example, a fixed bed reactor was used for catalytic cracking of canola oil to biogasoline over a variety of zeolites under different reaction conditions. Among the various zeolites used, HZSM-5 was found to be the most effective catalyst with a 100% conversion of canola oil. The reaction was carried over a temperature range of 573–773 K. The reaction product contained a high yield of aromatic compounds [35].

Several carbon-based catalysts (multiwalled carbon nanotubes, CNT-P-SO_3H) have shown excellent performance for the transesterification of oils and fats. Apart from thermochemical routes, the non-edible biomass is converted to valuable products/platform chemicals via a catalytic process such as hydrolysis, solvolysis, etc. The platform chemicals obtained are further converted to valuable products through isomerization, dehydration, hydrodeoxygenation, hydrogenolysis, etc. The various microporous, mesoporous, and nanoparticle catalysts are presented in Table 1.

2.3 *Functionalized Heterogeneous Catalyst*

Heterogeneous catalysts are preferable over homogeneous ones due to the ease of separation, reusability, tolerance to moisture, and thermal stability. To make the biomass conversion process more energy efficient, multifunctional catalysts can play a major role with an adequate amount of acid, base, and redox-active sites. Various multifunctional catalysts are discussed in the following section accommodating such features and can be applied to biomass conversion. The multifunctional catalyst can reduce few energy-intensive steps in the overall process, thereby improving the process efficiency.

2.3.1 Carbon-Based Catalysts

Carbon material catalysts have a high surface area, tailorable porosity, and higher hydrophobicity. These properties make them suitable catalysts for biomass valorization. They can act as support as well as active phase catalyst. However, the

Table 1 Microporous, mesoporous, and nanoparticle catalysts used for biomass conversion

Reaction	Catalyst	Conv/ yield, %	Reaction conditions	Remark	Ref
Isomerization and dehydration of glucose to HMF	Mesoporous AlSiO in THF/ H_2O-NaCl biphasic system	91.7/63	Temp: 160 °C, Time: 90 min	High catalytic activity after four reaction cycles. High surface area and a large number of active sites	[20]
Dehydration of glucose to HMF	HZSM-5 zeolite	80/42	Biphasic aqueous NaCl+ MIBK system, 190 °C, 30 min	The activity of the zeolite catalyst is better than the silica catalyst, short reaction time	[36]
Hydrodeoxygenation of guaiacol to cyclohexane	Pt/HMFI-90	100/93	Liquid phase, 180 °C, 5 bar, 5 h	Higher activity of acidic support, reducibility in Pt has a significant effect	[37]
Hydrodeoxygenation of anisole to cyclohexane	Ni/Al-SBA-15	99.8/95	Liquid phase, 220 °C, 50 bar, 2 h	A synergetic effect between support and active phases	[38]
Hydrogenation of furfural to furan	Pd NPs/S-$_1$-OH	100/99.9	Gas-phase, 250 °C, atm pressure	Wettability-driven selective hydrogenation	[39]
Hydrogenation of furfural to tetrahydrofurfuryl alcohol	CuNi/MgAlO	99/95	Liquid phase, 150 °C, 40 bar, 3 h	High activity and selectivity compared to monometallic catalysts	[40]
Hydrogenation of HMF to DMF	Cu-Zn nanoalloy (<150 nm)	100/97	Temp: 220 °C, 20 bar, 18 h	A synergetic effect between Cu and Zn	[41]
Aerobic oxidation of HMF to 2,5-furan-carboxylic acid	Ni-doped MnO_x nanowires	100/94	Temp: 100 °C, 8 bar, 28 h	The special property makes oxygen to be easy come and easy go	[42]

yield of carbon catalysts such as CNTs and graphene is low, and the production cost is high that limits their applications. The preparation cost of carbon catalyst can be brought down by using low-cost substrate like biomass. The carbon catalysts made from various biomass sources are described below.

Biomass-Derived Carbon Catalysts

The widely used carbon catalysts are carbon black and activated carbon. They are primarily utilized as a support material for heterogeneous catalysts such as Ru/C and Pd/C in reductive catalytic fractionation process to separate cellulose, hemicellulose, and lignin [5]. The carbon catalyst from biomass (wood, bamboo, bagasse) can be obtained by various carbonization techniques such as pyrolysis, gasification, hydrothermal carbonization, etc. Sometimes, the carbon-based functionalized catalysts are prepared from municipal waste, complex industrial sludge, etc. This approach of converting biomass and waste into catalysts can benefit in two ways; the first one is the reduced cost of material fabrication, and the second one is the reduction in environmental pollution by utilizing waste. The properties of carbon material (surface area, pore configuration) are highly influenced by activation techniques and other key parameters such as source material, type of activation agent, time, and temperature [43].

Carbon material acts as excellent support for active catalyst phases. One such example is ionic liquids (ILs) supported on the carbon-based sulfonated catalyst. A high yield (47–65%) of 5-hydroxymethylfurfural was obtained when inulin was reacted at 100 ºC for 60 min using ILs supported on carbon material. The catalyst performed well compared to conventional solid acid catalysts with high reusability. The carbon-based catalysts are expected to perform at par with their conventional counterparts. To verify this, four amorphous carbon-based sulfonated catalysts were prepared from D-xylose, cellulose, lignin, cellulose, and wood and compared with cation resin, HZSM-5, sulfated zirconia, and Amberlyst-15. All four carbon-based catalysts showed comparable catalytic activity over the conventional solid acid catalysts [44]. In another study, a carbon catalyst prepared via hydrothermal carbonization of water hyacinth was used for oleic acid esterification and also for xylose dehydration to furfural. The solid acid bearing the highest acidity (WH-PTSA-220) showed maximum catalyst activity, whereas catalyst prepared with high temperature (WH-PTSA-240) had shown favorable reusability due to enhance graphitization and hydrophobicity of the carbon surface [45]. The one-pot catalytic synthesis, developed by the Sels group, converts crystalline cellulose into simple alkanes using a modified Ru/C catalyst [46]. A series of bimetallic nanocatalysts supported on carbon (PtMn/C, PtFe/C, PtNi/C, PtZn/C, etc.) are reported to be used for the efficient oxidative conversion of glycerol to glyceric acid. Ninety-one percent of glycerol was converted within 8 h at 60 °C, with a 50% yield of glyceric acid. Carbon support is chosen because of its inert behavior in acidic environment [47].

Graphene-Based Catalysts

The advancement in graphene-based catalysts has paved a new way for its application in biomass processing. Graphene, along with graphene oxide (GO) and reduced graphene oxide (rGO), is increasingly used for biomass conversion. Graphene oxide is synthesized by oxidation of graphite, and reduced graphene oxide is synthesized by reduction of graphene oxide. Graphene per se has limited catalyst activity, which can be enhanced by the doping of heteroatoms such as nitrogen, boron, or sulfur. Graphene-based supports can be synthesized from biomass, and biomass-derived chemicals, for example, glucose to graphene [48]. It also facilitates the anchoring of various acid-base functionalities and metal nanoparticles (NPs). Graphene-based materials are preferred for the process involving adsorption and surface reactions owing to its high BET surface area of about 2600 m^2/g [49]. Fructose dehydration to 5-hydroxymethylfurfural (5-HMF) was carried out using GO in the presence of isopropanol mediated dimethyl sulfoxide (DMSO), and 87% yield of HMF was obtained. The high performance of the catalyst was attributed to the synergistic effect between hydrogen bonding and fructose [50].

In the process of producing fuel precursors, the hydroxyalkylation/alkylation condensation of 2-methyl furan with hydroxyl group-containing compounds is catalyzed by improved GO (IGO) to yield C_{12} to C_{21} fuel precursors in liquid form. The IGO was highly selective to C_{15} fuel precursor (yield 95% at 60 °C) and found to be a promising acid catalyst for C-C coupling reactions when compared with commonly used framework zeolites [51]. GO-based materials have the potential to become alternative conventional catalysts and need focused efforts for their development. Though there are numerous advantages of graphene-based catalysts, the synthesis of graphene and its derivatives remains a challenge [48]. Also, attention is to be paid for possible health issues for humans.

Carbon Nanotubes (CNTs) as Catalysts

Carbon nanotubes are used as catalyst support and show excellent performance for stabilizing metal nanoparticles (NPs), metal oxides, and acid/base functionalities. It also prevents particle aggregation on the support surface, thereby suppressing the formation of metal complex on the catalyst surface. For example, sorbitol was converted to ethylene glycol and 1,2-propanediol over Ru/CNTs catalyst. The reaction results can be further improved by the addition of WOx to Ru/CNTs due to synergy between WO_x and Ru. The catalyst was recycled several times and found to be stable against leaching and poisoning. The yield of ethylene glycol and 1,2-propanediol was reported as 25.6% and 34.6%, respectively, when the reaction is conducted using Ru0.25WO_x/CNTs at 205 °C and 5.0 MPa. This can be the alternate route for the production of ethylene glycol and 1,2-propanediol, which, at present, produced commercially from petroleum-derived ethylene and propylene [52]. In another study, 2,5-diformylfuran (DFF) was produced by aerobic oxidation for biomass-based 5-hydroxymethylfurfural (5-HMF) over vanadium dioxide immobilized on polyaniline-functionalized CNTs (VO_2-PANI/CNT). The maximum yield of DFF was 96% when 100% 5-HMF was converted with O_2 as the oxidant. The selective adsorption of HMF on the catalyst surface inhibited the undesired oxidation of DFF, resulting in higher yield [53].

CNT-based solid acid catalyst (CNT-P-SO_3H) showed excellent results for transesterification as well as esterification reactions to produce biodiesel. The catalyst suffered a loss of partial activity after six cycles, which cannot be regenerated [54]. A multiwalled carbon nanotube (Net$_3$-MWCNT) catalyst with a grafted amino group is also reported for the transesterification reaction. The 77% conversion of glyceryl tributyrate was observed after 8 h. The conversion was on the higher side compared to commonly used hydrotalcite catalyst (51%

conversion) under identical conditions [55]. Thus, CNTs provide a good option as catalysts and support for the biomass conversion process.

2.3.2 Metal-Organic Frameworks (MOFs) as Catalysts

Zeolites are known for their well-defined porous structures. Similarly, the metal-organic frameworks (MOFs) exhibit zeolite-like structure and a potential alternative to zeolites as well as metal oxide catalysts. MOFs perform better in selected reactions such as fructose dehydration in dimethyl sulfoxide (DMSO). MOFs are highly crystalline and possess required acid, base, and redox functionalities. It can also allow the immobilization of functional groups like $–SO_3H$ and $-NH_2$ as well as metal nanoparticles such as Ru, Pd, Cu, etc. MOFs exhibit mesoporous structures and are highly tunable materials in terms of pore size and anchoring of active phases. Approximately 20,000 MOFs are reported in the literature, but all may not be suitable for biomass conversion. The MOFs with a certain degree of thermal, chemical, and water stability only are suitable for biomass conversion. For example, zinc-carboxylate MOFs have shown poor water tolerance and are not suitable, whereas MIL-type compounds (MIL101-Cr, MIL-53Al-NH_2, UiO-66) exhibit higher water stability [56]. MOFs have also been used as active catalyst phase, catalyst support as well as a precursor material for the catalyst. MOFs and their composites are discussed in the following section.

MOF-Supported Metal Nanoparticles (NPs)

MOFs have shown greater properties to prevent agglomeration of NPs, hence improving their catalytic activities. Ning et al. [57] prepared Pt/MOF-5 by confining Pt nanoparticles into the pores of MOF-5 and used for conversion of furfural derived from biomass. Furan-2-acrolein was selectively produced from furfural (selectivity 90.7%) using Pt/MOF-5 as a catalyst. The catalyst showed good activity for the conversion of furfural (84.1%) in the presence of ethanol as a solvent. The catalyst was active after five reaction cycles due to the synergistic effect between NPs and MOF. The other MOF-supported catalysts used for furfural conversion are Pt/UIO-66-NH_2 and Pt/UIO-66. Hydrogenation of furfural to furfuryl alcohol was carried out with Ru NPs supported on several MOFs supports such as Zr6-NDC, UiO-66, MIL-140A, and UiO-67. High selectivity of furfuryl alcohol was obtained under mild reaction conditions. Ru/UiO-66 was found to be the most stable catalyst resulting in the highest activity and reusability for five reaction cycles without appreciable loss of activity.

γ-Valerolactone (GVL) is an important platform chemical and produced from ethyl levulinate derived from biomass via hydrogenation and transesterification reactions. Ethyl levulinate can also be obtained by esterification of levulinic acid with ethanol [58]. The MOF catalyst (UiO-66) with various functionalities ($-SO_3H$,

-NH_3, and –NO_2) is used for this reaction. The catalytic activity of UiO-66 reduced when functionalized with –NH_2 and –NO_2 for both hydrogenation and transesterification reactions owing to the poor dispersion of Ru. On the other hand, –SO_3H-functionalized MOF showed increased activity (22% higher yield of GVL) for transesterification reaction when compared with Ru/UiO-66 [59].

Acid-Functionalized MOFs

The reaction that is primarily explored using acid MOFs is the production of a 5-HMF form of glucose, which is a two-step reaction that involves isomerization (glucose to fructose) followed by dehydration (fructose to 5-HMF). The isomerization requires Lewis acidity, and dehydration requires Brønsted acidity. It is, therefore, beneficial if the catalyst possesses Lewis as well as Brønsted acidity for the single-step conversion of glucose. These bifunctional characteristics can be induced by partial modification of the metal-organic framework. UiO-66 is one such example where the organic linker of the zirconium organic framework is replaced with 2-monocular-benzene-1,4-dicarboxylate. The catalyst was recyclable and showed higher selectivity for 5-HMF and fructose up to 90%. Similarly, NU-1000 (acidic zirconia modified by phosphate) was used for glucose conversion via the isomerization-dehydration mechanism with higher selectivity [7]. To prevent the side reactions, the Lewis and Brønsted active sites were purposely poisoned as both Lewis and Brønsted acidities were required, but at reduced level. It was also observed through the isotope tracer studies that the isomerization-dehydration mechanism is the favored mechanism over the direct-dehydration mechanism. The direct-dehydration mechanism utilizes phosphate-modified titania and bare niobia as catalysts [60]. The presence of water as a solvent is essential to carry out glucose to 5-HMF conversion. This was verified by conducting a reaction with MIL-101Cr (MIL-SO_3H) catalysts in pure tetrahydrofuran (THF) as a solvent. No product was formed. The findings suggest that the presence of water for glucose conversion is indispensable. Therefore, the catalyst should have tolerance for water as a large amount of water is generated during a dehydration reaction.

Productions of levulinic acid and 5-HMF from glucose are competing reactions and highly sensitive to the catalyst used. For example, MIL-SO_3H favored the formation of 5-HMF over levulinic acid (molar ratio 1:0.3). On the other hand, Amberlyst-15 and H_2SO_4 favored levulinic acid over 5-HMF with molar ratio of 3:1 and 10:1, respectively. The catalyst did not show good reusability, and reactivation remains a challenge [61]. The kinetics of conversion of fructose to 5-HMF reveal that MIL-101Cr-SO_3H-promoted reaction follows pseudo-first-order kinetics with an activation energy of 55 kJ/mol. The reaction was conducted in the presence of dimethyl sulfoxide (DMSO) at 120 °C for 60 min. The high yield (90%) of 5-HMF was obtained with the full conversion of fructose [62]. The results highlight MOFs as promising alternative solid acid catalysts for biomass conversion.

Bifunctionalized MOFs

MOFs are tailorable and offer the opportunity to introduce acid, base, or both functionality and metal-active sites. This property of MOFs makes them an ideal material to be used as a bifunctional catalyst. For example, palladium supported on amine-functionalized MOF (Pd/MIL-101(Al)-NH_2) is used for hydrogenation of 5-HMF to 2,5-hydroxymethyl-tetrahydrofuran (DHMTHF). The metallic site and free amine moiety are observed to be the controlling factors in the conversion of 5-HMF to DHMTHF. The amine moiety in the MOF is crucial in uniform dispersion of Pd nanoparticles on amine-functionalized support. When 5-HMF is fully converted, a 96% yield of DHMTHF is obtained under optimal reaction conditions. The reaction was carried out at a low temperature of 30 °C in an aqueous medium. The MOF support could stabilize the Pd nanoparticles efficiently as only a marginal (0.03%) amount of Pd was leached after five cycles (60 h) of operation. However, the selectivity for DHMTHF was reduced from 96% to 80% [63].

An important platform chemical is γ-valerolactone (GVL), which is used for the synthesis of useful chemicals. GVL is synthesized by hydrogenation of levulinic acid and further converted to ethyl valerate (EV yield 83%) in the presence of ethanol via hydrodeoxygenation (HDO) over a bimetallic catalyst (Pd/MIL-101-SO_3H) [64]. GVL can also be produced from methyl levulinate (ML) by using Ru nanoparticles deposited on the Zr-based metal-organic framework (SO_3H-UiO-66). The catalyst showed duel functionality, and about 100% yield of GVL was obtained. Alternately, if GVL is produced by a two-step method, i.e., hydrogenation of methyl levulinate over Ru/C catalyst to produce intermediate (4-hydroxypentanoic acid methyl ester) followed by conversion of this intermediate in the absence of metal catalyst, the yield was very limited [65].

Sorbitol is an important chemical and widely used as a sweetener in the food industry as a moisture controller in medical and cosmetic applications and feedstock for hydrogen and alkane production. Sorbitol can be obtained by hydrogenation of cellulose and also by hydrolysis of cellobiose. Both the reactions can be catalyzed by the bifunctional catalyst supported on MOF, i.e., Ru-PTA/MIL-100(Cr). The important factor for cellulose and cellobiose conversion was the ratio of active acid sites (n_A) to the number of *Ru* surface atoms (n_{Ru}). The optimum ratio of two catalytic activities for maximum conversion was $8.84 < (n_A/n_{Ru}) < 12.90$. Ruthenium (Ru) promoted hydrogenation reaction, and PTA/MIL-100(Cr) was active for hydrolysis reactions. Though the leaching of metal was not significant (0.006%), the catalyst activity decreased significantly. The yield of sorbitol was 95.1% for fresh catalysts and decreased to 8.5% when the catalyst was reused for the reaction. The loss in activity was attributed to the catalyst poisoning by insoluble substrates [66]. It is, therefore, expected that the MOF catalysts could serve as novel catalysts for biomass upgrading by metal/acid dual functionality but need improvement in catalyst stability. The synchronized effect among the metal and acid functionality in the presence of an environmentally benign solvent will be the key to the catalytic process.

Bimetallic MOF-Derived Catalysts

The MOF catalysts suffer from low hydrothermal and chemical stability, which can be addressed by MOF-derived carbon-based metal and metal oxides. The carbon material has high stability for the chemical and hydrothermal environment. A bimetallic catalyst (CuNi@C), prepared by impregnation of nickel nitrate onto Cu-based MOFs, was utilized for conversion of furfural to cyclopentanone at 130 °C, 5 MPa for 5 h. As a result, a 96.9% yield of the product was obtained. Cyclopentanone has wide applications in insecticide, medicine, and perfume industries. It can also be used as a solvent in the electronics industry [67]. In another work, the $CuCo_{0.4}/C$-873 catalyst is tested for the conversion of furfural to furfuryl alcohol. The catalyst is derived from Co-doped Cu-BTC MOF by thermolysis in a nitrogen environment at a temperature ranging from 773 K to 1073 K.; the doping of the cobalt helped inefficient dispersion of Co and Cu nanoparticles. The thermolysis temperature has an effect on the chemical state of the catalyst. At the best catalytic performance, 98.7% furfural was converted with high selectivity of furfural alcohol (97.7%) [68].

The Ni nanoparticle catalyst generated in situ with the help of MOF precursor (MIL-77(Ni)) is used for hydrotreatment of lignocellulosic biomass to avoid the disadvantages of supported catalysts such as metal leaching, coke deposition, polymerization of unstable species, less water tolerance, etc. The catalyst was found to be ten times more active than a conventional catalyst, i.e., Ni/SiO_2-Al_2O_3. The higher activity is attributed to high purity and crystallinity due to in situ generation and the robust MOF network [69].

Overall, MOFs are a good alternative to microporous zeolites, mesoporous silica, and carbon-based catalysts. It offers numerous advantages such as reduced mass transfer resistance, improved surface properties, and efficient immobilization of functional groups. However, its uses as a catalyst get restricted due to high synthesis cost, leaching of active species, and low hydrothermal stability. Thus, directed efforts are required toward the structure-activity analysis of MOFs to be widely accepted as a catalyst for biomass conversion [5].

2.3.3 Solid-Phase Ionic Liquid (IL)-Based Catalyst

Ionic liquids (ILs) are generally in the liquid state at room temperature and have a melting point below 100 °C. They are organic salts and are increasingly used as an alternative solvent to conventional volatile solvents. They consist of organic cation and inorganic or organic anions. The advantages of ILs are their extremely low vapor pressure and high thermal stability, which are helpful in developing the greener technologies and sometimes referred to as green solvents [70]. Additionally, ILs possess tunable physical properties by virtue of the different combination of cations and anions. The properties of ILs, such as viscosity, density, melting point, solubility, and acidity, can be tuned. Theoretically, it is possible to synthesize 10^{18}

types of ILs, but only about 1000 types of ionic liquids have been synthesized to date. The drawbacks of ionic liquids are high preparation cost, active phase leaching, and poor recyclability that can be overcome by solid-phase ILs [5].

Depolymerization of cellulose is a critical step to obtain platform chemicals such as fructose, glucose, xylose, etc. Cellulose is insoluble in most of the common industrial solvents due to its high degree of crystallinity, thus hampering the catalytic activity in the depolymerization step and demanding for harsh reaction conditions. Due to this reason, depolymerization of cellulose to glucose under mild reaction conditions still remains a challenge [70]. ILs are excellent solvents for cellulose dissolution that can be helpful in the depolymerization of cellulose through hydrolysis, alcoholysis, etc. The key advantages of ILs are efficient functionalization, promising reusability, and lower amount requirement for the reaction. The cost of functionalized ILs is a crucial factor that needs due consideration. Depending on the solubility of biomass molecule in ILs, a careful selection of coupled catalyst-solvent system is necessary. An understanding of molecular interaction between the feedstock molecule, catalyst, and solvent is necessary for the development of new catalytic systems. The post-reaction separation technologies for catalyst, solvent, and biomass products are necessary. There is a limited success for the depolymerization of lignin using ILs. Therefore, more opportunities are available for research in this domain [71]. Even though the ILs have several advantages over conventional catalysts, handling of ILs is difficult owing to its viscous nature. Also, the leaching of ILs in reaction mixture limits their practical applications in biomass conversion. To address these issues, researchers have combined ILs with solid catalyst and developed a new class of functionalized catalyst, namely, “solid-state ILs.” The ILs are deposited in the form of a film on the support material with a high specific surface area, thus creating a homogeneous environment for reactions [5]. This way, the use of solid-state ILs is more practical in biomass conversion.

Supported IL-Based Catalysts

The ionic liquid immobilized on solid support offers several advantages than using the ILs themselves. Both inorganic and organic materials can be used as supports. Inorganic supports offer better thermal stability and low on cost and easy to prepare, i.e., alumina and silica [72]. Various carbohydrates (cellulose, sucrose, glucose) were converted to furans with a functional ILs supported on silica nanoparticles with different acidity. The dual acid-functionalized supported ionic liquid (SIL) (IL-SO_3H-HSO_4/SiO_2) was effective for high conversion (99%) of sugars. The reusability of the ILs/SiO_2 was also investigated for dehydration of fructose with IL-SO_3H-HSO_4/SiO_2 at the optimized conditions. Consistent conversion (99%) of fructose was obtained for five reaction cycles that suggest no leaching of immobilized functional groups (SO_3H and –HSO_4) during the repeated process [73]. ILs immobilized on mixed metal oxides, and silica gels are investigated for biodiesel synthesis from waste cooking oil. The mixed oxide catalysts (Mg + Al), in its pristine form, exhibited low activity for the conversion of waste cooking oil by transesterification due to the high acidity of the oil. Their activity improved after the immobilization of ILs due to increased basic strength and basicity of supports. The biodiesel yields catalyzed by IL/Mg-Al and IL/Mg-Al-La catalysts were 85.4% and 98.7%, respectively [74]. When waste cooking oil is transesterified with methanol at 60 °C for 20 h with ILs supported on silica gel, 87.58% yield of biodiesel was observed [75].

Polymeric IL-Based Catalysts

The ionic liquids are promising candidates for various applications and named after the mobility of ions in ionic liquids. The ILs are neither liquids nor solids and do not have advantages of liquids or solids. This limits their applicability due to leakage issues and high viscosity. Polymeric ionic liquids (PILs) can address this problem without losing the features of ILs. PILs are formed by the polymerization of ionic liquids [76]. They can combine the functionalities of polymer and ILs and act as bifunctional catalysts. They have high thermal stability, better corrosion resistance, and flexibility of available structures. The dehydration process of 5-HMF from glucose/fructose can be catalyzed by a series of PILs (mono- and bifunctional polymeric ionic liquids). The PILs performed well compared to solid-supported ionic liquids like ILs on silica and showed consistent activity for five reaction cycles without significant loss of activity [77]. Among the other reusable PILs are poly(3-butyl-1-vinylimidazolium chloride) combined with $CrCl_2$, P[BVIM]Cl-$CrCl_2$, which was found suitable for dehydration of glucose and fructose to yield 68.8% HMF at 120 °C for 3 h. However, the recyclability test indicates poor performance compared to its analogous catalyst, i.e., P[BVIM]Cl-Et_2ALCl [78]. PILs are also found suitable for oleic acid esterification to yield 92.6% biodiesel. The biodiesel yield slightly decreased to 89.3% after six runs, indicating the consistent performance of the catalyst. The catalyst, 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate [VSIM][HSO_4], was synthesized from Brønsted acidic ionic liquid through free radical polymerization from a novel approach, where Fe_3O_4 particles acted as hard template [79].

2.3.4 Magnetic Iron Oxide-Based Catalysts

Magnetic catalysts are different from other solid catalysts due to their easy separation from the reaction mixture by the permanent magnet. They are mainly represented by ferrous, cobalt, and nickel, especially ferrous. The commonly used magnetic catalyst/support includes alloys (FePt, CoPt), metals (Fe, Co, Ni), and iron oxides (FeO, Fe_2O_3, Fe_2O_4). Among them, Fe_2O_4 is widely used for catalytic purposes [80]. Magnetic acid catalysts are used for the conversion of cellulose to glucose, fructose to 5-hydroxymethylfurfural (5-HMF), and 5-HMF to 5-ethoxymethylfurfural (5-EMF) via hydrolysis, dehydration, and etherification processes, respectively. These catalysts also find their use in transesterification reactions to synthesize biodiesel. The catalysts

Table 2 Summary of functionalized heterogeneous catalyst used for biomass conversion

Reaction	Class	Catalyst	Conv/ yield, %	P, bar	T, K	Remark	Ref
Oxidation of glycerol to glyceric acid	Carbon-based	Pt_9Sn_1/C	91/50	1	333	The catalyst was active for four reaction cycles without loss of activity	[47]
Hydrogenolysis of glycerol to lactic acid	Carbon-based	Cu-Pd/RGO	56.2/49.5	14	413	Reasonably good activity for three cycles	[82]
Fructose to lactic acid	MOF	MIL-100(Fe)	>99/32	1	463	Catalyst was active for four reaction cycles	[83]
Methyl levulinate—GVL	MOF	Ru-SO_3H-UiO-66	100/81	5	353	The catalyst was active for five reaction cycles	[65]
Dehydration of glucose to HMF	ILs	$CrCl_2$-Im-SBA-15	50/35	1	423	Catalyst deactivation after two reaction cycles	[84]
Esterification of oleic acid to biodiesel	ILs	Microporous poly-IL	92.6/92.6	1	353	The catalyst was active for six reaction cycles	[79]

mentioned in Sect. 2.3.2 are effective for biomass conversion, but sometimes they are difficult to separate due to the viscous nature of the reaction mixture. This provides an opportunity for the use of a magnetic catalyst as it can be easily separated with external magnate material. Core-shell $Fe_3O_4@SiO_2$ magnetic nanoparticle is one such catalyst used for biodiesel production [81]. Magnetic sulfonated mesoporous silica (Fe_3O_4-SBA-SO_3H) was used as a catalyst for hydrolysis of cellobiose and found efficient for 98% conversion of cellobiose at 120 °C, whereas the conversion is only 54% when H_2SO_4 is used as a catalyst under identical conditions. The catalyst can be easily recyclable from the hydrolysis solution with the help of an external magnet. The catalyst is also stable and showed consistent activity for three experimental runs. A summary of the functionalized heterogeneous catalyst used for biomass conversion is presented in Table 2.

2.4 *Bimetallic Catalysts*

Biomass conversion processes such as reforming, hydrogenolysis, hydrogenation, and oxidation are catalyzed by metals and yield product as well as byproducts. Byproducts can complicate the separation process and seriously affect the yield of the desired product. It is necessary to minimize the production of side products. It can be done by the addition of a second metal, as a support or promoter, to enhance selectivity to a particular product. The second metal can alter the catalytic activity, selectivity, and stability of the first one. It can be achieved by one of the methods mentioned here:

- Altering the geometry
- Altering the electron properties of active sites
- Stabilizing the active metal
- Chemical bonding with a reaction intermediate and transition state
- Bifunctional effects by providing different functions in the reaction mechanism

The use of a bimetallic catalyst is advantageous, but the exact mechanism is not known. The information on the molecular and electronic level can help to establish the relationship between experimental results and catalyst modification. One may propose an analogy between catalysts used in petroleum refining and biomass conversion, but may not be appropriate as petroleum refining needs the addition of functional groups, whereas biomass conversion requires removal/replacement of functional groups. The transformation of cellulose, hemicelluloses, and lignin using bimetallic catalysts is discussed in the following section.

2.4.1 Cellulose Conversion Using the Bimetallic Catalyst

Cellulose is made up of biopolymers and depolymerized to its monomer, glucose ($C_6H_{12}O_6$), by hydrolysis. Glucose is further converted to platform chemicals such as levulinic acid and 5-hydroxymethylfurfural (5-HMF) by a dehydration reaction. Glucose can be upgraded to valuable chemicals by decreasing the functionality (aqueous-phase reforming) as well as increasing the functionality (oxidation). Aqueous-phase reforming produces H_2 and alkanes, whereas oxidation yields acids. Glucose mainly consists of aldehydes and alcohols. Oxidation of aldehydes produces carboxylic acid (gluconic acid) and that of alcohol produces glucuronic and keto acids. The most common monometallic catalysts used for glucose conversion are Pt and Pd. A second metal, Bi, is added to increase their activity as well as selectivity toward gluconic acid. The presence of Bi prevents the deactivation of Pd (by absorbing O_2 that would otherwise oxidize Pd) and limits the formation of byproducts. The promotion of Pd with other metals was not as effective as PdBi [85]. The possible oxidation products that can be produced from glucose are glucuronic acid, gluconic acid, 5-keto-glucose, glucaric acid, 5-keto-gluconic acid, and 2,5-diketogluconic acid. Other catalysts used for cellulose oxidation are PbPt, AuPt, AuRh, etc.

Glucose, the monomer of cellulose, can also be converted to various alcohols such as hexitols, sorbitols, and diols by hydrogenation. Ni and Ni-based catalysts are primarily used for glucose hydrogenation, but leaching of catalysts is a real issue. To improve the catalyst activity, promoters like Sn, Mo, Cr, and Fe are used that increase the rate of glucose formation by four to five times. When Fe/Cr is added to Ni, the selectivity of sorbitol was reached to as high as 98% [86]. Ru-based catalyst is reportedly stable for hydrogenation of glucose to produce sorbitols, but is expensive. Hexitols can be produced by hydrogenolysis (hydrogenation followed by dehydration) over the Pt-Ni catalyst. The yield of hexitols was 47.4% at 100% conversion of glucose over the Pt-Ni catalyst. The results were even better with hexitol yield up to 53.2% and 54.2%, respectively, for Pd-Ni and Ru-Ni catalyst at 100% conversion of glucose.

2.4.2 Hemicellulose Conversion Using the Bimetallic Catalyst

Hemicellulose is a polymer with C_5 sugars, mainly xylose. Xylose is converted to xylitol by hydrogenation using a different metal catalyst. The catalyst Ru-Ni is commonly used to produce xylitol. For catalyst deactivation due to leaching, deposition is a common issue. Xylitol is a common sweetener used in the food industry. A platform chemical, furfural, can be obtained by dehydration of xylose and further hydrogenated to 2-methylfuran, furfural alcohol, and furan. The Cu-chromite is the most widely used commercial catalyst for hydrogenation [87]. The other bimetallic catalysts used for hemicellulose conversion are Cu/C, Cu/MgO, NiCu/SiO_2, CuCO/SiO_2, etc. Furfural yield of 98% was reported at 473 K over Cu/MgO and CuCo/SiO_2 catalyst [6].

2.4.3 Lignin Conversion Using the Bimetallic Catalyst

Lignin is a significant fraction of biomass, and its effective utilization will ensure the economic feasibility of the biomass conversion. Commercially, lignin is used in a very inefficient manner as 98% of it is burned to fulfill energy demand in pulp mills, whereas only 2% is utilized toward chemical production. So for the sustainable operation of biorefinery, lignin conversion to chemicals through technological advancement is necessary [88, 89]. Lignin possesses aromatic functionality, and products like benzene, phenol, and cyclohexanes can be made from it through cracking via hydrogenation and hydrodeoxygenation (HDO). Bimetallic catalysts such as sulfide, CoMo, and NiMo are used for lignin hydrogenation and HDO. The catalysts PtSn and PtRh are also reported to be used for lignin conversion. Among the catalysts, at a lower temperature (<673 K), all Rh-based catalysts are active than sulfide, CoMo, and NiMo catalysts. Owing to its complexity, model components such as phenol, cresol, anisole, etc. are used to study the conversion of lignin. Zhang et al. (2014) [90] conducted the catalytic hydrogenolysis of lignin using NiRu (Ni = 85% and Ru = 15%) to obtain aromatic chemicals and fuel-grade hydrocarbons. The results with bimetallic catalysts show better performance than monometallic Ni and Ru. The best result for pinene transformation was obtained using bimetallic Au-Cu/TiO_2 catalyst with higher selectivity for verbenone product due to the synchronized effect between bimetals and their support [91].

2.4.4 Catalytic Conversion of Glycerol Using the Bimetallic Catalyst

Bimetallic catalysts are used for the conversion of biomass-derived glycerol to valuable chemicals. Glycerol can be valorized through hydrogenolysis, hydrogenation, and oxidation reactions. Hydrogenolysis involves breaking of bonds with the help of hydrogen. Glycerol is converted to polyols, alcohols via hydrogenolysis over the temperature range of 373–523 K and at 200 bar using monometallic catalysts. The selectivity and yield of hydrogenolysis can be greatly improved over bimetallic catalysts. Hydrogenolysis is sometimes referred to as hydrodeoxygenation (HDO) when used for the removal of oxygen. For example, the ethylene glycol was produced over Ni/Al_2O_3, but the selectivity was improved when palladium/iridium/rhodium was added to Ni/Al_2O_3 as the second metal. Glycerol can be oxidized in two ways: (1) oxidation of secondary alcohol to give dihydroxyacetone and hydroxypiruvic acid and (2) oxidation of primary alcohol to give glyceraldehydes and glyceric acid. The most commonly used bimetallic catalyst for glycerol oxidation was AuPd in basic medium and PtBi in acidic medium [6]. The summary of the bimetallic catalysts used for the conversion of biomass-derived chemicals is given in Table 3.

Table 3 Summary of bimetallic catalysts used for the conversion of biomass-derived chemicals

Feedstock	Reaction	Catalysts	Conv.	Selectivity	P, bar	T, K	Remark	Ref
Ethylene glycol	Aqueous-phase reforming	Pt/Al_2O_3	>90%	88% (H_2), 8% (alkane)	56	338	90% activity lost in 2 days. No restoration of activity	[92]
Sorbitol	Aqueous-phase reforming	RANEY® $Ni_{14}Sn$	>90%	46% (H_2), 31% (alkane)	51	538	Consistent activity for H_2 production for 340 h without regeneration	[92]
Glycerol	Hydrogenolysis	Ru-Co/ ZrO_2	56.2%	70.3% (1,2 PDO), 18.0% (EG)	50	453	A synergetic effect between Ru and Co observed	[93]
Glycerol	Hydrogenolysis	CuAg/ Al_2O_3	27%	96% (1,2 PDO)	15	473	The catalyst showed higher activity than commercial chromite catalyst	[94]
Guaiacol (lignin)	Deoxygenation	PtSn/ Inconel	>80%	–	1	673	Higher rate of catalyst deactivation	[95]
o-Cresol (lignin)	Hydrodeoxygenation	CoMO/ Al_2O_3	23%	65% (C_6H_6)	50	573	Activity of the catalyst is low	[96]

3 Current Challenges and Future Opportunities

In order to reduce the dependence on fossil fuels, large-scale production of fuels and chemicals from lignocellulosic biomass is necessary. But this is very challenging due to variations in supply, composition, and properties. Many technologies devised at laboratory/pilot plant scale are technically viable but economically not feasible. To make the process economically feasible, a multidisciplinary approach, including chemistry, material science, and process engineering, is required. The efficiency of various technologies and yield of the products depends on many factors such as type of biomass, pretreatment method, biomass composition, catalyst activity, etc. In the following section, the major concerns regarding technologies and the use of catalysts for biomass conversion are discussed.

3.1 The Selectivity of Desirable Products

It is essential to tune the porosity and structure of the catalyst to selectively produce the desired products. The pore dimension of the solid catalyst influences the diffusion properties of the reacting species. Zeolites ordered mesoporous silica and metal-organic frameworks (MOFs) are the materials that can be used as a catalyst for biomass conversion. These materials also act as support for metals and metal oxides with excellent stabilizing effects. One of the reasons for low conversion and selectivity of complex and viscous biomass molecules is the inaccessibility of active catalyst sites. The active sites are located inside the porous catalyst materials and become difficult to access due to diffusional limitations. Due to this reason, multimode porous materials are preferred over single-mode porous materials for enhanced selectivity. For example, large biomass molecules (lignin, triglycerides, polysaccharides) cannot access the catalytically active sites in zeolites due to small pore diameters. In that case, catalyst materials with mixed pores (micro, meso, and macro) such as hierarchical zeolites are useful. Zeolites offer numerous advantages, such as acidity, porosity, and shape selectivity. Of these, tunable Brønsted/Lewis acidity is a vital feature for biomass conversion and can influence conversion and selectivity. Both Brønsted and Lewis acidities are required for effective biomass conversion. For example, during the conversion of 2,5-dimethylfuran, zeolites with strong Lewis acid sites (Na-Y) favored the formation of toluene, whereas Brønsted acid zeolites (H-β and H-Y) favored *p*-xylene formation.

Another parameter that can affect the selectivity of the desired product is the biomass to catalyst ratio. In fast catalytic pyrolysis of *Pongamia pinnata* seeds using USY zeolites, more aromatic hydrocarbons were produced (4.7% to 52.5%) when the ratio of biomass to catalyst increased for five times [2]. Mesoporous SiO_2-based materials (SBA, KIT, MSU, COK) offer similar properties to zeolites but with larger pores. Larger pores can offer access to active catalyst sites, thereby enhancing the biomass conversion. During the condensation of furfuryl alcohol to butyl levulinate, propylsulfonic acid-functionalized SBA-15 offered 96% yield of butyl levulinate with 100% selectivity [5]. Hence, it is important to select a catalyst with appropriate porosity, pore structure, and acidity to achieve maximum conversion and selectivity of the desired product.

3.2 Deactivation and Reusability of the Catalyst

Deactivation of the catalyst is evaluated by subjecting it to the loss of activity with increasing time on stream. Among the various reasons for deactivation, coking is a major one for the deactivation of catalysts in biomass conversion reactions. The other possible ways of catalyst deactivation are blockage of pore or active sites by insoluble byproducts/intermediates, metal leaching, sintering, decrease in specific surface area, loss of pore volume, etc. Sometimes, the basic metal oxides (MgO) can form hydroxides, which are more soluble in water and tend to leach. Also, the reaction byproducts can accumulate on the active catalytic site, thereby restricting the accessibility resulting in a low conversion. In the case of zeolites, degradation due to desilication or dealumination at harsh hydrothermal conditions is one of the ways of catalyst deactivation [2]. In order to avoid pore blockage in microporous zeolites, incorporation of larger size metal should be avoided. Many of the catalysts presented in this chapter showed good catalytic activity up to five reaction cycles, but their applicability at commercial scale and for real biomass feedstock needs to be tested. Fouling of MOF catalysts by humin formation is common in biomass conversion that can be prevented by using a proper solvent such as ethanol in case of selective conversion of glucose to 5-HMF [61]. Temperature can also influence deactivation as observed in catalytic cracking of fatty acid mixture; the order of deactivation over the composite catalyst was almost constant at moderate rate, whereas ZSM-5 deactivation order decreased with increasing temperature. The same order of deactivation was also observed for used palm oil cracking [97].

3.3 Kinetic/Mechanistic Aspects

Kinetic data obtained by careful evaluation of reaction parameters helps in process scale-up, technology transfer, and evaluation of economic feasibility. Due to the large number of complex reactions taking place in biomass conversion, it is not easy to explain kinetics at the molecular level. Few kinetic studies are discussed here. In the case of catalytic cracking of vegetable oil, a simplified lumped kinetics is presented by the grouping of components having similar chemical functions [34]. The complexity of the model varies according to the degree of lumping. Adding more lumps will make the process of kinetic parameters more intrinsic; thus, more kinetic parameters need to be estimated, and accordingly, more experimental information is required. For vegetable oil cracking, three, four, and six lumped models were reported. The cracking of palm fatty acid mixture and used palm oil was reported to follow first-order kinetics [97], whereas the cracking of used vegetable oil over sulfated zirconia followed second-order kinetics. The reactions were carried out over a temperature range of 673–723 K and in the presence of composite catalysts (HZSM-5 and MCM-41/ZSM-5) in a fixed bed microreactor. The proposed model was adequate with a 10% deviation in the experimental and predicted values [98].

Kinetic of fructose to 5-HMF reaction reveals that MIL-101Cr-SO_3H-promoted reaction follows the pseudo-first-order kinetics with the observed activation energy of 55 kJ/mol [62]. In the case of glucose to 5-HMF reaction, the isomerization-dehydration mechanism is the prominent reaction pathway, compared to the phosphate-modified titania and bare niobia, which proposes direct-dehydration mechanism [61]. Though the use of bimetallic catalyst is advantageous, the exact mechanism is not known. The information on the molecular and electronic level can help to establish the relationship between experimental results and catalyst modification. Proposing a robust kinetic model still remains a challenge due to multiple and complex reactions that take place during biomass conversion.

4 Conclusions

The chapter has summarized various aspects of biomass conversion to useful chemicals having properties similar to those obtained from petrochemicals. It can be achieved by various processes such as hydration, solvolysis, pyrolysis, gasification, etc. Numerous catalysts with varying degrees of efficiency and reusability are presented in this chapter. The advantages and disadvantages of such catalysts are presented for a wide range of feedstocks and intermediate components. The commonly used catalyst, microporous zeolites, mesoporous silica, metal nanoparticles, and bimetallic materials have shown promising performance for model components of biomass. But their performance with real biomass feedstock remains a challenge. Due to this reason, not many commercial technologies are available. For example, the biomass pyrolysis to produce bio-oil is still an immature technology compared to fossil oil. It has to overcome many technical and economic challenges.

Overall, more opportunities are available for research in biomass conversion, but one needs to follow certain restraints for efficient utilization of biomass. These are as follows:

(a) Detailed understanding of the properties of components such as cellulose, hemicelluloses, and lignin. This will help to understand the mechanism of its catalytic conversion.
(b) Identification of the specific sources for cellulose, hemicelluloses, and lignin components and targeted product out of it.

(c) Preparation of the suitable catalysts based on their acidity/basicity, operating conditions, reusability, shape of catalyst particle, metal interaction, etc.
(d) As the product of lignocellulosic biomass is a complex one, novel reactor and separators should be developed. Process intensification to reduce waste and maximize product and energy efficiency will lead to an economically feasible design.

References

1. Jahirul MI, Rasul MG, Chowdhury AA, Ashwath N (2012) Biofuels production through biomass pyrolysis—a technological review. Energies 5:4952–5001. https://doi.org/10.3390/en5124952
2. Sudarsanam P, Peeters E, Makshina EV, Parvulescu VI, Sels BF (2019) Advances in porous and nanoscale catalysts for viable biomass conversion. Chem Soc Rev 48:2366–2421. https://doi.org/10.1039/c8cs00452h
3. Bauen A, Berndes G, Junginger M, Londo M, Vuille F (2009) Bioenergy—a sustainable and reliable energy source—a review of status and prospects. IEA Bioenergy:1–108
4. Global Bioenergy Statistics (2019) World Bioenergy Association 2019, p 58
5. Sudarsanam P, Zhong R, Van Den Bosch S, Coman SM, Parvulescu VI et al (2018) Functionalised heterogeneous catalysts for sustainable biomass valorisation. Chem Soc Rev 47:8349–8402. https://doi.org/10.1039/C8CS00410B
6. Alonso DM, Wettstein SG, Dumesic JA (2012) Bimetallic catalysts for upgrading of biomass to fuels and chemicals. Chem Soc Rev 41:8075–8098. https://doi.org/10.1039/c2cs35188a
7. Amin MH, Sudarsanam P, Field MR, Patel J, Bhargava SK (2017) Effect of a swelling agent on the performance of Ni/Porous Silica catalyst for CH4-CO2 reforming. Langmuir 33:10632–10644. https://doi.org/10.1021/acs.langmuir.7b02753
8. Fernando S, Adhikari S, Chandrapal C, Murali N (2006) Biorefineries: current status, challenges, and future direction. Energy Fuel 20:1727–1737. https://doi.org/10.1021/ef060097w
9. Zhou C, Xia X, Lin C, Tong D, Beltramini J (2011) Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. Chem Soc Rev 40:5588–5617. https://doi.org/10.1039/c1cs15124j
10. Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind Eng Chem Res 48:3713–3729. https://doi.org/10.1021/ie801542g
11. Cheng S, DCruz I, Wang M, Leitch M, Xu C (2010) Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. Energy Fuel 24:4659–4667. https://doi.org/10.1021/ef901218w
12. Han J, Kim H (2008) The reduction and control technology of tar during biomass gasification / pyrolysis: an overview. Renew Sustain Energy Rev 12:397–416. https://doi.org/10.1016/j.rser.2006.07.015
13. Dobele G, Rossinskaja G, Dizhbite T, Telysheva G, Meier D, Faix O (2005) Application of catalysts for obtaining 1, 6-anhydrosaccharides from cellulose and wood by fast pyrolysis. J Anal Appl Pyrolysis 74:401–405. https://doi.org/10.1016/j.jaap.2004.11.031
14. Kawamoto H, Saito S, Hatanaka W, Saka S (2007) Catalytic pyrolysis of cellulose in sulfolane with some acidic catalysts. J Wood Sci 53:127–133. https://doi.org/10.1007/s10086-006-0835-y
15. Chen MQ, Wang J, Zhang MX, Chen MG, Zhu XF, Min FF et al (2008) Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating. J Anal Appl Pyrolysis 82:145–150. https://doi.org/10.1016/j.jaap.2008.03.001

16. Pattiya A, Titiloye JO, Bridgwater AV (2008) Fast pyrolysis of cassava rhizome in the presence of catalysts. J Anal Appl Pyrolysis 81:72–79. https://doi.org/10.1016/j.jaap.2007.09.002
17. Osada M, Sato T, Watanabe M, Adschiri T, Arai K (2004) Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water. Energy Fuel 18:327–333
18. Li N, Tompsett GA, Zhang T, Shi J, Wyman CE, Huber GW (2011) Renewable gasoline from aqueous phase hydrodeoxygenation of aqueous sugar solutions prepared by hydrolysis of maple wood. Green Chem 13:91–101. https://doi.org/10.1039/c0gc00501k
19. Wang D, Astruc D (2017) The recent development of efficient Earth-abundant transition-metal nanocatalysts. Chem Soc Rev 46:816–854. https://doi.org/10.1039/c6cs00629a
20. Li X, Xia Q, Nguyen VC, Peng K, Liu X, Essayem N et al (2016) High yield production of HMF from carbohydrates over silica-alumina composite catalysts. Cat Sci Technol 6:7586–7596. https://doi.org/10.1039/c6cy01628f
21. Custodis VBF, Karakoulia SA, Triantafyllidis KS, Van Bokhoven JA (2016) Catalytic fast pyrolysis of lignin over high-surface-area mesoporous aluminosilicates: effect of porosity and acidity. ChemSusChem 9:1134–1145. https://doi.org/10.1002/cssc.201600105
22. Jeenpadiphat S, Kasiban C, Tungasmita DN (2016) Corncob to value-added chemical transformation by metal/beta zeolite and metal/mesoporous SBA-15 catalytic pyrolysis. J Chem Technol Biotechnol 91:2519–2528. https://doi.org/10.1002/jctb.4852
23. Haishi T, Kasai K, Iwamoto M (2011) Fast and quantitative dehydration of lower alcohols to corresponding olefins on mesoporous silica catalyst. Chem Lett 40:614–616. https://doi.org/10.1246/cl.2011.614
24. Grams J, Potrzebowska N, Goscianska J, Michalkiewicz B, Ruppert AM (2016) Mesoporous silicas as supports for Ni catalyst used in cellulose conversion to hydrogen rich gas. Int J Hydrogen Energy 41:8656–8667. https://doi.org/10.1016/j.ijhydene.2015.12.146
25. Li S, Wang Y, Gao L, Wu Y, Yang X, Sheng P et al (2018) Short channeled Ni-Co/SBA-15 catalysts for highly selective hydrogenation of biomass derived furfural to tetrahydrofurfuryl alcohol. Microporous Mesoporous Mater 262:154–165. https://doi.org/10.1016/j.micromeso.2017.11.027
26. Hashmi ASK, Hutchings GJ (2006) Gold catalysis. Angew Chem Int Ed 45:7896–7936. https://doi.org/10.1002/anie.200602454
27. Chakinala AG, Chinthaginjala JK, Seshan K, Van Swaaij WPM, Kersten SRA, Brilman DWF (2012) Catalyst screening for the hydrothermal gasification of aqueous phase of bio-oil. Catal Today 195:83–92. https://doi.org/10.1016/j.cattod.2012.07.042
28. Tauster SJ, Fung SC, Garten RL (1978) Strong metal-support interactions. Group 8 Noble Metals supported on TiO2. J Am Chem Soc 100:170–175. https://doi.org/10.1021/ja00469a029
29. Tathod AP, Dhepe PL (2015) Efficient method for the conversion of agricultural waste into sugar alcohols over supported bimetallic catalysts. Bioresour Technol 178:36–44. https://doi.org/10.1016/j.biortech.2014.10.036
30. Varkolu M, Raju Burri D, Rao Kamaraju SR, Jonnalagadda SB, van Zyl WE (2017) Hydrogenation of levulinic acid using formic acid as a hydrogen source over Ni/SiO2 catalysts. Chem Eng Technol 40:719–726. https://doi.org/10.1002/ceat.201600429
31. Bhoi R, Sen N, Singh KK, Mahajani SM, Shenoy KT, Rao H et al (2014) Transesterification of sunflower oil in microreactors. Int J Chem React Eng 12. https://doi.org/10.1515/ijcre-2013-0105
32. Singh D, Bhoi R, Ganesh A, Mahajani S (2014) Synthesis of biodiesel from vegetable oil using supported metal oxide catalysts. Energy Fuel 28:2743–2753. https://doi.org/10.1021/ef500045x
33. Bhoi R, Mahajani S (2018) Investigation of spontaneous emulsification and its relevance in biodiesel synthesis. React Chem Eng 3:171–181. https://doi.org/10.1039/c7re00205j
34. Taufiqurrahmi N, Bhatia S (2011) Catalytic cracking of edible and non-edible oils for the production of biofuels. Energ Environ Sci 4:1087–1112. https://doi.org/10.1039/c0ee00460j

35. Uatikaneni SPR, Adjaye JD, Bakhshp NN (1995) Catalytic conversion of Canola oil to fuels and chemicals over various cracking catalysts. Can J Chem Eng 73:484–497
36. Moreno-Recio M, Santamaría-González J, Maireles-Torres P (2016) Brönsted and Lewis acid ZSM-5 zeolites for the catalytic dehydration of glucose into 5-hydroxymethylfurfural. Chem Eng J 303:22–30. https://doi.org/10.1016/j.cej.2016.05.120
37. Hellinger M, Carvalho HWP, Baier S, Wang D, Kleist W, Grunwaldt JD (2015) Catalytic hydrodeoxygenation of guaiacol over platinum supported on metal oxides and zeolites. Appl Catal A Gen 490:181–192. https://doi.org/10.1016/j.apcata.2014.10.043
38. Sankaranarayanan TM, Berenguer A, Ochoa-Hernández C, Moreno I, Jana P, Coronado JM et al (2015) Hydrodeoxygenation of anisole as bio-oil model compound over supported Ni and Co catalysts: effect of metal and support properties. Catal Today 243:163–172. https://doi.org/10.1016/j.cattod.2014.09.004
39. Wang C, Liu Z, Wang L, Dong X, Zhang J, Wang G et al (2018) Importance of Zeolite wettability for selective hydrogenation of Furfural over Pd@Zeolite catalysts. ACS Catal 8:474–481. https://doi.org/10.1021/acscatal.7b03443
40. Wu J, Gao G, Li J, Sun P, Long X, Li F (2017) Efficient and versatile CuNi alloy nanocatalysts for the highly selective hydrogenation of furfural. Appl Catal Environ 203:227–236. https://doi.org/10.1016/j.apcatb.2016.10.038
41. Bottari G, Kumalaputri AJ, Krawczyk KK, Feringa BL, Heeres HJ, Barta K (2015) Copper-Zinc alloy nanopowder: a robust precious-metal-free catalyst for the conversion of 5-Hydroxymethylfurfural. ChemSusChem 8:1323–1327. https://doi.org/10.1002/cssc.201403453
42. Yu K, Liu Y, Lei D, Jiang Y, Wang Y, Feng Y et al (2018) M3+O(-Mn4+)2 clusters in doped MnO: X catalysts as promoted active sites for the aerobic oxidation of 5-hydroxymethylfurfural. Cat Sci Technol 8:2299–2303. https://doi.org/10.1039/c7cy02455j
43. Ma Q, Yu Y, Sindoro M, Fane AG, Wang R, Zhang H (2017) Carbon-based functional materials derived from waste for water remediation and energy storage. Adv Mater 29:1605361. https://doi.org/10.1002/adma.201605361
44. Kang S, Ye J, Zhang Y, Chang J (2013) Preparation of biomass hydrochar derived sulfonated catalysts and their catalytic effects for 5-hydroxymethylfurfural production. RSC Adv 3:7360–7366. https://doi.org/10.1039/c3ra23314f
45. Laohapornchaiphan J, Smith CB, Smith SM (2017) One-step preparation of carbon-based solid acid catalyst from Water Hyacinth leaves for esterification of oleic acid and dehydration of xylose. Chem Asian J 12:3178–3186. https://doi.org/10.1002/asia.201701369
46. Op De Beeck B, Dusselier M, Geboers J, Holsbeek J, Morré E, Oswald S et al (2015) Direct catalytic conversion of cellulose to liquid straight-chain alkanes. Energ Environ Sci 8:230–240. https://doi.org/10.1039/c4ee01523a
47. Dou J, Zhang B, Liu H, Hong J, Yin S, Huang Y et al (2016) Carbon supported Pt9Sn1 nanoparticles as an efficient nanocatalyst for glycerol oxidation. Appl Catal Environ 180:78–85. https://doi.org/10.1016/j.apcatb.2015.06.007
48. Das VK, Shifrina ZB, Bronstein LM (2017) Graphene and graphene-like materials in biomass conversion: paving the way to the future. J Mater Chem A 5:25131–25143. https://doi.org/10.1039/c7ta09418c
49. Bai S, Shen X (2012) Graphene-inorganic nanocomposites. RSC Adv 2:64–98. https://doi.org/10.1039/c1ra00260k
50. Wang H, Kong Q, Wang Y, Deng T, Chen C, Hou X et al (2014) Graphene oxide catalyzed dehydration of fructose into 5-hydroxymethylfurfural with isopropanol as cosolvent. ChemCatChem 6:728–732. https://doi.org/10.1002/cctc.201301067
51. Dutta S, Bohre A, Zheng W, Jenness GR, Núñez M, Saha B et al (2017) Solventless C-C Coupling of low carbon Furanics to high carbon fuel precursors using an improved graphene oxide carbocatalyst. ACS Catal 7:3905–3915. https://doi.org/10.1021/acscatal.6b03113

52. Guo X, Guan J, Li B, Wang X, Mu X, Liu H (2015) Conversion of biomass-derived sorbitol to glycols over carbon-materials supported Ru-based catalysts. Sci Rep 5:1–9. https://doi.org/10.1038/srep16451
53. Guo Y, Chen J (2015) Bicomponent assembly of VO2 and polyaniline-functionalized carbon nanotubes for the selective oxidation of biomass-based 5-Hydroxymethylfurfural to 2,5-Diformylfuran. ChemPlusChem 80:1760–1768. https://doi.org/10.1002/cplu.201500292
54. Liu H, Chen J, Chen L, Xu Y, Guo X, Fang D (2016) Carbon nanotube-based solid sulfonic acids as catalysts for production of fatty acid methyl ester via transesterification and esterification. ACS Sustain Chem Eng 4:3140–3150. https://doi.org/10.1021/acssuschemeng.6b00156
55. Tessonnier JP, Villa A, Majoulet O, Su DS, Schlögl R (2009) Defect-mediated functionalization of carbon nanotubes as a route to design single-site basic heterogeneous catalysts for biomass conversion. Angew Chem Int Ed 48:6543–6546. https://doi.org/10.1002/anie.200901658
56. Herbst A, Janiak C (2017) MOF catalysts in biomass upgrading towards value-added fine chemicals. CrstEngComm 19:4092–4117. https://doi.org/10.1039/c6ce01782g
57. Ning L, Liao S, Cui H, Yu L, Tong X (2018) Selective conversion of renewable Furfural with Ethanol to produce Furan-2-acrolein mediated by Pt@MOF-5. ACS Sustain Chem Eng 6:135–142. https://doi.org/10.1021/acssuschemeng.7b01929
58. Ahmad E, Alam MI, Pant KK, Haider MA (2016) Catalytic and mechanistic insights into the production of ethyl levulinate from biorenewable feedstocks. Green Chem 18:4804–4823. https://doi.org/10.1039/c6gc01523a
59. Yang J, Huang W, Liu Y, Zhou T (2018) Enhancing the conversion of ethyl levulinate to γ-valerolactone over Ru/UiO-66 by introducing sulfonic groups into the framework. RSC Adv 8:16611–16618. https://doi.org/10.1039/c8ra01314d
60. Oozeerally R, Burnett DL, Chamberlain TW, Walton RI, Degirmenci V (2018) Exceptionally efficient and recyclable heterogeneous metal–organic framework catalyst for glucose isomerization in water. ChemCatChem 10:706–709. https://doi.org/10.1002/cctc.201701825
61. Herbst A, Janiak C (2016) Selective glucose conversion to 5-hydroxymethylfurfural (5-HMF) instead of levulinic acid with MIL-101Cr MOF-derivatives. New J Chem 40:7958–7967. https://doi.org/10.1039/c6nj01399f
62. Chen J, Li K, Chen L, Liu R, Huang X, Ye D (2014) Conversion of fructose into 5-hydroxymethylfurfural catalyzed by recyclable sulfonic acid-functionalized metal-organic frameworks. Green Chem 16:2490–2499. https://doi.org/10.1039/c3gc42414f
63. Chen J, Liu R, Guo Y, Chen L, Gao H (2015) Selective hydrogenation of biomass-based 5-hydroxymethylfurfural over catalyst of palladium immobilized on amine-functionalized metal-organic frameworks. ACS Catal 5:722–733. https://doi.org/10.1021/cs5012926
64. Zhang D, Ye F, Guan Y, Wang Y, Hensen EJM (2014) Hydrogenation of γ-valerolactone in ethanol over Pd nanoparticles supported on sulfonic acid functionalized MIL-101. RSC Adv 4:39558–39564. https://doi.org/10.1039/c4ra05250a
65. Lin Z, Cai X, Fu Y, Zhu W, Zhang F (2017) Cascade catalytic hydrogenation-cyclization of methyl levulinate to form γ-valerolactone over Ru nanoparticles supported on a sulfonic acid-functionalized UiO-66 catalyst. RSC Adv 7:44082–44088. https://doi.org/10.1039/c7ra06293a
66. Chen J, Wang S, Huang J, Chen L, Ma L, Huang X (2013) Conversion of cellulose and cellobiose into sorbitol catalyzed by ruthenium supported on a polyoxometalate/metal-organic framework hybrid. ChemSusChem 6:1545–1555. https://doi.org/10.1002/cssc.201200914
67. Wang Y, Sang S, Zhu W, Gao L, Xiao G (2016) CuNi@C catalysts with high activity derived from metal-organic frameworks precursor for conversion of furfural to cyclopentanone. Chem Eng J 299:104–111. https://doi.org/10.1016/j.cej.2016.04.068
68. Wang Y, Miao Y, Li S, Gao L, Xiao G (2017) Metal-organic frameworks derived bimetallic Cu-Co catalyst for efficient and selective hydrogenation of biomass-derived furfural to furfuryl alcohol. Mol Catal 436:128–137. https://doi.org/10.1016/j.mcat.2017.04.018
69. Čelič TB, Grilc M, Likozar B, Tušar NN (2015) In situ generation of Ni nanoparticles from metal-organic framework precursors and their use for biomass hydrodeoxygenation. ChemSusChem 8:1703–1710. https://doi.org/10.1002/cssc.201403300

70. Zhang Q, Zhang S, Deng Y (2011) Recent advances in ionic liquid catalysis. Green Chem 13:2619–2637. https://doi.org/10.1039/c1gc15334j
71. Zhang Z, Song J, Han B (2017) Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. Chem Rev 117:6834–6880. https://doi.org/10.1021/acs.chemrev.6b00457
72. Skoda-Földes R (2014) The use of supported acidic ionic liquids in organic synthesis. Molecules 19:8840–8884. https://doi.org/10.3390/molecules19078840
73. Xu H, Zhao H, Song H, Miao Z, Yang J, Zhao J et al (2015) Functionalized ionic liquids supported on silica as mild and effective heterogeneous catalysts for dehydration of biomass to furan derivatives. J Mol Catal A Chem 410:235–241. https://doi.org/10.1016/j.molcata.2015.09.020
74. Sun J, Yang J, Li S, Xu X (2016) Basic ionic liquid immobilized oxides as heterogeneous catalyst for biodiesel synthesis from waste cooking oil. Cat Com 83:35–38. https://doi.org/10.1016/j.catcom.2016.05.002
75. Cao Y, Zhou H, Li J (2016) Preparation of a supported acidic ionic liquid on silica-gel and its application to the synthesis of biodiesel from waste cooking oil. Renew Sustain Energy Rev 58:871–875. https://doi.org/10.1016/j.rser.2015.12.237
76. Eftekhari A, Saito T (2017) Synthesis and properties of polymerized ionic liquids. Eur Polym J 90:245–272. https://doi.org/10.1016/j.eurpolymj.2017.03.033
77. Li H, Zhang Q, Liu X, Chang F, Zhang Y, Xue W et al (2013) Immobilizing Cr3+ with SO3H-functionalized solid polymeric ionic liquids as efficient and reusable catalysts for selective transformation of carbohydrates into 5-hydroxymethylfurfural. Bioresour Technol 144:21–27. https://doi.org/10.1016/j.biortech.2013.06.063
78. Liu DDJ, Chen EYX (2013) Polymeric ionic liquid (PIL)-supported recyclable catalysts for biomass conversion into HMF. Biomass Bioenergy 48:181–190. https://doi.org/10.1016/j.biombioe.2012.11.020
79. Wu Z, Chen C, Guo Q, Li B, Que Y, Wang L et al (2016) Novel approach for preparation of poly (ionic liquid) catalyst with macroporous structure for biodiesel production. Fuel 184:128–135. https://doi.org/10.1016/j.fuel.2016.07.004
80. Liu B, Zhang Z (2016) Catalytic conversion of biomass into chemicals and fuels over magnetic catalysts. ACS Catal 6:326–338. https://doi.org/10.1021/acscatal.5b02094
81. Chiang YD, Dutta S, Chen CT, Huang YT, Lin KS, Wu JCS et al (2015) Functionalized Fe3O4@Silica Core-Shell Nanoparticles as Microalgae Harvester and Catalyst for Biodiesel Production. ChemSusChem 8:789–794. https://doi.org/10.1002/cssc.201402996
82. Jin X, Dang L, Lohrman J, Subramaniam B, Ren S, Chaudhari RV (2013) Lattice-matched bimetallic CuPd-graphene nanocatalysts for facile conversion of biomass-derived polyols to chemicals. ACS Nano 7:1309–1316. https://doi.org/10.1021/nn304820v
83. Huang S, Yang KL, Liu XF, Pan H, Zhang H, Yang S (2017) MIL-100(Fe)-catalyzed efficient conversion of hexoses to lactic acid. RSC Adv 7:5621–5627. https://doi.org/10.1039/c6ra26469g
84. Degirmenci V, Pidko EA, Magusin PCMM, Hensen EJM (2011) Towards a selective heterogeneous catalyst for glucose dehydration to 5-Hydroxymethylfurfural in water: CrCl2 catalysis in a thin immobilized ionic liquid layer. ChemCatChem 3:969–972. https://doi.org/10.1002/cctc.201000426
85. Karski S, Paryjczak T, Witoñska I (2003) Selective oxidation of glucose to gluconic acid over bimetallic Pd-Me catalysts (Me = Bi, Tl, Sn, Co). Kinet Catal 44:618–622. https://doi.org/10.1023/A:1026133820538
86. Hoffer BW, Crezee E, Mooijman PRM, Van Langeveld AD, Kapteijn F, Moulijn JA (2003) Carbon supported Ru catalysts as promising alternative for Raney-type Ni in the selective hydrogenation of D-glucose. Catal Today 79–80:35–41. https://doi.org/10.1016/S0920-5861(03)00040-3
87. Rao R, Dandekar A, Baker RTK, Vannice MA (1997) Properties of copper chromite catalysts in hydrogenation reactions. J Catal 171:406–419. https://doi.org/10.1006/jcat.1997.1832

88. Zakzeski J, Weckhuysen BM (2011) Lignin solubilization and aqueous phase reforming for the production of aromatic chemicals and hydrogen. ChemSusChem 4:369–378. https://doi.org/10.1002/cssc.201000299
89. Ahmad E, Pant KK (2018) Lignin conversion: A key to the concept of lignocellulosic biomass-based integrated biorefinery. Elsevier B.V., Amsterdam. https://doi.org/10.1016/B978-0-444-63992-9.00014-8
90. Zhang J, Teo J, Chen X, Asakura H, Tanaka T, Teramura K et al (2014) A series of NiM (M = Ru, Rh, and Pd) bimetallic catalysts for effective lignin hydrogenolysis in water. ACS Catal 4:1574–1583. https://doi.org/10.1021/cs401199f
91. Ajaikumar S, Ahlkvist J, Larsson W, Shchukarev A, Leino AR, Kordas K et al (2011) Oxidation of α-pinene over gold containing bimetallic nanoparticles supported on reducible TiO2 by deposition-precipitation method. Appl Catal A Gen 392:11–18. https://doi.org/10.1016/j.apcata.2010.10.015
92. Shabaker JW, Huber GW, Dumesic JA (2004) Aqueous-phase reforming of oxygenated hydrocarbons over Sn-modified Ni catalysts. J Catal 222:180–191. https://doi.org/10.1016/j.jcat.2003.10.022
93. Feng J, Zhang Y, Xiong W, Ding H, He B (2016) Hydrogenolysis of glycerol to 1,2-propanediol and ethylene glycol over ru-co/zro2 catalysts. Catalysts 6:1–13. https://doi.org/10.3390/catal6040051
94. Zhou J, Guo L, Guo X, Mao J, Zhang S (2010) Selective hydrogenolysis of glycerol to propanediols on supported Cu-containing bimetallic catalysts. Green Chem 12:1835–1843. https://doi.org/10.1039/c0gc00058b
95. González-Borja MÁ, Resasco DE (2011) Anisole and guaiacol hydrodeoxygenation over monolithic Pt-Sn catalysts. Energy Fuel 25:4155–4162. https://doi.org/10.1021/ef200728r
96. Jongerius AL, Jastrzebski R, Bruijnincx PCA, Weckhuysen BM (2012) CoMo sulfide-catalyzed hydrodeoxygenation of lignin model compounds: an extended reaction network for the conversion of monomeric and dimeric substrates. J Catal 285:315–323. https://doi.org/10.1016/j.jcat.2011.10.006
97. Ooi YS, Zakaria R, Mohamed AR, Bhatia S (2004) Catalytic cracking of used palm oil and palm oil fatty acids mixture for the production of liquid fuel: kinetic modeling. Energy Fuel 18:1555–1561. https://doi.org/10.1021/ef049948v
98. Charusiri W, Yongchareon W, Vitidsant T (2006) Conversion of used vegetable oils to liquid fuels and chemicals over HZSM-5, sulfated zirconia and hybrid catalysts. Korean J Chem Eng 23:349–355. https://doi.org/10.1007/BF02706733