Environmental Chemistry Letters (2021) 19:4119–4136
https://doi.org/10.1007/s10311-021-01284-x

REVIEW

Catalytic conversion of lignocellulosic polysaccharides to commodity biochemicals: a review

Falguni Pattnaik[1,2] · **Shreya Tripathi**[2] · **Biswa R. Patra**[1] · **Sonil Nanda**[1] · **Vivek Kumar**[2] · **Ajay K. Dalai**[1] · **Satyanarayan Naik**[2]

Received: 9 June 2021 / Accepted: 11 July 2021 / Published online: 4 August 2021

Abstract

The applications of green chemistry and industrial bioprocessing are becoming more popular to address concerns of pollution, climate change, global warming, circular bioeconomy, sustainable development goals and energy security. Both biological and thermochemical routes can play vital roles in transforming waste lignocellulosic biomass to high-value bioproducts. Lignocellulosic biomass contains essential building blocks that could be tapped to generate biofuels, biochemicals and biomaterials to replace petroleum-derived fuels and chemicals. Besides containing extractives and ash, lignocellulosic feedstocks are made up of cellulose, hemicellulose and lignin typically in the ranges of 35–55 wt%, 20–40 wt% and 10–25 wt%, respectively. Catalytic thermochemical approaches are effective for biomass conversion with a significant yield of various platform chemicals, such as furfural, 5-hydroxymethylfurfural, levulinic acid and other furan or non-furan-based chemicals. These chemicals play a crucial part in the synthesis of different fuel-based materials, which can successfully replace petroleum-based chemicals or fuels. Lignocellulosic biomass and their derived monomeric sugars can be catalytically converted into various platform chemicals using different homogeneous and heterogeneous catalysts. In this review paper, we have highlighted some promising catalysts such as mineral acids, mesoporous silica materials, zeolites, metal–organic frameworks, metal oxides and ionic liquids used in biorefining to generate biochemicals. We have also reviewed a few pieces of notable literature presenting the catalytic conversion of cellulose, hemicellulose, cellobiose, glucose, fructose and xylose into various high-value chemicals.

Keywords Lignocellulosic biomass · Mesoporous silica · Zeolites · Metal oxides · Ionic liquids · Metal–organic frameworks

Abbreviations

Al^{+3}	Aluminum ion
Al_2O_3	Aluminum oxide
Sn-β-NH_2	Amino functionalized tin impregnated beta-zeolite
NH_2	Amino group
NH_4^+	Ammonium
HSO_3/ZSM-5	Bisulfite functionalized Zeolite Socony Mobil–5
HSO_3	Bisulfite
CO_2	Carbon dioxide
CO	Carbon monoxide
COK	Centre for Research Chemistry and Catalysis
Co	Cobalt
CAGR	Compound annual growth rate
°C	Degree Celsius
g	Gram
h	Hour
HCl	Hydrochloric acid
H^+	Hydrogen ion or proton
H_2	Hydrogen molecule
H_3O^+	Hydronium ion
kJ/mol	Kilojoule per mole
KIT	Korea Advanced Institute of Science and Technology
Lys-PM_2	Lysine functionalized phosphotungstic acid

✉ Ajay K. Dalai
ajay.dalai@usask.ca

[1] Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

[2] Centre for Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi, India

MPa	Megapascal
MOF	Metal–organic framework
Methane	CH_4
MSU	Michigan State University
min	Minute
MCM-41	Mobil Composition of Matter-41
MCM-48	Mobil Composition of Matter-48
MCM-50	Mobil Composition of Matter-50
M	Molar
Mo_2O_3	Molybdenum oxide
H-Mordenite	Mordenite in protonic form
NiCo/H-ZSM-5	Nickel and Cobalt biofunctionalized Zeolite Socony Mobil–5 in the protonic form
Ni	Nickel
Nb/SBA-15	Niobium impregnated Santa Barbara Amorphous-15
Nb_2O_5	Niobium oxide
HNO_3	Nitric acid
PO_4^{3-}/NU-1000	Phosphated Zr-based metal–organic framework
H_3PO_4	Phosphoric acid
PO_4^{3-}/TiO_2	Phosporated titanium oxide
Pt	Platinum
Ru/MCM-48	Ruthenium impregnated Mobil Composition of Matter-48
Ru	Ruthenium
SBA-15	Santa Barbara Amorphous-15
SBA-16	Santa Barbara Amorphous-16
s	Second
SiO_2	Silicon dioxide
Si^{+4}	Silicon ion
Si/Al	Silicon to aluminum ratio
Si/Nb	Silicon to niobium ratio
$H_4SiW_{12}O_{40}$	Silicotungstic acid
NaOH	Sodium hydroxide
Na^+	Sodium ion
MIL-101(Cr)-SO_3H	Sulfonic acid-modified chromium terephthalate-based metal–organic framework (Matérial Institut Lavoisier)
Pt/SBA-15/SO_3H	Sulfonic acid-modified Platinum impregnated Santa Barbara Amorphous-15
H_2SO_4	Sulfuric acid
SO_3H	Sulphonic acid
Ta_3O_5	Tantalum oxide
Sn-β zeolite	Tin impregnated beta zeolite
SnO_2	Tin oxide
Sn	Tin
TiO_2	Titanium oxide
WO_3-Ta_3O_5	Tungsten trioxide impregnated tantalum oxide
WO_3-TiO_2	Tungsten trioxide impregnated titanium oxide
WO_3-ZrO_2	Tungsten trioxide impregnated zirconium oxide
WO_3	Tungsten trioxide
H-USY	Ultrastable Y in the protonic form
U.S.$	United State Dollar
H_2O	Water
wt%	Weight percentage
ZSM-5	Zeolite Socony Mobil–5
H-Zeolite Y	Zeolite Y in protonic form
$Cu_{0.89}Zn_{0.11}O$	Zinc doped copper oxide
ZrO_2	Zirconium oxide
ZrO_2–TiO_2	Zirconium-titanium mixed oxide

Introduction

With the increasing consumption and rising prices of fossil fuels and petrochemical products, significant research is being invested in alternative energy sources. The chemicals derived from petroleum sources have diverse applications in the industrial, transportation sectors and for various consumer-based products. In the context of renewable sources, a vast part of these applications depends on the different biomass generated platform chemicals such as bio-alcohols, levulinic acid, 5-hydroxymethylfurfural, furfural, ethyl levulinate, lactic acid, 5-ethoxymethylfurfural and other furan or non-furan-based chemicals (Okolie et al. 2021a) (Fig. 1). These higher demands for the various chemicals and fuels have increased adequately due to the modernization of society with growing numbers of industries (Srivastava et al. 2020; Tang et al. 2020). Therefore, to fulfill the requirement of these chemicals through renewable ways, there is an increment of the research in the conversion of lignocellulosic biomasses by implementing different environmentally friendly approaches like hydrothermal, solvothermal and thermocatalytic techniques (Nanda et al. 2018; Quereshi et al. 2019; Kaloudas et al. 2021).

Lignocellulosic biomasses are majorly comprised of cellulose, hemicellulose and lignin in the ranges of 35-55 wt%, 20–40 wt% and 10–25 wt%, respectively (Nanda et al. 2013; Pattanaik et al. 2019). In this review, we have attempted to provide an insight into the conversion of these components and their monomeric or oligomeric building blocks, such as glucose, xylose, cellobiose, mannose, galactose and arabinose into various platform chemicals with the catalytic effects of various homogeneous and heterogeneous catalysts.

The thermocatalytic conversion of biomacss using heterogeneous or homogeneous catalysts has become prevalent for converting pentose and hexose sugars into biochemicals. Various acid catalysts viz. zeolites, metal oxides, mesoporous silica, mineral acids, acidic ionic liquids and

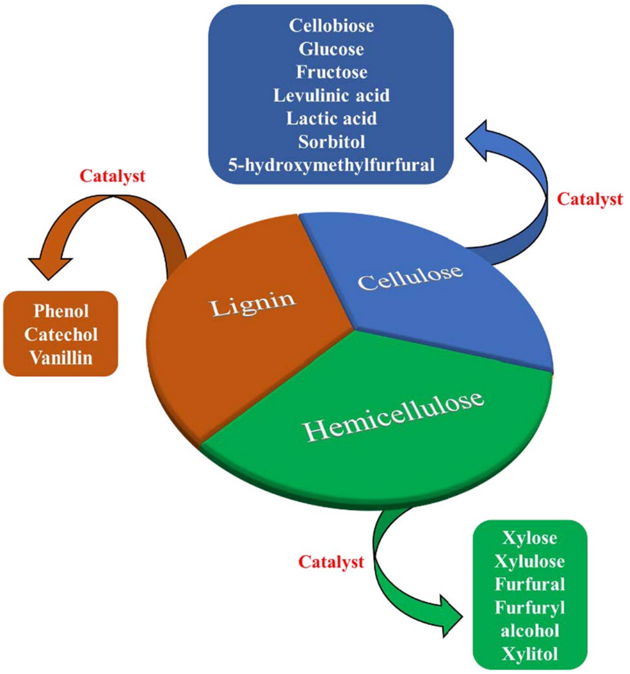

Fig. 1 List of platform biochemicals derived from lignocellulosic biomass. Some notable sugars and biochemicals produced from cellulose include cellobiose, glucose, fructose, 5-hydroxymethylfurfural, levulinic acid, lactic acid and sorbitol. On the other hand, hemicellulose can yield sugars and biochemicals such as xylose, xylulose, furfural, furfuryl alcohol and xylitol. The basic biochemicals produced from lignin are phenols, catechol and vanillin. Catalysts play selective and significant roles in converting cellulose, hemicellulose and lignin to biochemicals of commercial and industrial relevance

metal-organic frameworks have been reported to convert sugars into platform biochemicals such as levulinic acid, furfurals and 5-hydroxymethylfurfural (Acharjee and Lee 2018). Water-resistance is a primary characteristic of acid catalysts during the conversion of sugars to chemicals during aqueous reactions. Heterogeneous acid catalysts are highly popularized for their thermal stability, lower separation cost and other environmental and industrial advantages. On the other hand, homogeneous catalysts including mineral acids such as HCl, H_2SO_4 and H_3PO_4 are well-established and commercialized materials for the conversion of carbohydrates into various platform chemicals like furfural, 5-hydroxymethylfurfural and levulinic acid.

Besides different chemical catalysts, biocatalysts such as hydrolytic enzymes play a vital role in the depolymerization of the complex carbohydrates and polysaccharides into monomeric sugars and their conversion into various liquid chemicals (Nanda et al. 2017). However, compared with the other chemical-based catalysis, biocatalysis is comparatively expensive with lesser outcomes (Chua et al. 2020). Investigating various aspects of different catalytic processes, heterogeneous acid catalysts, including ionic liquids, are found to be economically and environmentally sustainable for the biomass conversion process.

Global market of commodity chemicals

Furfural

The renewability and abundance of lignocellulosic biomass provide a reliable source to produce furfural. The hydrolysis of pentosans in lignocellulose followed by dehydration of the released pentose sugars results in the formation of furfural and its derivatives. Commercially it is produced by acid hydrolysis of agricultural and woody biomass. (Kabbour and Luque 2020). The market price for furfural is U.S.$ 1500/ton and its demand has reached 600 kilotons annually with a global market size of U.S.$ 815 million in 2020 (Grand View Research 2020a). The U.S. and Germany are accounted to consume 30% of furfural and Japan with 11% consumption. China using corn cobs as the principal feedstock material, having 200 furfural production units is the leading global producer of furfural, which accounted for over 70% of world supplies (Lee and Wu 2021). Furfural and its derivatives being versatile chemicals can be used as transportation fuels, resins, decolorizing agents, intermediate in the synthesis of fine chemicals, biopolymers and pharmaceuticals. It also finds its application in the role of soil enhancers, organic fertilizers, jet fuel blendstock and flavor enhancers for drinks and food.

Levulinic acid

Levulinic acid is produced from lignocellulosic biomass typically by the following steps such as: (i) pretreatment of biomass, (ii) hydrolysis of cellulose into glucose monomers, (iii) isomerization of glucose monomers to fructose monomers, (iv) dehydration of hexose sugars to 5-hydroxymethylfurfural, and (v) rehydration of 5-hydroxymethylfurfural to levulinic acid (Kang et al. 2018). The global market demand for levulinic acid was 2,606 tons in 2013 and it is expected to be 3,820 tons by 2021 (Grand View Research 2015). The global market size for levulinic acid was U.S.$ 19.7 million in 2020 demonstrating a compound annual growth rate or CAGR of 4.8% (Grand View Research 2015). The agriculture and pharmaceutical sectors accounted for over 66% of the overall volume in 2013 and are anticipated to grow at 5.4% CAGR (Grand View Research 2015). North America is the leading producer of levulinic acid by contributing to more than 41% of world supplies in 2013 while Europe and the Asia-Pacific are the emerging markets of levulinic acid. The outlook of levulinic acid application is outrageous in pharmaceuticals, agriculture, food additives and cosmetics (Grand View Research 2015).

Bioethanol

Bioethanol is a promising future fuel, which is produced by the hydrolysis of lignocellulosic biomass followed by fermentation (Karimi et al. 2021). The market size for bioethanol was U.S.$ 33.7 billion in 2020 and is expected to reach around U.S.$ 65 billion by 2025 at a CAGR of 14% between 2020 and 2025 (Markets and Markets 2020a). North America is the largest market for bioethanol due to large production facilities, while U.S., Canada and Mexico are the growing consumers (Intrado 2020). Bioethanol and biobutanol can be used as a transportation fuel, feedstock in the chemical industry, fuel for fuel cells, in the cosmetics industry and manufacturing processes owing to its clean-burning and easy availability (Nanda et al. 2014; Kumar et al. 2018).

Ferulic acid

Ferulic acid, recognized as a phytochemical, is found in the cell walls of plants. Ferulic acid is produced by the usage of dilute acid pretreatment and enzymatic hydrolysis of lignocellulosic biomass. While the market size of ferulic acid was U.S.$ 60 million in 2020, its consumption could exceed 750 tons by 2025 (Osorio-González et al. 2019; TBinsights 2020). Owing to its usage in different fields like pharmaceutical, cosmeceuticals and food sectors, Europe, Asia Pacific and North America shared U.S.$ 12.7, 24.2 and 14.6 million, respectively in the global market in 2020 (Barbara et al. 2015; TBinsights 2020).

Vanillin

Vanillin is one of the lignin-derived aromatic compounds and the bacterial consortium is found to be a good biocatalyst for its production from lignocellulosic biomass (Harshvardhan et al. 2017). The global market size for vanillin was estimated to be U.S.$ 395 million in 2016, which was increased to U.S.$ 480 million in 2020 (Grand Research View 2017). In 2016, the Asia-Pacific was dominating the market which accounted for 39.7% of the total revenue followed by Europe, which accounted for 27% and it is expected to demonstrate a CAGR of 7.1% from 2019 to 2025 (Grand Research View 2017). It is used in perfumery and beverage as well as an intermediate in pharmaceutical industries. It is also used as a flavoring agent in the food processing industries.

Eugenol

Eugenol is a phenolic component that can be obtained from clove oil, nutmeg oil and cinnamon extract and many wide ranges of plant sources like basil, ginger, pepper, oregano, thyme and turmeric. It was the first natural compound used in the synthesis of vanillin in the late 19th century and it is an industrial source to produce iso-eugenol and methyl eugenol. It can be produced by drying of biomass followed by roasting, staged condensation and purification of the mixture (Khalil et al. 2017).

Various chemicals like 5-hydroxymethylfurfural, lactic acid, furfuryl alcohol, xylitol, sorbitol and mannitol had the global market value of U.S.$ 55, 1100, 473, 877, 1470 and 382 million in 2020 (Fig. 2) (Market and Research 2019; Markets and Markets 2020b; Grand View Research 2020b, 2021; EMR 2020a, 2020b). These biochemicals are potentially used in biofuels, pharmaceuticals, food industries, confectioneries and several other value-added sectors.

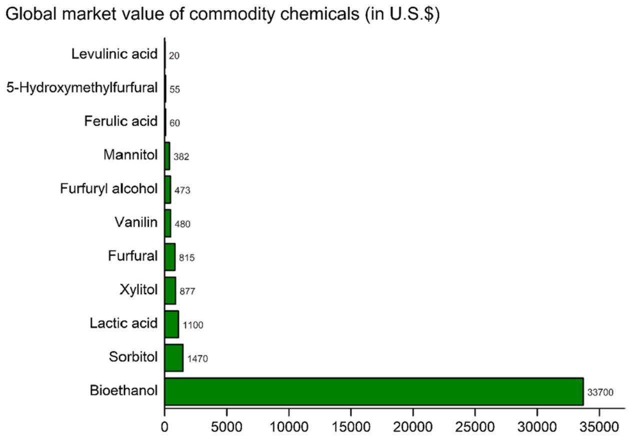

Fig. 2 Global market size of different commodity biochemicals in 2019–2020. (Data source: Market and Research 2019; Markets and Markets 2020b; Grand View Research 2020b; EMR 2020a; EMR 2020b; Grand View Research 2021). Note the highest market share of bioethanol followed by sorbitol, lactic acid, xylitol and furfural. Bioethanol has the highest market share globally because of its diverse applications as a laboratory chemical, industrial commodity, biofuel and precursor for other value-added products. Other biochemicals have found applications in specialty industries such as food processing, beverages, pharmaceuticals, laboratory chemical manufacturing, bioplastics and fuel processing, to name a few

Table 1 Composition of various lignocellulosic biomasses

Lignocellulosic biomass	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	References
Aspen wood	45	19	25	Wu et al. (2021)
Cassava peels	42	44	12	Awoyale and Lokhat (2021)
Coffee husk	43	7	9	Rambabu et al. (2016)
Corn stover	35	21	22	Shi et al. (2021)
Corncob	39	43	8	Boonsombuti et al. (2016)
Olive tree pruning	39	16	19	Galletti et al. (2012)
Pine wood	42	20	30	Gürbüz et al. (2013)
Poplar sawdust	58	14	18	Galletti et al. (2012)
Rice straw	49	33	17	Amiri et al. (2014)
Sugarcane bagasse	44	26	22	de Lucas et al. (2021)
Sunflower stalk	34	21	30	Monlau et al. (2012)
Switchgrass	32	19	20	Shi et al. (2021)
Switchgrass	34	28	19	Gürbüz et al. (2013)
Wheat bran	33	34	7	Tirpanalan et al. (2015)

Components of lignocellulosic biomass

The lignocellulosic biomasses are primarily made up of cellulose, hemicellulose and lignin. The proportion of these chief biopolymers vary for different biomasses (Table 1). For instance, the crop residues are comprised of 30-50 wt% cellulose, 20-38 wt% hemicellulose and 7-21 wt% lignin, whereas the biomass obtained from agro-processing industries consist of 21-45 wt% cellulose, 15-33 wt% hemicellulose and 5-24 wt% lignin (Pattanaik et al. 2019). The composition of given lignocellulosic biomass also changes with the environment, harvesting practice, collection time and anatomical portion (Srivastava et al. 2019). The selection of required lignocellulosic biomass depends on the targeted end product. For the synthesis of most commodity biochemicals, biomass rich in polysaccharides and containing a low amount of lignin is preferred (Srivastava et al. 2017; Pattanaik et al. 2019). However, depolymerization of lignin also results in some aromatic monomers, which are of significance for biofuel generation and other applications (Gall et al. 2017).

Cellulose is the most abundantly available homopolysaccharide consisting of linear chains of D-glucose units attached by β-1,4-glycosidic linkage whereas hemicellulose is a complex polysaccharide comprised of xylose, mannose, galactose, arabinose, glucose and acetic acid (Okolie et al. 2019). Lignin is the second most abundant biopolymer made of coniferyl, sinapyl and coumaryl alcohol (Okolie et al. 2021b).

Different routes for the conversion of lignocellulosic biomasses to bioproducts

Biological conversion route

Figure 3 represents different biological and thermochemical routes for the conversion of lignocellulosic biomass into various commodity chemicals, syngas, sugars and bio-oil. The biological route for converting lignocellulosic biomass involves enzymatic hydrolysis of polysaccharides such as cellulose and hemicellulose to monomeric sugars, which further undergo fermentation and distillation to produce biofuels such as bioethanol and biobutanol (Nanda et al. 2014; Nanda and Berruti 2021a). The biological process for converting biomass is well explored and preferred for obtaining valuable chemicals and fuel at a large scale due to its environmentally benign nature. The robust structure of lignocellulosic biomass impedes the effective enzymatic hydrolysis and fermentation, thereby necessitating the pretreatment of biomass (Zeng et al. 2014; Nanda and Berruti 2021b).

There are various possible approaches for the pretreatment of biomass to facilitate its bioconversion. The chemical pretreatment method involves the use of acids, bases or organic solvents. Various greener pretreatment methods such as grinding, milling, ultrasound, microwave and steam explosion are found to enhance biomass hydrolysis to a significant extent (Zhang et al. 2021). The pretreated biomass is subjected to enzymatic hydrolysis during the biochemical conversion process to generate sugar monomers. The sugar monomers are further converted into valuable commodities during the fermentation stage. The lignin content and its structure were the most crucial factor affecting the enzymatic hydrolysis process. Higher lignin content and a

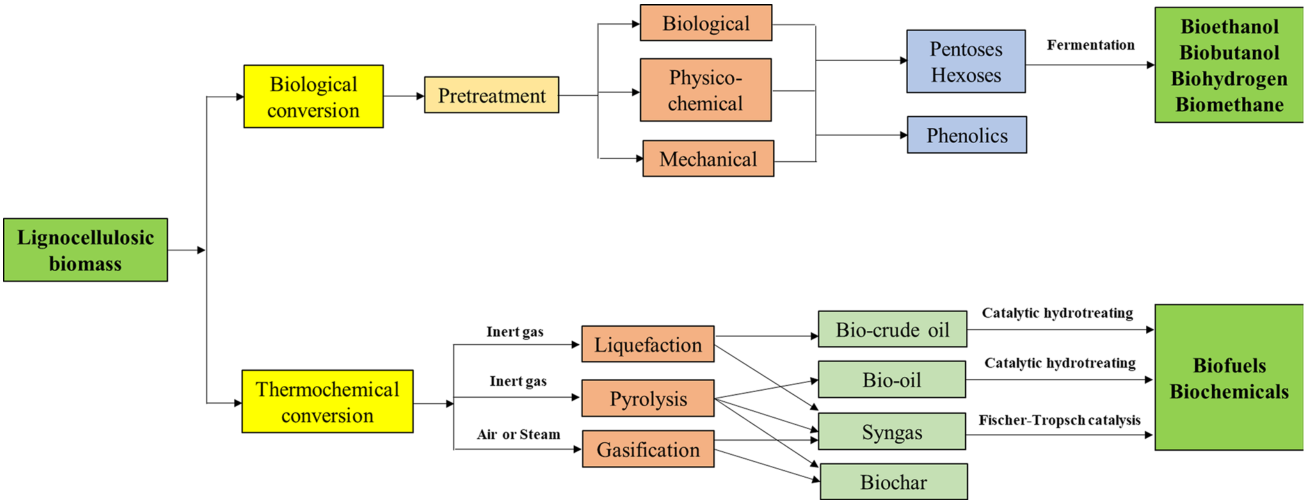

Fig. 3 Different routes for the conversion of lignocellulosic biomass to biofuel and biochemicals. The biological conversion processes involve microorganisms and their enzymes to degrade lignocellulosic biomass to monomeric sugars and further to bioethanol, biobutanol, biohydrogen and biomethane. On the contrary, thermochemical conversion technologies involving liquefaction, pyrolysis and gasification transform waste biomass to specific biofuel products such as bio-oil, bio-crude oil, syngas and biochar. Through catalytic hydrotreating and upgrading processes, bio-crude oil and bio-oil can be transformed into synthetic transportation fuels such as biodiesel, aviation fuels and bio-gasoline as well as biochemicals and high-value clean hydrocarbons

lower ratio of syringyl/guaiacyl led to reduced accessibility of enzymes to the polysaccharides, thereby decreasing its efficiency (Santos et al. 2012). Besides generating fermentable sugars to be used for further production of biofuels and some added value chemicals, the enzymatic hydrolysis of lignocellulosic biomasses itself leads to the production of many valuable commodity chemicals. For example, the enzymatic hydrolysis of biomasses such as de-starched wheat bran, corn stover and sugarcane bagasse can produce ferulic acid (Damásio et al. 2013; Cao et al. 2015; Zhang et al. 2015).

Fermentation of monomeric sugar molecules produced by enzymatic hydrolysis of polysaccharides is another important step during the biochemical conversion of biomass to biofuel. The metabolic activities of microorganisms under aerobic or anaerobic conditions convert the organic matter present in the biomass to biofuels (Patinvoh and Taherzadeh 2019; Sarangi and Nanda 2020). The fermentation process can be operated in different modes such as batch, continuous, fed-batch and consolidated bioprocessing by the digestion. To make the biochemical conversion process cost-effective, integration of various stages, including pretreatment, saccharification and fermentation using a single reactor and microorganisms have been suggested.

Thermochemical conversion routes

The thermochemical conversion routes mostly involve high temperatures, optimal reaction times and catalysts to break down the organic compounds to volatile gases and liquids, which are further processed for use as biofuels or precursors for biochemicals. Thermochemical conversion routes are broadly categorized into pyrolysis, gasification and liquefaction for fuel and chemical production (Aravind et al. 2020; Parakh et al. 2020; Patra et al. 2021; Suresh et al. 2021).

Pyrolysis is an endothermic process, which induces mild depolymerization of lignocellulosic biomass under an inert atmosphere producing mainly a liquid intermediate product called bio-oil at a temperature 300–700°C, a high heating rate of up to 1000°C/s and residence time up to 2 s (Aravind et al. 2020; Patra et al. 2021). The bio-oil obtained via pyrolysis can be subjected to catalytic hydrotreating processes to produce hydrocarbon liquid fuels with the removal of heteroatoms such as oxygen, nitrogen and sulfur. Besides, liquefaction technology can also convert lignocellulosic biomass into bio-oil upon heating at 250–374°C in an aqueous or organic solvent medium at pressures higher than 22 MPa (Tekin et al. 2014). It is considered an advantageous methodology to process wet biomass. Liquefaction can be used to produce bio-crude oil and tar from biomass (Aresta et al. 2005; Zhang et al. 2019). Biochar obtained from pyrolysis and gasification can be used as a solid fuel, adsorbent for wastewater treatment, catalyst support and precursor for carbon-based high-performance materials (Nanda et al. 2016;

Balajii and Niju 2019; Gunarathne et al. 2019; Chen et al. 2019; Gopinath et al. 2021).

Gasification is a thermochemical technique, which involves complete depolymerization of biomass in the presence of gasifying agents such as oxygen and steam to syngas at temperatures typically above 800 °C. The produced gas mainly comprises a mixture of H_2, CO_2, CO and CH_4 (Nanda et al. 2019). Furthermore, gasification of biomass at temperature and pressures greater than 374°C and 22.1 MPa, respectively under supercritical water medium is termed supercritical water gasification. Supercritical water gasification is considered economically feasible as it reduces the energy input. The biomass components under supercritical conditions are decomposed into glycerol, alcohols, organic acids, phenolics, aromatics and permanent gases (Akalın et al. 2017; Kumar et al. 2019; Nanda et al. 2015, 2019). Syngas obtained from gasification can be converted to methanol and dimethyl ether can also be produced by dehydrating methanol. Gasification can also be utilized for the generation of fuels and electricity (Okolie et al. 2021c).

Catalytic conversion of polysaccharides

Homogeneous catalysts

Homogeneous catalysis infers to the condition when the catalyst is in the same phase as the reaction medium. Homogeneous acid catalysis plays an essential role throughout the biomass conversion process, starting from hydrolytic cleavage of bonds in polysaccharides to form monomers to upgrading steps for delivering valuable products from platform chemicals. The mineral acids such as sulfuric acid or H_2SO_4, hydrochloric acid or HCl and nitric acid or HNO_3 are among the oldest and most effective homogeneous catalysts to produce biofuel and other value-added commodities like furfural and 5-hydroxymethylfurfural with high selectivity.

Table 2 shows various examples of the catalytic conversion of polysaccharides into different platform chemicals. The promising application of homogeneous catalysts for furfural synthesis has led to an increased interest of researchers (Zhao et al. 2021). Tan-Soetedjo et al. (2017) have reported a 22% conversion of sucrose into 5-hydroxymethylfurfural using 0.05 M H_2SO_4 at 140℃. The conversion of sucrose into platform chemicals was found to be susceptible to temperature and concentration of acid.

When the monomeric sugar fructose was directly used as the substrate, 53 mol% of 5-hydroxymethylfurfural was obtained at 166℃ with 0.005 M H_2SO_4 and 0.1 M of initial fructose concentration (Fachri et al. 2015). Approximately 27% yield of furfural was obtained from *Miscanthus* at 185℃ and 0.5 M H_2SO_4 (Dussan et al. 2013). 5-hydroxymethylfurfural can further be converted to levulinic acid and 2,5-furan dicarboxylic acid, which are important value-added chemicals. Acid-catalyzed hydrolysis of lignocellulosic biomass is among the most widely used process to produce levulinic acid (Kang et al. 2018). The most frequently reported acids used are H_2SO_4 and HCl, whereas HNO_3, not being too strong, cannot produce levulinic acid significantly. This emphasizes the role of acid strength in converting biomass feedstock into levulinic acid (Rackemann and Doherty 2011).

Galletti et al. (2012) used HCl to produce levulinic acid from waste biomasses such as poplar sawdust, tobacco chops, paper sludge, wheat straw and tree pruning olive. The optimization of reaction temperature and time of 200℃ and 1 h, respectively led to a 12-32 wt% yield of levulinic acid with the lowest yield from olive tree pruning and the highest yield from paper sludge. The utilization of other biomasses and optimization of reaction parameters can further enhance the yield of levulinic acid obtained.

Lignin is an integral component of lignocellulosic biomass that has several applications in fuel, chemical and biomedicine (Spiridon 2020). Lignin depolymerization with the homogeneous catalyst to produce valuable polymer precursors and aromatic monomers has been studied (Wanmolee et al. 2016). The ether bonds of lignin can be cleaved by acid or base catalysts such as triflic acid and NaOH. Lavoie et al. (2011) used NaOH for the synthesis of monomers such as phenol, catechol and vanillin from lignin obtained by steam processing of softwood and hemp. The monomeric composition obtained was different for lignin from hemp and softwood, which could be attributed to the difference in the structure of the original lignin. Additionally, the composition varied with the temperature of the depolymerization process.

In the catalytic conversion of lignocellulosic biomasses or biomass-derived pentose and hexose sugars such as xylose and glucose, the first step is the hydrolysis of polysaccharides into monomeric sugars. The second step is the isomerization of the sugars, and the most important part is the dehydration of the isomerized sugars into high-value compounds like furfural, 5-hydroxymethylfurfural and other furanics. In this catalytic process, hydrolysis and dehydration reactions are catalyzed by the Brønsted acid sites present in the acid catalysts, whereas the isomerization process is catalyzed by the Lewis acid sites (Pattnaik et al. 2021).

Although mineral acid-based homogeneous catalysts show a significant yield of various platform chemicals, due to the absence of a prominent level of Lewis acid sites, mineral acid does not significantly catalyze the isomerization reactions, which is mentioned as the rate-determining step. Therefore, these catalysts show comparatively lower yields than the various heterogeneous catalysts. Other major drawbacks of the homogeneous catalysts are the environmental toxicity caused by the different mineral acids in addition to

Table 2 Summary of works on the catalytic conversion of polysaccharides

Catalysts	Substrates	Process parameters	Key outcomes	References
Homogeneous catalysts				
0.05 M H_2SO_4	Sucrose	Temperature: 140 ℃	5-hydroxymethylfurfural yield: 22%	Tan-Soetedjo et al. (2017)
HCl	Paper sludge	Temperature: 200 ℃ Time: 1 h	Levulinic acid yield: 32%	Galletti et al. (2012)
0.5 M H_2SO_4	*Miscanthus*	Temperature: 185 ℃	Furfural yield: 27%	Dussan et al. (2013)
Mesoporous silica				
Mesoporous MCM-41	Xylose	Temperature: 170 ℃ Time: 3 h Reaction medium: Water/1-butanol, 1:1.5	Xylose conversion: 97% Furfural yield: 44%	Zhang et al. (2012)
Nb/SBA-15; Si/Nb = 1:40	Glucose	Temperature: 165 ℃ Time: 3 h Reaction medium: Water/tetrahydrofuran	Glucose conversion: 94% 5-hydroxymethylfurfural yield: 62%	Peng et al. (2017)
Nb/SBA-15; Si/Nb = 1:40	Cellulose	Temperature: 165 ℃ Time: 3 h Reaction medium: Water/tetrahydrofuran	Cellulose conversion: 92% 5-hydroxymethylfurfural yield: 51%	Peng et al. (2017)
Ru/MCM-48; Ru = 4.04 wt%	Cellulose and Glucose	Temperature: 200 ℃ Time: 0.1 h Reaction medium: Supercritical water Pressure: 5 MPa	Hexitol including mannitol and sorbitol yield: 49% from cellulose Sorbitol yield: 90% from glucose	Romero et al. (2016)
Pt/SBA-15/SO_3H; SO_3H = 12%	Xylose	Temperature: 130 ℃ Time: 6 h Reaction medium: water/isopropanol, 1:1 Pressure: 3 MPa	Xylose conversion: 65% Xylitol yield: 1% Xylulose yield: 10% Furfuryl alcohol yield: 54%	Canhaci et al. (2017)
Zeolites				
Ru/H-Zeolite Y; Ru = 1 wt% and Si/Al = 80	Xylose	Temperature: 120 ℃ Time: 2 h Pressure: 5 MPa	Xylose conversion: 62% Xylitol yield: 61%	Mishra et al. (2013)
H-USY; Si/Al = 15	Hemicellulose or Xylan	Temperature: 170 ℃ Time: 6 h Reaction medium: Water/p-xylene	Furfural yield: 17% from water medium Furfural yield: 56% from biphasic medium	Sahu and Dhepe (2012)
H-Mordenite	Cellulose, glucose and fructose	Temperature: 180 ℃ Time: 2 h	Levulinic acid yield: 56% from cellulose Levulinic acid yield: 52% from glucose Levulinic acid yield: 43% from fructose	Velaga et al. (2019)
HSO_3/ZSM-5	Corncob	Temperature: 150 ℃ Time: 5 h Reaction medium: Water/tetrahydrofuran	5-hydroxymethylfurfural yield: 49% Furfural yield: 89%	Hoang and Cuong (2021)
Sn-β-NH_2	Glucose	Temperature: 190 ℃ Time: 2 h Reaction medium: Water	Lactic acid yield: 56% 5-hydroxymethylfurfural yield: 7%	Shen et al. (2019)
NiCo/H-ZSM-5	Cellobiose and glucose	Temperature: 180 ℃ Time: 5 h Reaction medium: Water Catalyst weight: 100 mg Pressure: 5 MPa	Sorbitol yield: 87% from cellobiose Sorbitol yield: 99% from glucose	Zada et al. (2018)

Table 2 (continued)

Catalysts	Substrates	Process parameters	Key outcomes	References
Sn-β zeolite; Sn = 0.4 wt%	Glucose	Temperature: 120 °C Time: 24 h Reaction medium: Water/dioxane	Glucose conversion: 98% 5-hydroxymethylfurfural yield: 42%	Saenluang et al. (2020)
Metal oxides				
WO_3-ZrO_2	Hydrolysate from subcritical water hydrolysis of *Phragmites karka*	Temperature: 170 °C Time: 2 h Reaction medium: Water/1-butanol	Sugar conversion: 92% Furfural yield: 51% Levulinic acid yield: 34%	Pattnaik et al. (2021)
Nb_2O_5	Xylose	Temperature: 120 °C Time: 2 h Reaction medium: Water/toluene	Xylose conversion: 93% Furfural yield:72%	Gupta et al. (2017)
PO_4^{3-}/TiO_2	Cellulose, starch, sucrose, cellobiose, glucose and fructose	Temperature: 175 °C Time: 105 min Reaction medium: Water/tetrahydrofuran = 1:4 with 4 g NaCl to increase the polarity Glucose/catalyst = 4:1 Pressure: 2 MPa	Cellulose yield: 33% Starch yield: 80% Sucrose yield: 98% Cellobiose yield: 94% Glucose yield: 90% Fructose yield: 98%	Atanda et al. (2015)
WO_3-TiO_2	Glucose	Temperature: 170 °C Time: 2 h Reaction medium: Water/methyl isobutyl ketone = 3:7	Glucose conversion: 90% 5-hydroxymethylfurfural yield: 58%	Ganji and Roy (2019)
$Cu_{0.89}Zn_{0.11}O$	Xylose	Temperature: 150 °C Time: 12 h Reaction medium: Water	Furfural yield: 86%	Mishra et al. (2019)
Ionic liquids				
1-(3-sulfopropyl)-3-methylimidazolium hydrogen sulfate	Pine wood	Temperature: 180 °C Time: 7.5 min Reaction medium: Ionic liquid	Levulinic acid yield: 33% Furfural yield: 60%	López et al. (2020)
1,1,3,3-tetramethylguanidine tetrafluoroborate	Fructose	Temperature: 160 °C Time: 2 h Reaction medium: Ionic liquid, water and dimethyl sulfoxide	5-hydroxymethylfurfural yield: 74%	Du et al. (2017)
Metal–organic frameworks (MOFs)				
Lys-PM_2	Glucose	Temperature: 150 °C Time: 9 h Reaction medium: Water	Levulinic acid yield: 58%	Qu et al. (2019)
PO_4^{3-}/NU-1000	Glucose	Temperature: 140 °C Time: 5 h Reaction medium: Water/2-propanol, 1:9	Glucose conversion: 94% 5-hydroxymethylfurfural yield: 24%	Yabushita et al. (2017)
MIL-101(Cr)-SO_3H	Xylose	Temperature: 170 °C Time: 3 h Reaction medium: Cyclopentyl metyl ether and water containing 26 wt% NaCl	Xylose conversion: 98% Furfural yield: 71%	Liu et al. (2018)
Tin Phosphate and MIL-101 (Cr) composite	Xylose	Temperature: 150 °C Time: 3 h Reaction medium: Water/toluene, 3:7	Xylose conversion: 96% Furfural yield: 92%	Chatterjee et al. (2018)

the higher cost of the downstream processes for the separation of the chemicals from the reaction medium. Therefore, heterogeneous acid catalysts and ionic liquids are promising for their cost-effective and environmentally friendly approaches towards biomass conversion.

Mesoporous silica-based catalysts

For the catalytic conversion of the biomass, mesoporous SiO_2 catalysts are used due to their larger pore size, which can produce convenient passage to the larger polysaccharide molecules and other derived chemicals. For the synthesis of the mesoporous SiO_2 catalysts, two major synthetic routes are adopted, such as the soft templating method and the hard templating method (Shi et al. 2011). In the silica material, the Si atoms are replaced with Al atoms, which enhances the acidic property of the catalysts, and they are categorized as aluminosilicates. The discovery of the M41S family by Mobil's corporation made a breakthrough in the mesoporous aluminosilicate catalyst materials. In the footprint of Mobil's corporation, various other families of aluminosilicates were developed such as SBA, KIT, COK and MSU. Under this category of catalysts, MCM-41, MCM-50, MCM-48, SBA-15, and SBA-16 are well established for the conversion of lignocellulosic biomass into liquid chemicals.

Zhang et al. (2012) used the mesoporous MCM-41 for the conversion of biomass-derived xylose into furfural. They have performed the experiments using the catalyst at the temperature of 170 °C for 3 h in a biphasic medium containing water and 1-butanol in the ratio of 1:1.5. In this study, there was a xylose conversion of 97% and furfural yield of 44%, showing a comparatively better selectivity for the synthesis of furfural.

The major bottleneck of the aluminosilicates catalysis is the hydrothermally unstable nature of the various materials, especially at higher temperatures or prolong catalytic processes (Xiong et al. 2014). However, some of the doped mesoporous silica has proved to be hydrothermally stable. Peng et al. (2017) performed catalytic conversion of glucose to 5-hydroxymethylfurfural by using Niobium or Nb doped SBA-15 at the Si/Nb ratio of 1:40. The authors reported a significant glucose conversion and 5-hydroxymethylfurfural yield of 94% and 62%, respectively. The above catalytic conversion was performed at the temperature of 165 °C for 3 h and using tetrahydrofuran as a co-solvent in the reaction medium. In this study, the researchers have performed the catalytic conversion of cellulose into 5-hydroxymethylfurfural, where they have concluded with the cellulose conversion of 92% and 5-hydroxymethylfurfural yield of 51% at the reaction temperature of 170 °C for 8 h. However, with the increase in the temperature to 190 °C, the 5-hydroxymethylfurfural yield decreased to 21% due to the polymerization of glucose into humin.

5-ethoxymethylfurfural is another high-value platform chemical like 5-hydroxymethylfurfural, which can be synthesized from various carbohydrates by using selective catalysts. Rao et al. (2020) used the SBA-15 catalyst modified by Sn-doped heteropolysilicate for the selective conversion of fructose to 5-ethoxymethylfurfural. The higher selectivity of the catalyst was attributed towards the appropriate Brønsted to Lewis acid site. In this conversion process, fructose was dehydrated to produce 5-hydroxymethylfurfural by the Brønsted site. On the other hand, the catalytic effect of the Lewis sites resulted in the conversion of 5-hydroxymethylfurfural into 5-ethoxymethylfurfural (Rao et al. 2020).

In various studies, aluminosilicates are used as the support materials for various solid acid catalysts like sulfonic acids, tungsten oxide, heteropoly acids and other metal oxides, which catalyze a wide range of lignocellulosic biomasses, and biomass-derived carbohydrates to obtain various platform chemicals. However, aluminosilicates such as amorphous zeolites are widely used solid acid catalysts with a well-defined porous and crystalline structure. These materials are also hydrothermally stable to several high-temperature reactions.

Zeolite-based catalysts

Zeolites are also considered solid acid catalysts under the category of aluminosilicates. However, unlike the previously described aluminosilicates such as MCM or SBA, zeolites are microporous crystalline materials and possess significant stability towards the high-temperature water-based reaction medium. Zeolites consist of SiO_4 tetrahedra where some of the Si-point is replaced by the Al^{+3} ion creating AlO_3 linkages and leaving a negative charge to the zeolite framework. Moreover, to compensate for this negative charge, positive ions such as ammonium ions or NH_4^+, sodium ions or Na^+ and proton or H^+ reside over the framework. Among these ions, zeolites containing H^+ are known for their acidic sites, where the Al_2O_3 provides the Lewis acid sites, and the H^+ ion provides the Brønsted acid sites (Fig. 4). Therefore, the proper synchronization of these Lewis and Brønsted sites can catalyze various acid-catalyzed reactions like isomerization, dehydration and hydrogenation. There are several pieces of literature available for the catalytic conversion of lignocellulosic biomasses and sugar into different furan-based chemicals such as furfural, 5-hydroxymethylfurfural, organic acids like levulinic acid and sugar alcohols like xylitol, sorbitol and mannitol.

The biphasic systems have been proved to be the efficient reaction media compared to the water. When an organic

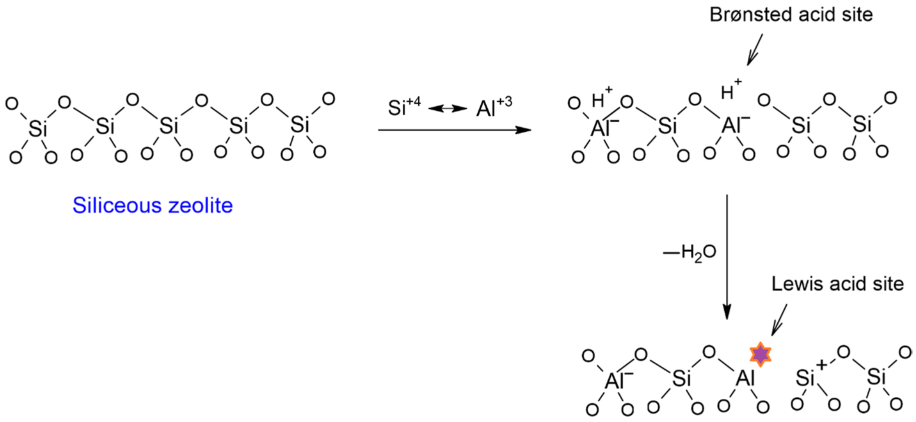

Fig. 4 Development of Brønsted and Lewis acid sites in zeolites. In the zeolite framework, when tetravalent silicon ions are replaced by trivalent aluminum ions, extra negative charges are formed. These negative ions are compensated by the monovalent positive ions such as protons. These protons behave as the Brønsted acid sites in the zeolite catalytic framework. It should also be noted that by the dehydration of aluminum-doped silicon-based zeolites, Lewis acid sites are formed as vacant orbitals. The synergistic effects of the Brønsted and Lewis acid sites in zeolites can catalyze various biomass conversion processes

solvent is present in the reaction medium, the degraded products such as furfural and 5-hydroxymethylfurfural obtained from the catalytic conversion of sugars are extracted to the organic medium due to their higher solubility in the organic solvent than the water. Therefore, the products further do not react to the various polymeric products like humin, which subsequently increases the yield of decided products from the sugars.

Sahu and Dhepe (2012) reported using various zeolite catalysts such as H-β, H-USY and H-mordenite to convert the hemicelluloses present in lignocellulosic biomass into furfural. In this study, the yield of furfural in the water medium and water/p-xylene medium was obtained to be 17% and 56%, respectively, in the case of H-USY with Si/Al ratio of 15 at 170 °C for 6 h, where other zeolites were concluded with a comparatively lesser yield of furfural.

Among the various zeolitic catalysts, ZSM-5 or various modified ZSM-5 are highly implemented for their cost-effective aspects. However, in the catalytic conversion of the lignocellulosic biomass, there exist three significant reactions, such as hydrolysis of polysaccharides to mono-or oligomers, isomerization of monomers and finally dehydration of the isomeric sugars, in which the hydrolysis and isomerization can be performed by the Lewis sites present in ZSM-5 or other zeolites whereas the hydration step needs strong acid sites. Therefore, sometimes the modification of zeolites with a stronger acid catalyst can increase the acidity and catalytic activity.

Bisulfite or HSO_3 modified ZSM-5 can be used to convert the corncob to obtain 5-hydroxymethylfurfural and furfural. Here, this modification using HSO_3 enhances the acid properties of the parent catalyst by increasing the strong acid sites, for which the conversion of corn cob was efficiently performed, yielding 49% 5-hydroxymethylfurfural and 89% furfural at the temperature of 150 °C for 5 h in a biphasic system containing tetrahydrofuran and water (Hoang and Cuong 2021). In some reports, as with the HSO_3, heteropoly acids are used as the Brønsted acid modifier in the zeolites. Heteropolyacids are strong solid acids and can provide their Brønsted acidity in the acid catalytic conversion of carbohydrates. Zhou et al. (2019) used $H_4SiW_{12}O_{40}$ modified Sn-β-zeolite for the conversion of alpha-cellulose and microcrystalline cellulose to produce methyl levulinate in the presence of methanol in the reaction medium. The authors reported methyl levulinate yields of 55% and 62% from α-cellulose and microcrystalline cellulose, respectively.

Zeolites are widely used for the conversion of lignocellulosic biomasses or biomass-derived sugars into various platform chemicals. However, a few disadvantages associated with zeolitic catalysts are encountered such as lower hydrothermal stability, deactivation of acid sites and blocking of micropores leading to the hampered synthesis of large molecules (Silva et al. 2020). In the conversion of sugars, the catalysts should be hydrothermally stable, as the reaction medium in this catalytic process is water. Therefore, for the catalytic conversion of polysaccharides, metal oxides are proven to be potential catalysts with a higher level of hydrothermal stability.

Metal oxides

Since the sugars are soluble in water, the reaction is usually performed under aqueous conditions. Therefore, under such conditions, the tolerance of acid catalysts to convert sugars into chemicals is a critical feature. Furthermore, some water-resistant metal oxides such as ZrO_2, TiO_2, SnO_2, Ta_3O_5, Nb_2O_5 and Mo_2O_3 as well as mixed metal oxides such as WO_3–TiO_2, WO_3–ZrO_2, ZrO_2–TiO_2 and WO_3–Ta_3O_5 can be potentially implemented to transform lignocellulosic biomass into fine chemical precursors. The metal oxides mentioned above consist of unsaturated metal ions, which are responsible for the Lewis acidity of the metal oxides and can catalyze the isomerization process of the monomeric sugars. Moreover, these metal oxides with pre-existing Lewis acid sites can be modified by some solid Brønsted acids, which subsequently aid the dehydration of isomerized sugars including fructose or xylulose.

With the synchronizing effect of these two types of catalytic sites, polysaccharides present in the lignocellulosic biomass can be converted into liquid chemicals. Therefore, to enhance the Brønsted sites, the metal oxides can be mixed with tungsten trioxide or WO_3, sulfuric acid or H_2SO_4, phosphoric acid or H_3PO_4 and heteropoly acids, which will provide strong acidity to the conversion reactions. Among the various Brønsted acids, WO_3 is the most common dopant used by several researchers (Pattnaik et al. 2021).

Pattnaik et al. (2021) used several metal oxides and mixed metal oxides for the conversion of sugar mixture obtained from the subcritical hydrolysis of common reed or *Phragmites karka*. WO_3-ZrO_2 showed significant catalytic activity with 92% sugar conversion, 51% furfural yield and 34% levulinic acid at 170 ℃ for 2 h when compared with other catalysts such as ZrO_2, TiO_2, ZrO_2-TiO_2, WO_3-TiO_2 and WO_3-ZrO_2-TiO_2. The higher yield of levulinic acid and furfural than the other used catalysts is due to the synchronization of the basic sites present in ZrO_2 and Brønsted sites of the WO_3. Figure 5 shows the dehydration of xylose and glucose into specific products (Pattnaik et al. 2021).

Besides the mixed metal oxides, individual metal oxides like TiO_2, ZrO_2 and Nb_2O_5 are used as the catalyst for the conversion of sugars or carbohydrates into respective dehydrated chemicals. In a catalytic reaction, one of the significant factors is the lower activation energy, which establishes an energy-efficient catalytic conversion. In a study by Gupta et al. (2017), Nb_2O_5 showed comparatively lower activation energy (83 kJ/mol) than the conventional homogeneous catalysts and a mineral acid such as HCl (107-131 kJ/mol). With Nb_2O_5, xylose conversion and furfural yield were found to be 93% and 72%, respectively at 120 ℃ in a biphasic system containing toluene and water.

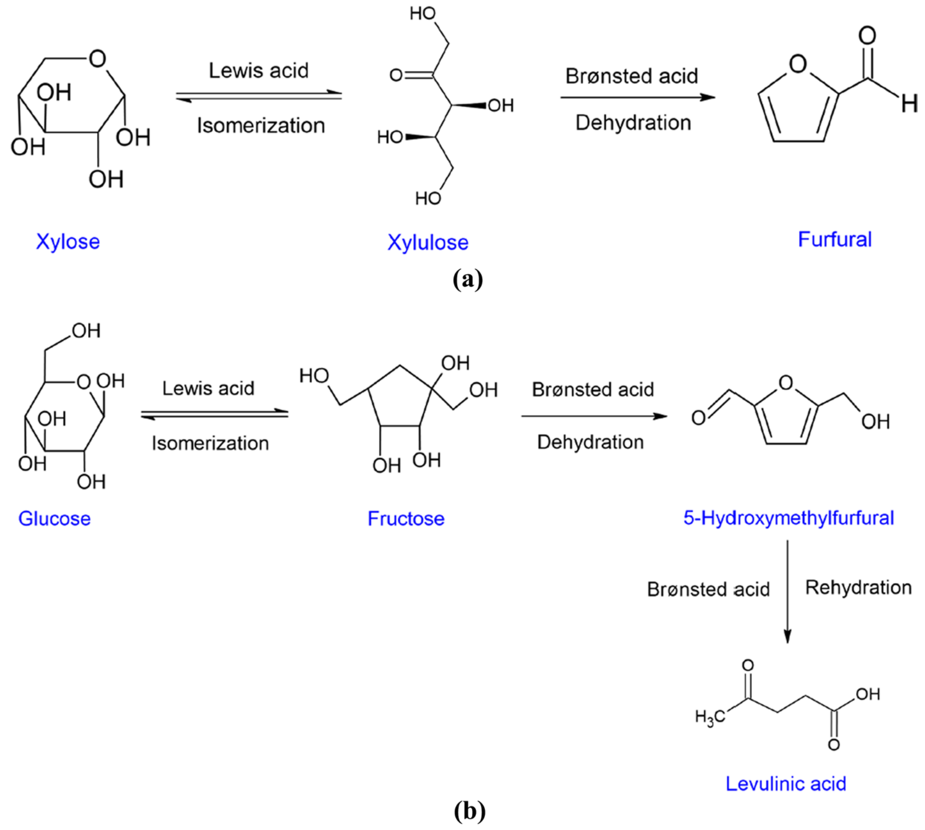

Fig. 5 **a** Dehydration of xylose into furfural, and **b** dehydration of glucose into 5-hydroxymethylfurfural and levulinic acid. Note that in the catalytic conversion of xylose to furfural, two consecutive steps occur such as isomerization of xylose to xylulose and dehydration of xylose to furfural. Likewise, in the catalytic conversion of glucose, the first step is the isomerization of glucose to fructose followed by the dehydration of fructose to 5-hydroxymethylfurfural and rehydration to form levulinic acid. The isomerization reactions are catalyzed by the Lewis acid sites, whereas the dehydration and rehydration are promoted by the Brønsted acid sites

To increase the acidity of the metal oxides, these are modified by several Brønsted acids. Moreover, sulfated and phosphate metal oxides show comparatively higher performance than the WO_3 based catalysts. Anatase phase TiO_2 impregnated with H_3PO_4 is known as phosphate TiO_2, which showed tremendous activity in the conversion of cellulose, starch, sucrose, cellobiose, glucose and fructose, obtaining a yield of 33%, 80%, 98%, 94%, 90% and 98%, respectively at the temperature of 175 °C for glucose and fructose whereas 180 °C for remaining of the substrates. Among the above substrates, cellulose delivered a relatively lower yield of 5-hydroxymethylfurfural compared with the other substrates due to the existence of slow rate-determining step and hydrolysis of cellulose into its monomeric sugars (Atanda et al. 2015). Although most of the metal oxides are highly resistant to hydrothermal processes, some tungsten-based oxides such as WO_3 are slightly unstable in the water-based single-phase system. However, the reactions conducted in bi-phase or multi-phase systems provide a higher level of stability to the unstable metal oxide catalysts (Choi et al. 2018).

Ionic liquids

Unlike other conventional organic solvents, ionic liquids are composed of different inorganic or organic ions in cationic and anionic forms. They possess various potential characteristics like lower vapor pressure, higher thermal stability and excellent solubility in water. Ionic liquids are used for the dissolution of the various components of lignocellulosic biomasses such as cellulose, lignin and hemicellulose by taking multiple combinations of the anions and cations. According to the need of the processes, the combinations of anions and cations are tailored, which are raised with acidic, basic or other prominent properties.

Some notable ionic liquids such as 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium acetate and their chlorides, especially chloride of 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations can solubilize lignocellulosic biomass components such as cellulose, hemicellulose and lignin (da Costa Lopes and Bogel-Łukasik 2015). Furthermore, some phosphorous-based ionic liquids and sulfate-based ionic liquids are reported to selectively dissolve cellulose and lignin, respectively. Besides degrading lignin, ionic liquids are also used as the reaction medium for hydrolysis of cellulose and hemicellulose as well as the conversion of monomeric or oligomeric sugars into furan and non-furan-based biochemicals such as furfural, 5-hydroxymethylfurfural and levulinic acid.

In the biomass conversion process, the major bottleneck is the hydrolysis of complex polysaccharides like cellulose and hemicellulose into mono-or oligomeric sugars, which is a Brønsted acid-catalyzed reaction. Among various green processes, performing conversion reactions in ionic liquids has been tremendously established and well propagated by researchers worldwide. Amarasekara and Owereh (2009) have synthesized acidic ionic liquids by functionalizing the sulfonic acid group or $–SO_3H$ with imidazolium and pyridine-based ionic liquids. In the acid hydrolysis reaction, water plays a vital role in the reaction, which produces hydronium ion or H_3O^+ by reacting with H^+ ions generated from the acidic ionic liquids. These hydronium ions react with the β-(1,4)-glycosidic linkages to disintegrate the bonds or interaction, resulting in pentose or hexose sugars, including some oligomeric sugars like cellobiose and raffinose. In the conclusion of this study, the researchers found methylimidazolium ionic liquids to be the efficient medium to produce the highest reducing sugars yield from cellulose than the pyridinium ionic liquids (Amarasekara and Owereh 2009; da Costa Lopes and Bogel-Łukasik 2015).

Some alkaline ionic liquids such as 1-butyl-3-methylimidazolium carbonate, 1-butyl-3-methylimidazolium benzoate, 1-butyl-3-methylimidazolium acetate, ethanolamine tetrafluoroborate and 1-butyl-3-methylimidazolium hydroxide are widely implemented for the acid-catalyzed reactions for the conversion of monomeric sugars, namely glucose, xylose and fructose, oligomeric sugars like cellobiose and pure microcrystalline cellulose into furfural, 5-hydroxymethylfurfural, levulinic acid and other furanics.

Du et al. (2017) reported an alkaline ionic liquid named 1,1,3,3-tetramethylguanidine tetrafluoroborate showing an excellent yield of 74% for 5-hydroxymethylfurfural from fructose. Both the acidic and alkaline ionic liquids are considered greener solvents or catalysts for the pretreatment of lignocellulosic biomasses. However, the separation of synthesized products from the reaction medium can increase the cost of the downstream process.

Metal–organic frameworks

Metal-organic frameworks or MOFs are three-dimensional solid catalysts, which comprise metal clusters connected with the organic ligands with the coordinate bonds (Tran et al. 2019; Cong et al. 2021). MOFs are often known for their hierarchal porosity and have attracted the attention of many researchers for their heterogeneity, considerably higher surface area and adaptable pore dimension. Although a majority of MOFs have Lewis acid sites, there exist few MOFs containing both Lewis and Brønsted acid sites. MOFs can also be modified with certain Brønsted acid. These modified MOFs and MOFs with both Lewis and Brønsted acid sites are used for the catalytic conversion of carbohydrates to produce various liquid chemicals.

Qu et al. (2019) have used Lysin coordinated phosphotungstic acid or Lys-PM_2 as the MOF for the conversion of glucose into levulinic acid. The most important advantages of the above heterogeneous catalyst are the convenient or cost-effective synthesis of the catalyst and higher stability in the aqueous medium with the least leaching of the catalyst elements into the reaction medium. In this study, with the synchronizing effect of Lewis and Brønsted sites, a levulinic acid yield of 57% was obtained at the temperature of 150 ℃ for 9 h in the single-phase aqueous medium. Besides this significant yield of levulinic acid, the intactness of the Brønsted acid sites makes the catalysts be used significantly for four consecutive catalytic runs without losing the effectiveness of the catalytic process (Qu et al. 2019).

NU-1000 is another thermodynamically and chemically stable MOF-based catalyst similar to Lys-PM_2. It is a MOF made up of ZrO_2 clusters isolated by pyrene linkers. Due to the presence of Lewis acid sites, it is used as the catalyst for the isomerization of glucose to fructose. Yabushita et al. (2017) used phosphoric acid-modified NU-1000, where the phosphoric acid provided Brønsted acidity for the dehydration of fructose into 5-hydroxymethylfurfural. With the simultaneous effect of the Lewis and Brønsted sites, a glucose conversion of 94% and 5-hydroxymethylfurfural yield of 24% were reported at 140 ℃ in 5 h using a biphasic system containing water and 2-propanol in a ratio of 1:9 (Yabushita et al. 2017). Although MOFs establish a green technique for the catalytic conversion of the lignocellulosic biomass or biomass-derived carbohydrates, the absence of Brønsted sites adds up the process cost for the modification of the MOFs to have Brønsted acidity.

Conclusion

The production of biofuel platform chemicals from diverse integral units of lignocellulosic biomasses is anticipated to be the chief facet of the biobased economy. The conversion of biomass into platform chemicals can be acquired by a thermochemical or biochemical pathway. The biochemical route is an entirely green approach but is somewhat more expensive and results in lower yields requiring thorough scientific investigations and innovations for enhancing the competency of the process. The thermochemical approach utilizing various homogeneous or heterogeneous catalysts is successfully applied to biofuel and platform chemicals production. The use of homogeneous mineral acids as the catalyst for this bioconversion is most widely commercialized, but the toxicity associated with these mineral acids leads to the utilization of environmentally benign heterogeneous catalysts. Mesoporous silica-based catalysts, zeolite-based catalysts, metal oxides, ionic liquids and metal-organic frameworks are profitably being employed for effective and efficient greener conversion of polysaccharides into biofuel platform chemicals. The catalytic processes postulate immense possibilities for driving the world towards the biobased economy.

Funding The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Research Chairs (CRC) program for funding this bioenergy research.

Declarations

Conflicts of interest The authors declare that they have no competing interests.

Consent for publication All authors agree to publish this article in Environmental Chemistry Letters.

Informed consent No informed consent.

Research involving human participants and/or animals No human or animalrights applicable.

References

Acharjee TC, Lee YY (2018) Production of levulinic acid from glucose by dual solid-acid catalysts. Environ Prog Sustain Energy 37:471–480. https://doi.org/10.1002/ep.12659

Akalın MK, Tekin K, Karagöz S (2017) Supercritical fluid extraction of biofuels from biomass. Environ Chem Lett 15:29–41. https://doi.org/10.1007/s10311-016-0593-z

Amarasekara AS, Owereh OS (2009) Hydrolysis and decomposition of cellulose in Bronsted acidic ionic liquids under mild conditions. Ind Eng Chem Res 48:10152–10155. https://doi.org/10.1021/ie901047u

Amiri H, Karimi K, Zilouei H (2014) Organosolv pretreatment of rice straw for efficient acetone, butanol, and ethanol production. Bioresour Technol 152:450–456. https://doi.org/10.1016/j.biortech.2013.11.038

Aravind S, Kumar PS, Kumar NS, Siddarth N (2020) Conversion of green algal biomass into bioenergy by pyrolysis. A Rev Environ Chem Lett 18:829–849. https://doi.org/10.1007/s10311-020-00990-2

Aresta M, Dibenedetto A, Carone M, Colonna T, Fragale C (2005) Production of biodiesel from macroalgae by supercritical CO_2 extraction and thermochemical liquefaction. Environ Chem Lett 3:136–139. https://doi.org/10.1007/s10311-005-0020-3

Atanda L, Shrotri A, Mukundan S, Ma Q, Konarova M, Beltramini J (2015) Direct production of 5-hydroxymethylfurfural via catalytic conversion of simple and complex sugars over phosphated TiO_2. Chemsuschem 8:2907–2916. https://doi.org/10.1002/cssc.201500395

Awoyale AA, Lokhat D (2021) Experimental determination of the effects of pretreatment on selected Nigerian lignocellulosic biomass in bioethanol production. Sci Rep 11:1–16. https://doi.org/10.1038/s41598-020-78105-8

Balajii M, Niju S (2019) Biochar-derived heterogeneous catalysts for biodiesel production. Environ Chem Lett 17:1447–1469. https://doi.org/10.1007/s10311-019-00885-x

Barbara I, Flourat AL, Allais F (2015) Renewable polymers derived from ferulic acid and biobased diols via ADMET. Eur Polym J 62:236–243. https://doi.org/10.1016/j.eurpolymj.2014.11.035

Boonsombuti A, Tangmanasakul K, Nantapipat J, Komolpis K, Luengnaruemitchai A, Wongkasemjit S (2016) Production of biobutanol from acid-pretreated corncob using *Clostridium beijerinckii* TISTR 1461: process optimization studies. Prep Biochem Biotechnol 46:141–149. https://doi.org/10.1080/10826068.2014.995810

Canhaci SJ, Perez RF, Borges LEP, Fraga MA (2017) Direct conversion of xylose to furfuryl alcohol on single organic–inorganic hybrid mesoporous silica-supported catalysts. Appl Catal B Environ 207:279–285. https://doi.org/10.1016/j.apcatb.2017.01.085

Cao L, Chen R, Xie W, Liu Y (2015) Enhancing the thermostability of feruloyl esterase EstF27 by directed evolution and the underlying structural basis. J Agric Food Chem 63:8225–8233. https://doi.org/10.1021/acs.jafc.5b03424

Chatterjee A, Hu X, Lam FL-Y (2018) A dual acidic hydrothermally stable MOF-composite for upgrading xylose to furfural. Appl Catal A Gen 566:130–139. https://doi.org/10.1016/j.apcata.2018.04.016

Chen L, Li F, Wei Y, Li G, Shen K, He HJ (2019) High cadmium adsorption on nanoscale zero-valent iron coated *Eichhornia crassipes* biochar. Environ Chem Lett 17:589–594. https://doi.org/10.1007/s10311-018-0811-y

Choi IH, Kim HR, Moon G, Jyothi RK, Lee JY (2018) Spent V_2O_5-WO_3/TiO_2 catalyst processing for valuable metals by soda roasting-water leaching. Hydrometallurgy 175:292–299. https://doi.org/10.1016/j.hydromet.2017.12.010

Chua SY, Periasamy LAP, Goh CMH, Tan YH, Mubarak NM, Kansedo J, Khalid M, Walvekar R, Abdullah EC (2020) Biodiesel synthesis using natural solid catalyst derived from biomass waste—a review. J Ind Eng Chem 81:41–60. https://doi.org/10.1016/j.jiec.2019.09.022

Cong W-J, Nanda S, Li H, Fang Z, Dalai AK, Kozinski JA (2021) Metal-organic framework-based functional catalytic materials for biodiesel production: a review. Green Chem 23:2595–2618. https://doi.org/10.1039/D1GC00233C

da Costa Lopes AM, Bogel-Łukasik R (2015) Acidic ionic liquids as sustainable approach of cellulose and lignocellulosic biomass conversion without additional catalysts. Chemsuschem 8:947–965. https://doi.org/10.1002/cssc.201402950

Damásio ARL, Braga CMP, Brenelli LB, Citadini AP, Mandelli F, Cota J, de Almeida RF, Salvador VH, Paixao DAA, Segato F, Mercadante AZ, de Oliveira Neto NM, do Santosde Squina NMWDFM (2013) Biomass-to-bio-products application of feruloyl esterase from *Aspergillus clavatus*. Appl Microbiol Biotechnol 97:6759–6767. https://doi.org/10.1007/s00253-012-4548-4

de Lucas RC, de Oliveira TB, Lima MS, Pasin TM, de Almeid Scarcella AS, Ribeiro LFC, Carvalho C, de Lima Damasio AR, Buckeridge MS, Prade RA, Segato F, de Lourdes Teixeira de Moraes Polizeli M (2021) The profile secretion of *Aspergillus clavatus*: Different pre-treatments of sugarcane bagasse distinctly induces holocellulases for the lignocellulosic biomass conversion into sugar. Renew Energy 165:748–757. https://doi.org/10.1016/j.renene.2020.11.072

Du X, Zhang J, Wang Y, Qu Y (2017) Conversion of carbohydrates into platform chemicals catalyzed by alkaline ionic liquids. Catalysts 7:245. https://doi.org/10.3390/catal7090245

Dussan K, Girisuta B, Haverty D, Leahy JJ, Hayes MHB (2013) Kinetics of levulinic acid and furfural production from *Miscanthus* × *giganteus*. Bioresour Technol 149:216–224. https://doi.org/10.1016/j.biortech.2013.09.006

EMR (2020a) Global xylitol market: by form: solid, liquid; by application: chewing gum, confectionery, pharmaceuticals and personal care, others; regional analysis; historical market and forecast (2016–2026); market dynamics; value chain analysis; price analysis; manufacturing process; competitive landscape; industry events and developments, https://www.expertmarketresearch.com/reports/xylitol-market#:~:text=Global%20Xylitol%20Market%20Outlook,USD%201209.2%20million%20by%202026. Accessed 25 Apr 2021

EMR (2020b) Global mannitol market: by form: powder, granular; by application: food industry, industrial, surfactants, pharmaceuticals, personal care, others; regional analysis; historical market and forecast (2016–2026); SWOT analysis; value chain analysis; price analysis; competitive landscape; industry events and developments, https://www.expertmarketresearch.com/reports/mannitol-market#:~:text=The%20global%20mannitol%20market%20attained,USD%20497%20million%20in%202026.&text=The%20Asia%20Pacific%20is%20the%20leading%20market%20in%20the%20industry. Accessed 25 Apr 2021

Fachri BA, Abdilla RM, Bovenkamp HHVD, Rasrendra CB, Heeres HJ (2015) Experimental and kinetic modeling studies on the sulfuric acid catalyzed conversion of d-fructose to 5-hydroxymethylfurfural and levulinic acid in water. ACS Sustain Chem Eng 3:3024–3034. https://doi.org/10.1021/acssuschemeng.5b00023

Gall DL, Ralph J, Donohue TJ, Noguera DR (2017) Biochemical transformation of lignin for deriving valued commodities from lignocellulose. Curr Opin Biotechnol 45:120–126. https://doi.org/10.1016/j.copbio.2017.02.015

Galletti AMR, Antonetti C, De Luise V, Licursi D, Nasso NN (2012) Levulinic acid production from waste biomass. BioResources 7:1824–1835

Ganji P, Roy S (2019) Trade-off between acidic sites and crystallinity of the WO_3-TiO_2 catalyst toward dehydration of glucose to 5-hydroxymethylfurfural. Energy Fuels 33:5293–5303. https://doi.org/10.1021/acs.energyfuels.9b00461

Gopinath KP, Vo DVN, Prakash DG, Joseph AA, Viswanathan S, Arun J (2021) Environmental applications of carbon-based materials: a review. Environ Chem Lett 19:557–582. https://doi.org/10.1007/s10311-020-01084-9

Grand view research (2015) https://www.grandviewresearch.com/industry-analysis/levulinic-acid-market. Accessed 22 Feb 2021

Grand view research (2017) Vanillin market size, share & trends analysis report by end-use (food & beverage, fragrance, pharmaceutical), by region (North America, Europe, Asia Pacific, Central & South America, MEA), and segment forecasts, 2018–2025. https://www.grandviewresearch.com/industry-analysis/vanillin-market/toc. Accessed 22 Feb 2021

Grand View Research (2020a) Furfural market size, share & trends analysis report by process, by raw material (corncob, sugarcane bagasse), by application (furfuryl alcohol, solvent), by end-use (pharmaceutical, refineries), and segment forecasts, 2020 – 2027. https://www.grandviewresearch.com/industry-analysis/furfural-market. Accessed on 24 Apr 2021

Grand View Research (2020b) Furfuryl alcohol market size, share & trends analysis report by application (resins, solvent, corrosion inhibitor), by end use (Foundry, Agriculture), By Region, And Segment Forecasts, 2020–2027. https://www.grandviewresearch.com/industry-analysis/furfuryl-alcohol-market. Accessed on 25 Apr 2021

Grand View Research (2021) Sorbitol market size, share & trends analysis report by product (liquid, crystal), by application (diabetic & dietetic F&B, Vitamin C), by end-use (food, personal care), by region, and segment forecasts, 2021–2028. https://www.grandviewresearch.com/industry-analysis/sorbitol-market. Accessed 25 Apr 2021

Gunarathne V, Ashiq A, Ramanayaka S, Wijekoon P, Vithanage M (2019) Biochar from municipal solid waste for resource recovery and pollution remediation. Environ Chem Lett 17:1225–1235. https://doi.org/10.1007/s10311-019-00866-0

Gupta NK, Fukuoka A, Nakajima K (2017) Amorphous Nb_2O_5 as a selective and reusable catalyst for furfural production from xylose in biphasic water and toluene. ACS Catal 7:2430–2436. https://doi.org/10.1021/acscatal.6b03682

Gürbüz E, Bond JQ, Dumesic JA, Román-Leshkov Y (2013) Role of acid catalysis in the conversion of lignocellulosic biomass to fuels and chemicals. In: Triantafyllidis KS, Lappas AA, Stöcker M (eds) The role of catalysis for the sustainable production of bio-fuels and bio-chemicals. Elsevier, Amsterdam, pp 261–288

Harshvardhan K, Suri M, Goswami A, Goswami T (2017) Biological approach for the production of vanillin from lignocellulosic biomass (*Bambusa tulda*). J Clean Prod 149:485–490. https://doi.org/10.1016/j.jclepro.2017.02.125

Hoang PH, Cuong TD (2021) Simultaneous direct production of 5-hydroxymethylfurfural (HMF) and furfural from corncob biomass using porous HSO_3-ZSM-5 zeolite catalyst. Energy Fuels 35:546–551. https://doi.org/10.1021/acs.energyfuels.0c03431

Intrado (2020) The global bioethanol market size is projected to grow from USD 33.7 billion in 2020 to USD 64.8 billion by 2025, at a Compound Annual Growth Rate (CAGR) of 14.0% from 2020 to 2025. https://www.globenewswire.com/news-release/2020/06/08/2044734/0/en/The-global-bioethanol-market-size-is-projected-to-grow-from-USD-33-7-billion-in-2020-to-USD-64-8-billion-by-2025-at-a-Compound-Annual-Growth-Rate-CAGR-of-14-0-from-2020-to-2025.html. Accessed 22 Feb 2021

Kabbour M, Luque R (2020) Furfural as a platform chemical: from production to applications. In: Saravanamurugan S, Pandey A, Li H, Riisager A (eds) Recent Advances in Development of Platform Chemicals, Elsevier, pp 283–297. https://doi.org/10.1016/B978-0-444-64307-0.00010-X

Kaloudas D, Pavlova N, Penchovsky R (2021) Lignocellulose, algal biomass, biofuels and biohydrogen: a review. Environ Chem Lett 19:2809–2824. https://doi.org/10.1007/s10311-021-01213-y

Kang S, Fu J, Zhang G (2018) From lignocellulosic biomass to levulinic acid: a review on acid-catalyzed hydrolysis. Renew Sustain Energy Rev 94:340–362. https://doi.org/10.1016/j.rser.2018.06.016

Karimi S, Karri RR, Yaraki MT, Koduru JR (2021) Processes and separation technologies for the production of fuel-grade bioethanol: a review. Environ Chem Lett 19:2873–2890. https://doi.org/10.1007/s10311-021-01208-9

Khalil AA, ur Rahman U, Khan MR, Sahar A, Mehmood T, Khan M, (2017) Essential oil eugenol: sources, extraction techniques and nutraceutical perspectives. RSC Adv 7:32669–32681. https://doi.org/10.1039/C7RA04803C

Kumar G, Dharmaraja J, Arvindnarayan S, Shoban S, Bakonyi P, Saratale GD, Nemestóthy N, Bélafi-Bakó K, Yoon J-J, Kim S-H (2019) A comprehensive review on thermochemical, biological, biochemical and hybrid conversion methods of bio-derived lignocellulosic molecules into renewable fuels. Fuel 251:352–367. https://doi.org/10.1016/j.fuel.2019.04.049

Kumar V, Binod P, Sindhu R, Gnansounou E, Ahluwalia V (2018) Bioconversion of pentose sugars to value added chemicals and fuels: Recent trends, challenges and possibilities. Bioresour Technol 269:443–451. https://doi.org/10.1016/j.biortech.2018.08.042

Lavoie JM, Baré W, Bilodeau M (2011) Depolymerization of steam-treated lignin for the production of green chemicals. Bioresour Technol 102:4917–4920. https://doi.org/10.1016/j.biortech.2011.01.010

Lee CBTL, Wu TY (2021) A review on solvent systems for furfural production from lignocellulosic biomass. Renew Sustain Energy Rev 137:110172. https://doi.org/10.1016/j.rser.2020.110172

Liu Y, Ma C, Huang C, Fu Y, Chang J (2018) Efficient conversion of xylose into furfural using sulfonic acid-functionalized metal-organic frameworks in a biphasic system. Ind Eng Chem Res 57:16628–16634. https://doi.org/10.1021/acs.iecr.8b04070

López M, Vila C, Santos V, Parajó JC (2020) Manufacture of platform chemicals from pine wood polysaccharides in media containing acidic ionic liquids. Polymers 12:1215. https://doi.org/10.3390/polym12061215

Market and Research (2019) Global 5-hydroxymethylfurfural (5-HMF) (CAS 67–47–0) Market Growth 2019–2024. https://www.marketandresearch.biz/report/100081/global-5-hydroxymethylfurfural-5-hmf-cas-67-47-0-market-growth-2019-2024. Accessed 25 Apr 2021

Markets and Markets (2020a) Bioethanol Market by Feedstock (Starch based, sugar based, cellulose based), End-use Industry (transportation, pharmaceuticals, cosmetics, alcoholic beverages), Fuel blend (E5, E10, E15 to E70, E75 & E85), and Region - Global Forecast to 2025. https://www.marketsandmarkets.com/Market-Reports/bioethanol-market-131222570.html. Accessed 24 Apr 2021

Markets and Markets (2020b) Lactic acid market by application (biodegradable polymers, food & beverages, pharmaceutical products), form, and region, polylactic acid market, by application (Packaging, Fiber & Fabrics, Agriculture), form, and region - global forecast to 2025. https://www.marketsandmarkets.com/Market-Reports/polylacticacid-387.html. Accessed 25 Apr 2021

Mishra DK, Dabbawala AA, Hwang J-S (2013) Ruthenium nanoparticles supported on zeolite Y as an efficient catalyst for selective hydrogenation of xylose to xylitol. J Mol Catal A Chem 376:63–70. https://doi.org/10.1016/j.molcata.2013.04.011

Mishra RK, Kumar VB, Victor A, Pulidindi IN, Gedanken A (2019) Selective production of furfural from the dehydration of xylose using Zn doped CuO catalyst. Ultrason Sonochem 56:55–62. https://doi.org/10.1016/j.ultsonch.2019.03.015

Monlau F, Barakat A, Steyer J-P, Carrère H (2012) Comparison of seven types of thermo-chemical pretreatments on the structural features and anaerobic digestion of sunflower stalks. Bioresour Technol 120:241–247. https://doi.org/10.1016/j.biortech.2012.06.040

Nanda S, Berruti F (2021a) Municipal solid waste management and landfilling technologies: a review. Environ Chem Lett 19:1433–1456. https://doi.org/10.1007/s10311-020-01100-y

Nanda S, Berruti F (2021b) Thermochemical conversion of plastic waste to fuels: a review. Environ Chem Lett 19:123–148. https://doi.org/10.1007/s10311-020-01094-7

Nanda S, Dalai AK, Berruti F, Kozinski JA (2016) Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials. Waste Biomass Valor 7:201–235. https://doi.org/10.1007/s12649-015-9459-z

Nanda S, Dalai AK, Kozinski JA (2014) Butanol and ethanol production from lignocellulosic feedstock: biomass pretreatment and bioconversion. Energy Sci Eng 2:138–148. https://doi.org/10.1002/ese3.41

Nanda S, Golemi-Kotra D, McDermott JC, Dalai AK, Gökalp I, Kozinski JA (2017) Fermentative production of butanol: Perspectives on synthetic biology. New Biotechnol 37:210–221. https://doi.org/10.1016/j.nbt.2017.02.006

Nanda S, Mohanty P, Pant KK, Naik S, Kozinski JA, Dalai AK (2013) Characterization of North American lignocellulosic biomass and biochars in terms of their candidacy for alternate renewable fuels. Bioenergy Res 6:663–677. https://doi.org/10.1007/s12155-012-9281-4

Nanda S, Rana R, Hunter HN, Fang Z, Dalai AK, Kozinski JA (2019) Hydrothermal catalytic processing of waste cooking oil for hydrogen-rich syngas production. Chem Eng Sci 195:935–945. https://doi.org/10.1016/j.ces.2018.10.039

Nanda S, Reddy SN, Hunter HN, Dalai AK, Kozinski JA (2015) Supercritical water gasification of fructose as a model compound for waste fruits and vegetables. J Supercrit Fluids 104:112–121. https://doi.org/10.1016/j.supflu.2015.05.009

Nanda S, Reddy SN, Vo DVN, Sahoo BN, Kozinski JA (2018) Catalytic gasification of wheat straw in hot compressed (subcritical and supercritical) water for hydrogen production. Energy Sci Eng 6:448–459. https://doi.org/10.1002/ese3.219

Okolie JA, Mukherjee A, Nanda S, Dalai AK, Kozinski JA (2021a) Next-generation biofuels and platform biochemicals from lignocellulosic biomass. Int J Energy Res 45:14145–14169. https://doi.org/10.1002/er.6697

Okolie JA, Nanda S, Dalai AK, Kozinski JA (2021b) Chemistry and specialty industrial applications of lignocellulosic biomass. Waste Biomass Valor 12:2145–2169. https://doi.org/10.1007/s12649-020-01123-0

Okolie JA, Patra BR, Mukherjee A, Nanda S, Dalai AK, Kozinski JA (2021c) Futuristic applications of hydrogen in energy, biorefining, aerospace, pharmaceuticals and metallurgy. Int J Hydrogen Energy 46:8885–8905. https://doi.org/10.1016/j.ijhydene.2021.01.014

Okolie JA, Rana R, Nanda S, Dalai AK, Kozinski JA (2019) Supercritical water gasification of biomass: a state-of-the-art review of process parameters, reaction mechanisms and catalysis. Sustain Energy & Fuels 3:578–598. https://doi.org/10.1039/C8SE00565F

Osorio-González CS, Hegde K, Brar SK, Kermanshahipour A, Avalos-Ramírez A (2019) Data set of green extraction of valuable chemicals from lignocellulosic biomass using microwave method. Data Br 26:104347. https://doi.org/10.1016/j.dib.2019.104347

Parakh PD, Nanda S, Kozinski JA (2020) Eco-friendly transformation of waste biomass to biofuels. Curr Biochem Eng 6:120–134. https://doi.org/10.2174/2212711906999200425235946

Patinvoh RJ, Taherzadeh MJ (2019) Fermentation processes for second-generation biofuels. In: Basile A, Dalena F (eds) Second and third generation of feedstocks. Elsevier, Amsterdam, pp 241–271

Patra BR, Mukherjee A, Nanda S, Dalai AK (2021) Biochar production, activation and adsorptive applications: a review. Environ Chem Lett 19:2237–2259. https://doi.org/10.1007/s10311-020-01165-9

Pattanaik L, Pattnaik F, Saxena DK, Naik SN (2019) Biofuels from agricultural wastes. In: Basile A, Dalena F (eds) second and third generation of feedstocks. Elsevier, Amsterdam, pp 103–142

Pattnaik F, Nanda S, Kumar V, Naik S, Dalai AK (2021) Subcritical water hydrolysis of Phragmites for sugar extraction and catalytic conversion to platform chemicals. Biomass Bioenergy 145:105965. https://doi.org/10.1016/j.biombioe.2021.105965

Peng K, Li X, Liu X, Wang Y (2017) Hydrothermally stable Nb-SBA-15 catalysts applied in carbohydrate conversion to 5-hydroxymethyl furfural. Mol Catal 441:72–80. https://doi.org/10.1016/j.mcat.2017.04.034

Qu H, Liu B, Gao G, Ma Y, Zhou Y, Zhou H, Li L, Li Y, Liu S (2019) Metal-organic framework containing Brønsted acidity and Lewis acidity for efficient conversion glucose to levulinic acid. Process Technol 193:1–6. https://doi.org/10.1016/j.fuproc.2019.04.035

Quereshi, S, Dutta S, Naiya TK (2019) Catalytic conversion of lignocellulosic biomass into fuels and value-added chemicals. In: Nanda S, Sarangi PK, Vo DVN (eds.) Fuel Processing and Energy Utilization, CRC Press, Boca Raton, pp 31–51

Rackemann DW, Doherty WOS (2011) The conversion of lignocellulosics to levulinic acid. Biofuels, Bioprod Bioref 5:198–214. https://doi.org/10.1002/bbb.267

Rambabu N, Panthapulakkal S, Sain M, Dalai AK (2016) Production of nanocellulose fibers from pinecone biomass: evaluation and optimization of chemical and mechanical treatment conditions on mechanical properties of nanocellulose films. Ind Crops Prod 83:746–754. https://doi.org/10.1016/j.indcrop.2015.11.083

Rao BS, Lakshmi DD, Kumari PK, Rajitha P, Lingaiah N (2020) Dehydrative etherification of carbohydrates to 5-ethoxymethylfurfural over SBA-15-supported Sn-modified heteropolysilicate catalysts. Sustain Energy Fuels 4:3428–3437. https://doi.org/10.1039/D0SE00509F

Romero A, Alonso E, Sastre Á, Nieto-Márquez A (2016) Conversion of biomass into sorbitol: Cellulose hydrolysis on MCM-48 and d-Glucose hydrogenation on Ru/MCM-48. Micropor Mesopor Mater 224:1–8. https://doi.org/10.1016/j.micromeso.2015.11.013

Saenluang K, Thivasasith A, Dugkhuntod P, Salakhum S, Namuangruk S, Wattanakit C (2020) In situ synthesis of sn-beta zeolite nanocrystals for glucose to hydroxymethylfurfural (HMF). Catalysts 10:1249. https://doi.org/10.3390/catal10111249

Sahu R, Dhepe PL (2012) A one-pot method for the selective conversion of hemicellulose from crop waste into C5 sugars and furfural by using solid acid catalysts. Chemsuschem 5:751–761. https://doi.org/10.1002/cssc.201100448

Santos RB, Lee JM, Jameel H, Chang JM, Lucia LA (2012) Effects of hardwood structural and chemical characteristics on enzymatic hydrolysis for biofuel production. Bioresour Technol 110:232–238. https://doi.org/10.1016/j.biortech.2012.01.085

Sarangi PK, Nanda S (2020) Biohydrogen production through dark fermentation. Chem Eng Technol 43:601–612. https://doi.org/10.1002/ceat.201900452

Shen Z, Kong L, Zhang W, Gu M, Xia M, Zhou X, Zhang Y (2019) Surface amino-functionalization of Sn-Beta zeolite catalyst for lactic acid production from glucose. RSC Adv 9:18989–18995. https://doi.org/10.1039/C9RA01264H

Shi S, Guan W, Blersch D, Li J (2021) Improving the enzymatic digestibility of alkaline-pretreated lignocellulosic biomass using polyDADMAC. Ind Crops Prod 162:113244. https://doi.org/10.1016/j.indcrop.2021.113244

Shi Y, Wan Y, Zhao D (2011) Ordered mesoporous non-oxide materials. Chem Soc Rev 40:3854–3878. https://doi.org/10.1039/C0CS00186D

Silva BJB, Sousa LV, Sarmento LRA, Alencar SL, Quintela PH, Silva AO (2020) Kinetic study of thermocatalytic degradation of UHMWPE over microporous and hierarchical ZSM-23 zeolite. Appl Catal B Environ 267:118699. https://doi.org/10.1016/j.apcatb.2020.118699

Spiridon I (2020) Extraction of lignin and therapeutic applications of lignin-derived compounds. A Rev Environ Chem Lett 18:771–785. https://doi.org/10.1007/s10311-020-00981-3

Srivastava N, Mishra K, Srivastava M, Srivastava KR, Gupta VK, Ramteke PW, Mishra PK (2019) Role of compositional analysis of lignocellulosic biomass for efficient biofuel production. In: Srivastava N, Srivastava M, Mishra PK, Ramteke PW, Singh RL (eds) New and future developments in microbial biotechnology and bioengineering. Elsevier, Amsterdam, pp 29–43

Srivastava N, Srivastava M, Manikanta A, Singh P, Ramteke PW, Mishra PK (2017) Nanomaterials for biofuel production using lignocellulosic waste. Environ Chem Lett 15:179–184. https://doi.org/10.1007/s10311-017-0622-6

Srivastava RK, Shetti NP, Reddy KR, Aminabhavi TM (2020) Biofuels, biodiesel and biohydrogen production using bioprocesses. A Review Environ Chem Lett 18:1049–1072. https://doi.org/10.1007/s10311-020-00999-7

Suresh A, Alagusundaram A, Kumar PS, Vo DVN, Christopher FC, Balaji B, Viswanathan V, Sankar S (2021) Microwave pyrolysis of coal, biomass and plastic waste: a review. Environ Chem Lett. https://doi.org/10.1007/s10311-021-01245-4

Tang DYY, Yew GY, Koyande AK, Chew JW, Vo DVN, Show PL (2020) Green technology for the industrial production of biofuels and bioproducts from microalgae: a review. Environ Chem Lett 18:1967–1985. https://doi.org/10.1007/s10311-020-01052-3

Tan-Soetedjo JNM, van de Bovenkamp HH, Abdilla RM, Rasrendra CB, van Ginkel J, Heeres HJ (2017) Experimental and kinetic modeling studies on the conversion of sucrose to levulinic acid and 5-hydroxymethylfurfural using sulfuric acid in water. Ind Eng Chem Res 56:13228–13239. https://doi.org/10.1021/acs.iecr.7b01611

TBinsights (2020) Global Ferulic Acid Market 2020 (Includes Business Impact of COVID-19), https://www.trustedbusinessinsights.com/details/ferulic-acid-market-2020. Accessed 24 Apr 2021

Tekin K, Karagöz S, Bektaş S (2014) A review of hydrothermal biomass processing. Renew Sustain Energy Rev 40:673–687. https://doi.org/10.1016/j.rser.2014.07.216

Tirpanalan Ö, Reisinger M, Smerilli M, Huber F, Neureiter M, Kneifel W, Novalin S (2015) Wheat bran biorefinery–an insight into the process chain for the production of lactic acid. Bioresour Technol 180:242–249. https://doi.org/10.1016/j.biortech.2015.01.021

Van Tran T, Nguyen DT, Nguyen HT, Nanda S, Vo DV, Do ST, Van Nguyen T, Thi TA, Bach LG, Nguyen TD (2019) Application of Fe-based metal-organic framework and its pyrolysis products for sulfonamide treatment. Environ Sci Pollut Res 26:28106–28126. https://doi.org/10.1007/s11356-019-06011-2

Velaga B, Parde RP, Soni J, Peela NR (2019) Synthesized hierarchical mordenite zeolites for the biomass conversion to levulinic acid and the mechanistic insights into humins formation. Micropor Mesopor Mater 287:18–28. https://doi.org/10.1016/j.micromeso.2019.05.049

Wanmolee W, Daorattanachai P, Laosiripojana N (2016) Depolymerization of organosolv lignin to valuable chemicals over homogeneous and heterogeneous acid catalysts. Energy Proc 100:173–177. https://doi.org/10.1016/j.egypro.2016.10.161

Wu Y, Ge S, Xia C, Mei C, Kim KH, Cai L, Smith LM, Lee J, Shi SQ (2021) Application of intermittent ball milling to enzymatic hydrolysis for efficient conversion of lignocellulosic biomass into glucose. Renew Sustain Energy Rev 136:110442. https://doi.org/10.1016/j.rser.2020.110442

Xiong H, Pham HN, Datye AK (2014) Hydrothermally stable heterogeneous catalysts for conversion of biorenewables. Green Chem 16:4627–4643. https://doi.org/10.1039/C4GC01152J

Yabushita M, Li P, Islamoglu T, Kobayashi H, Fukuoka A, Farha OK, Katz A (2017) Selective metal–organic framework catalysis of glucose to 5-hydroxymethylfurfural using phosphate-modified NU-1000. Ind Eng Chem Res 56:7141–7148. https://doi.org/10.1021/acs.iecr.7b01164

Zada B, Yan L, Fu Y (2018) Effective conversion of cellobiose and glucose to sorbitol using non-noble bimetallic NiCo/HZSM-5 catalyst. Sci China Chem 61:1167–1174. https://doi.org/10.1007/s11426-018-9321-0

Zeng Y, Zhao S, Yang S, Ding SY (2014) Lignin plays a negative role in the biochemical process for producing lignocellulosic biofuels. Curr Opin Biotechnol 27:38–45. https://doi.org/10.1016/j.copbio.2013.09.008

Zhang H, Han L, Dong H (2021) An insight to pre-treatment, enzyme adsorption and enzymatic hydrolysis of lignocellulosic biomass: Experimental and modelling studies. Renew Sustain Energy Rev 140:110758. https://doi.org/10.1016/j.rser.2021.110758

Zhang J, Zhuang J, Lin L, Liu S, Zhang Z (2012) Conversion of D-xylose into furfural with mesoporous molecular sieve MCM-41 as catalyst and butanol as the extraction phase. Biomass Bioenergy 39:73–77. https://doi.org/10.1016/j.biombioe.2010.07.028

Zhang S, Yang X, Zhang H, Chu C, Zheng K, Ju M, Liu L (2019) Liquefaction of biomass and upgrading of bio-oil: a review. Molecules 24:2250. https://doi.org/10.3390/molecules24122250

Zhang T, Kumar R, Tsai YD, Elander RT, Wyman CE (2015) Xylose yields and relationship to combined severity for dilute acid post hydrolysis of xylooligomers from hydrothermal pretreatment of corn stover. Green Chem 17:394–403. https://doi.org/10.1039/C4GC01283F

Zhao Y, Lu K, Xu H, Zhu L, Wang S (2021) A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion. Renew Sustain Energy Rev 139:110706. https://doi.org/10.1016/j.rser.2021.110706

Zhou S, Yang X, Zhang Y, Jiang L, Zhou L, Lu T, Su Y (2019) Efficient conversion of cellulose to methyl levulinate over heteropoly acid promoted by Sn-Beta zeolite. Cellulose 26:9135–9147. https://doi.org/10.1007/s10570-019-02743-z