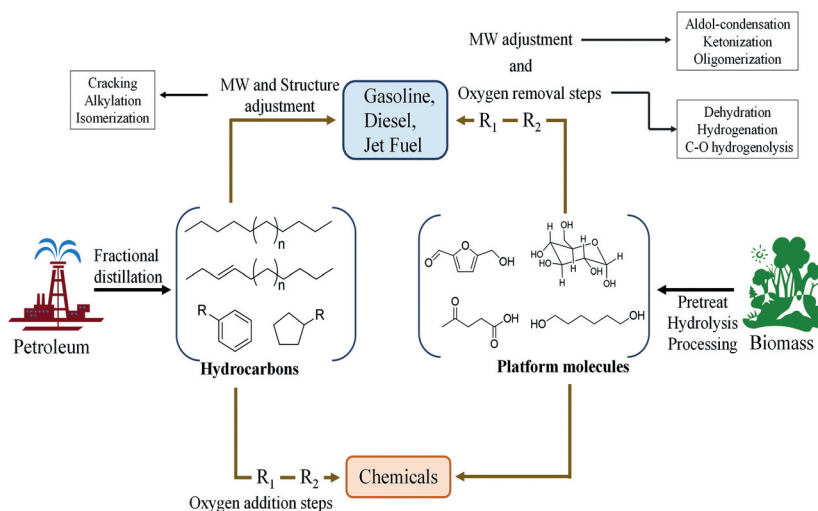


Heterogeneous Catalysis for Sustainable Energy

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Abstract The dominance of fossil fuels in the energy sector is associated with greenhouse-gas emission and release of atmospheric pollutants. Biomass-based energy generation is considered a potential alternative for replacement of fossil fuels, and it has been used as a sustainable source of heat and power for a long time. Biomass as a feedstock can be used for the synthesis of different energy products. Catalysts play a significant role in various conversion routes and affect the yield of major products. Researchers have mainly focused on starchy feedstock, lignocellulosic biomass, and triglyceride containing biomass for bioenergy production. Catalytic reactions for biomass feedstock mainly involve deoxygenation, hydrolysis, hydrogenation, dehydrogenation, and oxidation etc. This review provides an overview of catalytic reactions for the conversion of different classes of biomass feedstock for biofuel production. The primary aim of this review is to summarize catalytic strategies for conversion of lignocellulosic biomass into value-added products.

Keywords biomass, heterogeneous catalysis, catalytic conversion, sustainable energy

1 Introduction

The use of biomass as an alternate energy source has gained much attention in the past decade owing to its efficient production of a range of petrochemical products.^{1,2} Among various renewable energy sources, biomass has the

potential to produce carbon-containing products as the carbon-content in biomass resources is quite high.^{3,4} In this era where population is continuously rising and to satisfy their basic needs, the requirement for transportation fuels is continuously increasing. Currently, petroleum products that are obtained from fossil fuels are the primary source for transportation fuel. The disadvantage of using fossil fuel as a resource is the imbalance between its production and consumption; the consumption rate is much higher than its production rate. Thus, there is a strong demand to find other sources of transportation fuel that are based on renewable energy sources.^{5,6}

For the production of fuel from renewable feedstock such as biomass, the focus has been on three major components of biomass: (1) Starchy feedstock, which includes glucose, fructose, and other sugars, (2) lignocellulosic biomass, which includes cellulose, hemicelluloses, and lignin part, and (3) triglycerides, including fatty acids of hydrocarbon chains ranging from C4 to C24.

Starchy feedstocks are dominated by the long complex chain of sugar molecules found in wheat, corn, sugarcane, sweet potatoes etc. However, these are edible substances, which are not suitable to use for conversion.⁷ There is another branch of starchy feedstock that is non-edible and is comprised of inedible nuts (e.g., horse chestnut and buckeye) that can be utilized to produce ethanol; although edible starch can be used for bio-ethanol production, the use of edible starch for ethanol production is not sustainable in light of the current global food crisis. On the other hand, triglyceride feedstock was the first to be used as fuel in a diesel engine in 1920 (soyabean oil) due to its chemical and physical properties.⁸ However, triglycerides cannot be used

directly with modern diesel engines owing to their high density and viscosity;^{9,10} therefore, we need to explore alternative chemical structures of triglycerides, and different approaches to this have been reported. Two basic approaches that have been used by various researchers so far are *trans* esterification and hydrotreatment.¹¹

The third biomass resource, which is most abundant, is lignocellulosic biomass.¹² The lignocellulosic biomass is comprised of three main components: cellulose, hemicelluloses, and lignin, among which cellulose contributes 30–50%, hemicelluloses 20–30%, and lignin 10–20%.^{13–16} From the above data we can see that the major component of lignocellulosic biomass is cellulose, and great efforts have been made to convert cellulose into value added chemical in last two decades.

To utilize this biomass resource as fuel precursors, the first step is to depolymerize the highly crystallized polymer structure of lignocellulosic biomass to different fractions by application of pretreatment methodologies. The pretreatment includes physical, chemical, biological, and physiochemical processes such as ball milling, comminuting, steam distillation, or acid/base hydrolysis. The pretreatment step is important as it simplifies the highly complex chemical structure, which facilitates their further chemical transformations; although it costs approximately 20% of the cost of total conversion, it is economical do so.^{17–19} In this review we discuss the recent pretreatment pathways, chemical conversions via catalytic routes and subsequent biological transformations. Biomass has long been used as an energy source for cooking food and to provide heat in rural areas.¹⁸ Furthermore, the bio-oil or alcohols obtained from biomass have been identified as suitable transportation fuel since the beginning of the era of the combustion engine (first-generation biofuel).²⁰ However, these green fuels have not gained much attention as these were costlier than available petrol and diesel. Moreover, the first-genera-

tion biofuels were dependent on food resources (crops, sugars, starch oil etc). The present scenario, considering population growth and their continuous demand for food and fuel, has forced us to rethink the utilization of biomass resources for production of second-generation biofuels; i.e., utilizing non-edible feedstock. First-generation biofuels or bioethanol is the most abundantly produced alcohol, and numerous research studies are available in this field. Today the challenge is to render the process of producing bioethanol cost-effective and more efficient. The USA alone produced 341 billion liters of biofuel every year from biomass.²¹ The most abundant source of bioethanol is sugarcane and corn (food crops) and represents a good fuel precursor as it can be used directly along with gasoline in modern engines without much modification.

Lignocellulosic biomass, which is composed of lignin, hemicelluloses, and cellulose components, is a potential biomass resource for commodity chemicals. Lignocellulosic biomass provides structure rigidity to cell walls. Cellulose and hemicelluloses form the basic structure of the cell wall, and lignin provides rigidity by incorporation as a connector. Lignin is composed of aromatic building blocks such as polyphenols and polypropanoids,²² and it is the only source that has the potential to provide intermediates for various polymer, plastic, drug, and paint industries. Lignin can serve as a good raw material for polyphenolic resins due to the high content of aromatic components.^{23,24} Lignin can also be used as a simple source of heat and electricity by burning.²⁵ Without breaking the wall of lignin, accessing carbohydrates is very difficult.²⁶ Hemicelluloses are basically composed of five sugars: xylose, arabinose, glucose, galactose, and mannose, among which xylose is found in abundance. Hemicelluloses from lignocelluloses biomass has the greatest potential to be utilized as fuel precursors. Thus, extraction of hemicellulose from biomass resources is of great interest.

Biographical Sketches



Dr. Jaya Tuteja has been working as Assistant Professor, School of Sciences, Manav Rachna University since January 2018. She earned her PhD in Materials Science from Japan Advanced Institute of Science and Technology (JAIST), Japan in 2015, and was awarded 'Excellent Doctorate Student' by JAIST. She was also selected for the dual graduate school program between Delhi University, India and JAIST, Japan. She studied as a visiting

masters-course student in JAIST for one year from January 2011 to December 2011 and earned an M.S. in Material science from JAIST and M. Tech Chemical Synthesis and Process Technology from Delhi University in 2012. She has published seven research papers in reputed international journals with a sum of impact factor of >40. She also has two patents filed on her name from her PhD research work. She has been the editor of

three books and has eight book chapters in her account. Her research area includes development, characterization, and application of heterogeneous catalysts for effective conversion of biomass into value-added products, nanoparticles synthesis, and nanoparticle-based heterogeneous catalysts, bimetallic nanoparticles, carbohydrate chemistry, analytical techniques for compound identification.

2 Role of Catalyst in Pretreatment of Lignocellulosic Biomass

Catalysts can play a critical role in the pretreatment of lignocellulosic biomass, which is an essential step in the conversion of biomass into biofuels and other valuable products. Pretreatment is typically necessary to break down the complex structure of lignocellulosic biomass and make it more accessible to subsequent conversion processes such as enzymatic hydrolysis or fermentation. Catalysts can facilitate pretreatment by promoting chemical reactions that break down the lignocellulosic structure, making the biomass more amenable to further processing. For example, catalysts can help to hydrolyze hemicellulose and cellulose into simple sugars that can be more easily fermented to produce biofuels. Catalysts can also promote lignin depolymerization, which can make the biomass more reactive and easier to digest by enzymes.

Moreover, catalysts can enhance the efficiency of pretreatment by reducing the required reaction time and temperature, thus lowering energy consumption and operational costs. In some cases, catalysts can even improve the selectivity of the reaction, leading to the production of higher-quality products. However, the selection of an appropriate catalyst for lignocellulosic biomass pretreatment depends on various factors, including the type of biomass, the specific pretreatment method, and the desired end-product. In addition, catalysts may have drawbacks such as high cost or potential toxicity, which must be considered before their implementation in the pretreatment process.

3 Role of Catalyst in Conversion of Biomass into Bioenergy

With respect to the environment and disposal of chemicals in the atmosphere and via drainage systems, the use of heterogeneous catalytic systems serves as the optimum solution for transformation of raw materials obtained from biomass into value added products of petrochemical industry (Figure 1). However, although catalysts for petrochemical conversions are well developed (such as isomerization, hydrogenation, reforming, Fischer–Tropsch etc.) and studied thoroughly, the same catalyst cannot be applied for biomass conversion (hydrolysis, deoxygenation, depolymerization etc.) because fossil fuel feedstock and biomass feedstock differ greatly in their chemical structure. Whereas fossil fuel resources are rich in hydrocarbons, the biorenewable feedstocks are rich in oxygen. This is why catalysts already developed by petrochemical industries cannot be applied to conversion of biomass material. This creates a strong incentive to develop new catalytic systems for efficient conversion of biomass feedstock into commodity chemicals. Developing complete heterogeneous catalyst system offer new challenges as the existing market possess

only heterogeneous and enzymatic catalytic system, which involves significant disadvantages in terms of cost and separation.



Figure 1 Catalytic conversion of biomass feedstocks into fuel and chemicals

It has been observed that the compounds obtained from biomass have high boiling-point or low volatility at normal reaction temperatures. This imposes the necessity to work with condensed-phase systems as compared to gas-phase systems that are currently used for processing hydrocarbons. The condensed-phase system where liquid–solid phases are employed comes with the advantage of allowing the use of new catalytic materials with high stability and high transport properties to be explored. In general, the approach is to develop value-added commodity chemicals from biomass instead of forming hydrocarbons as the latter requires quite lengthy efforts and long processes for deoxygenation. Compounds containing oxygen such as acetic acid, bioethanol, glycerol, and glyceric acid can be easily produced via selective catalytic transformations. Ironically, these compounds can be prepared more efficiently from biomass than fossil fuels.

A platform molecule is a very interesting term being used for a group of chemicals or molecules that are produced from biomass and that possess versatile functionality. These platform molecules or building blocks represent a range of chemicals that can be further transformed into various value-added products. Examples of platform molecules are carbohydrates,²⁷ cellulose,^{28,29} furfural,^{30,31} glycerol,^{32–34} and hemicelluloses.^{35,36} To convert these platform molecules into commodity chemicals, various catalytic conversions have been designed, including hydrogenation reaction,³⁷ dehydrogenation reaction,³⁸ oxidation reaction,³⁹ dehydroxylation reaction,^{40,41} and acid-base catalyzed reactions for dehydration.^{42,43} Based on the desired product, the catalyst, catalytic reaction, and feedstock can be selected.

3.1 Hydrolysis

Inedible biomass sources that are not in competition with food crops, are considered best for the transformation. In this respect lignocellulosic biomass represents an attractive and ideal raw material resource to produce value-added chemicals. The first step in the transformation of these lignocellulosic biomass materials is hydrolysis, which can be achieved by catalysis using homogeneous or heteroge-

neous catalysts, based on the nature of the lignocellulosic biomass or polysaccharides. Although it is considered that acid hydrolysis is better than base catalytic hydrolysis owing to fewer side reactions, acid catalysis can break down the glycosidic bond to form sugar units from cellulose and hemicellulose. Figure 2 shows the general hydrolysis of lignocellulosic biomass. Among homogeneous catalysis systems, numerous dilute and concentrated acids can be used, for instance H_2SO_4 and HCl ; but these homogeneous acids come with the disadvantage of corrosion of the reaction vessel and disposal of acids, and the homogeneous catalyst is difficult to recover.^{44,45}

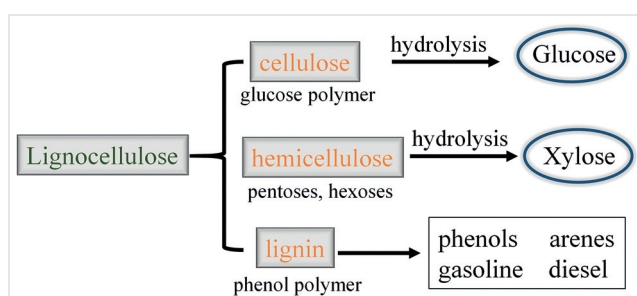


Figure 2 Hydrolysis reaction of lignocellulosic biomass

Considering the advantages of acid in breaking down the glycosidic linkage and the disadvantages it poses to the environment and to the reactor, researchers have developed heterogeneous catalysts that can overcome the disadvantages of liquid acids while maintaining similar or better performance, and multiple reports have been published in this area.^{46–49}

A variety of heterogeneous acid catalysts have been reported by researchers for biomass conversion, among which the zeolites have gained much attention. Numerous zeolites, such as H-Zeolites, ZSM-5, HY, HPA, and iron oxide-SBA, have been examined.^{50–52} After zeolites, transition-metal oxides including Nb_2O_5 , WO_3 , Ta_2O_5 - WO_3 , Nb-W oxide have been considered as valuable solid acid catalyst candidates. It has been known for centuries that metal oxides contain both Lewis and Brønsted acid sites; these acidic sites are actually major contributors to the high catalytic efficiency of metal oxides and mixed metal oxides in hydrolysis reactions.^{53,54} The high catalytic-surface and large pore-volumes allow the reactants to interact with active sites in the pores.

Supported catalysts are prepared by imparting acidic functionality on solid surfaces of zeolites or carbon highly active solid surfaces. These catalysts exhibit anchoring properties for depolymerization of lignocellulosic biomass to produce cellulose, hemicellulose and further to produce glucose and Xylan etc., and the same catalyst can be reused in a number of cycles.^{55,56} Under the umbrella of supported

catalysts, metal oxide supported catalysts are also used due to their high mechanical and thermal stability. $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ and $\text{SO}_4^{2-}/\text{ZrO}_2$ provide many more acidic sites than any H^+ from HCl or H_2SO_4 homogeneous catalysts.⁵⁷

In today's era of commercial catalyst ion exchange resins, if we consider the commercially available, more benign solid acid metal supported catalysts, metal oxides supported catalysts, heteropoly acids, nanoparticle-based catalysts and ion-exchange resins such as Amberlyst-25, Nafion NR-50, superior catalytic properties and better thermal stability have been reported by various researchers. On a similar note, hemicellulose can be hydrolyzed to the sugar unit xylose via treatment with solid acid catalysis at moderate temperature. These obtained sugar units are further transformed into valuable chemicals by different routes.

3.2 Dehydration

Dehydration is a reaction in which one or more water molecules are removed from the parent organic compound to carry out the desired transformations. It represents a very important reaction as C-5 sugars, on dehydration, produces furfural, and C-6 sugars produce 5-hydroxymethyl furfural (HMF). The furans can be further transformed and used as liquid fuel additives to improve fuel efficiency, for instance by aqueous-phase hydrogenation and aldol condensation reactions as shown in Figure 3. Other applications include the production of industrial solvents via reduction of furan rings to tetrahydrofuran and tetrahydrofurfuryl alcohol, and oxidation of HMF to 2,5-furandicarboxylic acid (FDCA).

It may be thought that furan synthesis is quite simple as only dehydration of C-6 or C-5 sugars is required; but this is not entirely true. The synthesis of furans is, in fact, rather complex. For instance in the conversion of C-6 sugars into HMF, the HMF forms and is readily consumed either through decomposition into levulinic acid under same reaction conditions or through polymerization to form humins, which results in decreased overall yield of HMF. Under the acid-catalyzed dehydration of sugar units, simultaneous isomerization followed by dehydration, fragmentation and condensation can occur. Van Dam⁵⁸ and Cottier⁵⁹ reported that a mixture of 37 products are formed from decomposition of sugars in organic and aqueous solvents. It has been also found that polymerization to humins can occur in aqueous or organic solvents, whereas degradation only occurs in aqueous medium. To conclude the above findings, it should be mentioned that furan synthesis is more efficiently conducted from the ketose form of sugars than the aldose form; thus, an efficient way of synthesizing the desired products is to isomerize the aldoses to ketoses and immediately dehydrate these to the furan ring before other transformations can occur.

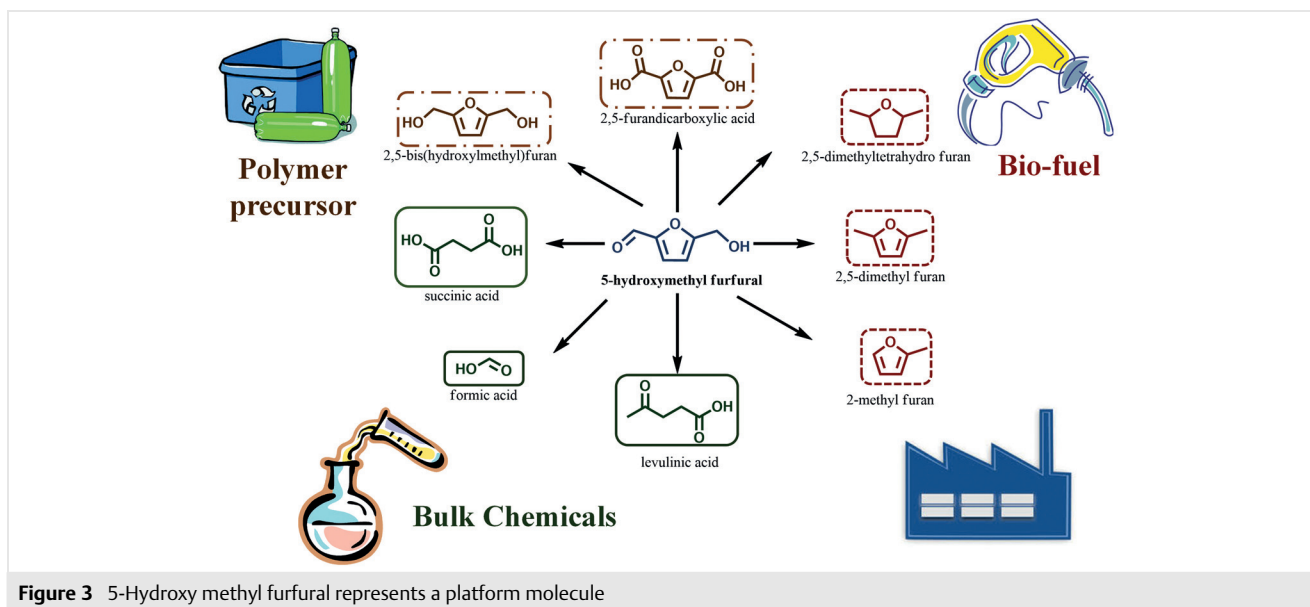


Figure 3 5-Hydroxy methyl furfural represents a platform molecule

Glucose, being cheap and easy availability, is of keen interest to industry for producing furan molecules, but the problem is that it is an aldose unit and thus requires base catalyst for its isomerization to ketose form. This is followed by acid-catalyzed dehydration to form furan rings. A direct one-step transformation of glucose into furan ring is difficult to achieve, but a one-pot synthesis of furans from carbohydrates can be accomplished using solid acid and base catalysts together. The transformation can be achieved in a variety of aqueous, non-aqueous, and biphasic solvents,^{60,61} and ionic liquids,^{62–64} over a range of catalysts including mineral acids, oxalic acid, solid acids, zeolites, and ion-exchange catalysts.

3.3 Hydrogenolysis

Hydrogenolysis involves the cleavage of C–C and C–O bond together when reacted in the presence of hydrogen. The reaction generally requires high temperature conditions (400–500 K), high pressure of hydrogen gas (13–400 bar), basic solution, and a metal-based heterogeneous catalytic system.^{65–68} Despite the harsh reaction conditions and risks associated with using high-pressure gas, this reaction is important. The reaction is crucial for targeting fossil-fuel-based compounds from biomass resources as it helps to remove oxygen. The major barrier of using lignocellulosic biomass as fuel precursor is its highly oxygenated nature; however, if a few oxygen atoms are removed we can use them as fuel precursors or in polymer synthesis. In Figure 4, various hydrogenolysis reactions are shown that have

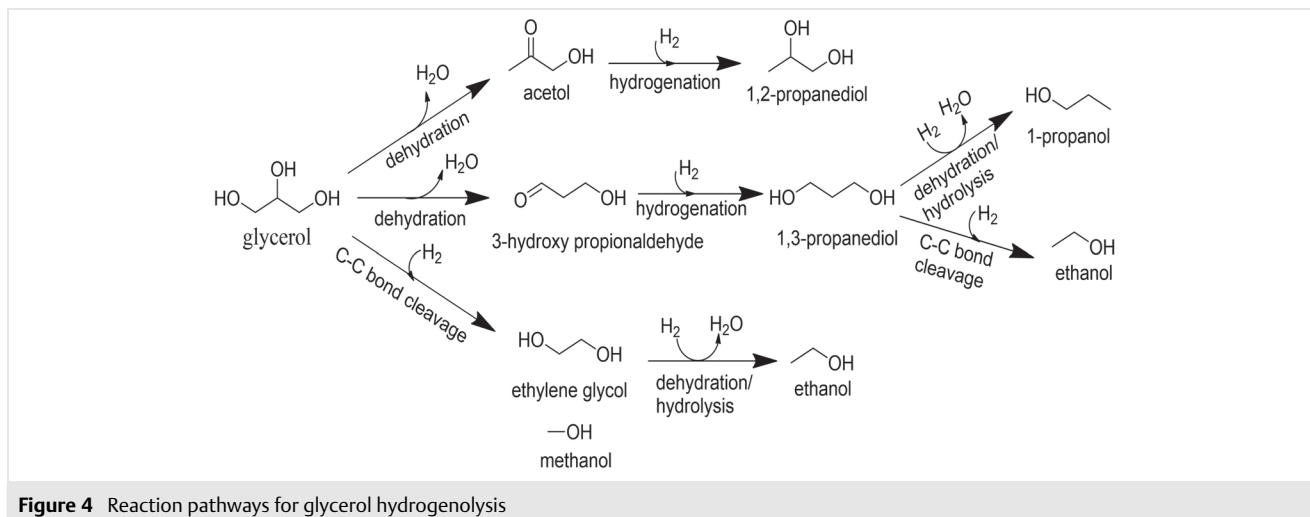


Figure 4 Reaction pathways for glycerol hydrogenolysis

gained considerable attention. The beauty of the reaction is that the product can be altered by changing catalyst or reaction conditions from the same reactant. Highly oxygenated glycerol can be converted into acetol, 1,3-propanediol, 1-propanol, or ethanol. Additionally the hydrogenolysis of glycerol is of utmost importance in generating diol or polyol from furan compounds.^{65,66}

3.4 Hydrogenation

As we have just seen, hydrogenolysis occurs in the presence of hydrogen gas. On a similar note, hydrogenation, as the name suggests, requires hydrogen gas. The basic purpose of using hydrogenation reaction in organic chemistry is to saturate olefinic compounds. In transforming biomass, the role of hydrogenation reaction is to saturate the C=O, C=C, and C–O–C bonds. Like the hydrogenolysis reaction, hydrogenation also occurs in the presence of high-pressure hydrogen gas and metal-based heterogeneous catalyst, but basic conditions are not required, and the temperature requirement is also more moderate (370–420 K). Figure 5 summarizes the hydrogenation of furan-based compounds such as furfural to tetrahydrofuran and tetrahydromethylfuran. These tetrahydrofuran compounds have been found to be suitable for the production of diesel fuel by undergoing aldol condensation reaction. Based on different reaction parameters and choice of catalysts, the furfural can be converted into furfuryl alcohol,⁶⁹ 2,5-dimethylfuran,^{70,71} and 2,5-bis-hydroxymethyl furan.^{72–73}

The latest research in this area is aimed at developing methods to selectively convert furfural into furfuryl alcohol. The research published to date have used copper chromite catalyst, which is not so eco-friendly. Thus, there remains a challenge to find a catalyst that is environmentally friendly and can be used to selectively hydrogenate C=O while preserving C=C bonds. Selective hydrogenation is the key to success in this method, which is affected by the choice of solvent, catalyst, pressure of hydrogen gas, and temperature.

3.5 Selective Oxidation

After selective hydrogenations, selective oxidation is also a very important reaction; these reactions require well-optimized parameters to produce the target compound with specific functionality while retaining the other groups. For example, in the selective oxidation of 1,6-hexanediol to 6-hydroxycaproic acid, both the –OH are terminal and susceptible to oxidations, yet only one is oxidized and other remains as –OH. In this type of selective reaction the challenge is to control the position that undergoes oxidation without using protection and deprotection. Figure 6 depicts a few examples of selective oxidation products produced from biomass conversion such as 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran, and gluconic acid.

The oxidation in general requires oxidizing agents such as H₂O₂ or high-pressure oxygen gas in the presence of metal-based heterogeneous catalyst or metal oxides, metal hydroxides etc. Metal derivatives such as V₂O₅, K₂Cr₂O₇, or KMnO₄ using aqueous or organic solvents in the presence or absence of oxygen gas pressure are also used. Again, the type of catalyst used, the polarity of the solvent, pH, pressure, and temperature, play major roles in the selective transformation.

For instance, when the reaction is carried out in basic solvent and low temperature, the oxidation of 5-hydroxymethyl furfural leads to the formation of FDCA as the major product;^{73,74} however, when the same reaction is conducted at neutral pH and high temperature with same catalyst it results in the formation of 2,5-diformylfuran as the major product over FDCA.⁷⁵ Another example is of oxidation of glycerol, which can result in the formation of dihydroxyacetone and glyceric acid. Here, the acidic conditions favor the oxidation of the secondary alcohol group over the primary alcohol group, leading to dihydroxyacetone (DHA) as the major product.^{76,77} In contrast, basic conditions results in primary alcohol oxidation, leading to glyceric acid as the major product.^{75–77} These days, the interest of researchers has shifted to the use of bimetallic catalysts

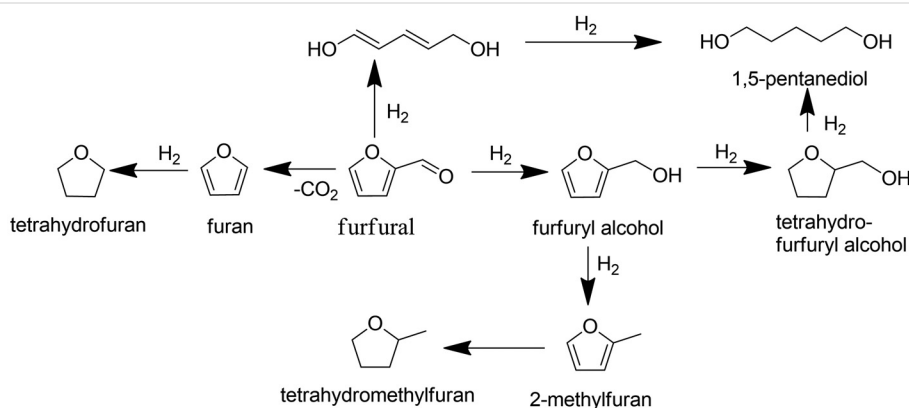


Figure 5 Hydrogenation of furfural

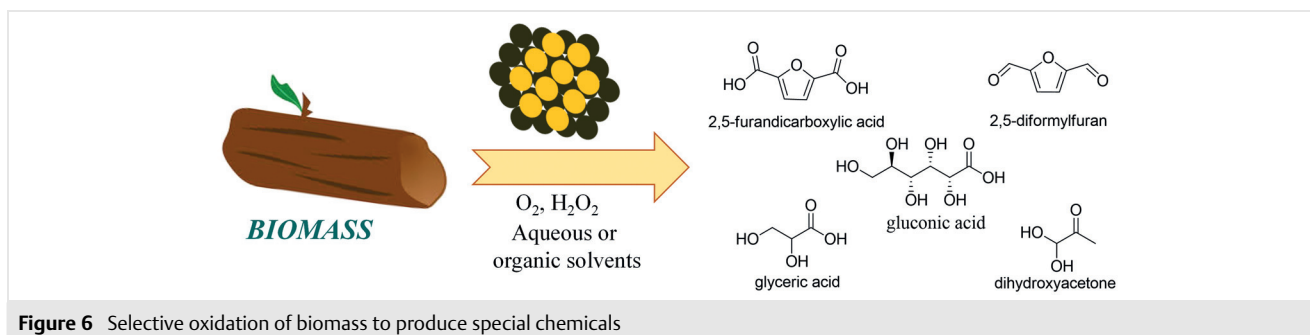


Figure 6 Selective oxidation of biomass to produce special chemicals

over mono-metallic catalysts because they can have the advantage of more selectivity, higher efficiency, and require less catalyst. For oxidation reactions, Au-Pd and Au-Pt bimetallic catalysts have been seen to be high value as compared to Au, Pd, Pt monometallic catalysts.⁷⁸ It has been considered that a synergistic effect of the bimetal is the key to achieving high selectivity and high efficiency. Other factors that play significant role in bimetallic based oxidation reactions are particle size and influence of capping agents.⁷⁹

4 Role of Catalyst in Thermochemical Conversion

There are two main approaches to the thermochemical conversion of biomass: gasification and pyrolysis. Gasification gives synthesis gas (syngas; CO/H_2), whereas the final product of pyrolysis is bio-oil, which maybe further treated to give fuel and value-added commodities. The thermochemical approach to biomass conversion offers significant advantages for the complete conversion of biomass including lignin, but at the cost of high energy input to provide high temperature. On the other side, the pyrolysis route produces products similar to the products obtained from hydrolysis.^{80,81}

Catalysts play an important role in the thermochemical conversion of lignocellulosic biomass, which refers to the process of converting biomass into biofuels or other useful chemicals through high-temperature and high-pressure reactions. In the pyrolysis process, which involves heating biomass in the absence of oxygen to produce bio-oil, gas, and char, catalysts can improve the yield and quality of bio-oil. Catalysts can promote the cracking of biomass molecules and reduce the formation of char, which can improve the yield of bio-oil. Additionally, catalysts can improve the stability of bio-oil by reducing the amount of oxygenated compounds, which tend to degrade over time.

In the gasification process, which involves heating biomass in the presence of a gasifying agent to produce syngas, which can be used to produce biofuels or other chemicals, catalysts can improve the efficiency of the process by promoting the conversion of tar and other impurities in the syngas into useful products. Overall, the use of catalysts in the thermochemical conversion of lignocellulosic biomass can lead to higher yields, improved product quality, and increased process efficiency. However, the selection and design of appropriate catalysts requires careful consideration of the specific reaction conditions and the properties of the biomass feedstock.

5 Conclusion

From above discussion it can be concluded that biomass can be utilized to meet our energy demands in the future, contingent on a suitable catalyst for the desired conversions being developed. The design and synthesis of catalysts are key factors that regulate the transformation of lignocellulosic biomass. To use lignocellulosic biomass, we need to start from the deconstruction of biomass, which leads to the generation of furfural, glycerol, levulinic acid, 5-hydroxymethyl furfural, and 1,6-hexanedion, which are collectively called platform molecules (Figure 7). These platform molecules are known as chemical building blocks and they possess numerous structural functionalities. These functionalities can be further transformed into various value-added or commercially valuable precursors by chemical or biochemical pathways.

The first approach or first thing we should think of before using these biomass resources as fuel precursors is to remove the oxygen. If we examine the differences in chemical structure of existing fuel precursors and biomass-based platform molecules, we observe that the existing fuel precursors consist of hydrocarbon units, while biomass-based platform molecules are generally highly oxygenated species. Thus, the priority is to reduce the number of oxygen atoms without reducing the carbon content (Figure 7).

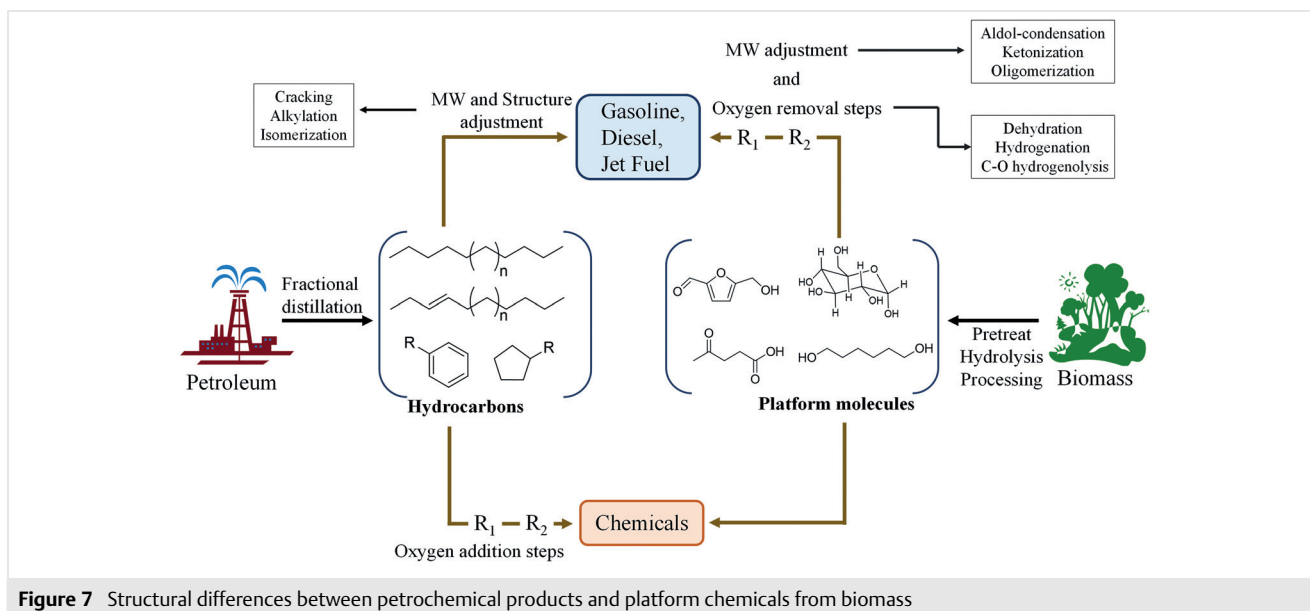


Figure 7 Structural differences between petrochemical products and platform chemicals from biomass

Another significant difference between existing fuel chemical compounds and biomass-based components is their nature: hydrocarbons are hydrophobic in nature while biomass-based precursors are generally hydrophilic. This leads to a strong drive to develop new catalytic pathways for converting biomass-based precursors because existing catalytic pathways have been developed for less oxygenated species and hydrophobic compounds. While previous catalytic methodologies were focused on fractional distillation and cracking of hydrocarbons, new catalytic pathways for developing platform molecules as fuel-based precursors are more focused on the aqueous phase, with multipurpose catalysts for removal of oxygen than can be used to conduct reactions at moderate temperature reaction conditions, considering green chemistry principles. This review has presented an overview of the development of environmentally friendly and sustainable reaction routes to access value-added commercial commodities from biomass resources.

Conflict of Interest

The authors declare no conflict of interest.

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