



A review on the heterogeneous catalyst for effective conversion of lignocellulosic biomass

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ABSTRACT

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This study examines a review of the heterogeneous catalyst for effective conversion of lignocellulosic biomass. In light of the challenges posed by a growing global population and the depletion of natural resources, there is an urgent need for alternative solutions. One such solution is the conversion of biomass into fuel, which has the potential to be a cost-effective and widely available substitute for fossil fuels. Solid catalysis and a range of chemical conversions effectively convert biomass into value-added chemicals. A critical factor in this process is the development of a highly efficient and selective catalysis system, along with the necessary chemical reactions. This review provides a comprehensive discussion of the various sources of biomass and their essential chemical composition. It also covers the conversion of biomass into a value-added chemical and the indispensable role of catalysis in the conversion process. Additionally, the review explores various conversion techniques for transforming biomass into useful forms of energy, and highlights their potential applications. By providing a detailed analysis of this process, this review aims to contribute constructively to the ongoing search for sustainable and effective solutions to energy challenges.

Contribution/Originality: The review here highlights the importance of using biomass as a renewable energy source for fulfilling the energy demand of future generations as compared to others owing to the C content present in them. The major concern in utilizing them is the complex structure of biomass, for which various strategies have been offered in this review via use of heterogeneous catalysts.

1. INTRODUCTION

Fossil fuels are the major energy source that meets the energy demands worldwide. It's impossible to think about the life without these fossil fuel resources. The urbanization has led to an increase in consumption of these fossil fuel resources on a much larger scale than their production, which makes it difficult to sustain or rely on the natural fossil fuel resources. This creates a pressing need to explore the alternative, sustainable, and renewable energy sources to meet our energy needs. Though there are various growing renewable energy sources that are being employed and are under research, such as electric, hydroelectric, wind, and solar energy. But the uses of these resources are limited and cannot be employed to generate value-added chemicals as they lack C content in them. Thus, to meet the criteria, we need to look for the alternatives that are carbon-rich and can be converted to fine chemicals.

1.1. Biomass

One such great source of C from renewable energy sources is biomass. The governments of various countries have motivated the companies to work in this area to shift from the fossil fuel resources to the ones that can be generated by biomass resources (Energy, 2018; Longley, 2020). Being the only C source available in nature that can be converted to produce various chemical compounds of our need has gained tremendous attention of researchers in past decades (Ragauskas et al., 2006). The only barrier to utilizing them as precursors for fuel compounds is their effective transformation, as they possess high oxygen content are quite complex in nature. Thus effective catalytic routes are required to convert the complex oxygenated species to petrochemical products (De, Burange, & Luque, 2022; Luque, 2014; Tuteja, 2023; Tuteja, Nishimura, & Ebitani, 2012). The same approach that is applied to convert fossil fuel resources to petrochemical products can't be applied to process the biomass resources to produce value-added commodities, as they both differ in their starting materials. In processing fossil fuel precursor cracking, isomerization and alkylation are major footsteps; for converting biomass, deoxygenation, hydrolysis, and hydrogenolysis are the important reactions to start with.⁶ (Figure 1).

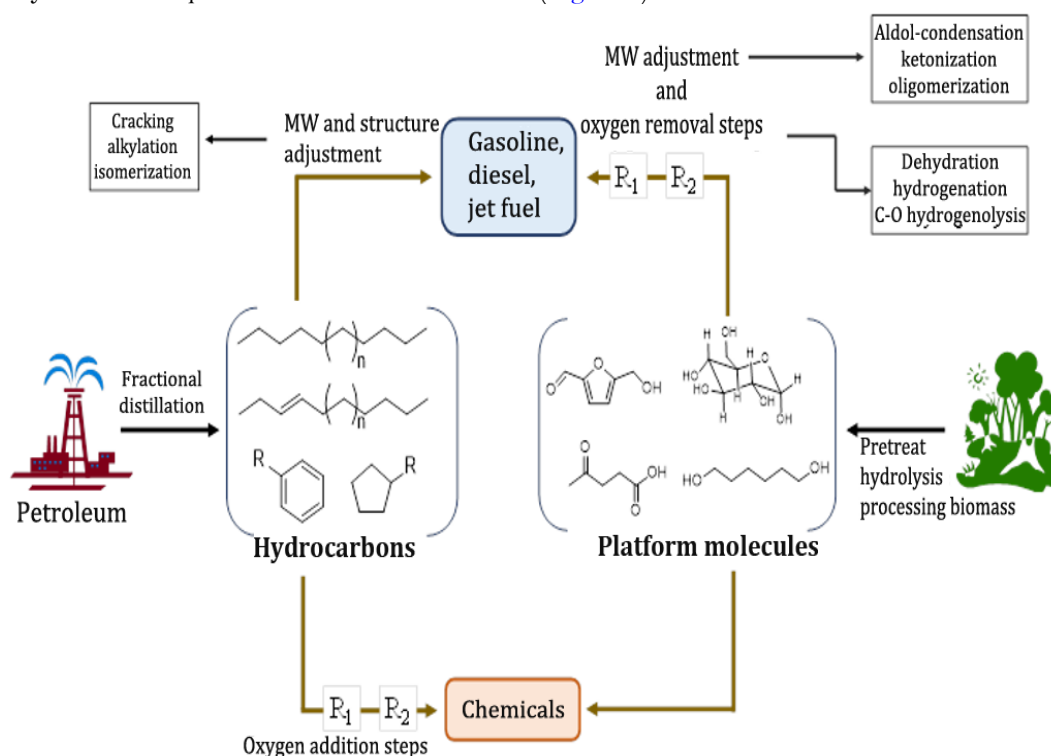


Figure 1. Important Reactions to process value added products from fossil fuel resources and biomass resources.

1.2. Chemical Composition of Lignocellulosic Biomass

The major components of lignocellulosic biomass are lignin, hemicellulose, and cellulose, which together provide structural support to plant cell walls. To make use of these resources for fruitful energy applications, it is necessary to understand their structural composition. Cellulose, the most abundant organic compound on Earth, is a strong, resistant material made up of glucose molecules. The glucose molecules are connected to each other *via* β -1,4-glycosidic bonds. Hemicellulose is a flexible, amorphous polymer consisting of various sugar monomers, it is heterogeneous in comparison to cellulose, as it is composed of various 5-C and 6-C sugar units. It's basically a soft, flexible matrix structure that surrounds the cellulose. Hydrolysis of hemicellulose is considered easier than the hydrolysis of cellulose. While lignin, is composed of aromatic hydrocarbons, phenolic compounds, a complex and resistant polymer, provide rigidity to plant cell walls and protect cellulose and hemicellulose from degradation.

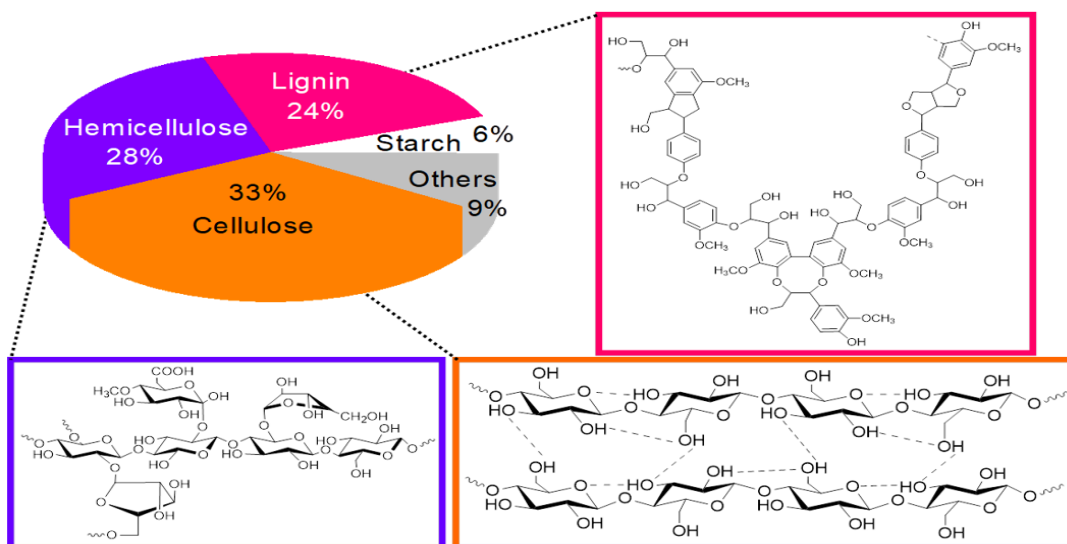


Figure 2. Composition of Lignocellulosic biomass.

1.3. Processing of Lignocellulosic Biomass

To use the biomass precursors as potential fuel precursors, the primary step involves the breaking down of their complex structure into simpler units. As biomass, specifically lignocellulosic biomass is basically composed of 3 units, namely cellulose, hemicellulose, and lignin (Boerjan, Ralph, & Baucher, 2003; Iriondo, Agirre, Viar, & Requies, 2020; Shuai & Pan, 2010; Taarning et al., 2011). Upon simplifying the complex biomass units via pre-treatment (ball milling and hydrolysis), these are sent to biorefinery units, where they are converted to materials, energy, and fuel as required. After the destruction of biomass after its preliminary treatment, they are converted into platform molecules; they are named as platform molecules based on their utility. These platform molecules or chemical building blocks, which carry a plenty of functional groups, are further converted into a range of value-added products via various catalytic routes (Anastas & Warner, 1998; Corma, Iborra, & Velty, 2007; Hara, Nakajima, & Kamata, 2015; Van Putten et al., 2013).

1.4. Biomass Conversion Selectivity

As we are aware, biomass is composed of a complex mixture of various C-containing organic compounds. Thus, the key success of biomass conversion is truly dependent on the ability to form accurate chemical compositions of valuable chemical compounds from complex biomass feedstock. The effective conversion of biomass also necessitates the selectivity of the biomass conversion by directing the reaction method to form desired product selectively. Which will not only maximize the product formation but also reduce the cost of purifying the valuable chemical from multiple products. However, attaining selectivity is a challenging process owing to the heterogeneity of biomass; the chemical composition of biomass varies from its growth environments, plant genetics, harvest and storage conditions, and much more. This heterogeneity of biomass makes it impossible to generalize any method of preparation of valuable chemicals from biomass. This demands the need for robust analytical tools for real-time analysis of conversion of complex mixtures to attain maximum selectivity.

Along with these, many of the feedstocks used for production of valuable chemicals are the by-products of another process. For instance, baggase produced from the conversion of sugarcane into sugar is used as feedstock for another conversion. In this scenario, the efficiency of first process directly influences the efficiency of the other. With all these variations, it's next to impossible to control the biomass conversion to a selective formation. Only way to achieve the desired target is the real-time analysis of biomass conversion with effective analytical tools, such that process optimization can be done at every stage of the conversion.

1.5. Various Catalysts for Conversion of Lignocellulosic Biomass

1.5.1. Thermo Catalysts

For biomass conversion, thermocatalysts play a crucial role and facilitate the conversion of biomass conversion into valuable chemical products. The thermo-catalysts have the unique characteristics of robust thermal stability, which makes them suitable to work under high temperature conditions, which is utmost required for biomass conversion. High thermal stability ensures prolonged sustainable performance of catalyst over multiple reaction cycles, which helps to reduce the cost to use fresh catalyst at every cycle. In addition to the same, the tailor-made activity of thermocatalysts makes them suitable for various reactions like dehydration, hydrolysis, deoxygenation, etc., which enhances the ability to produce more selective product and minimizes the side reactions.

1.5.2. Electrocatalysts

Electrocatalysts play a significant role in biomass conversion to valuable chemical commodities through electrochemical processes. The catalysts designed for electrochemical activity precisely control the reaction kinetics and selectivity by promoting electron transfer. This method is especially beneficial for the production of alcohols, organic acids, and hydrogen from biomass resources with minimal energy input. The typical reactions involved in electrochemical reaction pathways are oxygen reduction and hydrogen evolution. The electrocatalysts have made themselves an inevitable tool for advancing renewable energy sources. They are efficiently useful for the integration of solar or wind into biomass conversion systems.

1.5.3. Photocatalysis

Photocatalysts possess significant roles for biomass conversion to sustainable energy production. These catalysts enable the transformation of solar energy into energy production, making them feasible to drive chemical transformations. They are environmentally friendly catalysts that utilize abundant sunlight as a feedstock. This special characteristic of them helps to release the burden on fossil fuel resources and minimizes the global warming by compressing the production of CO₂. They are known to exhibit excellent catalytic activity at lower temperatures, which minimizes the energy input and maximizes the product selectivity. The specific feature to work under ambient conditions makes them suitable choice for the conversion of temperature sensitive biomass. The tailormode activity by optimizing catalyst composition and surface properties helps researchers promote selective reactions by minimizing side reactions. The utmost importance of photocatalysts in biomass conversions is due to their ability to perform the direct conversion of biomass without any requirement of pre-treatment.

1.5.4. Photoelectron Catalysis

Photoelectron catalysts are the catalysts that possess distinctive characteristics to promote both light energy and electrocatalytic processes for the successful transformation of biomass feedstock into valuable products. It offers an environmentally friendly route as it allows the solar energy to drive the chemical transformation involved in biomass conversion. As already discussed for photocatalysts, photoelectron catalysts offer the advantage of working under mild reaction conditions. And they can work with direct biomass for effective conversions without the urge for pre-treatment.

2. FUNCTIONAL CATALYSTS FOR THE SYNTHESIS OF BIOMASS-DERIVED FUELS AND CHEMICALS

The production of biomass-derived fuels and chemicals frequently necessitates the use of catalysts to facilitate the conversion processes. Catalysts are substances that accelerate chemical reactions without being consumed in the process. Various functional catalysts have been employed in the conversion of biomass into valuable products. For example, metal catalysts or metal-supported heterogeneous catalysts/metal-based nanoparticles Ru, Pt, and Pd are

often used as catalysts in processes like hydrolysis, hydrogenation, and deoxygenation for the production of biofuels. Ni and Co-based catalysts for hydrodeoxygenation reactions. The other category of catalysts includes zeolite and solid acid catalysts. These microporous materials are used in processes such as catalytic cracking and pyrolysis to produce biofuels like biogasoline and biodiesel. This modern research has also focused on the use of solid acid catalysts for various biomass reactions, including esterification and dehydration reactions, such as converting biomass-derived sugars into various furan derivatives. Bi-functional catalysts like solid-acid catalysts, redox catalysts, and bimetallic catalysts that are fruitful for the conversion of hydrogenation and dehydrogenation reactions are essential in processes like upgrading bio-oil or converting biomass into liquid hydrocarbons. Processes like hydroxyalkylation also employ these catalysts, transforming biomass-derived compounds into variable chemicals. Combining Noble Metals with Base Metals: Bimetallic catalysts can offer synergistic effects, improving catalytic activity and selectivity in various biomass conversion reactions. The selection of a specific catalyst depends on the biomass feedstock, desired end products, and the reaction conditions. Ongoing research focuses on developing efficient and sustainable catalysts to improve the overall viability of biomass conversion processes.

2.1. Role of Homogeneous Catalysts

As we have already seen the importance of using renewable feedstock above, on the same grounds, the implication of catalysis also plays a crucial role in viewpoint of green chemistry (Thomas & Raja, 2005). The role of catalysts in chemical manufacturing of fine chemicals is irreplaceable. Unfortunately, after knowing the green chemistry principles and advantages of using solid catalysts, our manufacturing companies are working on the use of homogeneous acid and base catalysts, for instance, mineral acids like H_2SO_4 , HCl , and H_3PO_4 as acid catalyst; NaOH , KOH as base catalyst; oxidizing agents KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$; reduction using Na , Mg , and Zn metals; and much more. The use of these chemicals in stoichiometric ratios generates hazardous and carcinogenic effects; the only alternative to prohibit or reduce the emission of the hazardous substances is the use of heterogeneous catalytic systems (Hovárth, 2002; Pines & Haag, 1958; Sheldon, 2000; Tundo et al., 2000).

2.2. Application of Heterogeneous Catalytic Systems

Long back in the year 1958, researchers began to explore the possibility of using solid materials as acids and bases for catalytic reactions (Zhang, Hattori, & Tanabe, 1988). Though the basic characteristics of solid alumina were discovered in the 1930s. The history of using solid-base catalysts in chemical reactions is amazing. It has been seen, that with the course of time, its significance or utilization has increased. Materials with catalytic active sites on their surfaces serve as solid catalysts, facilitating a variety of chemical reactions. Unlike traditional liquid or homogeneous catalysts, solid catalysts are heterogeneous and exist in a solid phase. These catalysts have gained attention in various industrial and laboratory applications due to their advantages, such as ease of separation, reusability, and stability. In 1990's numerous metal oxides such as magnesium oxide (MgO) and calcium oxide (CaO), strontium oxide (SrO), barium oxide (BaO), lanthanum (III) oxide (LaO), and zirconium oxide (ZrO) were identified as effective solid-base catalysts (Hattori, 1988; Vaccari, 1998). After the implications of metal oxides as base catalysts further innovations in solid base catalysts emerge layered double hydroxides and hydrotalcites with innovative properties (Allada, Navrotsky, Berbeco, & Casey, 2002; Sels, De Vos, & Jacobs, 2001; Thomas, 1992).

2.3. Solid Acid Catalysts

It's interesting to know that solid acid catalysts were known earlier for industrial applications in petroleum industry (Tanabe, 1970). They catalyze crucial reactions for refining crude oil into valuable products. The hydrocarbons that are produced by petroleum industry involve interaction with solid acid catalysts at every step, including catalyst cracking, hydrocracking, isomerization, alkylation, etherification, and much more. On the contrary, solid-base catalysts came into picture almost 2 decades later but have found their significant contribution

in the catalytic world owing to their versatile properties (Tanabe & Hölderich, 1999). The solid-base catalysts are now being used in various industrial applications as they exhibit enhanced surface area, ease in separation of solid-base catalyst; highly porous and uniform basicity. These days, heterogeneous base catalysts have been used in various reactions such as dehydration, isomerization, hydrogenation, etc. According to Védrine (2017) the characteristics that made them suitable for industrial applications are their high activity, which signifies their ability to use the minimum energy to transform the reactant into desired product. High selectivity, which means the use of heterogeneous base catalysts prohibits the side reaction with maximum conversion of reactant to desired product. The heterogeneous catalysts also offer better stability as they do not undergo deactivation, leaching, etc., (Busca, 2009). Recyclability and easy recovery are the added advantages with the use of heterogeneous catalytic systems for various industrial applications.

2.4. Solid Base Catalysts

Solid-base catalysis is one of the topics that has gained tremendous attention in past 10-15 years (Figueras, 2004; Hattori, 2001, 2004, 2015; Ono, 2003; Weitkamp, Hunger, & Rymasa, 2001). Numerous publications can be seen in this era on the topic heterogeneous catalysis. This chapter will brief you on the recent advances in this field along with some basics about the synthesis, development, and characterization of solid catalysts for desired transformations. The chapter primarily focuses on sustainable development, which involves developing solid catalysis with new insights and transforming the reaction from homogeneous to heterogeneous catalysis. A list of solid base catalysts known from years is below in Table 1.

Table 1. Types of solid base catalysts.

S. No.	Solid base catalysts	Types	Examples
1	Metal oxides	Alkaline metal oxides:	CaO; MgO; BaO; SrO
		Rare metal oxides	La ₂ O ₃ ; Sm ₂ O ₃
		Other oxides	Al ₂ O ₃ ; ZrO ₂ ; ThO ₂ ; TiO ₂ ; Mo ₂ O ₃
2	Mixed-metal oxides	Double metal oxides	ZnO-Al ₂ O ₃ ; MgO-TiO ₂
		Layered double hydroxides	Anionic clays that contain positively charged layers of metal hydroxides.
3	Zeolites	Alkali ion-exchanged zeolites	Na-X, Cs-X
		Alkali ion-added zeolites:	Cs ₂ O/Cs-X
4	Supported alkali metal compounds	Alkali metal compounds on alumina	NaO/Al ₂ O ₃ , Na ₂ O/Al ₂ O ₃
		Alkali metal compounds on silica	NaO/SiO ₂ , Na ₂ O/SiO ₂
		Alkali metal Ions on alkaline earth oxides	Na ₂ O/MgO
5	Clay minerals	Hydrotalcite	Mg ₆ Al ₂ (OH) ₁₆ CO ₃ ·4H ₂ O
		Chrysolite	Mg ₃ (Si ₂ O ₅)O ₃ (OH) ₄
		Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂
6	Non-oxides	KF supported on alumina	KF/Al ₂ O ₃
		Lanthanide imide and nitride on zeolite	
		Metal oxynitrides:	ALPON, VALPON

Source: Hovárth (2002).

3. FEW IMPORTANT CHEMICAL REACTIONS FOR BIOMASS TO COMMODITY CHEMICALS

3.1. Deoxygenation Reaction

If we observe the platform molecules from biomass resources, they include highly oxygenated species, for instance carbohydrates like glucose, sucrose, xylose, etc., carboxylic acids like succinic, lactic, levulinic, itaconic acids, etc. These highly oxygenated products need to be converted into deoxygenated products like furan derivatives furfural, 5-hydroxymethylfurfural, and 2,5-dimethylfuran, which work as biofuels and alternatives for biofuels. The reason behind decreasing the oxygen content is an increase in their energy density along with

decrease in their chemical reactivity. It is necessary to consider them as potential fuel precursors. The deoxygenation of platform molecules obtained from biomass to value-added chemicals is a catalytic process that is being dominated by heterogeneous catalytic systems these days. In this process, major reactions involved are decarboxylation, which removes CO and CO₂; dehydration process of removing H₂O; hydrogenolysis to break C-O bond, etc. Despite the importance of deoxygenation, it's been observed that all these reactions require hydrogen gas, which is sourced from fossil fuel resources only. Thus, to make the process more effective, the focus should not be only on developing heterogeneous catalysts but also on the development of heterogeneous catalytic systems that can work on transferring hydrogenation liquids to rely on our dependency on formic acid, which can be obtained from renewable sources (Deng, Li, Lai, Fu, & Guo, 2009; Toledano et al., 2014; Tuteja, Nishimura, & Ebitani, 2014).

The utilization of formic acid as hydrogen source generates *in-situ* hydrogen, which is absorbed on the catalyst surface and utilized in the reaction when required. Lignin being an abundant source, its utility has not been seen much for value-added chemicals. Its major uses till date have been explored only in the heat and power uses and somewhere in pulp and paper industry through combustion owing to its high calorific value. Lignin is constituted with highly complex polymeric structure of phenylpropane units. Due to its rigid nature, it is prohibited from microbial attack and cannot be depolymerized by water treatment as it repels water molecules. R. Luque *et al.* are working on the utilization of lignin sources by developing various heterogeneous catalysis for almost a decade (Pineda et al., 2011; Toledano, et al., 2013; Toledano, et al., 2013). They have developed a microwave-assisted methodology on lignin deconstruction using Magnetic Nanoparticles MNP/Si-Al-Si (metal nanoparticles supported on the surface of aluminosilicates) employing hydrogenated solvent as hydrogen source (Toledano, et al., 2013). Metal nanoparticles opted for this study are combinations of precious/noble metals such as Pd, Pt, Ru, and Rh and non-Nobel metals/transition metals like Cu and Ni synthesized using dry milling approach and supported on the highly active surface of aluminosilicates.⁴⁴ the transfer hydrogenating agents were chosen from the range of tetralin; isopropanol, and formic acid; out of which formic acid was selected as best for donating hydrogen under the reaction conditions used for the depolymerization of lignin (Boddien, Loges, Junge, & Beller, 2008; Geboers et al., 2011).

3.2. Hydrolysis

Hydrolysis represents an important reaction to convert lignocellulosic biomass to value-added commodities, as it represents the first step to produce cellulose and hemicellulose from lignocellulosic biomass. Further hydrolysis forms the building blocks of C5 and C-6 sugar units.

Table 2. Solid acid catalysts used for hydrolysis of lignocellulosic biomass.

S. no.	Type	Solid acid catalyst	Reference
1.	Zeolites	HY-zeolite H-beta	Li et al. (2012)
2.	Heteropoly acid	H ₃ PW ₁₂ O ₄₀	Onda, Ochi, and Yanagisawa (2008)
3.	Metal oxide	HNbMoO ₆	Akiyama, Matsuda, Sato, Takata, and Kitagawa (2011)
4.	Acidic polymers	Amberlyst-15 Nafion NR-50	Kitano et al. (2009); Rinaldi, Palkovits, and Schüth (2008) and Kobayashi, Komanoya, Hara, and Fukuoka (2010)
5.	Metal supported catalysts	Pd/C Ru/CMK-3	Lai et al. (2011)
6.	Magnetic solid acid catalysts	Fe ₃ O ₄ /SBA-SO ₃ H MNPs/SiO ₂ -SO ₃ H Fe ₃ O ₄ /C-SO ₃ H	Takagaki, Nishimura, Nishimura, and Ebitani (2011); Zhang, Wang, Liu, Wang, and He (2013) and Van De Vyver et al. (2010)
7.	Inorganic-organic hybrid composites	Si _m C _n -SO ₃ H	Suganuma et al. (2008)

Suganuma et al. (2008) found that cellulose on hydrolysis results in glucose units, whereas hemicellulose on hydrolysis provides C5 sugars like arabinose, xylose, etc. The acid catalysts, specifically solid acid catalysts, have gained tremendous attention for hydrolysis of cellulose and hemicellulose. Solid acid is made up of solid surface with highly active acidic sites (Brønsted or Lewis), which function for the hydrolysis of cellulose. Apart from easy recovery and being eco-friendly, the important benefit of using solid catalysts is that they are corrosion-resistant to reaction vessels (Cai, Li, Wang, Xu, & Zhang, 2012). The list of solid acid catalysts used for hydrolysis of lignocellulosic biomass is listed below in Table 2.

When we are discussing the solid acid catalysts for hydrolysis, it's important to know whether the acidity is due to Brønsted sites or Lewis sites. Secondly, the acidic sites are imbedded on the surface or incorporated into inner of solid catalysts.

3.3. Hydrolysis of Hemicellulose to Various Sugars

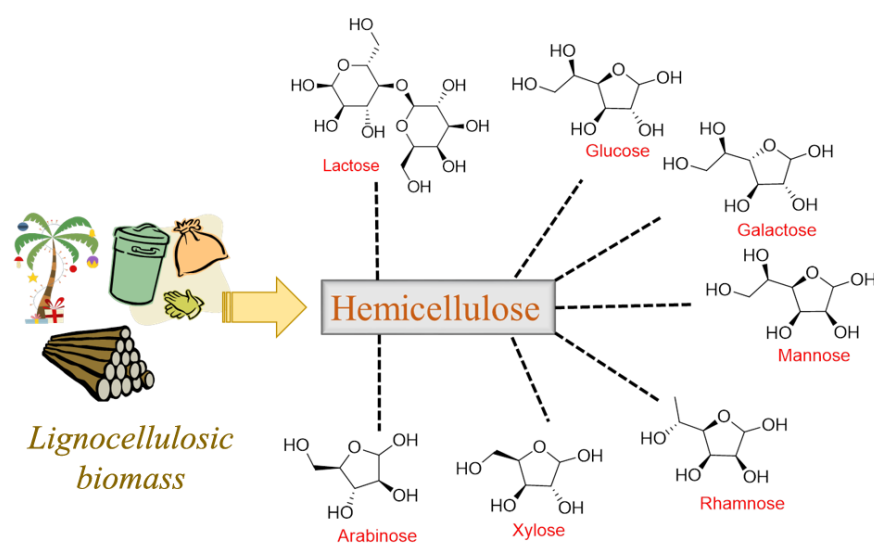


Figure 3. Hydrolysis of Hemicellulose to various sugars.

Hydrolysis of hemicellulose to various sugars is the key component of breakdown of complex hemicellulose to simple sugar units, making them suitable for the further conversions. The hydrolysis process involves the glycosidic bond cleavage under acidic conditions. You can also use enzymatic techniques to initiate the hydrolysis reaction. Apart from these, steam explosions can also be employed to rupture the structure of hemicellulose. Despite the methodology used for hydrolysis, it results in the formation of xylose, arabinose, mannose, galactose, rhamnose, and glucose.

3.4. Catalytic Activity of Acidic Sites

Strong Brønsted sites are provided by SO_3H group, which work by donating its H^+ to break β -1,4-glycosidic linkage of cellulose to form glucose units. There are commercially available catalysts like Amberlyst-15 and Nafion NR-50 that possess a sulfonic moiety on polymer beads; inorganic solid acids like sulfonated silica, etc, have been seen showing remarkable activity for hydrolysis of biomass-obtained molecules. Rinaldi et al. (2008); Harmer, Farneth, and Sun (1996) and Do Couto Fraga et al. (2016) the literature has suggested that the density or amount of SO_3H moiety is not the factor that depicts the catalytic activity (To, Chung, & Katz, 2015) it's the location and accessibility of the sulfonic moieties that play significant role in productivity and selectivity of the catalyst (Foo et al., 2015). For instance the sulfonated carbonaceous solid acid, if prepared under mild temperature conditions, has more surface acidic moieties that are easily accessible by cellulose to undergo hydrolysis. If same carbonaceous solid

acid is prepared under high temperature conditions, the SO_3H moieties are surrounded by polymeric C and are not easily approachable by the reactant. According to [Rastogi and Shrivastava \(2017\)](#) the only concern with these strongly acidic solid acids is their selectivity, as they don't stop the reaction of cellulose hydrolysis to glucose, but their further catalyze the reaction of glucose to 5-hydroxymethylfurfural and further to levulinic acid. [Onda et al. \(2008\)](#) thus fine tuning of acid sites and their location is must. There comes the role of weak solid acid sites of (COOH) to hydrolyze the glycosidic linkages of cellulose. A report in 2019 in green chemistry reported that the untreated C (without sulfonic acid treatment) catalyst also showed the activity to convert cellulose into glucose and suggested that the hydroxyl and carboxyl moiety on the activated C are behaving like acid to show the catalytic activity. [Kobayashi et al. \(2013\)](#) another report by Fukoka et.al., also signifies the same result with alkali-activated C (K26) without acid treatment ([Bozell & Petersen, 2010](#)). All these indicate the role of acidic sites, be they strong or weak, for the hydrolysis process of cellulose.

3.5. Dehydration

5-hydroxymethyl furfural (HMF), derived from the dehydration of C-6 sugars and furfural, derived from C-5 sugars are important building blocks from biomass. They both have been incorporated in the top 10 commodities or platform molecules from biomass to be converted into fuel additives or chemicals ([Hou et al., 2016](#)). Stoichiometrically, to convert C-6 sugars into HMF, we need to remove 3 water molecules, and the efficient catalysts discovered for this activity are solid acid catalysts. Numerous reports can be seen in this context, out of which few examples are listed here. The high yield of 94% of HMF can be seen from fructose with sulfonated grapheme oxide; ([Songo, Moutloali, & Ray, 2019](#)). $\text{TiO}_2/\text{Silica}$ is also found to be suitable for the said conversion with good efficiency (more than 90%) ([Marullo, Rizzo, & D'Anna, 2019](#)). Additionally, [Marullo, Rizzo, and D'Anna \(2019\)](#) reported using carboneous material after sulfonic acid treatment to effectively convert fructose (96%) into HMF (93.4%). [Vaccari \(1998\)](#) the application of commercially available Amberlyst-15 can also be seen working efficiently for moderate to high HMF yield and moderate reaction conditions. [Bisen, Niphadkar, Nandanwar, Simakova, and Bokade \(2021\)](#) the only disadvantage of all the processes mentioned above is that the starting material they used is fructose instead of glucose which is easily available and has low prices ([Román-Leshkov, Chheda, & Dumesic, 2006](#)). Thus, a strong urge to develop the methodology to produce HMF from glucose is a must. As the conversion from glucose to HMF involves the isomerization of glucose to fructose as first step, which is the major ([Figure 3](#)). To overcome the barrier with the use of same catalysts, scientists have used biphasic system, as isomerization needs an aqueous solvent and dehydration requires an organic solvent ([Nikolla, Román-Leshkov, Moliner, & Davis, 2011; Zunita, Yuan, & Syafi'Laksono, 2022](#)). Ionic liquids are also reported in the literature to avoid the hustle of biphasic system ([Serrano-Ruiz et al., 2012](#)). Brønsted acid site-based ionic liquids for conversion of C-5 sugars to furfural via microwave assisted reactions have been developed by [Li, Ho, Lim, and Zhang \(2017\)](#).

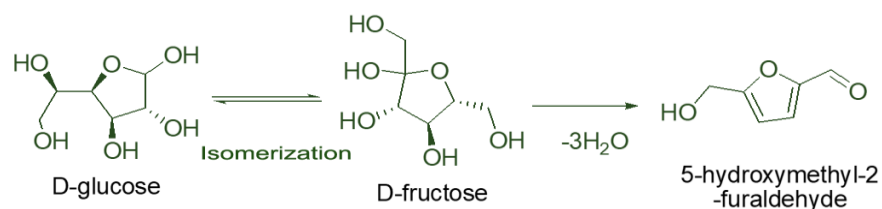


Figure 4. Mechanism of dehydration of glucose to 5-hydroxymethyl furfural.

3.5.1. Dehydration of Xylose to Furfural

For instance, if we consider the dehydration of xylose to furfural, [Table 3](#) summarizes the data of few reports that have used heterogeneous catalysts under numerous reaction conditions. ([Jiang et al., 2021](#)) optimize the

reaction parameters for variable temperature, reaction time, and solvent choice. The high efficiency of furfural was obtained with C-based heterogeneous catalysts for instances g-CN-SO₃H (entry No. 4 & 5 Table 2), which has shown a yield of 95% of furfural. In another study sulfonated palygorskite heterogeneous acid catalysts (PAL-SO₃H) have been used as solid acid catalysts in biphasic solvent media; the reaction produced 87% of furfural at 180°C in just 1 h (entry No. 7, Table 2). Some commercial solid acid catalysts, for example, Nafion 117, produce 60% of furfural yield from xylose at 180°C. Nb₂O₅, which is believed to have both Bronsted and Lewis acid sites, yields 72% furfural with a conversion of >99% of xylose.

Table 3. Heterogeneous Catalyzed Conversion of xylose to Furfural.

No.	Catalyst	Catalyst amount	Temperature	Time	Solvent	Conversion (%)	Y furfural (%)	Ref.
1	Nb ₂ O ₅	100 mg	120 °C	3 h	Toluene/H ₂ O	>99	72	Gupta, Fukuoka, and Nakajima (2017)
2	Nafion117	1.82 wt%	150 °C	2 h	DMSO	91	60	Lam et al. (2011)
3	g-CN-SO ₃ H	50 mg	100 °C	30 min	H ₂ O	---	95	Verma, Baig, Nadagouda, Len, and Varma (2017)
4	g-CN-SO ₃ H	50 mg	100 °C	25 min	DMSO	---	95	Verma et al. (2017)
5	Carbon-SO ₃ H	50 mg	170 °C	30 min	GVL/H ₂ O	99.5	75.1	Li et al. (2020)
6	Carbon-SO ₃ H	0.2 g	170 °C	30 min	GVL	---	78.5	Zhang et al. (2016)
7	PAL-SO ₃ H	50 mg	180 °C	60 min	GVL/H ₂ O	90.6	87	R. Wang et al. (2019)
8	Form-SO ₃ H	0.1 M acid sites	170 °C	10 min	Toluene/H ₂ O	---	70–80%	Krzelj, Ferrandez, and D'Angelo (2021)
9	CST	200 mg	170 °C	30 min	Toluene/H ₂ O	82.5	62.40%	Dulie, Woldeyes, and Demsash (2021)
10	SO ₄ ²⁻ /Sn-MMT	5 g/g	160 °C	90 min	2-MTHF/NaCl-H ₂ O	---	77.4	Lin et al. (2017)

Note: DMSO: Dimethyl sulfoxide; GVL: Gamma-valerolactone; MTHF: %-methyl tetra hydrofuran.

3.5.2. Dehydration of Glucose to 5-Hydroxymethyl Furfural

The research for the type of catalysts for the dehydration reaction of glucose to 5-hydroxymethyl furfural has already been achieved, and numerous publications can be seen in literature. Here I would like to enlighten an important aspect of the same reaction, *i.e.*, the solvent choice for the dehydration of glucose to HMF over heterogeneous catalytic system. The research indicated that the choice of solvent, whether we are choosing aqueous solvent or organic solvent; ionic liquids, biphasic or triphasic solvent mixtures, etc., (Xue, Ma, Li, & Mu, 2016). Table 4 depicts the various solvent choices for the conversion of glucose to 5-HMF (5-hydroxymethyl furfural).

Table 4. Catalytic conversion of glucose to 5-hydroxymethyl furfural.

No.	Catalyst	Solvent category	Solvent	Time	Temperature	Conversion (%)	Y Furfural (%)	Ref.
1	TiO ₂	Aqueous solvent	Water	MW heating for 5 min	200 °C	63.8	18.6	Qi, Watanabe, Aida, and Smith Jr (2008)
2	TiO ₂ -Cl-773K		Water	MW heating for 5 min	250 °C	79	28	Chareonlimkun, Champreda, Shotipruk, and Laosiripojana (2010)
3	SO ₄ ²⁻ /ZrO ₂	Organic solvent	DMSO	4 h	130 °C	95.2	19.2	Pan, Yang, Tong, Xiang, and Hu (2009)
4	SO ₄ ²⁻ /ZrO ₂ -Al ₂ O ₃		DMSO	4 h	130 °C	97.2	47.6	Pan et al. (2009)
5	Al ₂ O ₃ -B ₂ O ₃		DMSO	2 h	140 °C	94.8	41.4	Liu et al. (2015)
6	H β -zeolite (Si/Al = 25)	Ionic liquids	{Bmim} Cl	1 h	140 °C	80.6	50.3	Hu et al. (2014)
7	Zr-P-Cr		{Bmim}Cl	12 h	120 °C	94.7	43.2	Liu, Ba, Jin, and Zhang (2015)
8	Sn-MCM-41 (0.1 g)		{Bmim}Br	4 h	110 °C	99	87	Hu et al. (2014)
9	Sn-Mont	Biphasic solvents	DMSO-THF	3 h	160 °C	98	53.5	Wang et al. (2012)
10	lignin-derived carbonaceous catalyst.		DMSO- {Bmim}Cl	50 min	160 °C	99	68	Guo, Fang, and Zhou (2012)
11	Amberlyst 15		{Bmim}Cl- {Bmim}{BF ₄ }	2 h	25 °C	--	32	D'Anna et al. (2014)

3.6. Cascade Reactions

The next step after the production of furfural and its derivatives demands versatility from catalyst. The versatility can be achieved by employing multifunctional solid catalysts to achieve various reactions (hydrogenation, hydrogenolysis, dehydration, oxidation, etc.). The purpose of these reactions is to produce value-added commodities from furan derivatives (Figure 4).

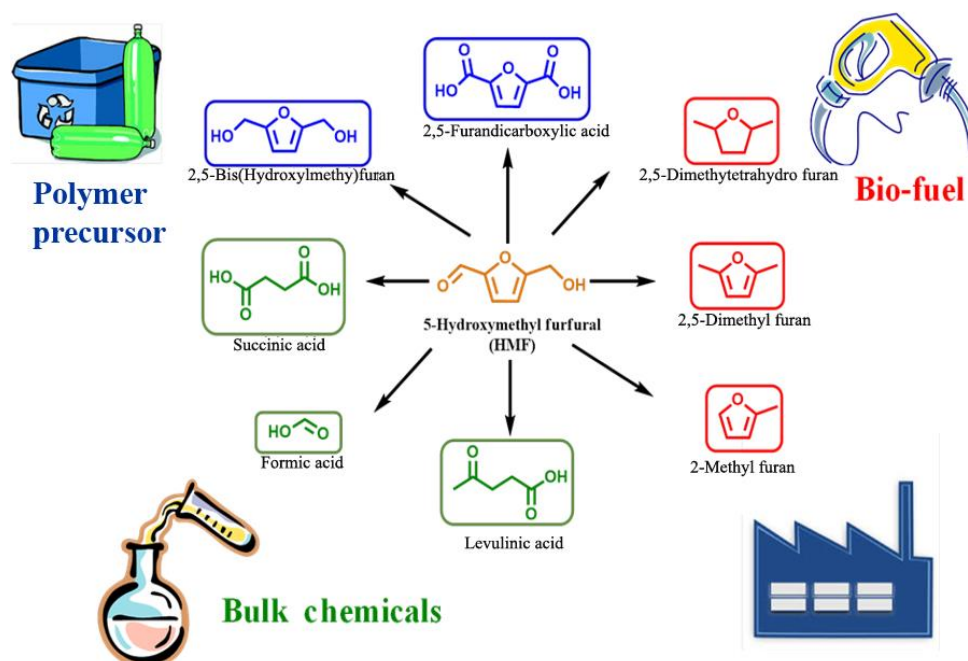


Figure 5. Commodity chemicals from chemical conversion of 5-hydroxymethyl furfural.

Figure 5 illustrates the ring opening oxidation of furfural/HMF to succinic acid, formic acid, and levulinic acid, 2,5-dimethyl furan, furan dicarboxylic acid, and 2,5-Bis (hydroxymethyl) furan. These commodity chemicals have gained tremendous attention owing to their application in plastidizer, surface coatings, pharmaceuticals, etc. (Alonso-Fagúndez, Granados, Mariscal, & Ojeda, 2012; Guo & Yin, 2011) Numerous heterogenous catalysts have been developed or are developing currently for the oxidative conversion to maleic acid, succinic acid, and formic acid. The reaction was initially studied in an aqueous organic biphasic system. Choudhary, Nishimura, and Ebitani (2012) within small time in Choudhary et al. (2012) developed the green oxidation method for conversion of furfural in water within a short time using Amberlyst-15 as catalyst and H_2O_2 as green oxidizing agent (Zhu et al., 2018). In 2018, metal-free grapheme oxide was employed as an efficient catalyst for the transformation of furfural to succinic acid with high yield (Palai, Shrotri, & Fukuoka, 2022). Lewis acidic sites of Sn-beta Zeolites are also observed to show great catalytic activity for the conversion very recently (Signoretto, Taghavi, Ghedini, & Menegazzo, 2019).

Similar to this, the conversion of HMF to levulinic acid over solid catalysts is also a very important reaction among biomass transitions to value-added chemicals. Liu et al. (2017) variety of solid acid catalysts based on carbon materials, metal oxides, polymer-supported acidic catalysts, zeolites, and heteropoly acids, have been developed. A new approach suggests that the optimization Brønsted/Lewis ratio has a significant impact on maximizing levulinic acid yield. Higher Brønsted acidic sites compared to Lewis one result in a high yield of levulinic acid of 64.2%. Wei and Wu (2018) Table 5 listed few solid acid catalysts for the effective production of levulinic acid from biomass.

Table 5. Synthesis of Levulinic acid from biomass over different solid acid catalysts.

S. no.	Starting material	Solid acid catalyst	LA yield	Reference
1.	Glucose	Cr/H-ZSM-5 (0.75 g)	64.4	Liu et al. (2017)
2.	Glucose	Fe-NbP (50 mg)	64.2	Pyo, Glaser, Rehnberg, and Hattikaul (2020)
3.	Fructose	H-Resin (30 wt%)	74.6	Bisen et al. (2021)
4.	Fructose	S-beta zeolite (3 wt%)	43.5	Wang et al. (2020)
5.	Cellulose	Ga ₂ O ₃ -UiO-66 (2.5%)	32	Pratama, Rahayu, and Krisnandi (2020)
6.	Rice husk	Mn ₃ O ₄ /ZSM-5, H ₃ PO ₄ (10%), H ₂ O ₂ (2%)	39.8	Wang, Zhao, Rodríguez-Padrón, and Len (2019)

Note: H-ZSM: Zeolite.

Another very important reaction is hydrogenation of furan derivatives to 2,5-dimethylfuran, 2-methylfuran, and 2,5-dimethyl tetrahydrofuran. A variety of precious metal (Au, Pd, Pt) and non-nobel (Cu, Co, Bi, Fe, Ru, Rh) metal-based catalysts have been used till date for the hydrogenation reaction (Wang, Zhu, Sang, Gao, & Xiao, 2017). Though precious metals have shown tremendous activity for the said reaction, here the focus is on the non-nobel catalysts, as the latest development is in this sector only. Among which Cu-based solid catalysts have been seen in a huge number of publications due to their low price, high activity, easy accessibility, and good performance in hydrogenation. To quote a few examples: Cu supported on both acidic and basic supports, such as Cu/ZSM-5; Cu/Al₂O₃; Cu/SiO₂; Cu/ZnO; and Cu/MgO, were thoroughly studied. The studies suggested that Cu on basic support gave much better results for hydrogenation with great selectivity, whereas Cu/Acidic support resulted in various side-product formations (Zhang et al., 2014). Another scientist proposed that to achieve high yield with high selectivity of Hydrogenation, it is necessary to have both Cu⁰ and Cu⁺ active sites (Srivastava, Jadeja, & Parikh, 2018). Further studies were done with Cu-based bimetallic catalysts where Co-Cu/Al₂O₃ was employed to study the hydrogenation reaction of furfural to methylfuran (Wei & Wu, 2018). Co-Ni; Co-Ni bimetallic systems have also received great attention in this regard, as have tetrahydrofuran and 2,5-dimethylfurans from furan derivatives (Zhang et al., 2014).

4. CONCLUSION

There is no doubt that owing SDG's (Sustainable Development Goals) and, in the process, making sustainable world use of renewable sources along with the use of solid catalysts has been considered an important aspect. From the viewpoint of the same, various scientists have developed and are currently developing various methodologies to achieve maximum efficiency in terms of yield of value-added products with highest selectivity following green chemistry principles. The focused products in this area are 2,5-dimethylfuran as a fuel precursor, hexanediol, pentanediol, levulinic acid, formic acid as polymer precursors, alcohols for biofuels, other products for bioplastics, etc. To achieve these target solid catalysts, comprising metal catalysts, metal supported catalysts, metal oxides, heteropoly acids, and sulfonated polymers have been considered as potential catalysts. To design the reaction for biomass to the desired product, we need to focus on which type of reaction it will undergo, considering the same the choice of solid catalyst can be made. We need to first optimize whether the reaction demands deoxygenation, ring-opening hydrogenation, ring-opening hydrogenolysis, oxidation, hydrolysis, or hydrogenation. Firstly, to convert cellulose and hemicellulose to C₅ and C₆ sugars, cation exchange resins and solid Brønsted acidic sites are considered effective. For more changes to furan derivatives from sugar, metal oxides that are supported on solid bases, both monometallic and bimetallic, are thought to be better. The ring opening hydrogenolysis again demands for solid Brønsted acidic sites. The oxidative reaction of HMF to FDCA (furan 2,5-dicarboxylic acid) is particularly achieved by monometallic or bimetallic catalysts with solid base as support.

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