



Advancements in the conversion of lingo biomass to glucose with photocatalysts.

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Abstract

Lignocellulosic biomass has been highlighted as a promising feedstock in the hunt for alternative resources to produce commercial chemicals and transportation fuels for decarbonization. Its yearly production rate is about 180 billion tonnes. The cutting-edge catalytic conversion of lignocellulosic biomass into glucose is the main topic of this review.

It is crucial to catalyze the conversion of plentiful and sustainable lignocellulosic biomass into value-added chemicals and fuels to replace fossil fuels. By depolymerizing carbohydrates and their derivatives, several C5-C6 monosaccharides (such as glucose and xylose) and platform compounds that are formed from them can be obtained.

A brief introduction to the structure, key resources, and several catalytic conversion processes of lignocellulosic biomass into glucose is followed by a thorough discussion of the catalytic conversion processes by enzyme, liquid acids, solid acids, and by photocatalysis into glucose. Due to its numerous applications, investigations about catalytic production of glucose, the primary platform chemical produced using biorefineries, recently gained popularity in catalysis studies and the chemicals/fuel sector.

By doing so, a new path toward sustainable chemical manufacturing and energy supply is made possible. Using a diversity of homogeneous and heterogeneous catalysts, this discussion seeks to summarize the latest innovations in the catalytic approaches for the digestion of carbohydrates from lignocellulosic biomass. Finally, the prospects, issues, and possibilities related to the valorisation of woody biomass are discussed.

Keywords Lignocellulose, Biomass, Catalytic conversion, Glucose, photocatalysis

Highlights

- Structure, resources, and Catalytic conversion of lignocellulosic biomass are introduced.
- Over 100 references related to the catalytic conversion of lignocellulosic biomass are discussed.
- Opportunities, challenges, and perspective of current approaches are discussed.

1.Introduction

Biomass, which is the term for organic materials generated from plants and animals, now makes up 10% of chemical feedstock and 9.4% of the world's energy supply [Deng et al., 2022]. It is recognized as the first fuel used by humans and the main energy source used up until the middle of the 19th century. As the sole substantial source of large-scale organic carbon for the production of organic fuels and chemicals, biomass resources have recently received a lot of interest once again. Among the numerous types of biomasses, lignocellulose is the most promising feedstock since it is a plentiful, affordable, and easily accessible non-edible resource.

Even though the usage of lignocellulosic biomass still relies on the carbon cycle and produces carbon dioxide as it goes along, the carbon footprint is balanced by plant growth during photosynthesis. Given the lack of

technological advancement in the hydrogen economy and the continued dependence of human activities on the carbon cycle, lignocellulosic biomass is seen as a key alternative for the future energy sector. According to estimates by [Yadav et al. 2020], biomass may be transformed into 6 MJ of energy or 0.8 kg of chemicals per kg of raw materials.

Lignocellulosic resources are currently underutilized despite their potential as feedstock in the production of biofuel and chemicals. Traditional methods of disposing of archaeological wastes included open-field burning or landfilling, both of which cause several environmental problems, including air pollution and soil erosion. Residues for energy production can be crushed into solid fuel pellets, including sawdust, rice husk, and sugarcane bagasse, although virgin biomass has lower calorific values than fossil fuels [Sivabalan et al., 2021]. The lignocellulosic biomass can be transformed into biofuels like bioethanol, biodiesel, and syngas to raise its energy density. Since cellulosic bioethanol facilities have been operating successfully for ten years, it is clear that they have the potential to replace starch-based bioethanol plants. [Rosales-Calderon et al. 2019, Arantes].

No matter how lignocellulosic biomass is converted into fuels or chemicals, such as glucose, good selectivity toward the desired products requires the use of catalysts. Effective breaking of C-C and C-O bonds, as well as the elimination of oxygen, are made possible by catalysis. As a result, this review offers a thorough overview of the catalytic conversion of lignocellulosic biomass into chemicals and fuels, either as individual components or as a whole.

This evaluation [Kobayashi and Fukuoka 2013] primarily focuses on documenting and assessing all elements of the investigations on glucose chemistry that have so far been reported. Some advancements in the catalytic digestion of carbohydrates with the developed reaction systems are described in depth [Kobayashi and Fukuoka 2013]. An outlook for this domain's future is provided in the review's last section. We believe that this study can give readers a useful overview and insights into this fascinating research topic because it is a discipline that is rapidly increasing.

1.1. Lignocellulosic biomass Structure and components

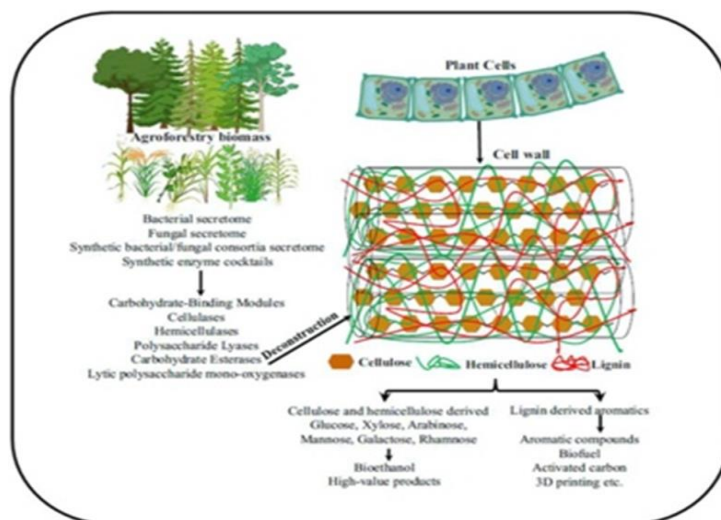


Figure 1. An overview of biomass composition and degradation. (Adapted from [Sethupathy et al. 2021] Open access CCBY 4.0)

High cellulose contents biomass is referred to as lignocellulosic biomass that also includes the two key components lignin and hemicellulose. Typically, between 40 and 60 percent of the overall biomass is composed of cellulose, with the remainder being made up of minerals, a small quantity of pectin, lignin polymer (10–25%), and hemicellulose (20–40%) [Tayyab et al., 2017] (Figure 1). Beta-glucosidase bonding surrounds each Cellulose polymeric structural unit, whereas in the linear structure, which is known as microfibrils, equal structures of hydroxyl groups present on both sides supported the crystal structure of cellulose in parallel alignment and

maintained it at the nanoscale [Kamm et al., 2017]. By creating hydrogen connections among the hydroxyl groups, these fibrils strengthen the cellulose structure. Additionally, the less compact, 3–30 times simpler to disintegrate cellulose structure known as the amorphous structure of cellulose is meant. Additionally, hemicellulose, the other companion polymer to cellulose, contains only an amorphous functional area due to its irregular structure and is composed of the monomeric sugar's glucose, pentose, xylose, arabinose, and mannose [Mitani, 2018, Paz-Cedeno et al., 2022, Yue et al., 2018]. Furthermore, hemicellulose has 150–200 smaller units than cellulose in its structure, which means that the hydrolysis of hemicellulose into monomeric sugars is simpler than the han hydrolysis of cellulose [Rezania et al., 2020]. Additionally, lignin, an aromatic polymer made up of three significant phenolic subunits—p-hydroxyphenyl, guaiacoll, and syringyl—maintains the hydrophobicity of LCB. An ester link connects the cellulose and hemicellulose structures, creating a strong structure that guards the polymer against outside threats such as microbial, enzymatic, and chemical hydrolysis [Sperandio and Ferreira Filho, 2019].

1.2. Major resources for Lignocellulosic Biomass

Primarily in nations with dynamic agricultural economies like Brazil, China, India, and the United States, agricultural waste represents a plentiful, affordable, and easily accessible source of lignocellulose. Various sources available for lignocellulosic biomass are depicted in Figure 2. The most widely produced grain worldwide is corn, which is followed by wheat and rice. Every year, the globe produces over 529 million tonnes of wheat straw. In human history, woody biomass has been used extensively as a heating source. 50 million tonnes of wood pallets and 1928 million m3 of roundwood were produced in 2020 for use in energy [F.a.a.O.O.T.U 2022]. The forest and timber leftovers, such as branches, barks, chips, and sawdust, are among these affordable sources of woody biomass. According to estimates by Titus et al. (2020), processing leftovers from harvesting and processing led to the production of 371 and 406 million tonnes of woody biomass, respectively. Perennial grasses are promising sources of lignocellulosic biomass because they have low water and fertilizer requirements, can be grown on poor soils, provide large and steady biomass yields, and have higher disease resistance

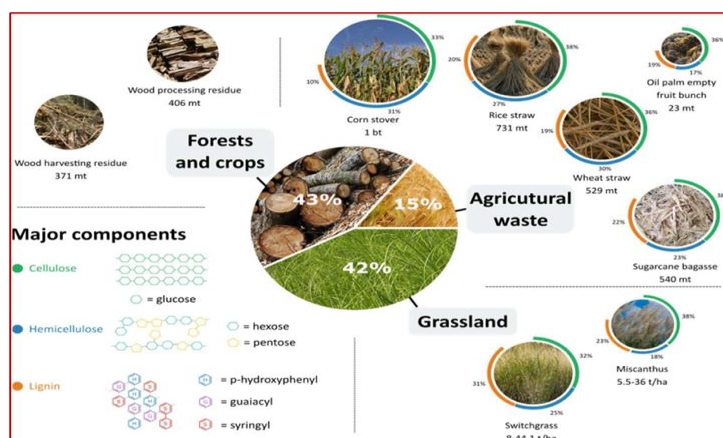


Figure 2. Different recourses of Lignocellulosic Biomass [Reference-Deng et al., 2023]

2. Conversion of lignocellulosic Biomass to glucose with various catalytic methods

2.1. Glucose production by enzyme

The enzymatic method is more desirable for converting cellulose or lignocellulosic biomass into saccharides, such as cellobiose and glucose, because it may be carried out under mild circumstances to create a high yield of the finished products. [Kobayashi and Fukuoka 2013]. Using pre-treated rice straw, banana plant debris, and maize cob as lignocellulosic materials, [El-Zawawy et al 2021] explores the utilization of acid and enzyme hydrolysis to produce glucose as a source for ethanol production. After testing the agricultural biomasses, a laboratory experimental setup was created to carry out the required conversions. Holocellulose and lignin concentrations in the biomass materials ranged from 57.46 to 85.28 and 14.55 to 26.12 percent, respectively. The pre-treatment

approach for the agricultural residues first applied chemical pulping, steam explosion method, as well as microwave treatment, then followed by two procedures, namely acid hydrolysis and enzyme hydrolysis, which was successful in converting the cellulose to glucose. *Trichoderma reesei* cellulases were employed in enzyme hydrolysis and 5% sulfuric acid was used in acid hydrolysis. These tests showed that the type of pre-treatment and type of hydrolysis affect the glucose concentration. Yeasts from *Saccharomyces cerevisiae* were used in the fermentation process to convert the glucose to ethanol. Using gas chromatography, the ethanol generation in the culture sample was observed. The findings suggest that depending on the pre-treatment and the amount of glucose generated by the hydrolysis process, ethanol can be created from the aforementioned wastes in a variety of yields. An enzyme complex called cellulase, which consists of three main enzymes, accelerates the conversion of cellulose into glucose. Figure below illustrates how such a procedure is carried out: To lessen the crystallinity, I endoglucanase randomly attacks and cuts the amorphous areas of long cellulose chains.; (ii) Cellobiose is successively released from the cellulose matrix by cellobiohydrolase; and (iii) -The produced cellobiose is converted into glucose units by glucosidase. The persistence of enzyme production throughout the reaction and the recyclability of the cellulase after the reaction are two important issues in cellulase-catalyzed reactions. After this, even though free cellulase has shown satisfactory results in the hydrolysis of cellulose, mounting cellulase onto compatible solid materials is a practical method to improve its tolerance of external conditions (such as temps and acidity values) and renewability.

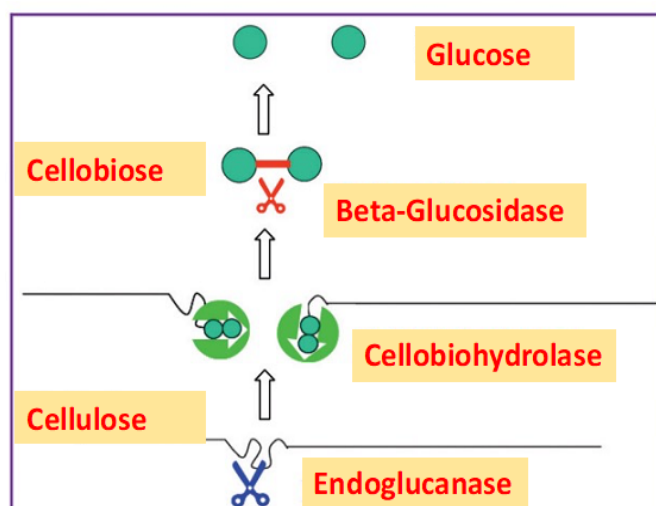


Figure 3. Cellulases' simultaneous induction of cellulose depolymerization. Nowadays, cellulose or lignocellulosic biomass may be depolymerized using an extremely selective method using enzymatic processes. Several demonstration factories or pilot plants, including those in Hiroshima are presently in operation. As is well known, there were significant issues with wastewater treatment due to the extremely low concentration of cellulose used for the transformation of cellulose to glucose via cellulase. Even though some levels of immobilized enzymes displayed remarkable utility, bigger amounts of enzymes, like cellulase, were necessary to enhance the glucose concentration, and this has ultimately exceeded the overall amount of expenses for conversion of glucose. Additionally, immobilized-cellulase-catalyzed cellulose transformation was often carried out under particular circumstances, such as cool temps as well as appropriate acid levels of the medium conditions. And adopting these, even at increased cellulose concentrations, the depolymerization activity of cellulose was remarkably low, necessitating longer reaction periods. The widespread use of enzymes or enzymes that have been immobilized All of these limitations would limit the commercial processing of cellulosic materials into saccharides (such as glucose and fructose) in the foreseeable.

Producing glucose syrup from starch using a twofold enzyme process: The double enzymatic approach uses a highly selective amylase and saccharification enzyme as a catalyst to hydrolyze starch into glucose. Starch

hydrolysis is conducted done twice to get a DE value of 98 percent or greater. In the first step, an elevated resistant a-amylase is used to liquefy the material, and in the second step, a starch saccharification enzyme is used to further hydrolysing the liquid substance into glucose. The key seven steps in the creation of glucose syrup are pulping, liquefaction, saccharification, deproteinization, decolorization, ion exchange, and focused evaporation. A description of how these steps work is given in Figure 4..

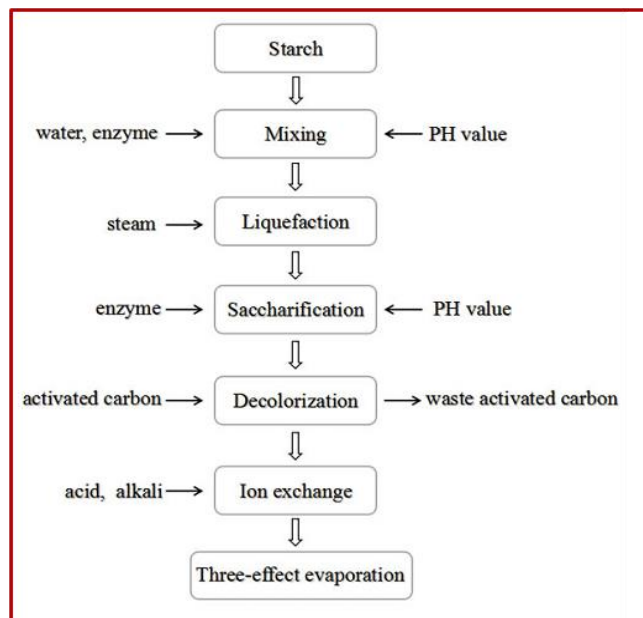


Figure 4. The twin enzyme technique for producing glucose syrup from starch.

2.2 Glucose production by liquid acids

Acid pre-treatments enhance enzymatic hydrolysis on the solid residue and boost recovery of hemicellulose sugars while reducing the generation of inhibitory chemicals. On the other hand, using alkali causes the biomass to swell, increasing its internal surface area while lowering its degree of polymerization and crystallinity. Switchgrass, sugar cane bagasse, wheat straw, rice straw, maize stover, Miscanthus, poplar, and agave plants are just a few examples of the lignocellulosic materials that have undergone these pre-treatments and are used as feedstock for the production of biofuel. [Kaparaju et al. 2010, Caspeta et al.2014, Banerjee et al. 2010, García, 2008, Saucedo-Luna et al. 2010, Nanda et al. 2014, Munir et al. 2015].

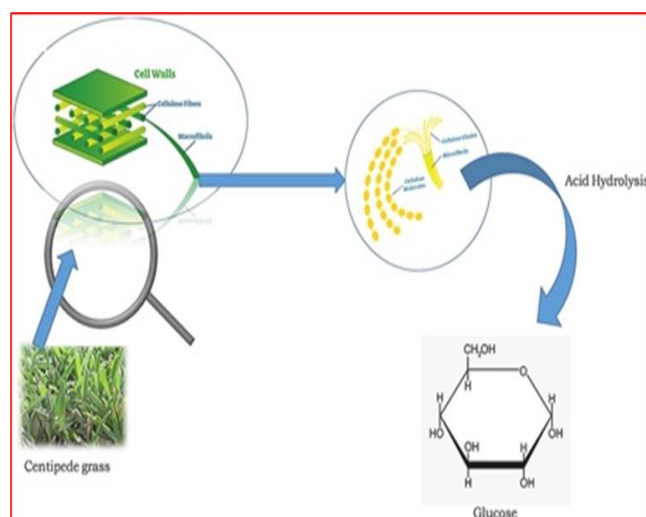


Figure 5. Conversion of Glucose by Liquid acids

The study by [Abbas et al., 2021] examined the generation of glucose through the hydrolysis of *Eremochloa ophiuroides*, a type of centipede grass (Figure 5). Before employing the centipede grass in the hydrolysis procedure to produce glucose, its moisture content, volatile matter, and fixed carbon were all analyzed. The content was increased (optimum) absorbance of glucose (0.36 equal to 17.24 mg glucose/10 g centipede grass) was achieved after 108 min of hydrolysis time at a temperature of 50.5 °C and a hydrochloric acid concentration of 8.94%. The purpose of the research carried out by Magdiel Láinez on *A. salmiana* was to determine how the lignocellulosic biomass of *A. salmiana* leaves would respond to the sequential application of acid-alkaline pre-treatments, followed by enzymatic saccharification. Reports on the breakdown of this plant's structure into sugar composites are incredibly rare. Therefore, research on this topic is very important, especially because it will be used as a feedstock for the production of biofuels. In order to assess the conversion of lignocellulosic biomass from *Agave salmiana* leaves into simple sugars, [Magdiel Láinez et al. 2018] conducted a series of successive acid-alkaline and enzymatic saccharification treatments (Figure 6). On lignocellulosic biomass, the effects of a catalytic reagent and residence time were assessed. Additionally, different degrees of cellulose and FPU loadings on the treated biomass were used throughout the enzymatic saccharification process. The resultant hemicellulose was fully hydrolyzed following an acid-alkaline pretreatment, but the residual cellulose achieved values of 91 and 84 percent (w/w) once the lignin was removed. Following acid pretreatment, the liquid by-product contained 0.50 g/L of glucose, 1.87 g/L of arabinose, 21.35 g/L of xylose, and 39.15 g/L of reducing sugars.

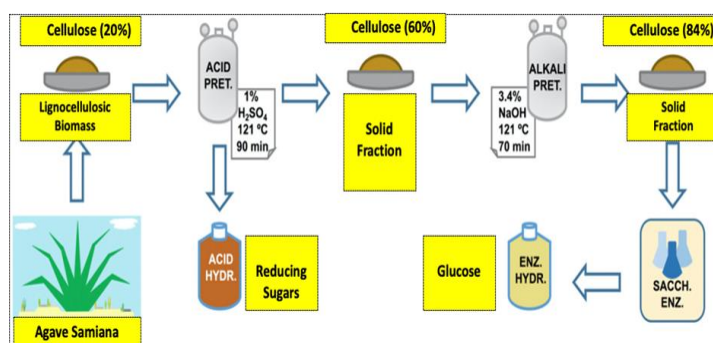


Figure 6. Illustrating the process for acid hydrolysis for Agave (lignocellulosic biomass)

a. Liquid mineral acid-catalyzed hydrolysis

The hydrolysis of cellulosic materials is a crucial step in the production of carbohydrates and biocomposite platform chemicals. To evaluate the time-dependent production of furfurals, organic acids, and sugars (glucose, xylose, and mannose) at different hydrolysis temperatures (220, 200, 1800C) of one representative of every fundamental kind of lignocellulose: Pretreatment tests on hardwood, softwood, and grass were carried out in a semi-continuous facility using diluted hydrochloric acid as a catalyst. Early on in the process, mostly xylose and mannose were produced, whereas glucose was released gradually. Figure 7 is depicting the diagrammatic representation of use of Mineral acids for catalysis of Lignocellulosic Biomass. During the dilute acid pretreatment, hemicellulose and cellulose are hydrolyzed to produce soluble sugars. In general, the hydrolysis of hemicellulose results in the production of organic acids and sugars (glucose, xylose, mannose, and galactose) (formic, acetic acid). A pentose sugar called xylose can be further dehydrated to become furfural [Lange et al., 2007]. Along with its high degree of polymerization, crystallinity, and hydrogen bonding, cellulose is more stable than hemicellulose. In less extreme circumstances, this delays the beginning of cellulose hydrolysis [Jönsson et al., 2016]. The hydrolysis of cellulose to glucose under acidic circumstances might lead to the production of value-

added compounds such as HMF [Dautzenberg et al., 2011, Chheda et al., 2007, Yu et al., 2017, Körner et al., 2018]. Cellulose is more stable than hemicellulose due to its high level of polymerization, crystallinity, and hydrogen bonding. This postpones the start of cellulose hydrolysis under less severe conditions [Jönsson et al., 2016]. Under acidic conditions, the hydrolysis of cellulose to glucose may produce added-value chemicals such as HMF [Dautzenberg et al., 2011, Chheda et al., 2007, Yu et al., 2017, Körner et al., 2018]. A crucial stage in the valorization of cellulose, hemicelluloses, and lignin to create different sustainable fuels and chemicals is the fractionation of lignocellulose. One of the most often used processes, mineral acid fractionation causes the hydrolysis and solubilization of cellulose and hemicelluloses, while the majority of the lignin remains insoluble and can be removed from the extract. Salts, by-products of sugar breakdown, and phenolic compounds are in solution with the produced monomeric sugars in the acid extract. The sugars must first be purified to be further valorized by chemical or biological processes into fuels or chemicals. The fractionation of lignocellulosic biomass using mineral acids is covered in the first section of the picture. The purification of the resulting lignocellulosic hydrolysates, including glucose, is described in the second section. The best yields for transformation cellulose and hemicelluloses into monomeric sugars like glucose were found to be with a combination of hydrolyses, including one at a high sulfuric acid concentration at a lower temperatures (about 30 C), after which another action at a low sulfuric acid concentration at an elevated temp (about 4% (w/w)) (120 C). Because of these fractionation circumstances, an extract was created that not only contained all the sugars (including glucose) in their monomeric form, but also contained phenolic compounds, acetic acid, mineral acid, and furans.

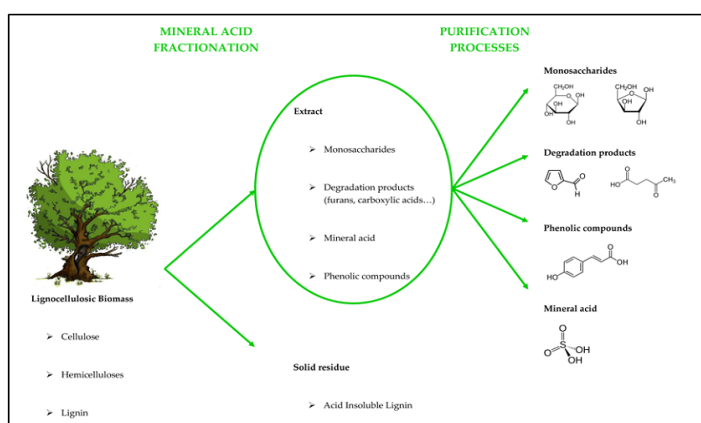


Figure 7. Diagrammatic illustration of Use of Mineral acids for catalysis of Lignocellulosic Biomass.

b. Water-soluble hetero-polyacid-catalyzed hydrolysis

H3PW12O40, another of the heteropolyacids (HPAs) and a superacid with strong acidity, is an effective approach which could be used in both homogeneous and heterogeneous acid-catalyzed reactions. It has the economic benefits of being simple to handle and delete, recyclable, stable, and possessing high catalytic activity. [Kozhevnikov, et al., 1998]. H3PW12O40 can also dissolve in water and completely dissociates the protons. According to Tian et al., cellulose can be transformed effectively over the H3PW12O40 catalyst, and at 180 °C for two hours, a 50.5 percent yield of glucose with 90 percent selectivity was produced. Additionally, as the saccharides soluble in water do not change into the diethyl solvent layer, the H3PW12O40 catalyst can be easily removed from the reaction solution with diethyl ether and repeatedly used. Up to 82 percent of the total reducing sugar output and 77 percent of the glucose yield can be produced in a cellulose-based 0.7 M H3PW12O40 solution at 60 °C. Additionally, the saccharification of natural lignocellulosic biomass, such as sawdust from Japanese cedar trees, the oil palm fruit bunch fiber, and rice plant straw, was successfully carried out with acceptable yields (77% total reducing sugar yield based on holocellulose). According to Li et al., cellulose could be effectively depolymerized in concentrated H3PW12O40 when microwave irradiation was used at low temperatures. At 90 °C for 3 hours, a

75.6 percent yield of glucose was obtained. Genuine biomass resources biomass, such as sugarcane, corncobs, and wheat straw, could likewise be saccharified under the same circumstances with respectable yields. [Li et al. 2012].

c. Conversion of cellulose component of lignocellulosic to Glucose

The heteropoly acid H₃PW₁₂O₄₀ was created by [Tian et al., 2010]. to convert the cellulose in a specific manner (Figure 8). At 180°C for two hours with 0.10 g of cellulose, the heteropoly acid catalyst may facilitate cellulosic hydrolysis, resulting in glucose selectivity and yield of 92.3 and 50.5 percent, respectively. The most effective circumstances for a reaction were identified by the authors after they researched and adjusted the reaction parameters impacting cellulose hydrolysis. With the same reaction circumstances and with the same acid concentration, H₃PW₁₂O₄₀ demonstrated higher catalytic activity and glucose selectivity in comparison to HCl. The total loss of H₃PW₁₂O₄₀ was 8.8% of its initial loss after assessing its catalytic activity across six successive reaction cycles [Tian et al., 2010]. The acid catalyst H₃PW₁₂O₄₀ was discovered to be typically stable and capable of recycling through diethyl ether extraction. The yield of TRS and glucose, however, was somewhat reduced due to a modest loss of catalyst activity. The total loss of H₃PW₁₂O₄₀ was 8.9% of its primary reduction after assessing its catalytic activity across six successive reaction cycles [Tian et al., 2010]. The acid catalyst H₃PW₁₂O₄₀ was discovered to be typically stable and capable of recycling through diethyl ether extraction. The yield of TRS and glucose, however, was somewhat reduced due to a modest loss of catalyst activity.

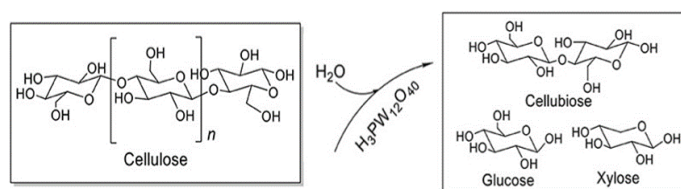


Figure 8 . Products and by-products of the acid catalyst H₃PW₁₂O₄₀'s conversion of cellulose.

TABLE 1. cellulose hydrolysis using various acid catalysts [Tian et al., 2010].

Catalyst	Solvents	Temp (°C)	Time (h)	Glucose/TRS yield TRS yield/%	References
Amberlyst-15	[BMIm]Cl/H ₂ O	100	5	11.0	Rinaldi et al., 2010
PCPs-SO ₃ H	H ₂ O	120	3	5.30	Akiyama et al., 2011
BC-SO ₃ H	H ₂ O	90	1	19.8	Wu et al., 2010
CMK-3-SO ₃ H	H ₂ O	150	24	74.5	Pang et al., 2010
Zn-Ca-Fe	H ₂ O	160	20	29	Zhang et al., 2011
CaH ₂ PW ₁₂ O ₄₀	H ₂ O	160	6	27.0	Tian et al., 2011
Ru/CMK-3	H ₂ O	230	24	34.2	Kobayashi et al., 2010
Fe ₃ O ₄ -SBA-SO ₃ H	H ₂ O	150	3	26.0	Lai et al., 2011
CaFe ₂ O ₄	H ₂ O	150	24	36.0	Komanoya et al., 2011
H ₃ PW ₁₂ O ₄₀	H ₂ O	180	2	50.5	Tian et al., 2010
H ₅ BW ₁₂ O ₄₀	H ₂ O	60	6	77.0	Ogasawara et al., 2011
H ₅ AW ₁₂ O ₄₀	H ₂ O	60	24	68.0	Ogasawara et al., 2011
H ₅ GalW ₁₂ O ₄₀	H ₂ O	60	24	62.0	Ogasawara et al., 2011
H ₅ CoW ₁₂ O ₄₀	H ₂ O	60	24	59.0	Ogasawara et al., 2011

In concentrated aqueous solutions, Ogasawara et al. demonstrated that the substantially negatively charged HPAs (such as H₅BW₁₂O₄₀, H₅AIW₁₂O₄₀, and H₅GalW₁₂O₄₀) could effectively facilitate the breakdown of cellulose

nanocrystals into glucose. [Ogasawara et al. 2011] Specifically, H₅BW₁₂O₄₀ demonstrated a better glucose yield (77 percent) for 48 hours in 0.7 mol/L cellulose solution at a lesser temperature (60°C), that prevented the generation of unwanted intermediates such humic compounds and dehydration compounds. Though unlike commonly used mineral acids and HPAs like H₂SO₄, HCl, H₃PW₁₂O₄₀, and H₄SiW₁₂O₄₀, its performance is significantly superior (Table 2).

No.	Acid catalysts	Concentration		Glucose yield (%)
		Anion (mol/L)	Proton (mol/L)	
1	H ₃ PW ₁₂ O ₄₀	0.70	2.1	8
2 ^a	H ₃ PW ₁₂ O ₄₀	0.60 ^b	3.5	18
3	H ₄ SiW ₁₂ O ₄₀	0.70	2.8	37
4 ^a	H ₄ SiW ₁₂ O ₄₀	0.70	3.5	61
5	H ₅ BW ₁₂ O ₄₀	0.70	3.5	77
6	H ₅ BW ₁₂ O ₄₀	0.40	2.0	4
7	H ₅ AlW ₁₂ O ₄₀	0.70	3.5	68
8	H ₅ GaW ₁₂ O ₄₀	0.70	3.5	62
9	H ₆ CoW ₁₂ O ₄₀	0.70	4.2	59
10	H ₂ SO ₄	1.75	3.5	<1
11	H ₂ SO ₄	4.5 ^c	9.0	5
12	HCl	3.5	3.5	4
13	HCl	6.0 ^c	6.0	9

^aThe proton concentration was adjusted using H₂SO₄.

^bSaturated concentration.

^cThe same as that of the H₅BW₁₂O₄₀ solution (0.7 mol/L).

Reaction conditions: crystalline cellulose (100 mg), aqueous acidic solution (2 mL), 60°C for 48 h.

[Ogasawara et al., 2011]

d. Liquid organic acid-catalyzed hydrolysis

Oxalic acid (OA), formic acid, and aryl sulfonic acid are a few organic acids with remarkably less acidity such that can depolymerize cellulose and generate oligosaccharides, total reducing sugars, or glucose. In contrary, strong fluid inorganic acids like H₂SO₄, H₃PO₄, and HPAs possess substantial catalytic activity. The hydrolysis of cellulosic materials is a crucial step in the production of sugars and biobased serve as a platform. Pre-treatment experiments in a semi-continuous plant using diluted sulfuric acid as a catalyst have been used to examine the time-dependent formation of sugars (glucose, xylose, and mannose), furfurals, and organic acids (acetic, formic, and levulinic acid) at various hydrolysis temperature changes (180, 200, and 220 °C) of one indicative of each type of lignocellulosic biomass: hardwood, softwood, and grass. The hydrolysis of cellulosic materials is a crucial step in the production of sugars and biobased serve as a platform. Pre-treatment experiments in a semi-continuous plant using diluted sulfuric acid as a catalyst have been used to examine the time-dependent formation of sugars (glucose, xylose, and mannose), furfurals, and organic acids (acetic, formic, and levulinic acid) at various hydrolysis temperature changes (180, 200, and 220 °C) of one indicative of each type of lignocellulosic biomass: hardwood, softwood, and grass. During the dilute acid pre-treatment, hemicellulose and cellulose are hydrolyzed to produce soluble sugars. In general, the hydrolysis of hemicellulose results in the production of organic acids and sugars (glucose, xylose, mannose, and galactose) (formic, acetic acid). A pentose sugar called xylose can be further dehydrated to become furfural [Lange et al., 2007]. In-depth research has been done on lignocellulosic hydrolysis utilising diluted acid solutions, which is reviewed by Steinbach et al. [Steinbach et al., 2017] and Kang et al. (2018). Additionally, hydrothermal treatment of beech wood was demonstrated in the studies of [Nitsos et al. 2013], [Kaková et al. 2013, and [Zhou et al. 2017] for *Miscanthus x giganteus*. According to [Lenihan et al. 2010], the majority of experimental experiments were carried out in batch settings, where intermediate molecules like sugars underwent numerous successive reactions. More information about the hydrolysis process can be gained by

closely examining the formation of intermediates using a semi-continuous reaction setup [Yu et al., 2010]. Woody biomass and rye straw were used for the conversion of biomass in a semi-continuous reaction setting [Matsunaga et al., 2008] and [Ingram et al., 2009]. Additionally, research on the hydrolysis of seaweed and corn stover in a continuous reactor were carried out by [Park et al. 2012] and Schell et al. [Schell et al., 2009], respectively. The operational variables used, such as reaction time or temperature, and the feedstock have a significant impact on the results.

e. Liquid hydrolysis aided by carbonic acid:

Aqua subcritical, especially when combined along with CO₂ to create carbonic acid (H₂CO₃), has recently gained attention as a potential replacement for diluted acid solutions and other biomass pre-treatment media. It is used to hydrolyze cellulose without the risks of severe corrosion, expensive separation, or the need to neutralise waste acids [Saka et al., 1999] This carbonic acid-catalyzed method is therefore eco-friendly. According to Brunner and colleagues, while depolymerizing cellulose in sub-critical water with pressurised CO₂, the yield of glucose can be greatly increased by acidifying the CO₂ in comparison to depolymerizing in pure water. [Rogalinski et al. 2008] Additionally, the faster breakdown of -1,4-glycosidic bonds aided by carbonic acid pushed the start of the synthesis of glucose to a lesser residence period (Zhou et al., 2011). For mixed hardwood and switchgrass, sugar concentrations of 185 and 149 g L⁻¹ were achieved, whilst the equivalent glucan to glucose outputs were well above 80% for both types of biomasses. Several substrates, including switchgrass and mixed hardwood, can also be effectively transformed [Rogalinski et al. 2008] [Rogalinski et al. 2008]. Another significant barrier to overcome is the insolubility of cellulose or lignocellulosic biomass. Despite appearing to be more environmentally friendly, this method proved too expensive to be used on a wide scale for the manufacturing of glucose. The above-mentioned procedures are contemporary methods for producing glucose from cellulose hydrolysis and depolymerization that are catalysed by liquid acid catalysts. Although liquid acid-catalytic processes are very effective at producing glucose, there are still a number of issues that need to be resolved in these systems, comprising product segregation, liquid acid distinction and recovery, rusting of reactor equipment, and the disposal of wastes effluent produced during acid neutralisation. So it's essential to look for environmentally friendly methods of hydrolyzing cellulose into glucose. Alternatives that are currently receiving a lot of interest for their ability to produce glucose while also resolving the aforementioned issues include solid acid catalysts. Bamboo was explored for H₂O/CO₂ hydrolysis in Sasaki and Ohsawa et al investigations in a semicontinuous (percolating) flow reactor at 9.8 MPa pressure. The study concentrated on the catalytic role of supercritical CO₂ in lignocellulosic material hydrolysis as a result of glucan and xylan degradation. We also took into account how fluid velocity affected the yield of solid products from hydrothermal processes.

2.3. The synthesis of glucose by solid acids

Relative to aqueous acid catalysts, the production of glucose from cellulosic hydrolysis process provides many advantages, including ease in catalyst/product separation, catalyst recyclability, lesser damage to the reactor, and a reduction produced in the neutralizing step. In a continuous flow fixed-bed reactor, solid acid catalysts may also be used with ease. Furthermore, catalysts exhibit a wide range of special physical or chemical properties, such as a large footprint, a unique surface structure, different channels, superior substrate adsorption, substrate association with surface functionalized groups on solid catalysts, and more. A biopolymer made of many glucose units united by -1,4-glycosidic linkages, cellulose is the primary component of lignocelluloses. Acids that break the 1,4-glycosidic linkages cause the cellulose polymers to hydrolyze, releasing the sugar molecules glucose or oligosaccharides (Figure 9). HCl and H₂SO₄ are examples of mineral acids that have been employed to hydrolyze cellulose. However, they struggle with issues such separation of materials, rusting of reactors, inadequate catalyst recycling, and the requirement for waste effluent treatment. Through the simplicity of product separation and excellent catalyst recyclability, Heterogeneous solid acids can be used to address some of these issues. This article covers current developments in the hydrolysis of cellulose by various solid acids, such as magnetic solid acids,

polymer-based acids, and sulfonated carbonaceous based acids. Effective hydrolysis processes depend heavily based on the substance's adsorption, acidity, density of the acid sites, and solid material micropores. Techniques to increase reaction efficiency are also covered, including the use of ionic salts or microwave - assisted extraction to speed up the process, as well as pre-treatment of the cellulose to reduce its crystallinity.

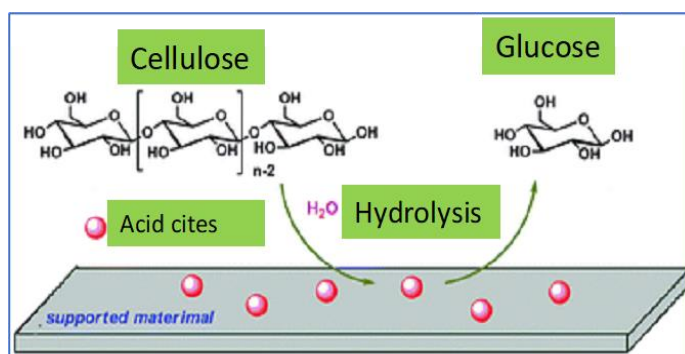


Figure 9. Cellulose hydrolysis by solid acids

More research is being done on the use of solid acids to hydrolyze cellulose into sugars. Solid acid catalysts have a number of benefits over liquid acid catalysts, including simpler product separation, greater recyclability, and reduced reactor damage. In addition, the application of solid acid catalysts can lower pollutants with negligible environmental impact. Numerous evaluations on the cellulose transformation with solid acids have been performed thus far. [Vigier et al., 2010], [Shimizu and Satsum 2011], [Guo et al., 2012], [Dhepe and Fukuoka, 2008]. We would like to summarise the most current developments in this area here.

2.3.1 Metal oxides

In addition to these solid acid catalysts with sulfonic acid groups functionalized, metal-based solid acid catalysts with large pore diameters and specific surface areas also perform admirably if cellulose or lignocellulosic biomass is hydrolyzed into saccharides (e.g., glucose). A layered transition-metal oxide of HNbMoO_6 was described by Domen's research team as having outstanding disaccharides like sucrose and cellobiose are being hydrolyzed. A form of solid catalyst with several Lewis acid sites is metal oxides. Metal oxides are always manufactured with very particular surfaces and hole diameters, making it simple for the reactants to get inside the metal oxide pores and make contact with the active sites there. These metal oxides may hydrolyze sugars like sucrose, cellobiose, and even cellulose. Transformation compounds with mesopores have been produced and used in organic chemical reactions as a type of strong solid acid. Tagusagawa and others, 2010 Mesoporous Nb-W oxide has been recently a reliable cellobiose and sucrose hydrolysis catalyst. When sucrose was hydrolyzed, glucose production and turnover frequency (TOF) were higher than they were for other solid acids (i.e. Amberlyst-15, Nb_2O_5). With the addition of W, the acid strength gradually rose until it reached the greatest reaction rate with mesoporous Nb_3W_7 oxide. The exceptional degradation activity of Nb_3W_7 oxide was credited to its strong acid sites and mesoporous structure with a large surface area. The Nb-W oxide catalyst exhibited reduced degradation efficiency of cellobiose as a result of the low Brnsted acid sites. Domen et al. reported that the concern required to be rectified with a multilayer transition-metal oxide, HNbMoO_6 , that shown Sucrose, cellobiose, starch, and cellulose hydrolysis with exceptional catalytic efficiency. [Takagaki et al., 2003]. The multilayer HNbMoO_6 catalyst had the maximum efficiency for sucrose and cellobiose breakdown, yielding glucose at a rate double that of Amberlyst-15. Strong acidity, water tolerance, and intercalation capacity were said to be the causes of HNbMoO_6 's high activity in these reactions.

2.3.2. Polymer based acids:

Many organic reactions, including hydrolysis reactions, have benefited from the use of polymer-based acids with Brnsted acid sites as efficient solid catalysts. [Uozumi et al., 2000]. Amberlyst, a type of these polymer-based acids, is composed of macroporous styrene divinylbenzene resins containing sulfonic groups. (-SO₃H). They are easily accessible, reasonably priced, and stable in the majority of solvents. These acids have macroporous architectures that let tiny molecules pass through and interact with more acidic sites. [Rinaldi et al. 2008] reported on recent ground-breaking research on Amberlyst 15DRY resin's degradation of beta-cellulose and crystalline phases cellulose. Purified cellulosic substrates were treated in 1-butyl-3-methylimidazolium chloride to increase their solubility and make the transit of cellulose chains to the acid sites a highly tedious process. ([BMIm]Cl). Cellulosic materials were hydrolyzed with Amberlyst 15DRY and then selectively transformed into sugars or cello-oligomers. The hydrolysis performances employing Amberlyst 15DRY revealed an induction duration of around 1.5 h as the reaction progressed. No induction period was given within the first 1.5 hours when soluble p-toluenesulfonic acid (p-TSA), which is similar to the acid sites of Amberlyst 15DRY, was utilised. While the process catalysed by p-TSA produced tiny sugars, HPLC examination of the reducing sugars revealed that essentially no mono- and disaccharides were formed within the first 1.5 hours. To compare the two systems, segregated cellulose preparations' outward appearance and degree of polymerization (DP) measurements were used.

2.3.3 Sulfonated carbonaceous based acids

Carbonaceous solid acids have the best catalytic activity when compared to other forms of solid acids for the hydrolysis of cellulose. These carbonaceous acids are excellent prospects for the synthesis of biofuel precursors due to their high capacity for recycling and affordable naturally occurring raw materials. The first carbonaceous acids were produced from sulfonated D-glucose/sucrose materials, according to [Hara et al. 2010] D-glucose and sucrose were first partially carbonised at low temperatures to create tiny polycyclic aromatic carbon rings. Then, they were sulfonated using sulfuric acid to create sulfonic groups(-SO₃H). They transesterified vegetable oils into biofuels using carbonaceous acids. Following their research, these new varieties of amorphous solid acids that may be utilised as degraders for the cellulose degradation reaction attracted a lot of attention. Sulfonation of incompletely carbonised natural polymers such sugars, cellulose, and starch as well as imperfect carbonization of sulfopolycyclic aromatic compounds in concentrated H₂SO₄ were used to create carbon-based solid acids. The technique of carbon material carrying -SO₃H groups from microcrystalline cellulose at 723 K over 5 h under N₂ flow was described by previous authors [Hara et al. in 2010], [Kitano et al. in 2009], and [Fukuhara et al. in 2011].

2.3.4. Hydrolysis of solid acids mediated by sulfonic groups

Among all types of acid catalysts for the production of glucose from cellulose, the sulfonated carbonaceous solid acid catalyst is an effective substitute for the liquid acid catalyst due to its lower cost, ease of production, greater reaction conditions, and high degree of adaptability. By carbonising cellulose and then sulfonating it with strong sulfuric acid, Hara and colleagues were able to create a sulfonated carbonaceous solid acid (MC-SO₃H). The materials in these solid acids were further characterised and revealed to be made of flexible polycyclic carbon sheets containing SO₃H, COOH, and phenolic hydroxyl (OH) groups. High catalytic performance for acid-catalyzed reactions resulted from the high density of these hydrophilic functional groups attached to the stretchable carbon sheets, which made the active sites more accessible to reactants in solution. At 100 °C for 3 hours, with 68% cellulose conversion, it was possible to produce 4% glucose and 64 percent soluble -1,4-glucan yields from microcrystalline cellulose. This conversion rate was higher than that catalysed by sulfuric acid (10% glucose and 38% -1,4-glucan).

By acting as a carbon source, natural lignocellulosic biomass can also be used to generate sulfonic carbonaceous solid acid on a budget. Wu et al. synthesised biomass char sulfonic acid (BC-SO₃H) from bamboo, cotton, and starch in order to investigate its function in the hydrolysis of microcrystalline cellulose into glucose [Wu et al.,

2010]. By using microwave irradiation, the rate of hydrolysis was accelerated while the reaction temperature was reduced.

3. Photocatalytic Conversion/ lignocellulosic biomass oxidation into glucose

The most prevalent monosaccharide in nature and the primary product of photosynthesis, glucose, may be selectively oxidised to produce a variety of useful compounds, including gluconic, glucaric, formic, levulinic, and lactic acids, arabinose, and erythrose [Colmenares et al., 2011]. The types of catalyst and solvent used, as well as the presence of metals, all affect how the various compounds are distributed [Navarro et al., 2005]. Despite the significant importance of this process, there aren't many studies in the literature reporting the photocatalytic glucose conversion. [Colmenares et al. 2011] carried out the reaction in water/acetonitrile mixes when commercial (Degussa P25) and synthetic TiO₂ samples were present. No intermediates were found when using pure water as the solvent, but when acetonitrile was added to the water, which stabilises the carboxylic acids via solvation limiting further oxidation, arabitol and glucaric and gluconic acid were generated. Additionally, CO₂, a product of glucose mineralization, was found in every system. When the volumetric ratio of water to acetonitrile was 1:1, the glucose conversion was 11%, and the total selectivity was 71% after 10 minutes of irradiation, the best results were obtained with the samples that were prepared at home. A growing number of academic papers have been published that discuss the photocatalysis of such as cellulose, glucose, and HMF into Valuable. But past analyses of these aspects weren't comprehensive. [Liu et al., 2019]; [Wu et al., 2020]. A timely and rigorous overview of recent developments in this field is required to encourage ongoing advancement in such a promising field. Therefore, the purpose of this study is to give an overview of the most recent advancements made in the field of selective photocatalytic transformation of carbohydrates and their derivatives. Emphasis will also be placed on problems and future perspectives in this area. The authors are hoping that by reviewing existing technology, they may design effective photocatalysts for the valuing of carbohydrates. The hydrolysis of polysaccharides like cellulose and starch yields glucose, the most common and least expensive monosaccharide in nature [Deng et al., 2014]; [Chatterjee et al., 2015]. Hexose is the term for glucose, which has six carbon atoms and can exist in both an open-chain and cyclic form. According to Han et al., TiO₂ supported Au nanoparticles were extremely effective and selective in oxidising glucose in Na₂CO₃ aqueous solution under both UV and visible light [Zhou et al., 2017]. Under visible light irradiation for 4 hours, both glucose conversion and gluconic acid production were up to 99 percent. It is intriguing that when exposed to visible and UV light, the electron creation and transport in Au NPs/TiO₂ are radically different. Under visible light, the LSPR action caused Au NPs to liberate electrons that were then injected into the TiO₂ conduction band. The oxidation of glucose was then further aided by the active superoxide radical ($\bullet\text{O}_2$) that was created when these photoactivated electrons activated O₂. Photogenerated holes were stimulated from the valence band of TiO₂ to the conduction band when UV light was shone on Au NPs/TiO₂. As reaction sites for the production of $\bullet\text{O}_2$, which oxidised the glucose into gluconic acid, Au NPs served as electron traps. Meanwhile, Na₂CO₃ suppressed reactive oxygen species with high oxidation potential, such as $\bullet\text{OH}$ and 1O_2 , resulting in a high selectivity of the desired product. In order to produce H₂ from cellulose photoreforming in water while being exposed to UV light, [Zou et al. 2018] coupled acid catalysed hydrolysis at 403 K with photocatalysis utilising Pt-TiO₂. By converting cellulose to carbohydrates (often glucose) by acid hydrolysis, cellulose serves as a sacrifice to encourage the creation of H₂. Fructose, 5-hydroxymethyl furfural (HMF), arabinose, and erythrose were other by-products of the metabolism of glucose. For the visible lightroom temperature photoreformation of cellulose, hemicellulose, and lignin to H₂ in alkaline aqueous solution, CdS/CdOx has proven to be a successful noble metal-free photocatalyst [Wakerley et al., 2017]. By biologically photocatalyzing the pre-treatment of lignocellulose in the presence of commercial TiO₂ (ST-01), Yasuda et al. [Yasuda et al., 2011] generated ethanol under UV irradiation. The photocatalyst's presence sped up the reaction time. On metal (e.g. Pt) loaded TiO₂, the initial step in creating hydrogen is photocatalysis-driven conversion of cellulose to glucose. However, even under photocatalysis, cellulose hydrolysis hardly ever happened in pure water, which unavoidably limits the conversion of cellulose due to the tight pH requirement. The first report on a simple and incredibly effective one-pot technique that combines acid hydrolysis and photocatalysis to address issues with cellulosic biomass conversion. In particular, photocatalytic reformation of cellulose to hydrogen was made possible

by conversion of cellulose in 0.6 M sulfuric acid solution at 403 K in the presence of a photocatalyst (such as platinumized TiO₂). Since the produced carbohydrates are particularly efficient, in situ creation of electron donors from direct cellulose conversion promotes the production of photocatalytic H₂. Photocatalytic conversion of glucose.

4. Conclusions and Perspectives

This review article, which has more than 100 references, gives a thorough overview of the potential for catalytic conversion of lignocellulosic biomass into chemicals and fuels. Numerous conversion paths to create value-added products are investigated on the basis of structural characteristics of the main lignocellulosic biomass portions. The entire chemical transformation process, from pretreatment through depolymerization and downstream transformation, significantly depends on catalytic conditions. Improved compound quality, reduced reaction times and temperatures, faster reaction rates, and more specificity for byproducts are the main advantages of using a catalytic process. Physicochemical, chemical, and biological pretreatments can help separate the components of lignocellulosic biomass. After being degraded into sugars by acids, enzymes, or autocatalysis, cellulose and hemicellulose are transformed into a variety of oxygen-containing, C₂ to C₆ platform compounds. More than 60% of lignocellulosic biomass is made up of carbohydrates, including cellulose and hemicellulose, making them the most prevalent natural source of renewable carbon. Photocatalysis is a "dream reaction" due to the unique photogenerated reactive species (such as h⁺, e⁻, •OH, •O₂, and 1O₂), as the source of energy, plentiful and unrestricted solar light, and moderate reaction conditions. It is a novel but well-established idea to use solar energy to selectively photocatalyze celluloses into significant compounds and fuels at room temperature and atmospheric pressure that may have benefits from an energy and environmental standpoint, such as lowering our reliance on fossil fuels and reducing our carbon footprint. It is safe to assume that biofuels will soon overtake fine chemicals as the most significant component of the world energy market, despite the fact that output of both is still modest and far from meeting societal demands. Despite the significant efforts made in this area, Organic matter photocatalytic transition is still in its infancy, and lags behind in terms of cost and efficiency. The fact that there haven't been many researches including photocatalytic hemicellulose, as far as we know, is what surprises us the most. To attain industrial applications, there is still a very long and difficult road to go. Recent developments on the catalytic synthesis of glucose from carbohydrates and their derivatives have been succinctly presented in this review. Even if the majority of the transformation techniques used today are technically and conceptually feasible, they are not cost-effective. But because of these helpful studies, a more positive future that includes biomass-based technologies is now more likely to come to pass.

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