International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843, Print ISSN: 2523-6075
Received: 01-08-2023, Accepted: 16-08-2023, Published: 02-09-2023
Volume 7, Issue 2, 2023, Page No. 5-9

Lignocellulose: A promising future resource for platform chemicals

Asawari Mokal
Assistant Professor, Department of Chemistry, Ramniranjan Jhunjhunwala College, Ghatkopar, Mumbai, Maharashtra, India

Abstract
Petroleum-based resources are employed to produce energy, chemicals, and industrial polymers in today's consumer driven society for technological development. However, the future is alarming due to the limited supply of oil reserves, global warming, and environmental regulations. The alternative is to find indigenous as well as sustainable feedstock. Since biomass-based materials are less affected by changing crude oil prices. Lignocellulosic biomass is a promising option for future renewable fuels. It is high in organic carbon content. This rich source of carbon can be utilized to make liquid fuels and chemicals. The low cost & easily available lignocellulosic wastes can be used to prepare platform chemicals or renewable monomers required for polymer production. This can in turn reduce dependency on the oil-field industry and the production cost of biopolymers due to the resource efficiency. This article discusses the structure and composition of lignocellulosic biomass, generic technologies used in the lignocellulose-based biorefinery, and conversion of lignocellulose to major platform chemicals or bio-based monomers. The article also includes a general overview of the potential platform chemicals or value-added products, which have various industrial applications.

Keywords: Biomass, biorefinery, lignocellulose, renewable, value-added chemicals

Introduction

A major part of the Indian economy is still based on the agricultural sector. Fiscal policy statements emphasize that the Indian agriculture sector is expected to grow by 3.5% in the financial year 2022-23. India has become self-reliant and rapidly emerged as an exporter of agricultural products, having exported a gigantic $50.2 Bn of agriculture-based products in FY 2022-23. India is the world's largest sugar-producing country, holding the second position in rice production after China. India is among the three largest wheat-producing countries in the world. with a share of around 14.14 per cent of the world's total production in 2020 [1].

With its mammoth agricultural production, about 500 million tons (MT) of crop residues are generated out of the total agricultural produce annually. This leads to major problems like the accumulation or disposal of residual plant biomass after harvesting. This lignocellulosic agro-waste cannot be simply discarded into the environment since it can lead to pollution of soil & water reservoirs. Although a part of it is used as fuel & animal fodder, majority of it remains underutilized. This surplus lignocellulosic biomass is an indigenous, renewable, and promising source of chemicals and fuels without competing with food industries such as starch & vegetable oils. Since the biomass-based economy is sustainable and carbon neutral, switching to a biomass-based economy is a feasible option with the support of government incentives, corporate sustainability objectives, and effective waste recycling.

Biorefinery

Biorefineries offer environmentally sustainable solutions to the waste biomass. A biorefinery, similar to a petroleum refinery, convert biomass to energy, fuel, chemicals and other beneficial byproducts, by integrating biological and/or chemical conversion processes. Based on the type of products, biorefineries can be classified into two platforms, energy-based or material-based. In energy-based platforms, biomass is used mainly for production of biofuels, heat, and electricity. In a material-based platform, chemicals and biomaterials are produced. Biorefinery, based on utilization of lignocellulosic material, aims to focus on enzyme mediated hydrolysis to release soluble and fermentable sugars. The major driving force for the initiation of biorefineries is the optimum utilization of vegetable biomass. Biomass includes starch and sugar-based sources, crop wastes, forestry residues, woody energy crops, industrial and municipal organic waste, urban wood, and food waste.

Biomass

Biomass is classified into two categories *viz*. first generation and second generation. The former involves renewable biomass, for example, corn starch, sugar cane, and sugar beet, which are not perceived as sustainable options in the long term as they, directly, or indirectly, compete with food production. In contrast, the use of second-generation renewable biomass, in the form of waste polysaccharides, such as lignocellulose [2] (plant dry matter from agricultural, and_forestry residues) and municipal food waste [3], is perceived as a sustainable long-term option for producing biofuels and commodity chemicals. Lignocellulosic biomass [4] with a production of approximately 1000 million tons per annum worldwide, is a natural, inexpensive, and renewable raw material. It is the most promising source as it includes agricultural wastes (corn stover, wheat straw) and forest waste (woody residues) [5].

Table: 1 shows the chemical composition of different biomass.

Biomass Type	% Cellulose	% Hemicellulose	% Lignin
Sugarcane straw	40-44	30-32	22-25
Sugarcane bagasse	32-48	19-24	23-32
Hard and soft wood	40-47	25-35	16-30
Corn cob	45	35	15
Wheat straw	30	50	15
Rice straw	43.3	26.4	16.3
Banana fiber	60-65	6-8	5-10
Lignocellulosic Biomass	30-50/35-50	20-40/20-35	10-30/10-225

Composition of lignocellulose

It refers to plant dry matter and is composed of two types of carbohydrate polymers, 1) cellulose, hemicellulose 2) aromatic rich polymer called lignin. Cellulose, the most abundant, is a polymer made up of linear chain of hundreds to thousands of D-glucose molecules, called polysaccharides. Cellulose on hydrolysis yields the monomer, glucose. Glucose is the most important source for a variety of chemicals. Cellulose is attached to hemicellulose via hydrogen bonding. Hemicellulose is a heterogeneous polymer, composed of varying proportions of C_5 sugars, like xylose, arabinose, and C_6 sugars like mannose, galactose, and glucose. Hemicellulose has high solubility in water compared to cellulose and hence readily hydrolyzes to the corresponding monomer sugars C_5 sugars. Lignin is an extremely complex, hydrophobic, phenolic polymer consisting of three aromatic subunits – coniferyl, sinapyl and, p-coumaryl alcohols which form a protective sheath around cellulose causing difficulty in hydrolysis and isolation of cellulose.

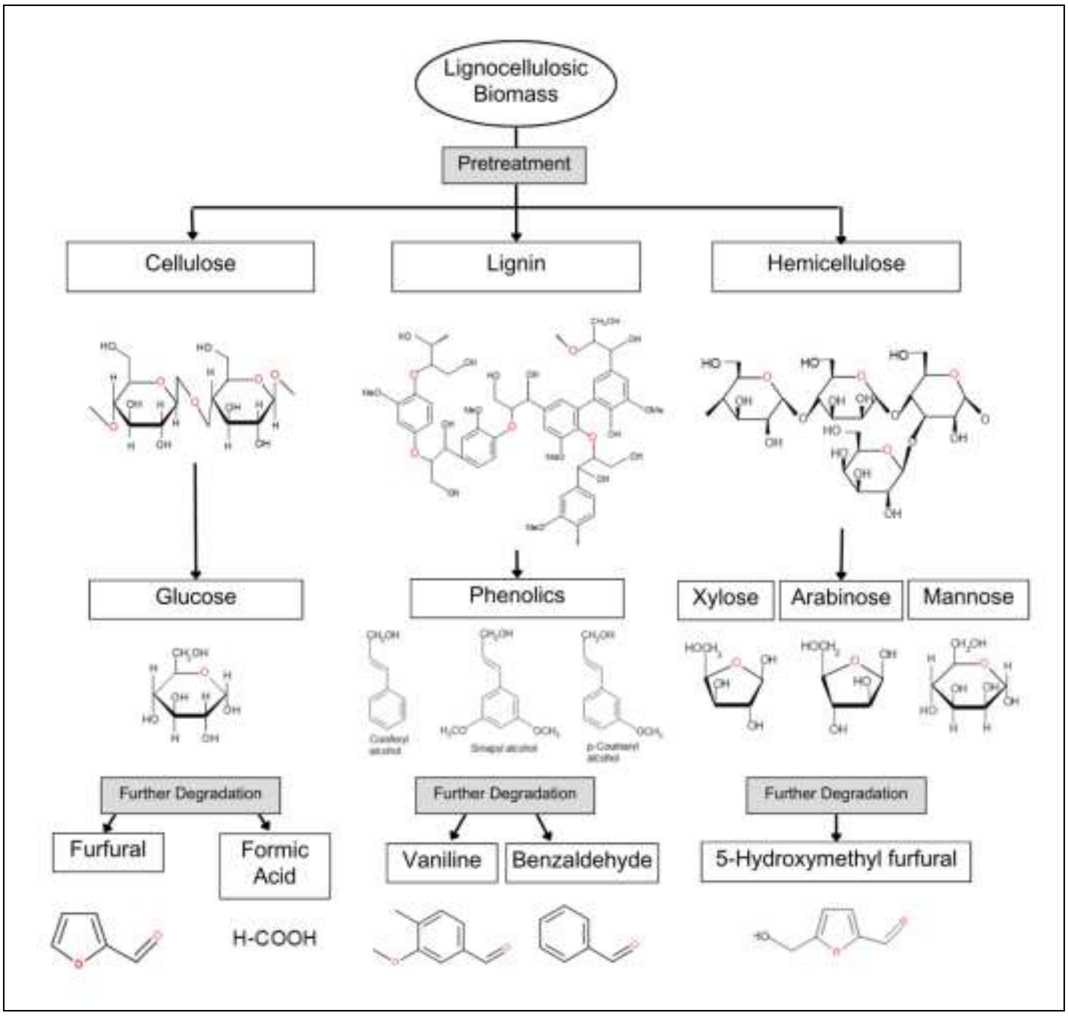

Fig 1: Pretreatment and hydrolysis of lignocellulose to commodity chemicals

In a biorefinery, lignocellulosic biomass is converted into platform chemicals. Prior to this, pretreatment is required to break the cell wall structure and make it amenable to enzyme action. Pretreatment [7] involves hydrolysis and fermentation. Acids and enzymes are employed for hydrolysis and fermentation is carried out using bacteria or yeast. During pretreatment, [8] carbohydrates shielded by naturally resistant lignin are disrupted so that cellulose and hemicellulose are accessible to enzyme action and the rate of hydrolysis increases. A high yield of fermentable sugars can be achieved by pretreatment. The C_5 and C_6 sugars sugar produced undergo chemical transformations such as isomerization fermentation, hydrogenation, and dehydration to obtain desired platform chemicals Fig.**2.**

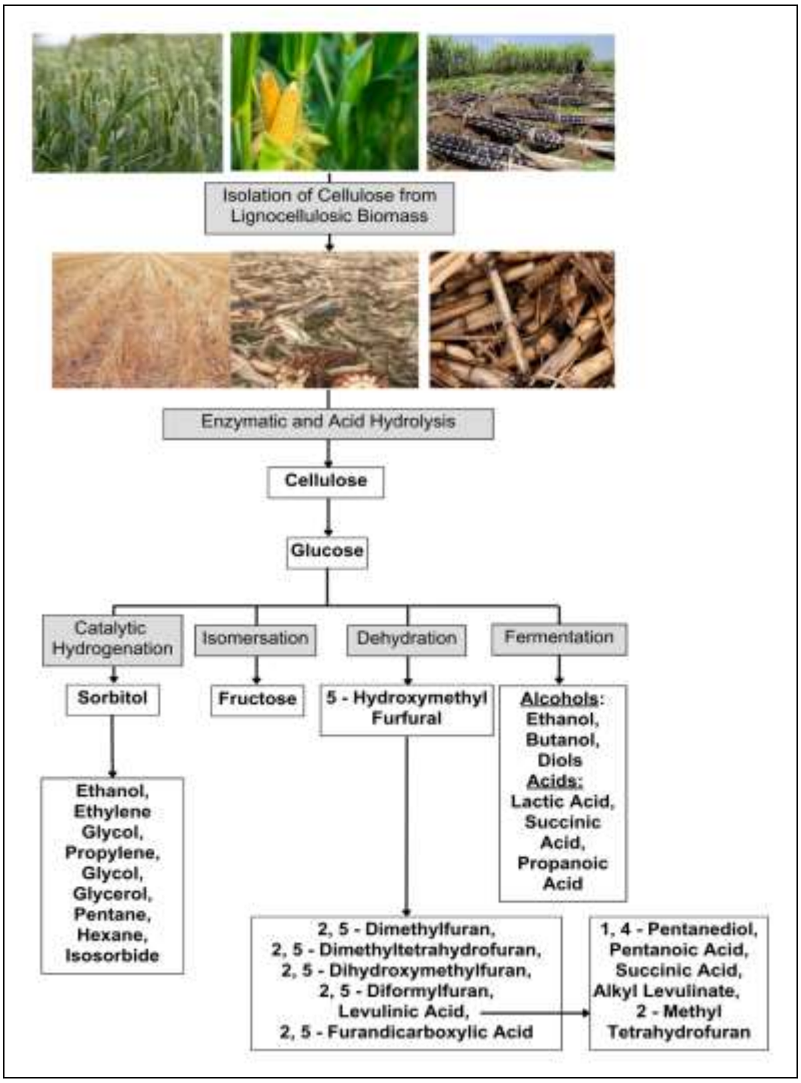

Fig 2: Conversion of sugars to commodity Chemicals[9]

According to the biofuelsdigest.com [10], the DOE updated the Platform Chemical List[11] which includes ethanol, furfural, hydroxymethylfurfural, 2,5-furandicarboxylic acid, glycerol, isoprene, succinic acid, 3-hydroxypropionic acid/aldehyde, levulinic acid, lactic acid, sorbitol, and xylitol. All these identified platform chemicals [12] can be produced from biomass-derived carbohydrate sources.

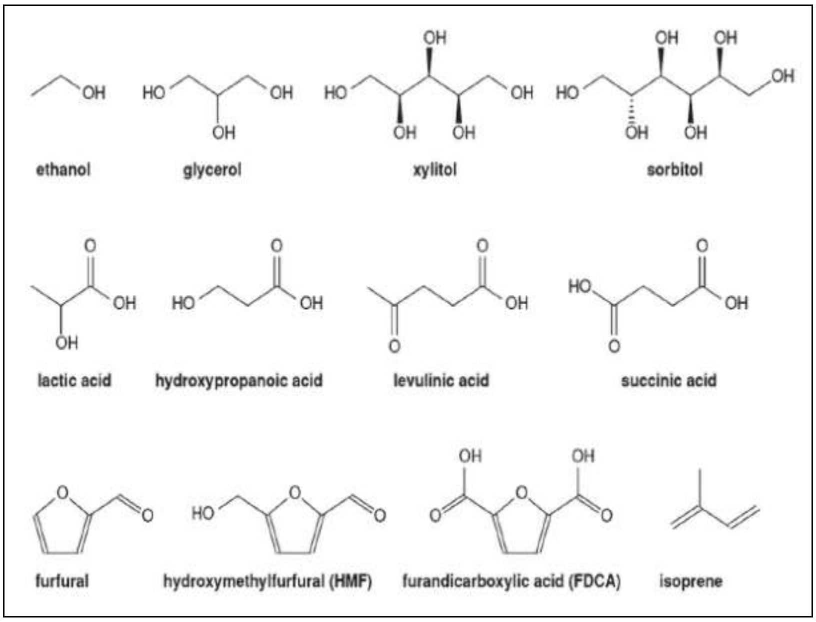

Fig 3: Bio-based monomers /platform chemicals derived from cellulose [10].

Brief Overview of platform chemicals/ Bio-based monomers

Ethanol

Most of it is used as green fuel additive to petrol. The rest of it serves as a renewable source to produce ethylene, propylene, and butadiene, which on polymerization give polyethylene, polypropylene, polybutadiene, polyethylene terphalate, and polyvinyl chloride. It can be easily converted to a variety of chemical compounds.

Glycerin produced from biomass can replace synthetic glycerin from propene. Glycerin is also widely used as a sweetener in the food industry and as a humectant in food and personal care products. glycerol can be converted to synthetic monomers, such as acrolein and epichlorohydrin [13].

Furfural

Furfural is a heterocyclic aldehyde, produced by the dehydration of xylose, a C5 sugar, primarily found in the hemicellulose fraction of lignocellulosic biomass. Furfural is not produced from fossil feedstocks and has extensive applications in biopolymers, pharmaceutical and agrochemical industries, and adhesives [14].

Isoprene

Isoprene is the monomer for the manufacture of polyisoprene polymer, which is used in rubber tires, footwear, medical appliances, sports goods, styrene co-polymers, etc. At present, all commercially available isoprene is derived from petroleum. Bio-based isoprene, produced by aerobic bioconversion of carbohydrates, is identical to petroleum-based isoprene [15].

Lactic Acid

Lactic acid is one of the most common alpha-hydroxy carboxylic acid found in nature. Commercially it is produced by microbial fermentation of sugars. Due to the presence of hydroxyl and carboxylic functional groups, it can be transformed into various chemical compounds and products. Lactic acid is used widely in food, pharmaceuticals, personal care products, industrial uses, and polymers. It's a biodegradable polymer, most popular in food packaging, disposable tableware, shrink wrap, 3-D printers, etc.

Succinic Acid

Succinic acid is a dicarboxylic acid that can be produced from petroleum or biomass. The biomass-derived succinic acid can be used to prepare bio-renewable polyester copolymer of succinic acid and 1, 4-butanediol [16]. It can be one of the possible precursors for commodity chemicals, polymers, and surfactants.

Xylitol

Xylitol is a naturally occurring C_5 sugar alcohol, which is 20 times sweeter than sucrose, but with 40% the calories [17]. In addition, the metabolism and assimilation of xylitol, is not dependent on insulin; thus, it is an ideal sugar substitute for people with diabetes [18]. Industrially, it is produced from xylose obtained from hemicellulose. Xylose on catalytic hydrogenation gives xylitol.

Levulinic Acid

Levulinic acid is produced in high yield by the acid-catalyzed hydrolysis of C_6 sugars [19]. It acts as a building block in many applications such as pharmaceuticals, plasticizers, fragrances, and cosmetics. Levulinic acid also has the potential for substituting petroleum-based chemicals. In addition, it can also be converted into various higher value-added products [20] such as levulinic acid esters, 5-aminolevulinic acid, valeric acid, γ-valerolactone, and 2-methyltetrahydrofuran.

Biorefineries in India

During the COP26, Union Minister of Science & Technology, Jitendra Singh, announced the launch of the mission "Integrated Biorefineries", an international collaboration to develop clean energy solutions under Mission Innovation Initiative [13].

Ethanol-blended petrol is the most preferred fuel blend. India aims to sell only E20, (Petrol blended with 20 percent ethanol) petrol from 2025. Until recently molasses and broken grains were used for production of ethanol competing with food vs fuel. Second generation (2G) bioethanol production technology processes agricultural lignocellulosic waste for its conversion to ethanol. Twelve commercial plants and ten demonstration plants of 2G biorefineries **(**2G technology can process agricultural waste such as rice straw, wheat straw, cotton stalk, corn cobs, and corn stover**)** have already been proposed to be built under the Pradhan Mantri JI-VAN (Jaiv Indhan-Vatavaran Anukool Fasal Awashesh Nivaran) Yojana in regions with adequate biomass supply. The scheme has sanctioned financial support of Rs 1,969.50 crores to commercialize this 2G bioethanol technology. On World Biofuel Day, August 10, Asia's first 2G ethanol biorefinery, built by a central public sector undertaking Indian Oil Corporation Ltd, was unveiled by honorable Prime Minister Narendra Modi in Panipat, Haryana.

Conclusion

These establishments/projects show India's initiative to explore biomass as an alternative to fossil-based fuels & sustainable economy. The integrated biorefineries have the capacity to produce bulk and fine chemicals in a robust, self-sufficient, and environmentally safe manner. Advanced technologies can recycle rich carbon resources from abundant lignocellulose waste to accommodate the needs of industries. This will serve the purpose of circular carbon economy instead of burning biomass, to reduce emission of greenhouse gases, health hazards, loss of biodiversity & soil fertility. The increased bioethanol production can be converted into a variety of chemicals via advanced catalytic processes [22]. Though there are still challenges that need further investigations, the future is promising, as the Indian government is aiming to this green push, through various domestic and international initiatives in coming years.

References

1. Ministry of Agriculture & Farmers Welfare Achieving Aatmanirbharta in Agriculture Posted On: 11 NOV 2022 https://pib.gov.in/FeaturesDeatils.aspx?NoteId=151185&ModuleId%20=%202
2. Liguori R, Faraco V, Biological processes for advancing lignocellulosic waste biorefinery by

advocating circular economy *Bioresour. Technol*.,2016:215:13-20.

3. Dahiya S, A Naresh, Kumar A, J Shanthi Sravan, Chatterjee S, Sarkar O S, Venkata Mohan S, Food waste biorefinery: Sustainable strategy for circular bioeconomy, Bioresource Technology,2018:248:2-12.
4. Sheldon R, Catalytic Oxidations in a Bio-Based Economy**.** Front. Chem.,2020:8(132):1-14.
5. Mülhaupt R, Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality Macromolecular Chemistry and Physics,2013:214(2):159-174.
6. Kaur R, Kaur P, Chemical valorization of cellulose from lignocellulosic biomass: A step towards sustainable development Cellulose Chem. Technol.,2021:55(3-4):207-222.
7. Binod P, Pandey A. *Introduction: Pretreatment of Biomass*, Processes and technologies,1st Edition, Sept, 2014, 3-6.
8. Hassan GA Williams, Jaiswal A, Emerging technologies for the pretreatment of lignocellulosic biomass., Bioresource Technology,2018: 262:310-318.
9. Kaur R, Kaur P, Chemical valorization of cellulose from lignocellulosic biomass: A step towards sustainable development Cellulose Chem.Technol,2021:55(3-4):207-222.
10. Jong D, Proposed biobased platform molecules/monomers. Biorefinery Concepts in Comparison to Petrochemical Refineries. Industrial Biorefineries & White Biotechnology. 2015, Page19.
11. Biddy M, Scarlata C, Kinchin C, Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential National Renewable Energy Laboratory Technical Report, NREL/TP-5100-65509 March 2016
12. Lane J, *biofuelsdigest.com* April 30,2015, In 2010
13. Yu B, "Glycerol". *Synlett*,2014:25(4):601-602.
14. Mamman *et al*. "Furfural: Hemicellulose/xylose derived biochemical." *Biofuels, Bioproducts and Biorefining*, Vol 2, No-5,2008, Pages 438-454.
15. Whited *et al*. Technology update: development of a gas-phase bioprocess for isoprene monomer production using metabolic pathway engineering. *Ind Biotechnol*,2010:5(4):152-163.
16. Adkins J, Pugh S, McKenna R, Nielsen DR, Engineering microbial chemical factories to produce renewable biomonomers. *Front. Microbiol*,2012:3:313.
17. Lugani Y, Oberoi S, Sooch B. Xylitol: a sugar substitute for patients of diabetes mellitus. *World J Pharm Pharm Sci*,23017:6:741-749.
18. Ur-Rehman S, Mushtaq Z, Zahoor T, Jamil A, Murtaza M. "Xylitol: A review on bio-production, application, health benefits, and related safety issues". Critical Reviews in Food Science and Nutrition,2015:55(11):1514-1528.
19. Takkellapati S, Tao L, Michael A, Gonzalez. An overview of biorefnery-derived platform chemicals from a cellulose and hemicellulose biorefnery, Clean Technologies and Environmental Policy,2018:20:1615-1630.
20. Pileidis F, Titirici M, Levulinic acid biorefineries: New challenges for efficient utilization of biomass. Chem Sus Chem,2016:6:562-582.
21. Jain Rahul, India's green push for second-generation bioethanol https://www.downtoearth.org.in/blog/energy/india-s-green-push-for-second-generation-bioethanol-85472 published: Friday 14 October 2022
22. Phung TK, Busca G. Selective Bioethanol Conversion to Chemicals and Fuels via Advanced Catalytic Approaches. In: Nanda S, N. Vo, DV, Sarangi, P. (eds) Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals. Springer, Singapore01 April 2020, https://doi.org/10.1007/978-981-15-1804-1_4, assessed on 22nd May 2023.