

“Green” Chemicals from Renewable Sources: A Mini Review

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ABSTRACT: The emerging field of interest around the world is “Utilization of Renewable Resources”. The advantages, such as their abundance and sustainability and rising oil prices with the negative effects of petroleum on the environment increased the demand of Renewable Sources. There is a growing interest in the replacement of fossil-based chemicals with biochemicals. The most popular feedstocks for commodity and specialty chemicals are carbohydrates, oils and fats of plant origin as they account for approximately 95% of the biomass produced annually. Production of green chemicals from renewable resources is a very broad topic. Herein, an introduction toward possible conversion pathways and products is discussed. In long- term, biochemicals will share markets with petroleum-based chemicals and ultimately replace them as biochemicals become price competitive.

KEY WORDS: Renewable sources, Green Chemicals, Conversion Pathways

I. INTRODUCTION

The emerging field of interest around the world is “Utilization of Renewable Resources.” Biomass, one of the important type of “Renewable Resources” refer to any material having recent biological origin, including plant materials, agricultural crops, and even animal manure that is available on a recurring basis [1]. It comprises of C, H, O and N, a composition similar to fossil feedstock which has C and H [2]. Among these sources Lignocellulosic materials can be the starting raw materials for a lot of valuable chemicals. Besides this oils and fats of vegetable and animal origin are important renewable raw materials for many “green” lubricants, surfactants, and resins. There is huge potential for bio-based chemicals to share markets with their fossil based counterparts. The applications of new and advanced technologies in chemical processing can provide new opportunities for the conversion of these enormous natural resources.

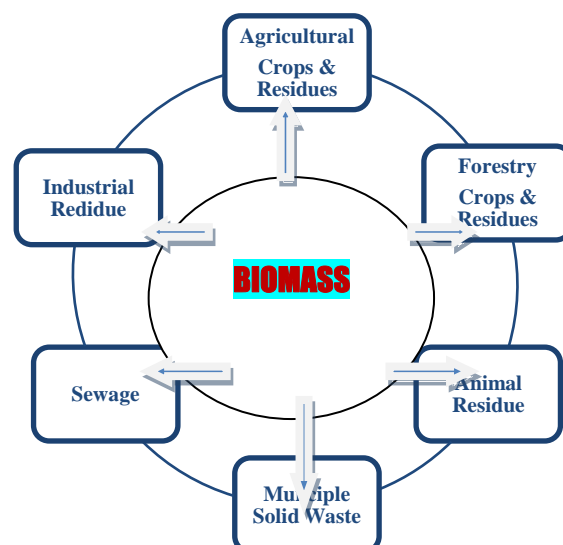


Figure 1. Sources of biomass

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II. METHODS

Chemical conversion - It refer to processes which directly convert biomass to chemicals at high temperature and pressure and in the presence of a catalyst. Eg. gasification, combustion and co-firing,etc. Many efforts have been made to design innovative alternative pathways to effectively convert biomass to chemicals. One area of research has focused on improving the efficiency of catalysts. Hydrothermal processing, using supercritical water as a reaction medium is the most promising for the conversion of biomass.

Biological conversions - It involves the utilization of biological enzymes or living organisms to catalyze the conversion of biomass into specialty and commodity chemicals. Use of yeast and bacterial fermentation processes are very old & Common,Genetic engineering & Recombinant DNA technology are the newer technologies.

Thermal conversion-It refer mainly to the pyrolysis i.e. breaking of molecule at high temperature in the absence of air/oxygen, it is a slow, irreversible, decomposition process used to obtain solid fuel like charcoal but to obtain liquid fuels pyrolysis is performed at moderate temperature with fast heating rate. Out of the wide range of the available biomass herein Lignocellulosic biomass is taken into consideration in detail.

III. LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass is a major source of non-edible carbohydrate which can be used for the synthesis of fuels and chemicals. Most agricultural and forest-derived biomass resources such as crop residues, wood and wood wastes are lignocellulosic biomass. It consists of cellulose (40–50%), hemicellulose (20–40%) and lignin (20–30%)[3].

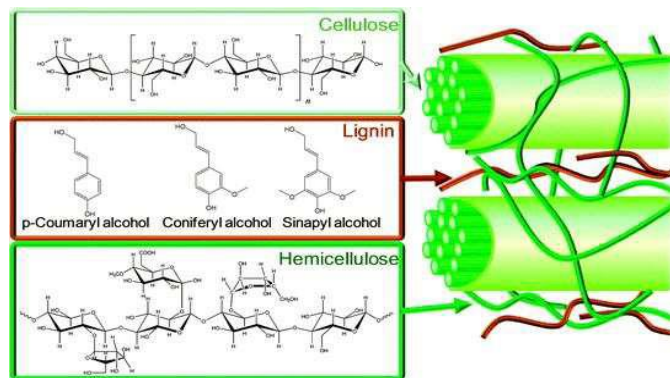


Figure .2 Components and structure of Lignocellulosic biomass [4]

Cellulose

Cellulose is a long, natural, linear homopolymer, consisting of long straight chains of six carbon sugar glucose, which are connected together end-to-end through β 1-4 glycosidic bonds, The molecular formula of cellulose is $(C_6H_{12}O_6)_n$; where n is an indication of the degree of polymerization and can range from several thousands to tens of thousands, The structure of cellulose is as shown in Figure 3.

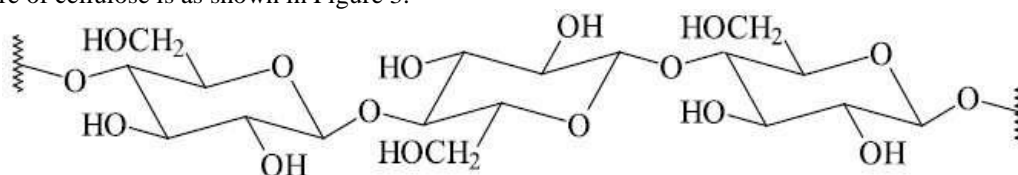


Fig. 3 Structure of cellulose

It has a highly microcrystalline structure and extensive intermolecular hydrogen bonding; therefore it is very hard to break the interconnections in the cellulose molecule. Cellulose is insoluble in water, but it absorbs 8-14% water under

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normal atmospheric conditions (20°C, 60% relative humidity) [5,6]. The solubility of cellulose increases with temperature. Cellulose is soluble in water at temperatures higher than 317°C[3]. This is because at higher temperatures, more energy is generated which breaks the hydrogen bonds between the cellulose molecules. However, at temperature of 180°C, cellulose starts to decompose[6]. The extensive hydrogen bonding between cellulose molecules and chains contributes greatly to the water-insoluble nature of cellulose[5,7].

Hemicellulose

Hemicellulose is a two-dimensional heteropolysaccharide which comprises of C-5 and C-6 monosaccharide sugars with short branched side connections [5,8]. Hemicellulose contains different kinds of sugar monomers such as xylose, mannose, galactose, glucose, rhamnose, arabinose [5,9]. The predominant sugar monomer found in hemicelluloses sugar is xylose[8]. Xylan has also been described as the most common type of polymers belonging to the hemicelluloses family of polysaccharides [6]. Hemicellulose also contains acetyl groups attached to the polymer chain, and its composition and structure vary, depending on their source and the extraction method[6]. Hemicelluloses have a degree of polymerization of 50 to 200 (much less than that of cellulose), thus they break down more easily than cellulose and many are soluble in alkaline solutions[9]. At low temperatures, hemicellulose is insoluble in water, but at elevated temperatures it becomes soluble [6].

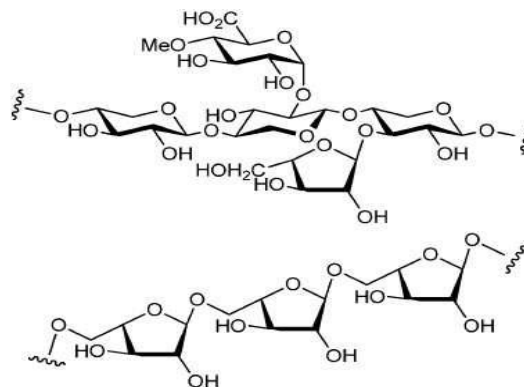


Figure 4. Hemicellulose top: glucuronoarabinoxylan, bottom: arabinan[3]

Lignin

Lignin is an amorphous, three-dimensional, non-carbohydrate heteropolymer. The main building blocks of lignin are phenylpropane units (figure 5), which form a complex and cross-linked aromatic structure [5,6].

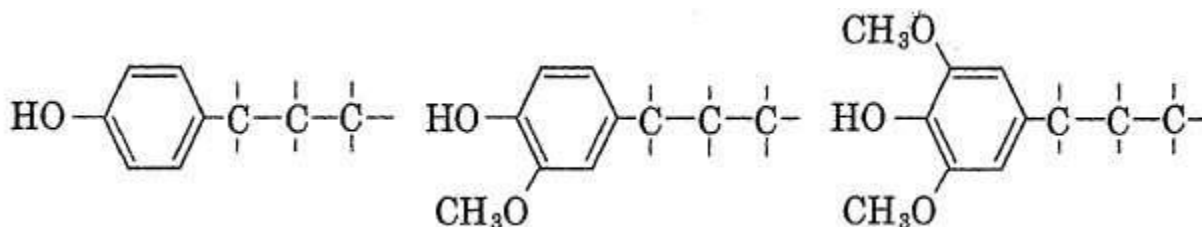


Figure 5. Main building blocks of lignin

The phenylpropane units are mainly methoxylated phenylpropylene alcohols[8], and they are linked by various types of linkages. The most common alcohols found in lignin are; p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 6.) [6,7]. The structures of the alcohols are shown in –

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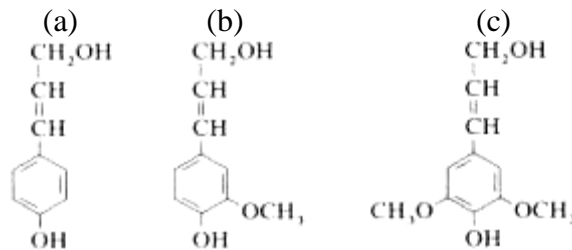


Figure 6(a) P-coumaryl (b)coniferyl (c) sinapyl alcohol

The exact composition of lignin depends on the source. Lignin from gymnosperms [8] (softwood, conifers, and needle trees) consists primarily of a product derived from the enzyme-mediated dehydrogenative polymerization of coniferyl alcohol, while the lignin from angiosperms is primarily a derivative of a mixture of coniferyl and sinapyl alcohol [6,8]. Coniferyl alcohol units account for more than 90% of softwood lignin, while the remaining is mainly p-coumaryl alcohol units [6]. Lignin from hardwood contains more sinapyl-derived units, and less coniferyl alcohol than softwood lignin [7]. Complete hydrolysis of the cellulose fraction in lignocellulosic biomass yields glucose, while complete hydrolysis of the hemicelluloses fraction yields pentoses (xylose and arabinose) and hexoses (glucose, galactose and mannose) [4]. The pentoses and hexoses hydrolyzed from the cellulose and hemicelluloses fractions are conveniently used for the production of various fuels and chemicals such as ethanol, butanol, hydrogen, methane, liquid alkanes, 5-hydroxymethyl furfural (5-HMF) and 2,5-dimethylfuran [5]. There are three major routes for the production of fuels and chemicals from Lignocellulosic biomass, and they include; Sugar or de-polymerization routes, Syn-gas routes, and Bio-oil routes [10,11]

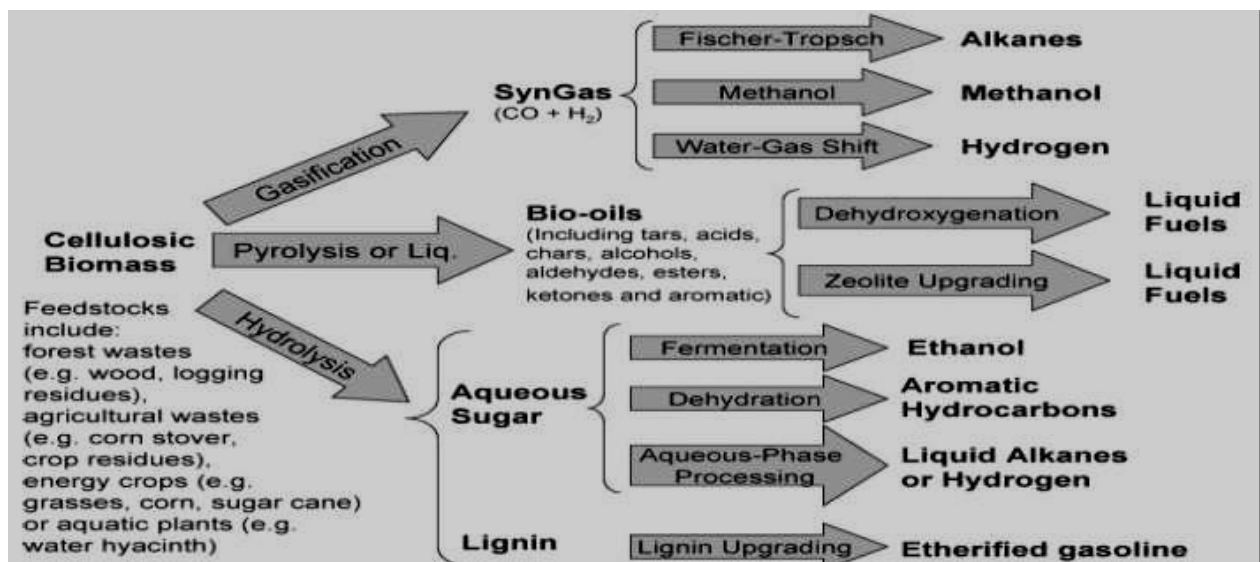


Figure 7. production of fuels from lignocellulosic biomass [10]

To obtain Various above products from lignocellulosic biomass, Pretreatment Step is the most essential & Crucial step which alters the crystalline structure of cellulosic biomass, by removing lignin and solubilizing hemicelluloses into hexoses and pentoses [5,6]. For the purpose of pretreatment, various physical, chemical, physico-chemical, and biological methods are available. The choice of a particular pretreatment method depends on the target component in the lignocellulosic biomass.

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IV. GREEN CHEMICALS FROM BIOMASS

The products listed here represent only a small portion of the biochemicals made by different research groups[12].

- Aspartic Acid
- 1,4 Diacids
- 2,5-furan dicarboxylic acid(FDA)
- Glucaric acid
- Glutamic acid
- Glycerol
- 5-hydroxymethyl furfural (5-HMF)
- 3-Hydroxypropionic acid
- 3-Hydroxy-butyrolactone
- Itaconic acid
- Levulinic acid
- Sorbitol
- Xylitol

V. CONCLUSION

The fossil fuel crisis and environmental concerns have opened newer ways for chemicals production from biomass. Further, low cost and sustainability, together with chemical compositions similar as fossil feedstocks, render biomass a promising raw material for production of biochemicals. Biorefineries, heterogeneous catalysis and genetic engineering are the main technologies which can develop new pathways for the production of green chemicals from biomass.

REFERENCES

- [1]. M.Crocker, C. Crofcheck, Biomass conversion to liquid fuels and chemicals, *Energieia*, vol.17, no.6, pp. 1-3, 2006.
- [2]. H.C.James, and I. D. Fabien, Introduction to chemical from biomass, John Wiley and Sons, United Kingdom, 2008.
- [3]. Hirokazu Kobayashi, Hidetoshi Ohta, Atsushi Fukuoka, Conversion of Lignocellulose into Renewable Chemicals by Heterogenous Catalysis, *Catalysis Science and Technology*, Volume 2, pp.869-883, 2012.
- [4]. David Martin Alonso, Stephanie G. Wettstein, James A. Dumesic, Bimetallic Catalysts for Upgrading of Biomass to Fuels and Chemicals. *Chemical Society Reviews*, vol.41, issue 24, pp.8075-8098, 2012.
- [5]. Feng Guo, Zhen Fang, C. Charles Xu, Richard L. Smith Jr, Solid Acid Mediated Hydrolysis of Biomass for Producing Biofuels, *Progress in Energy and Combustion Science*, vol.38, issue 5, pp.672-690, 2012.
- [6]. Paulinen Harmsen, Wouter Huijgen, Laura Bermudez, Robert Bakker, Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass, Wageningen: s.n. 2010.
- [7]. Anne Belinda Bjerre, Anette Skammelsen Schmidt, Development of Chemical and Biological Processes for Production of Bioethanol: Optimization of Wet oxidation Processes and Characterization of Products, RISO, 1997.
- [8]. Liu Shijie, Woody Biomass: Niche Position as a Source of Sustainable Renewable Chemicals and Energy and Kinetics of Hot-water Extraction/Hydrolysis. *Biotechnology Advances*, Volume 28, pp. 563-582, 2010.
- [9]. Yokohama et al., The Asian Biomass Handbook: A guide for Biomass Production and Utilization, The Japan Institute of Technology, Japan, 2008.
- [10]. George W. Huber, Sara Iborra, and Avelino Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.*, Volume 106, pp.4044- 4098, 2006.
- [11]. P. Shishir, S. Chundawat, T.Gregg, Beckham, E. Michael Himmel, E. Bruce Dale, Deconstruction of Lignocellulosic Biomass to Fuels and Chemicals, *The Annual Review of Chemical and Biomolecular Engineering*, Volume 2, pp.121-145, 2011.
- [12]. T. Werypy, G. Petersen, A. Aden, et Top value added chemicals from biomass. 2004, Volume 1: result of screening for potential candidates from sugar and synthesis gas.