

DOI:
10.22301/IJHMCR.2528-3189.1214

Article can be accessed online on:
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ORIGINAL ARTICLE

**INTERNATIONAL JOURNAL
OF HEALTH MEDICINE AND
CURRENT RESEARCH**

BIO-BASED CHEMICALS AND POLYMERS FROM BIOMASS OR BIOWASTE

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ARTICLE INFO

Article History:

Received 24th Dec, 2018

Received in revised form

22th Jan, 2019

Accepted 25th Feb, 2019

Published online 31st Mar, 2019

Key words:

Cellulose, lignocellulose,
biopolymers, fine chemicals,
biodegradable, biofuels, ionic
liquids.

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ABSTRACT

Biomass is one of the important renewable sources for securing future energy supply, production of fine chemicals, and high value biodegradable polymers, and sustainable development. Current biomass resources comprise primarily industrial waste materials such as sawdust or pulp process wastes, hog fuel, forest residues, clean wood waste from landfills, and agricultural prunings and residues from plants such as lignocellulosic materials. Recently, efforts have been devoted to the conversion of lignocellulosic materials into fine chemicals, biopolymers, and biofuels. There has been considerable interest in the use and optimization of biodegradable polymers as an alternative to conventional synthetic polymers / plastics and other applications such as packaging, medical, agriculture, pharmaceutical, cosmetics, adhesives, lubricants, textiles, electronics, high-strength structural materials, and biomedical applications. Uttarakhand is bestowed with rich and diverse vegetation. The wide topographical variations and excellent climatic condition have gifted the state with unique and varied species of medicinal plants. The plants play a vital role in our life and their therapeutic values are well known. It has lots of natural and renewable resources. The aim of this article is to provide an overview of importance and opportunities of biomass conversion towards the sustainable development.

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Citation: Shikha Baskar^{1*}, Rashmi², Amutha Chinnappan³, and Chinnappan Baskar^{4*}, 2019 "Bio-Based Chemicals And Polymers From Biomass Or Biowaste", *International Journal of Health Medicine and Current Research*, 4, (01), 1214-1217.

INTRODUCTION

In recent years, bio-based materials from biomass / biowaste have attracted increased attention due to the public concerns about the depletion of fossil fuels and climate change. Biomass is generated from available atmospheric CO₂, water and sunlight through biological photosynthesis. Therefore, biomass has been considered to be the only sustainable source of organic carbon in earth and the perfect equivalent to petroleum for the production of fuels and fine chemicals with net zero carbon emission. Biomass resources can provide an interesting sustainable platform to substitute partially, and to some extent totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with a positive environmental impact. Current biomass resources comprise primarily industrial waste materials such as sawdust or pulp process wastes, hog fuel, forest residues, clean wood waste from landfills, and agricultural prunings and residues from plants such as lignocellulosic materials. Lignocellulosic materials are natural complex composites primarily consisting of three biopolymers: cellulose (30-50%), hemicelluloses (25-30%), and lignin (10-25%). The cellulosic feedstock required to meet future bioenergy demand will be derived from a variety of settings including agricultural, grassland, forest, urban, and aquatic ecosystems. In recent years, there has been considerable interest in the use and optimization of biodegradable polymers as an alternative to conventional synthetic polymers / plastics and other applications such as packaging, medical, agriculture, pharmaceutical, cosmetics, adhesives, lubricants, textiles, electronics, high-strength structural materials, and biomedical applications.¹⁻⁵ Our research is mainly devoted to design and synthesis of functionalized ionic liquids and their role for chemical and biomass conversion for the production of fine-chemicals, biopolymers and bioplastics and their applications in energy, sensors, and wearable/flexible electronics.⁶⁻⁸ This report covers mini-review on biomass conversion into fine-chemicals and biodegradable polymers and their applications for sustainable development.

Biomass Conversion

Attempts to transfer biomass to produce industrially useful biopolymers and fine-chemicals by traditional biotechnological approaches have obtained only very limited success. An effective biomass conversion requires the interdisciplinary research field which is a unique combination of biotechnology,

chemistry, materials science and engineering, and may ultimately lead to cheap and effective processes for conversion of biomass into valuable-added products and biofuels. A schematic diagram of biomass conversion is shown in Fig 1. The transformation of biomass to chemicals and fuels can be generally realized by three different techniques: thermal, biochemical, and chemical routes. Thermal techniques, like pyrolysis and gasification, can take full advantage of the entire organic substance of this resource. Nevertheless, these techniques still suffer from the disadvantages of low selectivity and high energy input which are unacceptable. Bioconversion of biomass possesses the advantage of good selectivity, but sometimes suffers from low efficiency. Reasonable routes to promote biomass converted into high value-added chemicals under relative mild circumstance in liquid phase at a high selectivity are required. Biomass conversion can be classified as into three categories: Biomass is converted by depolymerization and/or fermentation into platform molecules that are subsequently employed as building blocks for the synthesis of intermediates and fine chemicals via heterogeneous and/or homogenous catalytic processes; Biomass is converted in one or few steps to a mixture of molecules with similar functionalities that are used without separation for the manufacture of high tonnage end-products; and Biopolymers are chemically modified in one step to introduce new functionalities along the polymer backbone.¹⁻⁵ Ionic liquids (ILs) play vital role as solvents and catalyst for the conversion of biomass into fine chemicals. ILs has been revealed as green reaction media owing to their negligible volatility, excellent thermal stability, and the variety of structures available. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristic as well as taking part in various new chemical and biomass conversion.⁹

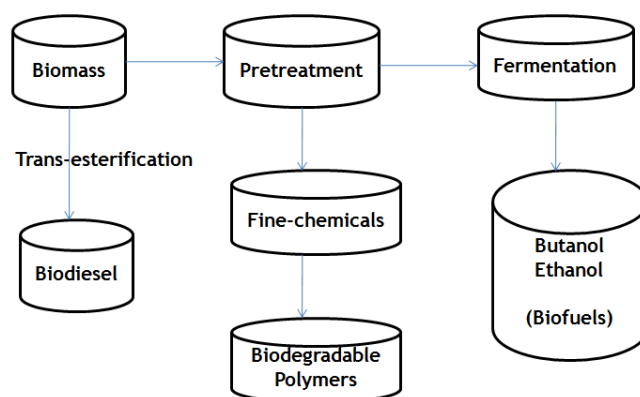


Figure 1. Schematic Diagram Of Biomass Conversion.

Cellulose and Hemicellulose Dissolution

At the beginning of the 20th century, cellulose recovered from biomass processed into chemical products. Cellulose is the major component of such biomass, which occupies 60–80% of biomass. Utilization of biomass, especially inedible cellulosic biomass, is highly desirable for the construction of sustainable society. Therefore, it is considered the most important bio-renewable resource to overcome challenges resulting from the depletion of the fossil fuels *via* its transformation into tailored biofuels or chemical products. The intermolecular and intramolecular hydrogen bonds give cellulose excellent mechanical properties, but also make it insoluble in most solvents. Its poor solubility in solvents limits its utilization.

Furthermore, most conventional cellulose solvents have severe drawbacks such as difficult and expensive recycling, poor solubility, polymer degradation, toxicity and harsh conditions. Generally, cellulose and hemicellulose can be used to produce bioethanol, and lignin offers a broad spectrum of conversion (thermal cracking, fast pyrolysis, and complete gasification) to achieve valuable chemicals and transportation fuels. So far, a great deal of effort has been put toward the degradation of cellulose with enzymes, mineral acids, bases, and supercritical water.

Enzymatic hydrolysis of cellulose is effective, but the system is sensitive to contaminants originating from other biomass components.¹⁰⁻¹³

Bio-based Monomers (Fine-chemicals)

Recently, efforts have been devoted to the conversion of lignocellulosic materials into fine chemicals, biopolymers, and biofuels. A schematic diagram of biomass conversion into bio-based monomers (fine-chemicals) and bio-based polymers (biodegradable polymers) is shown in Fig 2. Among fine-chemicals, 5-hydroxymethylfurfural (HMF), a versatile and one of the important key intermediates for the production of high industrial potential chemicals (such as 5-hydroxymethylfuranic acid, 2,5-furandicarboxylic acid, 2,5-bis(hydroxymethyl) furan, and 2,5-furandicarboxaldehyde), high value polymers (such as polyurethanes and polyamides), and biofuels. 5-Hydroxymethylfurfural (HMF) is one of the top biobased platform compounds and readily accessible from renewable resources like carbohydrates (cellulose, sucrose starch). HMF is a suitable starting material for the preparation of further furanic monomers required for the preparation of non-petroleum-derived polymeric materials such as polyesters, polyamides and polyurethanes. Ionic liquids play vital role as solvents

and catalyst for the conversion of biomass into fine chemicals. There are currently a number of catalysts that are active in the dehydration of sugars to form HMF.

However, most of them also promote side reactions that form undesired byproducts, and rehydrate HMF to form levulinic acid and formic acid. HMF production is currently still facing significant technical challenges to make it economically feasible in an industrial scale. A simple and an efficient method to produce pure HMF from abundant renewable carbohydrates in high yield at low energy cost must be developed before a biorefinery platform can be built on the basis of this substrate. Sugar molecules are potential feedstock for this purpose. According to the literature, the use of metal chlorides in ionic liquid [EMIm]Cl have been found to be effective catalyst for converting sugars such as fructose and glucose to HMF. It was found that ionic liquid mediated catalysis by chromium is the successful catalytic transformation of fructose and glucose to 5-HMF. The attraction of ionic liquids (ILs) lies in their remarkable set of properties when compared to conventional solvents. As salts consisting of distinct anions and cations, ILs are inherently binary (or higher order) systems. The anions and cations can be independently selected to tune the IL's physicochemical properties (melting point, conductivity, viscosity, density, refractive index, etc.) while at the same time introducing specific features for a given application (hydrophobicity vs. hydrophilicity, controlling solute solubility, adding functional groups for catalysis/reactivity purposes, chirality, etc.).^{7,12,14-17}

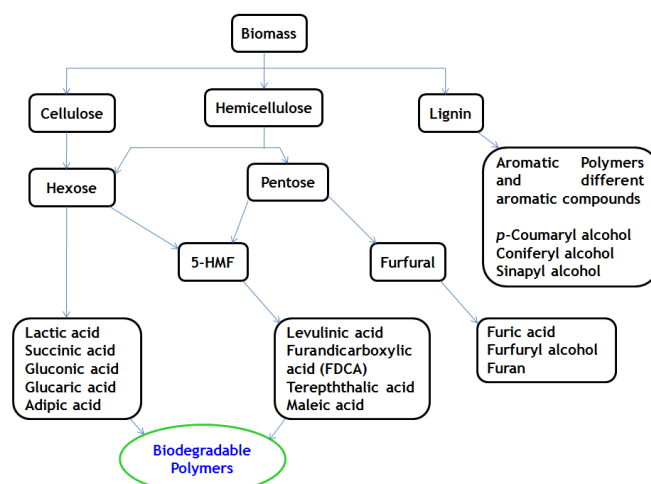


Figure 2. Schematic Diagram Of Biomass Conversion Into Bio-Based Monomers (Fine-Chemicals) And Bio-Based Polymers (Biodegradable Polymers).

Bio-based Polymers (Biodegradable Polymers)

Biodegradable polymers can be made based on either renewable or nonrenewable resources. Two criteria that define the classification of biopolymers or bioplastics are the source of raw materials and the biodegradability of the polymer. Many polymers that are known to be “biodegradable” are in fact “bio-erodible,” “hydrobiodegradable, or “photo-biodegradable.” These different polymer classes all come under the broader category of “environmentally degradable polymers.” The “biodegradability” of biopolymers is dependent on the chemical structure of the material and the constitution of the end product, not just on the raw materials used for its production. Worldwide production of high-volume consumer plastics continues to be dominated by nondegradable petroleum-based polymers. However, two factors have made biodegradable polymers economically attractive, environmental and economic concerns associated with waste disposal and the intensifying expenses of petroleum production resulting from the diminution of the most easily reachable reserves. Biodegradable plastics can be recycled to fruitful metabolites (monomers and oligomers) by microorganisms and enzymes. Biobased polymers can displace incumbent petroleum-based polymers in a market. They face challenges, like inferior mechanical properties and processability, that limit their potential in some high-volume markets like automotive, but their biodegradability can make them a valuable choice in markets such as biomedical and agriculture. Most biobased polymers, especially polybutylene succinate (PBS), polylactic acid (PLA) and polyhydroxyalanoate (PHA), exhibit biodegradability, something most petroleum-based polymers lack. For biomedical applications and in agriculture, this biodegradability and their low toxicity are valuable. More marketing are stating to use biopolymers, such as the building and construction industry, while existing ones continue to expand the range of products made from biopolymers. Products that show high growth rates are, among others, bags, catering products, mulch films, and food/beverage packaging.¹⁷⁻²⁰

Applications

Bio-based polymer applications are characterized either by biodegradability or by sustainability or both. Biopolymers are used in the field: service packaging (Examples: Films, bags, containers), food services (cups, trays, cutlery, bottles), agriculture/forestry/horticulture (delivery system for fertilizers and pesticides etc), fishing (fishing lines and nets, fishing hooks, fishing gear), consumer electronics (mobile phone casings, laptops, etc), automobile

industry (interior trim, spare tire covers etc.), textiles/fibers (carpets, clothing, upholstery etc.), medical / pharmaceutical sector (Medicine, implants) cosmetics, outdoor sports, building, construction industry.¹⁵⁻²⁰

CONCLUSIONS

Biomass is the most abundant renewable resource that can be converted to energy, chemicals, foods and feedstocks. An excellent strategy for providing a new energy source is the immediate use of the inedible biomass, such as cereal straws, bagasse and even used paper. Utilization of biomass, especially inedible cellulosic biomass, is highly desirable for the construction of sustainable society. Efficient and environmentally benign transformation of biomass into value-added chemicals, fuels and polymeric materials is not only a great importance, but also have a long-time task. Producing green chemicals from renewable resources is a very broad topic. Chemists and chemical companies have been actively searching for greener alternatives that can replace their current manufacturing practices. Significant progress has been made in several key research areas, such as the use of new multifunctional catalysts, environmentally benign solvents, ionic liquids prepared from renewable biomaterials. Since Uttarakhand is bestowed with rich and diverse vegetation and natural renewable resources; scientists should promote dedicated research on biomass conversion for the sustainable development.

ACKNOWLEDGMENTS

Authors thank the Department of Science and Technology, New Delhi for financial support.

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