

Biorefinery Concept: An Overview of Producing Energy, Fuels and Materials from Biomass Feedstocks

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Abstract: Biomass, as a renewable resource, has the potential to decrease our dependence on fossil fuels, provide energy security and mitigate environmental problems. Shifting dependence from petroleum-based to renewable biomass-based resources is generally viewed as key to the sustainable development and effective management of greenhouse gas emissions. There has been an increasing research interest in the assessment of bio-sourced materials recovered from residual biomass and their conversion techniques. Biomass which is generally considered as less important due to its light weight, bulkiness and less economic value can be a valuable feedstock in biorefineries. Many countries of the world are now on the way to effectively utilizing the so called neglected energy source for achieving greater and cleaner energy efficiency by adopting biorefinery approach. This review paper hereby critically examine the idea of biorefineries as a strategy for sustainability by using different available biomass feedstocks, techniques for their multipurpose conversion into useful chemicals, fuel and materials, and the associated challenges on the basis of relevant researches.

Keywords: Biomass; Biorefinery; Biofuels; Conversion Technologies; Energy.

1. INTRODUCTION

Increasing world population along with changing life style and high living standard led to change in energy-use pattern and an increase in global energy consumption. Presently, crude oil is a basic feedstock for the production of most of the commodity fuels and chemicals but its rapid depletion creates pressure on automobile and aviation industry. Coupled to this, there are clear scientific evidence that emissions of greenhouse gasses, such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), arising from fossil fuel combustion and land-use change are disturbing the Earth's climate (Cherubini & Stromman, 2011). In this regard there has been considerable interest in finding a low cost, and renewable energy resource that not only replaces petroleum dependency but also reduces green house gas emissions.

Among all renewable energy sources, biomass is the largest, most diverse and most readily available resource that offers the opportunity to generate a wide range of new polymers and bio-products (Cherubini, 2010). In recent years, there has been a tremendous research on biofuels generation, including bioethanol, biodiesel and other bio-based products by using various emerging technologies and conversion routes. Unlike conventional oil refinery processes, biorefinery is a facility that integrates biomass conversion processes and equipments to produce feed, food, fuels, value-added chemicals and energy (power and heat) from biomass (Amidon & Liu, 2009) (Figure 1).

Biorefinery approach can be a good example of a multifunctional process of generating multiple energy and material products (Cherubini, Strommana, & Ulgiati, 2011), thereby maximizing the economic value of the feedstock used while minimizing the waste streams production (Thomsen, 2005).

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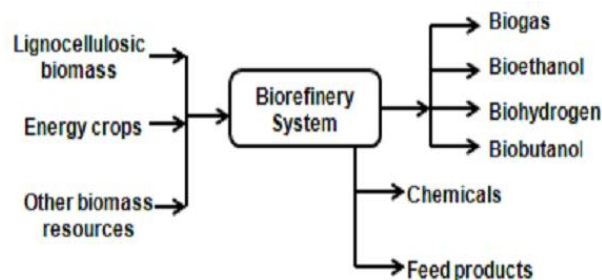


Figure 1 Biorefinery approach

Biomass feedstocks

The choice of feedstock and final products are important in biorefinery designing along with the availability and composition of initial feedstock's and their potential use in multiple production streams (Mabee, Gregg, & Saddler, 2005). In this context, there exists a high diversity of possible biomass feedstock sources like sugar- or starch-rich crops, lignocellulosic biomass and algae (Figure 2). Depending upon the raw materials employed, the conversion processes for biomass are often referred to as 1st and 2nd generation processes (Lyko, Deerberg, & Weidner, 2009). Currently, biofuels commercially produced from sugar, starch and oil-seed based feedstocks are collectively termed 1st generation biofuels. However, as compare to petroleum feedstocks, biomass feedstocks typically have low thermal stabilities and a high degree of

functionality thereby requiring unique reaction conditions (Huber & Dumesic, 2006).

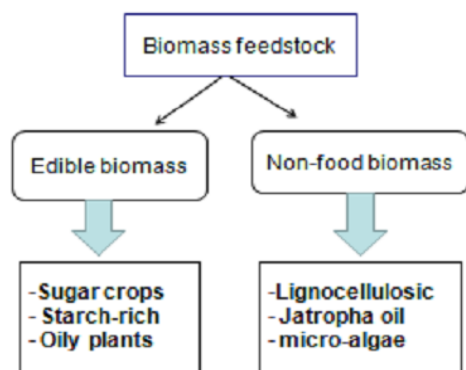


Figure 2 Biorefinery feedstock

Sugar based biorefineries uses sugar crops such as sugar cane, sugar beet or sweet sorghum as they have store large amounts of saccharose, which can be easily extracted from the plant material for subsequent fermentation to ethanol or bio-based chemicals. Brazil has been using sugarcane as raw material for large scale bioethanol production for more than 30 years mainly based on a biorefinery model in which sugars from the sugarcane juice are converted to ethanol and sugar, and the sugarcane bagasse is burnt to generate steam and power (Mariano et al., 2013). In India, Godavari Biorefineries Ltd. formerly the Godavari Sugar Mills Ltd., operates two sugar refineries and manufactures sugar, ethanol, and electricity from sugarcane along with more than 20 products from renewable sources using biorefinery approach. In Colombia, sugarcane based biorefineries, which simultaneously produces sugar from cane juice, fuel ethanol from molasses and electricity from cane bagasse, also moves forward for more profitable biorefinery configurations, which ensures greater capacity of sugar production to keep food security, larger ethanol production for the oxygenation programme, acceptable green house gases (GHG) emissions, low stillage effluents and positive social aspects through job generation (Moncada, El-Halwagi, & Cardona, 2013).

Starch-rich crops such as corn, wheat and cassava can be hydrolyzed enzymatically to deliver a sugar solution, which can subsequently be fermented and processed into fuels and chemicals. The processing of many starch crops also delivers valuable animal feed rich in proteins and energy as additional by-products. Sweet sorghum stems were explored in biorefinery to generate multiple valuable products, such as ethanol, butanol and wood plastic composites (Yu, Zhang, Zhong, Zhang, & Tanet, 2012). Plant oils contains various triacylglycerol based on fatty acids with 8–24 carbon length chains (Octave & Thomas, 2009). Oilseeds provide a unique opportunity for the production of biofuel and high-value fatty acids that can replace petrol sources of specialty chemicals, lubricants and detergents. Soybean, palm fruits and rapeseeds and canola seeds are the common feedstocks for biodiesel production (Demirbas, 2007). Bouaid, Martinez, and Aracil (2010) investigated an integrated process for producing valuable low and high molecular weight methyl ester fractions from coconut oil which could be used as

biodiesel and recovery of other additional valuable byproducts components like bio-lubricants or bio-solvents for sale, thereby helping in successfully developing a self sustained biorefinery. Rincon, Jaramilo, and Cardona (2014) developed an integrated approach to increase added value of palm oil by jointly producing biodiesel and alcohols from lignocellulosic residues (empty fruit bunches and palm press fiber) and crude glycerol or methanol from syngas, resulting in major number of products, low energy consumption and maximizing use of the feedstock.

The cost of using starch and sugar as a feedstock is high because grain and sugar crops are expensive. Consequently, there has been an increase in research based on lignocellulosic biomass processing, focusing particularly on agricultural and forestry residues which are comparatively cheaper, abundant, readily available, and renewable with no concurrency with food industries. Lignocelluloses are the most abundant biomass in the biosphere, accounting approximately 50% of the total. In general, lignocellulosic feedstocks are divided into three categories: (1) agricultural residues (e.g., crop residues and sugarcane bagasse), (2) forest residues, and (3) herbaceous and woody energy crops (Carriquiry, Du, & Timilsina, 2011). Lignocellulosic biomass, particularly agricultural and forestry residues, paper waste and energy crops, is becoming potential renewable energy resource (Zhang et al., 2010). Furthermore, compare with other feedstocks, lignocellulosic feedstock have a number of advantages as they: (i) mitigate competition for land and water used for food production; (ii) increase biomass production per unit of land; and (iii) require lesser inputs for growth (Schmer, Vogel, Mitchell, & Perrin, 2008). Being the most abundant type of biomass on the earth, lignocellulose can play a key role in successful substitution of fossil fuels, in proving desirable feedstock for the sustainable production of liquid fuels and chemical products, through the biorefinery approach. Several types of lignocellulosic biomass, regarding biorefinery feedstocks, have been proposed and reported in literature such as sugarcane bagasse (Rabelo, Carrere, Maciel-Filho, & Costa, 2011), wheat straw (Kaparaju, Serrano, Thomsen, Kongjan, & Angelidaki, 2009), Switchgrass (Cherubini & Jungmeier, 2010) etc. (Table 1). Among these types sugarcane bagasse is the major lignocellulosic feedstock available in huge quantities in tropical countries. India is one of the largest sugar cane growing countries, producing approximately 300 million tons/year, which generate about 75 million tons of sugarcane bagasse on dry weight basis (Adsul, Singhvi, Gaikawari, & Gokhale, 2011). Different experiments reported that, in term of eco-efficiency, the combined production of ethanol, succinic acid, acetic acid and electricity in lignocellulosic feedstock biorefinery shows better environmental performances. The CO₂ released during ethanol fermentation can be fixed in acid fermentation and has great potential in terms of profit compared to ethanol production (Furlan et al., 2013; Luo et al., 2010). The choice of the product combination is of crucial importance for biorefinery design. Multiple biofuels (bioethanol, biohydrogen and methane) production from wheat straw was found to be more

economical process for biomass utilization in biorefineries (Kaparaju, Serrano, Thomsen, Kongjan, & Angelidaki, 2009). In another study Soheli and Jack (2010), assessed the potential benefits of the thermodynamic performance of integrated geothermal heat into biochemical resulted in improved utilization of both biomass and/or geothermal resources. Many countries around the Pacific Rim have significant geothermal resources where this concept of co-locating geothermal and biomass resources for biorefineries can be feasible. However, the main limitation related to the use of agricultural residues is their typical low economic value and energy density associated with the long distance transportation (Mayfield, Darwin-Foster, Smith, Gan, & Fox, 2007). The delivered cost of biomass is a key component of the overall cost of recovering fuel or chemicals from biomass and constitutes 35-50% of the total production cost of biofuel. This could be eliminated to some extent by locating biorefinery industry in the proximity to the main agricultural or rural areas, having large availability of agricultural waste and residues (Lopolito, Nardone, Prosperi, Sisto, & Stasi, 2011). It may also stimulate the creation of job opportunities in non-agriculture sectors and enhance rural economic development (Bailey, Dyer, & Teeter, 2011). Further, in biorefinery feedstock delivery system, the transportation and traffic congestions can be reduced by increasing the bulk density and through combined delivery of agricultural residues in form of bales and wood chips (Sultana & Kumar, 2011).

Algal biomass (including seaweeds, micro-algae and blue-green algae) can be another promising alternative feedstock in biorefineries, because of their much higher photosynthetic efficiency (Singh, Nigam, & Murphy, 2011), productivity and oil content. In addition the algal biomass does not compete with food cultures, arable land, and potable water, and has the possibility of being harvested on a daily basis (Rosenberg, Mathias, Korth, Betenbaugh, & Oyler, 2011). Biofuels produced from lignocellulosic feedstocks are considered as 2nd generation biofuels, while those from algae and advanced processing of the 2nd generation biofuels are called 3rd generation biofuels (Gressel, 2008). In recent times microalgae have emerged as a potential energy crop for liquid biofuel production due to their high annual biomass productivity (175tons/ha/year) and ability to grow in poor quality waters and wastewaters (Jena, Vaidyanathan, Chinnasamy, & Das, 2011). One unique aspect of algae feedstocks include the availability of multiple species and the spectrum of different products such as recombinant proteins and omega-3 fatty acids that can be synthesized from algal biomass, making algae a perfect choice for biorefinery processing in future (Subhadra, 2010). Micro-alga *Nannochloropsis* sp. was demonstrated as potential biomass feedstock for the production of fatty acids for biodiesel, biohydrogen and high added-value compounds in biorefinery context. After the extraction of oils and pigments from the microalga, the remaining biomass could be used in a fermentation process as a substrate to produce hydrogen (Nobre et al., 2013). Agar and bioethanol was produced from red seaweed *Gracilaria verrucosa* algal pulp in an integrated biorefinery (Kumar, Gupta, Kumar,

Sahoo, & Kuhad, 2013). However, there is still limited information and research on integrated processes based on these microorganisms (particularly bacteria and yeast) for the production of biofuels and high value-added products (Lopes da Silva, Gouveia, & Reis, 2014).

Table1. Survey on the applications of feedstocks and raw material for production of value added products

Feedstocks for biorefinery approach	Bio-products	References
Wheat straw	Bioethanol, biohydrogen and biogas	Kaparaju et al., 2009
Bamboo	Bio-ethanol, bio-methane, natural food, flavonoids and functional xylo-oligosaccharides	He et al., 2014
Sweet sorghum stem	Ethanol, butanol and wood plastic composites	Yu et al., 2012
Sugarcane bagasse	Single cell oil as biodiesel, xylitol, xylanase	Kamat et al., 2013
Whole rape seed plant	Biodiesel, bioethanol, biohydrogen and methane	Luo et al., 2011
Sugarcane bagasse	Bioethanol, methane and heat	Rabelo et al., 2011

2. CONVERSION TECHNIQUES

In biorefinery system the conversion of biomass feedstock involve two platforms i.e. thermo-chemical and biochemical to promote different product routes (Figure 3). Thermo-chemical platform is based on thermo-chemical conversion processes (mainly pyrolysis and gasification) which involves the use of heat and chemical reagents to convert biomass into energetically more useful forms (Pravat, Das, & Naik, 2011). The basic processing steps in thermo-chemical plat-forms include: (i) feedstock preparation (drying, and size reduction), (ii) biomass conversion through feeding, gasification and/or pyrolysis, and (iii) product delivery with cleaning and conditioning (Carvalho, Duarte, & Gírio, 2008). In thermo-chemical conversion, pyrolysis characterizes the product yield into condensable tars, non-condensable gas and bio-char (Boateng, Jung, & Adler, 2006) whereas gasification converts the solid biomass feedstock into flammable syngas (Smolinski, Stanczyk, & Howaniec, 2010) having multiple uses. The syngas can be converted into chemicals like methanol, which is further converted into other chemicals such as formaldehyde and acetic acid (Difs, Wetterlund, Trygg, & Soderstrom, 2010). Thermo-chemical routes can present low cost, high efficiency and lower production of green house gases, with potential to accept a large range of biomass sources for biological routes (Forster-Carneiro, Berni, Dorileo, & Rostagno, 2013). Studies suggested that gasification followed by

Fischer-Tropsch process is a promising route for producing transportation fuel and combined heat and power (CHP) from lignocellulosic biomass, in a biorefinery (Ng & Sadhukhan, 2011).

A large percentage of proposed lignocellulosic biorefinery concepts are based on biochemical conversion platform where the lignocellulosic materials are converted to liquid biofuels, lignin bio-products and other extractives using enzymes and fermentation. Bioconversion of lignocellulosic biomass to bioethanol has received widespread interest due to their availability, abundance and relatively low cost. Lignocellulosic biomass is a tough feedstock owing to the compact packing of cellulose, hemicelluloses and lignin components. Lignocellulosic biomass could produce up to 442 billion/year of bioethanol (Bohlmann, 2006). In contrast to first generation sugar and corn crops feedstock, second generation lignocellulosic feedstocks are inherently recalcitrant, limiting the release of structural sugars and subsequently the amount of biofuel produced (Takara & Khanal, 2011).

The basic process steps in producing bioethanol from lignocellulosic materials are pretreatment, enzymatic hydrolysis, fermentation and product recovery (Balat, 2011). The aim of pretreatment is to increase the surface area and porosity of the substrate, reduce the crystallinity of cellulosic materials (Talebna, Karakashev, & Angelidaki, 2010). Pretreatment is always required to break this compact structure to make cellulose accessible for efficient enzymatic hydrolysis (Singh, Suhag, & Dhaka, 2015). After pretreatment, the remaining pretreated material is reacted with cellulase to hydrolyze cellulose to glucose, which is then fermented to bio-ethanol (Hasunuma et al., 2013). For the fermentation step, the yeast *Saccharomyces cerevisiae* was used as the process microorganism for the conversion of glucose into ethanol (Cardona-Alzate & Sanchez-Tore, 2006). Another application of glucose transformation by micro-organisms is the production of lactic acid which can be processed to make acrylic acid, used in polyester resins and polyurethane used as antifreeze (Sodergard & Stolt, 2007). Lactic acid can also be polymerized to form a bio-based polymer usually known as Polylactic acid having many industrial applications (Babu, Connor, & Seeram, 2013). Succinic acid, a derivative of glucose is very important and reactive molecule currently produced commercially by chemical processes. Interest in production of industrial chemicals from renewable resources has led to the development of several microorganisms that could produce succinic acid at concentrations sufficiently high to make the development of commercial fermentation processes economically feasible and attractive (Lee, Song, & Lee, 2006). It has been demonstrated that carbon dioxide produced in an ethanol fermentor can be used directly for succinic acid production in an adjacent fermentor without any impurities removal treatment (Nghiem, Hicks, & Johnston, 2010). All bioconversion platforms for ethanol production from lignocellulosic biomass produce a lignin-rich solid residue which can be combusted for on-site electricity production (Larsen,

Petersen, Thirup, Li, Iversen, 2008). Lignin is a good applicant in chemical industries, can be incorporated in resins to substitute phenols or as a cross-linker in epoxy-resins (Simionescu, Rusan, & Macoveanu, 1993). Lignin incorporation in polyolefin increases resistance to ultra-violet rays without major modification in mechanical properties (Gosselink et al., 2004). The conversion of lignin-rich solid residue to liquid fuels is presently possible by using various pathways such as fragmentation, hydro processing and thermal depolymerization (Sannigrahi, Pu, & Ragauskas, 2010). However, it is also recognized that still there is a lack of effective and cost competitive lignin depolymerization method to fully realize this potential (Zhang, Tu, & Paice, 2011).

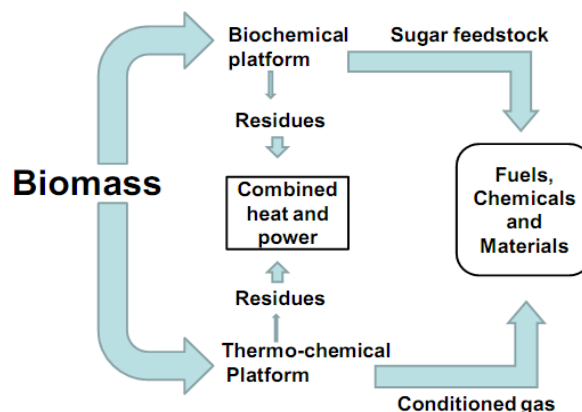


Figure 3 Biorefinery platforms

Biodiesel conversion technique known as Transesterification using plant or algal oil is a standardized process by which triglycerides are reacted with methanol in the presence of a catalyst to deliver fatty acid methyl esters popularly known as biodiesel and glycerol, which is a high value co-product (Lyko, Deerberg, & Weidner, 2009). Transesterification is a method of reducing the viscosity of the triglycerides and enhancing the physical properties of the fuel. Sunflower, rapeseed, soybean, palm oils and waste vegetable oil (requires refinement) are the main substrates to produce biodiesel. The recovery from rapeseed plant increased from 20% in the traditional process for biodiesel production to 60% in the biorefinery concept for production of biodiesel, bioethanol, biohydrogen and methane (Luo et al., 2011). Valuable low molecular weight methyl ester fractions like methyl caprylate, methyl laurate and methyl myristate are produced from coconut oil (Bouaid, Martinez, & Aracil, 2010) by using integrated process with a yield of 77.54% under optimum conditions. The use of this raw material as a renewable feedstock in an upgraded industrial process could help in successfully developing a self sustained biorefinery.

Biological catalysts (such as *Clostridium ljungdahlii*, *Clostridium autoethanogenum*, *Clostridium carboxidivorans*, *Acetobacterium woodii*, and *Peptostreptococcus* products) are also available to ferment syngas into liquid fuel more effectively than chemical catalysts (e.g. iron, copper or cobalt) in Fischer-Tropsch process. Biocatalysis can be used not only for production

of biofuel such as ethanol and biodiesel, but also for synthesis of biodegradable plastics such as polyesters (Tan, Xu, & Asano, 2009). Discovery of ethanol and acetate producers autotrophic bacteria *Clostridium ljungdahlii* and *Clostridium autoethanogenum* that use single-carbon gases, such as CO and CO₂, have sparked interest in the biological conversion of synthesis gas to solvents and acids (Cotter, Chinn, & Grunden, 2009). Thus bio-catalysis is a key technology in biorefinery process due to mild conversion condition and high efficiency. The establishment of biorefineries with Zygomycetes (filamentous fungi) as central catalysts hold great potential for the production of fine chemicals, enzymes, fungal biomass for food purposes, and lipids (Ferreira, Lennartsson, Edebo, & Taherzadeh, 2013).

3. CONCLUSIONS AND RECOMMENDATIONS

From the literature, it can be concluded that different types of biomass can be used in biorefineries. They are the industrial facilities, aiming sustainable transformation of biomass into their building blocks with the affiliated production of biofuels, energy, chemicals and materials, and can play an important role in the creation of sustainable and more environmentally friendly future. For sustainable economic growth many countries of the world including India, can be encouraging places for biorefinery approach due to abundance of different residual biomass substrates, along with left over agricultural and forest residues, bagasse etc. Coupled to this comparatively low labor and construction costs in India can be the additional encouraging factors. Most Life Cycle Assessments found reductions in global warming emissions and fossil energy consumption when the most common transportation biofuels were used to replace conventional diesel and gasoline (Blottnitz & Curran, 2007). However, a number of obstacles still stand in the way of biorefineries realizing their full economic potential. Still, bio-based products and fuels may also be associated with environmental disadvantages, e.g. an increased land use, the eutrophication of water or environmental contamination with pesticides (Uihlein & Schebek, 2009). From the economic point of view less energy-requiring and waste-generating biorefinery technologies should be designed and promoted for the assessment of lignocellulose and breakdown processes. More research and development by using other organic biomass like rice straw, municipal solid wastes, weeds like parthenium, and lantana, non-edible oil seeds and plants is recommended. In addition efficient microbial strains able to operate under industrial process conditions and more efficient and economic technology will be needed to make biorefinery approach a successful one.

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