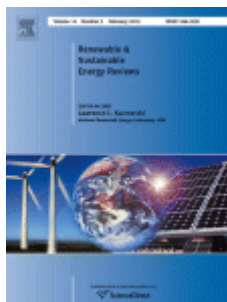




IITHLibrary
Transforming Information into Knowledge



Opportunities, Recent Trends and Challenges of Integrated Biorefinery: Part I

Sunil K. Maity

Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram-502205, Telangana, India.

Renewable and Sustainable Energy Reviews 43 (2015) 1427–1445.

Available online 18 December 2014

<http://dx.doi.org/10.1016/j.rser.2014.11.092>

This is author version post print archived in the official Institutional Repository of IIT-H
www.iith.ac.in

Opportunities, recent trends and challenges of integrated biorefinery: Part I

Sunil K. Maity¹

Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram-502205, Telangana, India.

Abstract

Sustainable production of energy, fuels, organic chemicals and polymers from biomass in an integrated biorefinery is extremely important to reduce enslavement on limited fossil fuels. In the present article, the biomass was classified into four general types based on their origin: energy crops, agricultural residues and waste, forestry waste and residues and industrial and municipal wastes. The article further elucidates the chemistry of various types of biomass used in the biorefinery. The biorefinery was classified into three broad categories based on the chemistry of biomass: triglyceride, sugar and starchy and lignocellulosic. The article further presents a comprehensive outlines of opportunities and recent trends of each type of biorefinery. A brief overview of original and revised list of platform chemicals, their sources from biomass and derivative potentials were also articulated. The article also provides comparisons of different types of biorefinery, broad challenges and availability of biomass. Furthermore, the article provides an overview of hydrocarbon biorefinery for production of hydrocarbon fuels and building block chemicals from biomass.

Keywords: Biorefinery; Biomass; Bio-fuels; Platform chemical; Lignocellulose; Starch.

Contents

Abstract	1
1. Introduction	2
2. Biomass	3-6
2.1. <i>Classification of biomass</i>	3
2.1.1. <i>Energy crops</i>	3
2.1.2. <i>Agricultural residues and waste</i>	3
2.1.3. <i>Forestry waste and residues</i>	3
2.1.4. <i>Industrial and municipal wastes</i>	3
2.2. <i>Chemistry of biomass</i>	4
2.2.1. <i>Triglycerides feedstock</i>	4
2.2.2. <i>Sugar and starchy feedstock</i>	4
2.2.3. <i>Lignocellulosic feedstock</i>	5
3. Biorefinery	6-19
3.1. <i>Analogy with petroleum refinery and petrochemical industry</i>	6
3.2. <i>Origin, definition and types of biorefinery</i>	7
3.3. <i>Triglyceride biorefinery</i>	8
3.4. <i>Sugar and starchy biorefinery</i>	9
3.5. <i>Lignocellulosic biorefinery</i>	11
3.5.1. <i>Combustion and gasification</i>	12
3.5.2. <i>Liquefaction and fast pyrolysis</i>	12
3.5.3. <i>Fermentation and anaerobic digestion</i>	12
3.5.4. <i>Lignin conversion</i>	13
3.5.5. <i>Biosynthetic pathways</i>	13
3.5.6. <i>Aqueous phase dehydration/hydrogenation</i>	13
3.6. <i>Platform chemicals</i>	14
3.7. <i>Comparisons of biorefinery</i>	16
3.7.1. <i>Availability and cost of feedstock</i>	16
3.7.2. <i>Feedstock diversity</i>	16
3.7.3. <i>Edible versus non-edible feedstock</i>	16
3.8. <i>Availability of biomass</i>	16
3.9. <i>Challenges of biorefinery</i>	18

¹ Corresponding author (Dr. Sunil K. Maity): Phone: +91-40-2301-6075; Fax: +91-40-2301 6003.

E-mail: sunil_maity@iith.ac.in

4. Hydrocarbon biorefinery.....	19
5. Conclusions.....	20
References.....	20-27

1. Introduction

At present our society is extremely dependent on finite fossil fuels (petroleum, coal and natural gas) to meet basic needs of energy, fuels, organic chemicals and polymers. At the moment, more than 80% of energy (Fig. 1) and ~90% of organic chemicals in the world are derived from fossil fuels alone [1-2]. Moreover, the energy and organic chemicals consumptions are growing (~7% per annum) incessantly due to rapid increase of world's population with improved standards of living. The increasing energy demands, gradual depletion of fossil fuels and hence rise of crude oils price are foremost motivations for exploration of renewable resources for sustainable production of electricity, heat, fuels, organic chemicals and polymers [3]. The deterioration of environmental cleanliness due to emissions of harmful and greenhouse gases (CO₂, CH₄, N₂O etc.) by large scale usage of fossil fuels is another motive for shifting dependency away from limited fossil fuels to carbon-neutral renewable resources.

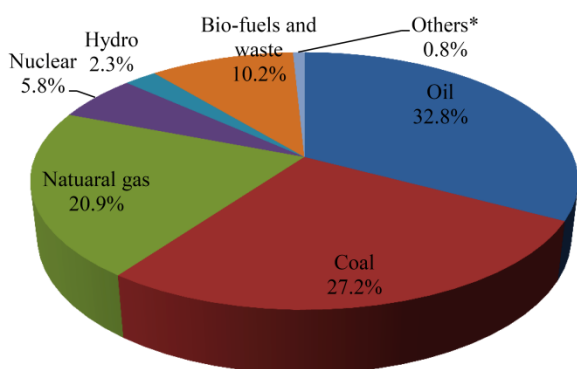


Fig. 1. Global energy scenario in the year 2009 [2].
* Other includes geothermal, solar, wind, heat, etc.

The global energy consumption was 12150 million tons equivalent in 2009 with only ~20% share of renewable energies (nuclear, hydro, bio-fuel and waste and others) (Fig. 1). The biomass (bio-fuels and waste together) alone contributes more than 50% of world's renewable energy. The contribution solar/pv to world's renewable energy is however negligibly small at the moment. But it has enormous forthcoming potentials if scientific advancements results novel materials for efficient capture of solar energy. However, with exception of biomass, all other renewable energies are incompetent to deliver societal needs of transportation fuels, organic chemicals and polymers. On the other hand, the biomass has tremendous potentials to deliver societal needs of

all useable forms of energies (electricity, heat and transportation fuels), organic chemicals and polymers. Therefore, new manufacturing concepts are continuously evolving to produce an array of bio-fuels and multitude of bio-products from biomass. These complex processing technologies are analogous to today's integrated petroleum refinery and petrochemical industries commonly known as biorefinery [1,4-5].

The transportation fuels are world's single largest energy consuming sector. The transportation sector alone consumed 28.58 quadrillion KJ in 2011 which was ~28% of world's energy consumption (103.08 quadrillion KJ) [6]. The consumption of petroleum products in India during 2010-11 was 14.18×10^7 metric tons with more than 50% share of transportation fuels (MoGas, ATF and HSDO) alone [7]. The annual consumption of the major liquid transportation fuels in India was 5.62×10^{10} metric tons during 2006-2007 and increased at a rate of ~8% per annum (Fig. 2).

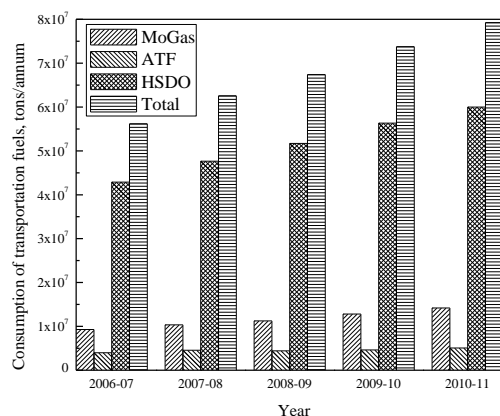


Fig. 2. Consumption of transportation fuels in India [7].

The government in few countries in the world mandated blending of biodiesel or bio-ethanol with petroleum derived fuels to limited extents. With exception of the blending of bio-fuels, the transportation fuels are exclusively obtained from petroleum at the moment. The sustainable production of transportation fuels and organic chemicals from biomass is thus essential in an integrated biorefinery to reduce enslavement on finite fossil fuels. Despite enormous potentials, only a few articles have published in the past on integrated biorefinery [1,4-5]. This may be partly due to versatile nature of the subject. Moreover, concepts of biorefinery have been evolving

continuously in response to novel scientific contributions in this area. Therefore, there are strong needs of scientific and technological advancements further in this area to develop economically viable biorefinery systems. An attempt was thus made in the present article to collate possible opportunities and challenges of biorefinery systems in coherent manner addressing both existing and emerging areas to the best of my capability.

2. Biomass

2.1. Classification of biomass

The biomass is “any organic matter that is available on a renewable or recurring basis (excluding old growth timber), including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes, and other waste materials” [4]. The most commonly used biomass for biorefinery is broadly classified into four major categories depending on their origin [8].

2.1.1. Energy crops

The energy crops are normally densely planted, high-yielding and short rotation crops. These crops are usually low cost and need low maintenance. These crops are grown dedicatedly to supply huge quantities of consistent-quality biomass for biorefinery. The energy crops mainly comprise of herbaceous energy crops, woody energy crops, agricultural crops and aquatic crops. *Herbaceous energy crops* are perennials that are harvested annually [9]. It takes 2-3 years to reach full productivity. These crops include grasses such as switchgrass, miscanthus, bamboo, sweet sorghum, tall fescue, kochia, wheatgrass, reed canary grass, coastal bermuda grass, alfalfa hay, timothy grass and others. The Biowert, Germany uses meadow grass to manufacture green electricity and innovative materials such as plastics, insulation materials and fertilisers [10]. *Woody energy crops* are fast growing hardwood trees that are harvested within 5-8 years of plantation. These crops include hybrid poplar, hybrid willow, silver maple, eastern cottonwood, green ash, black walnut, sweetgum, sycamore etc. The short rotation woody energy crops are traditionally used for manufacture of paper and pulp. Unlike agriculture crops and perennial grasses, the productivity of woody biomass is little affected by seasonal variations. *Agricultural crops* comprise of oil crops (e.g. jatropha, oilseed rape, linseed, field mustard, sunflower, castor oil, olive, palm, coconut, groundnut etc.), cereals (e.g. barley, wheat, oats, maize, rye etc.) and sugar and starchy crops (e.g. sweet sorghum, potato, sugar beet, sugarcane etc.) [11]. These crops are generally grown to produce vegetable oils, sugars and extractives. These crops

have potentials to produce plastics, chemicals and products as well. *Aquatic crops* include several varieties of aquatic biomass, for example, algae, giant kelp, other seaweed, marine microflora etc. The energy crops are extensively grown for production of bio-fuels, for example, sugar cane in Brazil for ethanol, maize in USA for ethanol and oilseed rape in Europe for biodiesel [11].

2.1.2. Agricultural residues and waste

Agricultural residues primarily comprise of stalks and leaves that are generally not harvested from fields for commercial use. Sugar cane bagasse, corn stover (stalks, leaves, husks and cobs), wheat straw, rice straw, rice hulls, nut hulls, barley straw, sweet sorghum bagasse, olive stones etc. are some of the examples of agricultural residues [12]. With vast areas of corn cultivated worldwide, corn stover is expected to be a major feedstock for biorefinery. The use of agricultural residues for biorefinery is beneficial as it eliminates the need of sacrificing arable lands [13]. The by-products and waste streams produced during biomass processing are collectively called *residues* that have substantial potentials as feedstock for biorefinery. Examples include unused sawdust, bark, branches and leaves/needles that are produced during processing of wood for bio-products or pulp. The wastes such as animal manure (from cattle, chicken and pigs) are also included within the agricultural residues [8]. The refuse derived waste generated from either domestic or industrial sources is another potential source of biomass.

2.1.3. Forestry waste and residues

The forestry waste and residues are referred to the biomass that is usually not harvested from logging sites in commercial hardwood and softwood stands. The forestry residues also include biomass resulting from forest management operations (thinning of young stands and removal of dead and dying trees). Utilization of these biomass for biorefinery near its source is highly desirable to avoid expensive transportation [13]. However, limited accessibility to dense forests largely increases operation costs for logging/collection activities.

2.1.4. Industrial and municipal wastes

These include municipal solid waste (MSW), sewage sludge and industrial waste. Residential, commercial and institutional post-consumer waste usually contains good amounts of plant derived organic materials that can be used as potential source of biomass. The waste paper, cardboard, wood waste and yard waste are examples of MSW. The waste product generated during wood pulping, called black liquor is an example of industrial waste.

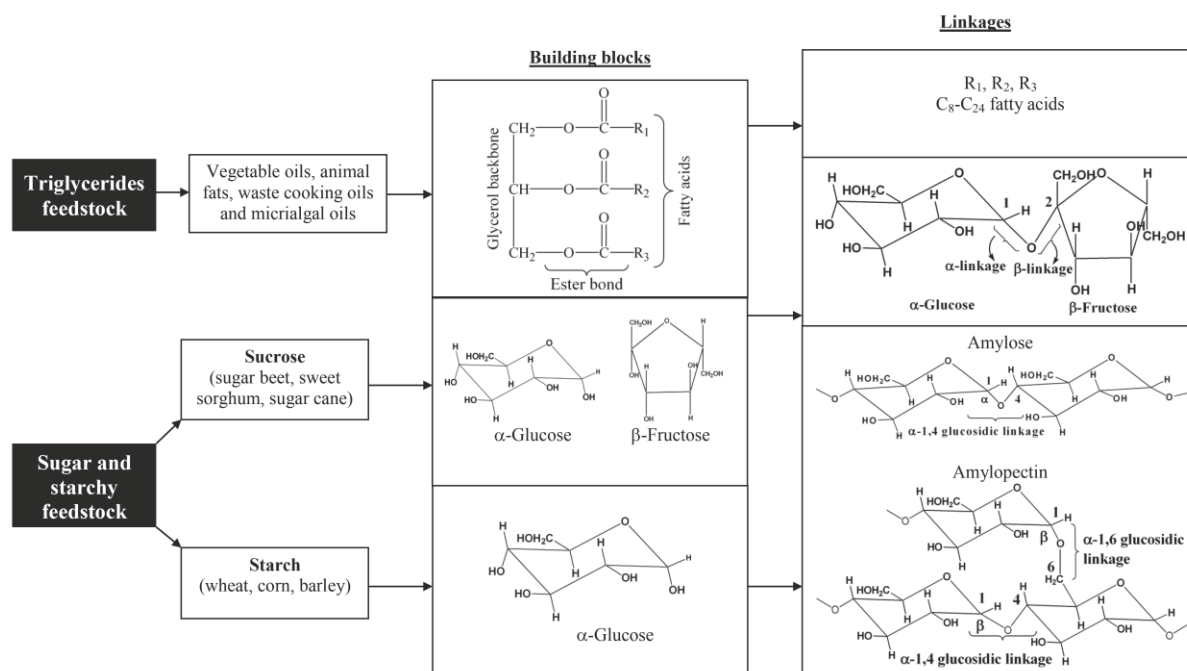


Fig. 3. Chemistry of triglycerides feedstock and sugar and starchy feedstock.

2.2. Chemistry of biomass

The knowledge of chemistry of biomass is extremely important for developments of energy-efficient biorefinery processes. In general, the chemistry of biomass is quite complex in nature involving extensive ranges of chemical compounds. The carbohydrates, lignin, proteins and fats are the primary chemical compounds present in the biomass together with lesser extents of several other chemicals such as vitamins, dyes and flavors. The chemistry of such wide ranges of biomass is beyond the scope of the present article. In the present article, the most commonly used biomass for biorefinery is classified into three broad categories based on their chemical nature [14].

- (i) triglycerides feedstock (TGF) (vegetable oils, animal fats, waste cooking oils and microalgal oils)
- (ii) sugar and starchy feedstock (SSF)
 - (a) sucrose containing biomass (e.g. sugar beet, sweet sorghum, sugar cane etc.)
 - (b) starchy biomass (e.g. wheat, corn, barley, maize etc.)
- (iii) lignocellulosic feedstock (LCF) (e.g. wood, straw, grasses etc.)

About 75% of the biomass is carbohydrate in nature mainly in the form of cellulose, starch and saccharose [15]. Only 20% of the biomass is composed of lignin and remaining 5% is natural compounds such as oils, proteins and other substances. Only 3-4% of these biomass are

currently used by human beings for food and non-food purposes.

2.2.1. Triglycerides feedstock

The TGF include vegetable oils, animal fats, waste cooking oils and microalgal oils. The vegetable oils are generally two types: edible (e.g. rapeseed, coconut, sunflower etc.) and non-edible (e.g. jatropha, mahua, karanja etc.). In TGF, one molecule of glycerol is bonded with three molecules of fatty acids by ester bonds (Fig. 3). The three fatty acids present in the TGF may be same or different. The fatty acid composition of TGF generally vary significantly depending on the source and geographical origin [16-17]. In general, vegetable oils are composed of C₈ - C₂₄ fatty acids with majority being C₁₆ and C₁₈ fatty acids [18-19]. The fatty acid composition of the microalgal oils are however somewhat broader compared to vegetable oils consisting of both lighter and heavier fatty acids [20-21]. The hydrocarbon backbone of fatty acids is either saturated or unsaturated. For some of the strains, microalgal oils are quite rich in polyunsaturated fatty acids with four or more double bonds. The animal fats are usually constituted of high molecular weight saturated fatty acids [22]. The TGF often contains large amounts of free fatty acids especially in non-edible oils, animal fats and microalgal oils [23].

2.2.2. Sugar and starchy feedstock

Sucrose is commonly known as table sugar or sometimes called saccharose. Chemically sucrose is a disaccharide composed of two different C₆ monosaccharides: α-glucose and β-fructose. These monosaccharides are linked together by α-1

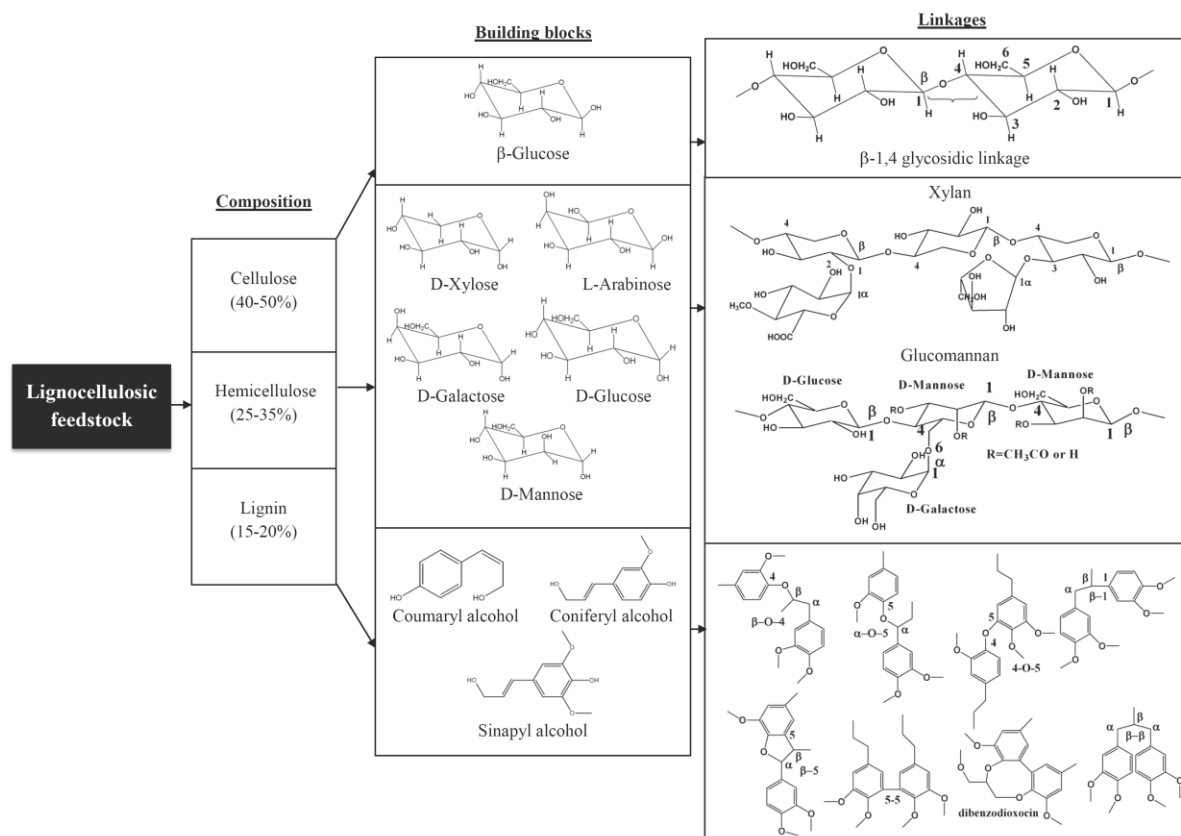


Fig. 4. Chemistry of lignocellulosic feedstock.

glucosidic- β -2 fructosidic bond (Fig. 3). The starch is a polymer of α -glucose linked by α -1,4 glucosidic bond (as in amylose) and α -1,6 glucosidic bond (as in amylopectin). Starch usually comprises of 20-25 wt% amylose and 75-80 wt% amylopectin depending on the source. The typical molecular weight of amylose is in the range of 10^5 - 10^6 kg kmol^{-1} [24]. On the other hand, the amylopectin is one of the largest biopolymers with typical molecular weight of about 10^8 kg kmol^{-1} [24]. In plants, the starch molecules arrange themselves in semi-crystalline granules. Starch is thus insoluble in cold water; but completely soluble in hot water.

2.2.3. Lignocellulosic feedstock

LCF is primarily composed of cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%) (Fig. 4) [14,25]. The LCF also contains small quantities of pectin, protein, extractives (nonstructural sugars, nitrogenous material, chlorophyll and waxes) and ash. The compositions of LCF vary significantly depending on types and geographical origin. The chemical compositions of some of the representative LCF are shown in Table 1 [26].

The cellulose is a high molecular weight (10^6 kg kmol^{-1} or more) linear polymer of β -glucose (5000-10000 units) linked together by β -1,4 glycosidic bonds. The polymer chains of cellulose

are bundled together by hydrogen and van der Waal bonds leading to high strength and highly resistant to biological attack. The cellulose is highly crystalline in nature with only a small fraction being amorphous. The crystalline property of cellulose makes it completely insoluble in aqueous solution. The crystalline property also leads to high resistance to hydrolysis that impedes efficient conversion of this polymer to monomers during biorefining processes. The annual cellulose production is ~ 1.5 trillion tons making it an unlimited resource for biorefinery [27].

The hemicellulose is an amorphous and branched polymer of five carbon (xylose and arabinose) and six carbon (galactose, glucose and mannose) sugars together with uronic acids substituents (e.g. 4-O-methylglucuronic, D-glucuronic and D-galactouronic acids). The hemicellulose is either homopolymer or heteropolymer with short branches [25]. The monosaccharides are linked together by β -1,4 glycosidic bonds and sometimes β -1,3 glycosidic bonds. The hemicellulose is highly substituted with acetic acid. The numbers of repeating monosaccharides are only ~ 150 in hemicellulose. The most abundant building block of hemicellulose in hardwood and agricultural plants (like grasses and straw) is xylan [28-30]. It is a polymer of xylose linked at 1 and 4 positions. While in softwoods, the abundant hemicellulose building block is glucomannan. It is a straight-chain

Table 1
Composition of various lignocellulosic biomass [26].

Feedstock	Cellulose	Hemicellulose	Lignin	Extractives	Ash	Protein
Corn stover	36.4%	22.6% (18% xylose, 3% arabinose, 1% galactose, 0.6% mannose)	16.6%	7.3%	9.7%	-
Wheat straw	38.2%	24.7% (21.1% xylose, 2.5% arabinose, 0.7% galactose, 0.3% mannose)	23.4%	13%	10.3%	-
Hardwood	43.3%	31.8% (27.8% xylose, 1.4% mannose)	24.4%	-	0.5%	-
Softwood	40.4%	31.1% (22.2% mannose, 8.9% xylose)	28%	-	0.5%	-
Switchgrass (late cut)	44.9%	31.4%	12%	-	4.6%	4.5%

Percent values are based on dry weight. Hardwood composition of beech (*Fagus sylvatica*) and softwood composition of spruce (*Picea abies*).

polymer of D-mannose and D-glucose linked by β -1,4 glucosidic bonds with small amounts of branching. The hemicellulose bridges lignin and cellulose fibers leading to a rigid network of cellulose-hemicellulose-lignin. The hemicellulose being amorphous in nature is highly soluble in water. The hydrolysis of hemicellulose to monomer sugars is thus relatively easy compared to cellulose.

The lignin is nature's most abundant high molecular weight aromatic polymer (6×10^5 - 15×10^6 kg kmol⁻¹). The lignin is an amorphous and three dimensional polymer composed of three different methoxylated phenylpropane units (coniferyl alcohol, sinapyl alcohol and coumaryl alcohol) that are bonded together by different kinds of linkages (Fig. 4). The distribution of these phenylpropane building blocks in lignin depends on types of biomass [31]. The softwood lignin is primarily build of coniferyl alcohol with small amounts of coumaryl alcohol. The lignin in hardwoods is composed of both coniferyl and sinapyl alcohol together with small quantity of coumaryl alcohol. The lignin obtained from grass and herbaceous crops composed of all three phenylpropane units together with *p*-hydroxycinnamic acids (*p*-coumaric acid, ferulic acid and sinapic acid). The plants cell walls are primarily composed of lignin that provides plants with structural supports, resistance against microbial attack and a hydrophobic vascular system for transportation of water and solutes.

3. Biorefinery

3.1. Analogy with petroleum refinery and petrochemical industry

After initial pretreatments, crude oil is segregated into assembly of products following distillation in petroleum refinery. These products are post processed using complex processing technologies to produce fuels for household and industry, transportation fuels and raw materials for petrochemical industry. The naphtha is one such raw material for production of several building block chemicals in petrochemical industry: (1) synthesis gas (SG), (2) olefins (ethylene, propylene, butylenes and butadiene) and (3) aromatics (benzene, toluene, xylene and ethyl benzene) [32-33]. In addition to naphtha, natural gas is another important raw material for petrochemical industry. The analysis of statistical data showed that ~10% of the total petroleum refinery output in the form of naphtha and ~30% of total offtake of natural gas is directed towards petrochemical industry in India for synthesis of these building block chemicals (Table 2). More than 90% of organic chemicals in the world are derived from these building block chemicals.

Before discovery of crude oils in the 19th century, the energy requirements of human civilization was primarily met by biomass [34]. The biomass in the form of wood, crop waste and animal waste or biomass derived charcoal still remained as primary source of fuels mainly for cooking in many developing countries. For example, biomass accounts for over 90% of total household fuels in poorer countries of Africa and Central America and 35% in Latin America and Asia [35]. Moreover, the fossil fuels were originated by natural decomposition of biomass under anaerobic conditions for period more than millions of years. Therefore, it is quite expected

Table 2
Share of petroleum for petrochemical industry [7].

		2005-06	2006-07	2007-08	2008-09	2009-10
Petroleum	Total production, MMT	119.750	135.260	144.930	150.516	179.769
	Naphtha, MMT	14.509	16.660	16.440	14.826	17.105
	Naphtha, %	12.1	12.3	11.3	9.8	9.5
Natural gas	Total offtakes, million m ³	31025	31368	30870	32989	44646
	Non-energy, %*	29	34	39	33	34

*Includes fertilizer industry, petrochemicals, and others.

that future needs of fuels and organic chemicals of fossil fuels deprived society will be met by biomass if technological advancements result cost-competitive production cost.

3.2. Origin, definition and types of biorefinery

The concept of biorefinery was originated in late 1990s as a result of scarcity of fossil fuels and increasing trends of use of biomass as a renewable feedstock for production of non-food products [1,4-5,36-37]. The term “Green Biorefinery” was first introduced in 1997 as: “*Green biorefineries represent complex (to fully integrated) systems of sustainable, environmentally and resource-friendly technologies for the comprehensive (holistic) material and energetic utilization as well as exploitation of biological raw materials in form of green and residue biomass from a targeted sustainable regional land utilization*” [36]. According to US Department of Energy (DOE) “*A biorefinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products*” [36-37]. The American National Renewable Energy Laboratory (NREL) defined biorefinery as: “*A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass*” [38]. These definitions of biorefinery are analogous to today’s integrated petroleum refinery and petrochemical industry that produces multitude of fuels and organic chemicals from petroleum.

The biorefinery was classified into three types, phase I, II and III, based on conversion technologies to produce various bio-products [1,5]. The phase I biorefinery has fixed processing capability. It uses grain as feedstock to produce fixed amounts of ethanol, other feed products and carbon dioxide. The low capacity dry mill primarily build for manufacture of ethanol is an example of phase I biorefinery [39]. The current wet milling technology with more processing flexibility is considered as phase II biorefinery. It also uses grain as feedstock to yield assembly of products such as starch, high fructose corn syrup, ethanol and corn oil depending on their demands and price [40].

The phase III biorefinery (whole-crop, green and LCF) uses mixture of biomass to produce multitude of products using combination of technologies [5]. The phase III is most advanced form of biorefinery. The whole-crop biorefinery uses entire crops such as cereals (rye, wheat and maize) as raw materials to obtain useful products [5]. The cereals are first mechanically separated into corn and straw. The cellulosic straw is further processed in LCF biorefinery. The corn is either converted into starch or meal by grinding. The meal is then converted into binder, adhesives and

filler by extrusion. Starch is further processed through plasticization, chemical modification and biological conversion via glucose. The green biorefinery uses natural wet biomass such as grass, green plants or green crops. It is a multiproduct system that handles its refinery cuts, products and fractions according to physiology of the corresponding plant materials [1,5]. The green biomass is first wet-fractionated to fiber-rich press cake and nutrient-rich green juice. The press cake comprises of cellulose, starch, valuable dyes and pigments, crude drugs and other organics. Whereas green juice contains proteins, free amino acids, organic acids, dyes, enzymes, hormones, other organic substances and minerals. The pressed cake can also be converted to green feed pellets, chemicals such as levulinic acid (LA), SG and synthetic fuels.

The LCF biorefinery uses naturally dry biomass such as cellulosic biomass and wastes. The raw biomass is first cleaned and then broken down into constitutive fractions (hemicellulose, cellulose and lignin) through chemical or enzymatic pretreatment. The hemicellulose and cellulose are converted to monomer sugars through hydrolysis. The glucose obtained from hydrolysis of cellulose is further converted to valuable products such as ethanol, acetic acid, acetone, butanol, succinic acid and other fermentation products. The xylose obtained from hydrolysis of hemicellulose is converted to furfural. The lignin is used as adhesive or binder and fuel for direct combustion.

The US DOE/NREL further described biomass conversion technologies based on five platforms: (1) sugar platform biorefinery (SPB), (2) thermochemical or syngas platform, (3) biogas platform, (4) carbon-rich chains platform and (5) plant products platform [1]. The SPB produces ethanol or other building block chemicals through fermentation of sugars. The syngas platform uses technology of biomass gasification to produce SG and liquid fuels. The biogas platform is useful for production of cooking gas by anaerobic digestion of biomass. The carbon-rich chains platform converts vegetable oils into biodiesel by transesterification with methanol for application as liquid fuel. The plant products platform performs biorefining in biological plants itself rather than in industrial plants.

Considering outstanding progress of biomass processing technologies in last two decades, an effort was made in the present article to provide a comprehensive overview of opportunities and challenges of various biorefinery systems. The biorefinery discussed in the present article is analogous to the definition of NREL. The classification of biorefinery is however highly debatable subject and depends largely on available biomass conversion technologies to produce spectrum of bio-products through various platforms

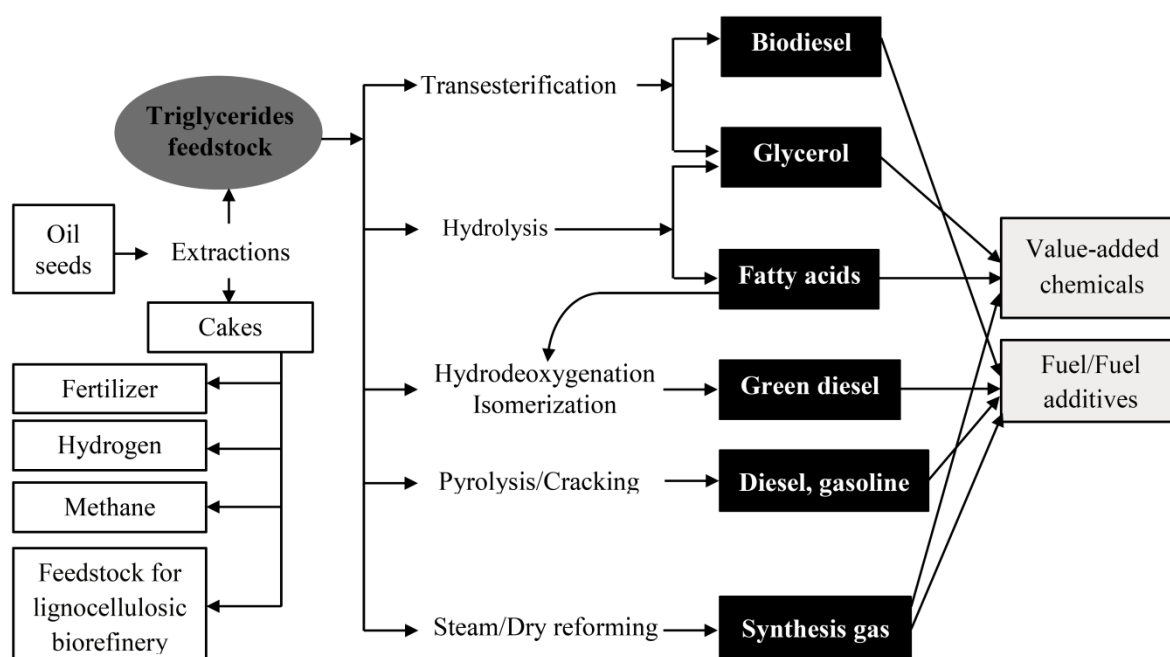


Fig. 5. Potential avenues of triglyceride biorefinery.

[41]. The conversion technologies are generally developed based on specific chemical nature of biomass. Therefore, the individual integrated biorefinery is expected to be developed based on specific type of feedstock. The biorefinery is thus classified into three broad categories based on chemical nature of biomass: (1) triglyceride biorefinery (TGB), (2) sugar and starchy biorefinery (SSB) and (3) lignocellulosic biorefinery (LCB) as shown in Fig. 5-7 respectively [14,42].

The present classification of biorefinery covers whole ranges of biomass and is based on known conversion technologies. However, conversion technologies and platform chemicals are expected to be expanded in near future in response to further scientific advancements and discovery of novel feedstock. The individual integrated biorefinery will be developed based on specific type of feedstock with the goals to produce certain ranges of products using specific conversion technologies. For example, LCB can be developed through gasification/fast pyrolysis, ethanol/butanol or other chemical intermediates.

3.3. Triglyceride biorefinery

The TGB has been received widespread appreciation throughout the globe primarily because of successful technological realization of biodiesel. The biodiesel is produced by transesterification of TGF with methanol in presence of alkali, acid or enzymes as catalyst under mild temperatures (323–353 K). The alkali catalyzed transesterification is most commonly employed especially for TGF with low free fatty

acid contents because of its faster reaction rate. The acid catalyzed followed by alkali catalyzed transesterification is generally used for TGF with high free fatty acid contents. During transesterification of TGF, glycerol is produced as a by-product (~10 wt% of biodiesel). The glycerol is mainly used in surfactant, cosmetics, medicines, sweetening agents and additives for food industries. When mass production of biodiesel is realized, novel processes for utilization of low-value glycerol must be developed to improve overall economics of the TGB [43-45]. The highly functionalized glycerol is either etherified with alcohols (e.g. ethanol or tert-butyl alcohol) or alkenes (e.g. isobutylene) or esterified with acetic acid or fatty acid to produce ethers/esters for application as fuels additives. Alternatively, glycerol can be converted to value-added chemical intermediates such as 1,2 propanediol and 1,3 propanediol (1,3 PDO) by reduction and acrolein by dehydration or SG by steam reforming. The acrolein is an important intermediate for chemical and agricultural industries [46]. 1,3 PDO is a key building block for polypropylene terephthalate. 1,3 PDO is generally produced by fermentation of glycerol using genes from natural strains [47]. The epichlorohydrin is another important chemical intermediate that can be produced from glycerol. It is mainly used for manufacture of epoxy resins and epichlorohydrin elastomers. Solvay recently developed epichlorohydrin manufacturing process from glycerol [48]. The process involves reaction between glycerol and hydrochloric acid to produce dichloropropanol. The dehydrochlorination of dichloropropanol leads to epichlorohydrin. Solvay developed another process for controlled

condensation of glycerol to manufacture polyglycerols (diglycerol and polyglycerol-3) [49]. The polyglycerols provides an opportunity to produce polyglycerol esters for applications as antifogging and antistatic additives, lubricants or plasticizers and in food and cosmetic industries.

The soap industries generally hydrolyze TGF to corresponding fatty acids and glycerol either directly in absence of any catalysts (at 483 K and high pressure) or in presence of small amounts of sulfuric acid or more usually zinc oxide (423 K) [50]. Following hydrolysis, water, volatile components and glycerol are separated by distillation to obtain crude fatty acids mixtures. A series of vacuum distillation in combination with crystallization or solvent extraction are generally used to obtain various fatty acid fractions from crude fatty acids mixture. The fatty acids are then converted to various oleochemicals (metal salts, fatty amides, nitriles, alcohols and alcohol ethoxylates) [39] for their applications as soaps (sodium salt of fatty acids), surfactants (fatty alcohol ethoxylates), plasticizer, emulsifiers and lubricants (fatty esters) [15,50-55]. The genetic engineering approaches made significant contribution for increasing concentration of a particular fatty acid in vegetable oils. For example, erucic acid in rapeseed oil can be increased from 0% to over 50%; while lauric acid can be varied from 0% to 37% [50]. The oleic acid contents in sunflower oils has been increased to over 92% [50].

The crude fatty acids mixture can also be used as feedstock for production of green diesel by deoxygenation in presence of supported metals catalysts [56]. The pyrolysis in absence of any catalyst in the temperatures range of 573–773 K under atmospheric pressures [57] or catalytic cracking over various solid acid catalysts in the temperature range of 623–773 K [58-59] provides another opportunity to produce gasoline or diesel range fuels directly from TGF. However, significant loss of TGF in the form of light hydrocarbon gaseous products and low yields of liquid hydrocarbon fuels limits their widespread acceptability so far. On the other hand, TGF can be hydrodeoxygenated to eliminate oxygen heteroatom in the form of water, CO and CO₂ over supported metals catalysts (e.g. NiMo and CoMo) in the temperature range of 523–693 K under high hydrogen pressures (up to 100 bars) [60-62]. The resultant hydrocarbons are hydro-isomerized to branched hydrocarbons in high yield with properties similar to petrodiesel. The hydro-isomerization step is necessary to adjust cold flow properties of the green diesel. In this process, the propane is obtained as a by-product that could be a potential feedstock for petrochemical industry. The possibility of using existing petroleum refinery infrastructure and co-processing with petroleum derived fuels are associated advantages of this

process. The TGF can be steam [19] or dry [18] reformed to produce SG suitable as feedstock for production of liquid hydrocarbon fuels [63-65], methanol, ethanol [66-67] or higher alcohols by Fischer-Tropsch synthesis (FTS) or other value-added chemicals.

During the processing and extraction of oils from seeds, huge quantities of cellulosic biomass (cakes, frond, trunk, fibre, shell, empty fruit bunches and straws) are generated. For example, ~10% of the whole palm tree forms palm oil, while remaining 90% biomass is full of fibre and cellulose [68]. These biomass are generally burnt as fuels for electricity generation. However, these biomass could be processed in LCB to produce hydrogen, methane and fertilizer [39,69-72]. The de-oiled cake generated during extraction of oils from seeds has potential to generate residual protein [39]. The edible protein can be utilized for production of essential amino acids for animal feeds and human consumption. The non-edible oil seeds cake like jatropha, neem, karanja, etc. can be used to produce bio-pesticides and amino acids for non-food applications. The residual biomass left after extraction of oils from microalgae can be utilized to produce bulk chemicals, food and feed ingredients [73-74]. The conventional thermochemical conversion technologies such as gasification, fast pyrolysis and direct combustion can be used to produce SG, bio-oils and electricity respectively from residual biomass [75]. The biochemical conversion processes such as anaerobic digestion and yeast fermentation can be used to produce biogas/bio-hydrogen and ethanol/butanols respectively [75].

3.4. Sugar and starchy biorefinery

The yeast fermentation of SSF to ethanol is widely practiced industrial process [76-77]. The concepts of SSB were thus commenced through ethanol for its application as gasoline additive. Currently, ethanol alone accounts for ~94% of global bio-fuels production [78]. In the fermentative conversion of starch to ethanol, starch is enzymatically broken down into glucose [39]. The mash (an aqueous solution typically containing 15–20% starch) is first prepared by grinding and mixing with water. The mash is then treated with enzyme, amylase to liberate maltodextrin oligosaccharides. The dextrin and oligosaccharides are further hydrolysed to glucose, maltose and isomaltose by enzymes such as pullulanase and glucoamylase. The mash is then fermented to ethanol by Baker's yeast under ambient temperature. The dilute aqueous solution containing 4-4.5% ethanol is subsequently separated by distillation followed by dehydration to fuel grade ethanol. The ethanol is generally used as solvents/chemicals and finding fresh applications

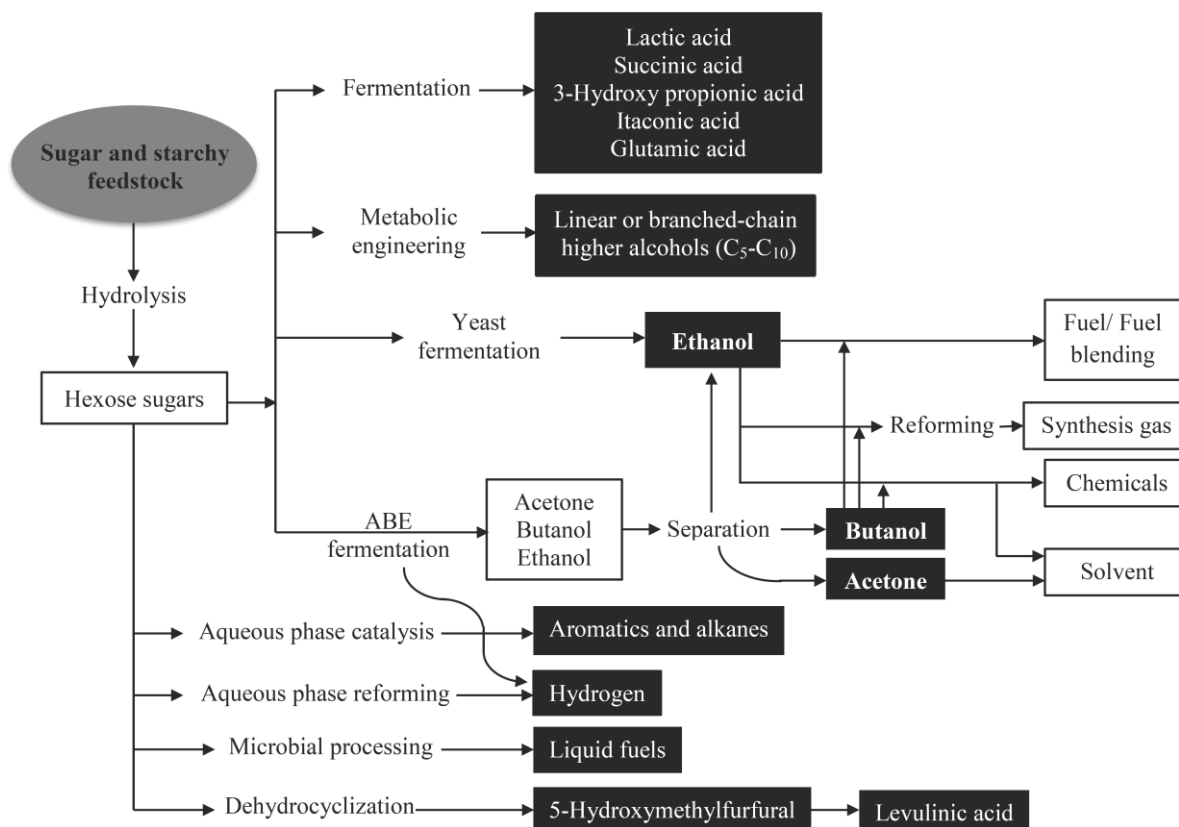


Fig. 6. Potential avenues of sugar and starchy biorefinery.

as precursor for hydrocarbon fuels, chemicals and aromatics in integrated biorefinery [79-80]. The ethanol can be converted to diethyl ether, ethylene, higher hydrocarbons or aromatics over zeolite catalysts especially HZSM-5 depending on operation temperatures. The ethanol can also be transformed to important petrochemical building block chemicals (propylene and butadiene) and organic chemicals (acetaldehyde and acetic acid).

Recently, bio-*n*-butanol has been received notable attentions as bio-fuel because of its superior fuel qualities over bio-ethanol and biodiesel [81-85]. The bio-*n*-butanol is produced by ABE (ratio of butanol, acetone and ethanol is 6:3:1) fermentation of aqueous hexose sugars using clostridia acetobutylicum bacteria. The isobutanol having lesser toxicity and higher octane number compared to *n*-butanol and same essential fuel potentials as *n*-butanol has been deliberated as one of the promising bio-fuels of the future. The ABE fermentation also produces carbon dioxide and hydrogen (typically $\sim 1/10^{\text{th}}$ of mass of butanol) as by-products that can be used to generate heat and power or as a source of renewable hydrogen [84]. The low butanol titer (~ 13 g/lit) in the fermentation broth however limits widespread acceptability of ABE fermentation so far. Additionally, bio-butanol has extensive array of market potentials as solvent and derivatives (butylenes and hydrocarbons) to fulfill the goals of integrated

biorefinery [86-88]. Additionally, SG can be produced by steam reforming of ethanol [89-91], butanol or acetone-butanol-ethanol mixture [92]. The metabolic engineering provides another opportunity to produce linear or branched-chain higher alcohols (C_5-C_{10}) from carbohydrates [93-96]. These alcohols especially branched C_5 alcohols have received remarkable attention in recent times as gasoline substitutes due to their higher energy density and lower hygroscopicity than ethanol. However, the low solvent titer debarred their immediate commercialization. The highest titer reported for 1-hexanol was ~ 210 mg/L [96].

The aqueous glucose solution is also fermented to various platform chemicals such as lactic acid, succinic acid, 3-hydroxy propionic acid, itaconic acid and glutamic acid [15]. The majority of lactic acid is currently produced by bacterial fermentation. It is traditionally used in food industry and finding newer applications in the field of organic chemicals (e.g. alkyl lactates, propylene glycol, propylene oxide, acrylic acid) and polymers production especially polylactic acid (PLA) [97]. At present, PLA has been received considerable interests throughout the globe as biodegradable plastics. The DuPont patented the technology for production of high-molecular weight PLA. Since then several industries have come forward to commercialize PLA including pioneering company,

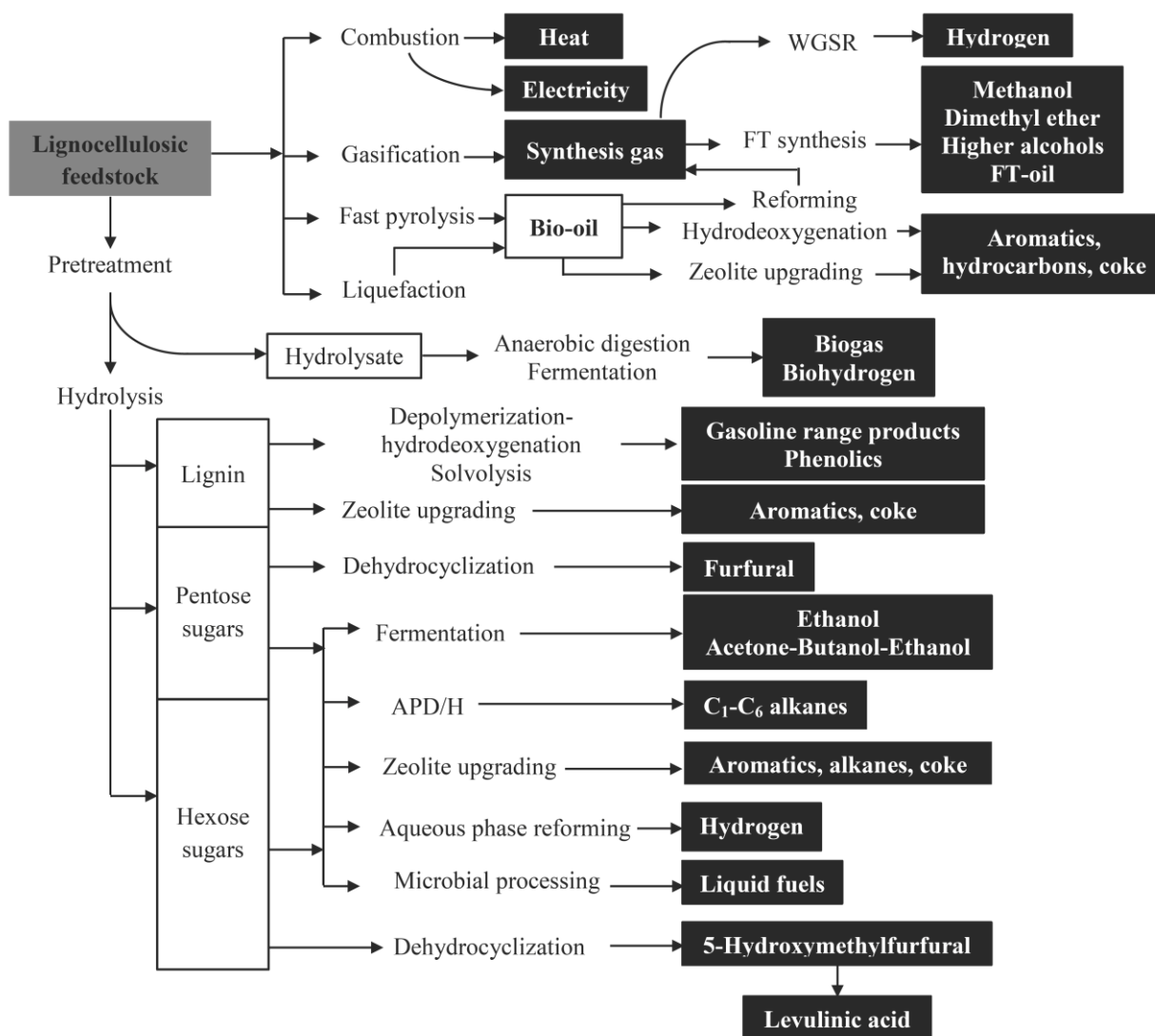


Fig. 7. Potential avenues of lignocellulosic biorefinery.

Nature Works LLC and Cargill Inc. [98]. The succinic acid is another important platform chemical in biorefinery. It has wide ranges of applications including raw material for polyurethanes, coatings, adhesives, sealants and personal care ingredients. The companies such as MBI and BioAmber are currently producing bio-based succinic acid through fermentation of carbohydrate using re-engineered bacteria at commercial scale [99-100]. The 3-hydroxypropionic acid is one of the top priority platform chemicals due to its multi-functionality that permits its transformation to spectrum of chemicals (e.g. acrylic acid, 1,3 PDO, methyl acrylate, acrylamide, malonic acid, propiolactone and acrylonitrile) and various polymers (e.g. propiolactone and polyesters) [101-102]. 3-Hydroxypropionic acid can be produced biologically from glucose and glycerol. However, the commercial production of 3-hydroxypropionic

acid is still limited due to its high toxicity that results product inhibition, low product yield and high production cost. 1,3 PDO can also be produced from carbohydrates. Genencor and DuPont have developed single organism catalytic route for direct conversion of D-glucose to 1,3 PDO. Joint venture of DuPont Tate & Lyle Bio Products is currently producing 63000 tons of 1,3 PDO annually from corn in their Loudon plant in Tennessee, USA [103].

3.5. Lignocellulosic biorefinery

The LCF is world's most abundant biomass with complex chemical compositions. The LCB thus provides potential avenues for spectrum of bio-products through multiple processing approaches [42,104-107]. The LCF can be processed directly through thermochemical processes such as combustion, gasification,

liquefaction and fast pyrolysis. The LCF can also be processed through biological routes like fermentation, digestion and microbial processing or chemical routes such as aqueous phase dehydration/hydrogenation (APD/H).

3.5.1. Combustion and gasification

The combustion of neat biomass or together with coal is an established technology for production of heat or combined heat and power using Rankine cycle. Huge numbers of combined heat and power plants are currently operating worldwide. The suitability of biomass combustion in micro, small and medium scale makes this technology as an ideal choice for decentralised biorefinery [108]. Alternatively, the LCF is gasified by sub-stoichiometric amounts of air at high temperatures (1073–1173 K) to produce SG for applications as a source of hydrogen in chemical industries or for conversion to fuels and organic chemicals by FTS [8,109–110]. However, presence of tars and methane in the resulting SG mandates complex downstream processing making biomass gasification gigantic in nature and economically unviable. In recent times, catalytic biomass gasification has been attracted widespread attention to improve efficiency of biomass gasification. The catalytic biomass gasification enhances the efficiency of biomass gasification to the extents ~10% [111].

3.5.2. Liquefaction and fast pyrolysis

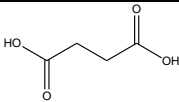
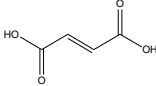
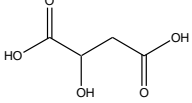
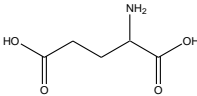
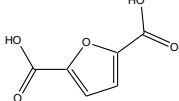
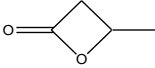
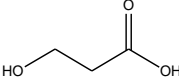
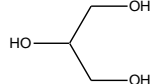
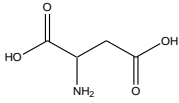
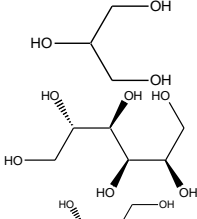
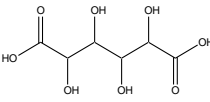
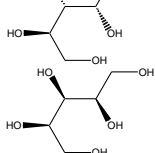
The liquefaction and fast pyrolysis are two thermochemical processes for direct conversion of LCF into liquid products commonly known as bio-oil or bio-crude. The liquefaction of biomass is usually carried out at moderate temperature (523–823 K) and high pressure (5–25 MPa) in presence of either water (hydrothermal liquefaction) or organic solvents (solvolytic liquefaction) [112]. The advantage of the liquefaction is that it can handle biomass with high levels of moisture contents. In this process, the macromolecules of the biomass are first disintegrated to smaller fragments by hydrolysis [113]. These fragments are further degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation reactions. The commercial applications of biomass liquefaction are however limited due to corrosive nature of the product (that requires expensive alloys) and high operating pressure that makes the process highly expensive [114]. In fast pyrolysis, LCF is thermally disintegrated in a fluidized bed reactor at ~773 K with a high heating and quenching rate [1,115]. The high water and oxygen contents and presence of large number of chemical compounds of many classes however debarred direct applications of bio-oil as fuels/fuels additives or chemicals feedstock. The bio-oil can be upgraded to liquid

hydrocarbon fuels by catalytic hydrodeoxygenation in presence of high hydrogen pressure (75–300 bars) at 523–723 K [78,116–118] or hydrocarbons/aromatics by zeolite upgrading under atmospheric pressure at 573–873 K or SG by steam reforming [119]. The former method is most promising one due to higher potential yields of oils with greater degrees of oxygen removal and lesser yields of coke.

3.5.3. Fermentation and anaerobic digestion

The LCF is recalcitrant in nature because of protective plant cell wall composed of lignin. The LCF is therefore subjected to pretreatment to disrupt cellulose-hemicellulose-lignin networks [120]. The pretreatment thus enhances accessibility of carbohydrates of LCF for subsequent hydrolysis and fermentation. The solid residue (containing mainly cellulose and remaining hemicellulose and lignin) recovered from pretreatment are subsequently hydrolyzed either enzymatically using cellulases (for cellulose) or hemicellulases (for hemicellulose) or chemically using sulfuric acid or other acids to monomer sugars [121–122]. The hexose sugars are easily fermented to either ethanol by Baker's yeast or butanols by ABE fermentation using clostridia acetobutylicum bacteria [29,123–124]. Ideally, pentose sugars should also be fermented to ethanol or acetone-butanol-ethanol either in separate reactors or together with hexose sugars in the same reactor using two different microorganisms called co-fermentation. However, limited availability of suitable strains together with slower fermentation rate compared to hexose sugars prohibits their proper utilization for alcoholic bio-fuels so far. At present, the cost of ethanol from LCF is almost double compared to corn ethanol due to expensive pretreatment step [125]. This restrains widespread acceptability of LCF for production of alcoholic bio-fuels so far. The economics of cellulosic ethanol however can be improved by two different approaches: (1) integration of cellulose hydrolysis and fermentation in single reactor commonly known as simultaneous saccharification and fermentation [126] or (2) consolidated bioprocessing where cellulase and hemicellulase production, hydrolysis of carbohydrates and co-fermentation of hexose and pentose sugars are integrated in single reactor [127–128]. The soluble hemicellulose fraction obtained from pretreatment step (called hydrolysate) containing mainly pentose sugars or effluents from fermentation can also be utilized to produce biohydrogen or biogas by dark/photo fermentation and anaerobic digestion respectively [70–72,129]. The MSW and biorefinery effluents containing good amounts of organic matters can also be utilized for biogas production.

Table 3
Original list of platform chemicals.

1,4-Diacids	 <p>Succinic acid</p>  <p>Fumaric acid</p>  <p>Malic acid</p>	Glutamic acid	
2,5-Furan dicarboxylic acid		3-Hydroxybutyrolactone	
3-Hydroxypropanoic acid		Glycerol	
Aspartic acid		Sorbitol	
Glucaric acid		Xylitol/arabinitol	

3.5.4. Lignin conversion

The huge quantities of lignin are produced as a by-product during the conversion of LCF to alcoholic bio-fuels or value-added organic chemicals. The overall economics of the LCB can be improved by proper utilization of such low-value (but high volume) lignin to valuable products. The lignin can be converted to gasoline range fuel additives or phenolic building block chemicals by either simultaneous lignin depolymerization and hydrodeoxygenation in single reactor, base catalyzed lignin depolymerization followed by hydrodeoxygenation in two different reactors or solvolysis using hydrogen donating solvents [130-133]. The world's most abundant aromatic polymer, lignin can also be upgraded to aromatic feedstock by zeolite upgrading using HZSM-5 catalysts [134].

3.5.5. Biosynthetic pathways

The biosynthetic pathways using genetically engineered microorganisms provides another opportunity for direct transformation of aqueous C₅ and C₆ sugars to short-chain, branched-chain and cyclic alcohols, alkanes, alkenes, esters and aromatics that separates spontaneously from aqueous phase [135-137].

3.5.6. Aqueous phase dehydration/hydrogenation

The APD/H provides wonderful opportunities for production of various platform chemicals such as furfurals (5-hydroxymethylfurfural (HMF) and furfural) and LA. These platform chemicals have huge derivative potentials for specialty chemicals, polymers, liquid alkanes and fuel additives. HMF can be converted to 2,5-dihydroxymethylfuran, 2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran, 2,5-diformylfuran, 2,5-furandicarboxylic acid (FDCA), LA and linear alkanes [138]. Furfural is transformed to various chemical intermediates (e.g. furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, furoic acid and maleic acid), linear alkanes, phenol-formaldehyde resin [138-140]. HMF and furfural are traditionally produced by dehydrocyclization of hexose and pentose sugars respectively. The reaction is usually carried out using either aqueous mineral acids such as HCl or H₂SO₄ or water-tolerant solid acids in a biphasic reactor to extract HMF/furfural continuously into organic phase thereby preventing over-reactions of intermediates in aqueous phase [77]. Large numbers of commercial processes are currently operating worldwide for production of furfurals using aqueous mineral acids as catalyst [141]. LA can be transformed to wide range of specialty chemicals and products including resins, plasticizers and textiles [142-143]. LA is generally

produced by hydration of HMF. LA can also be produced from hemicellulose derived pentose sugar, xylose. The process involves dehydration of xylose to furfural followed by its hydrogenation to furfuryl alcohol which is then hydrolyzed to LA. Recently, Biofine Technology, LLC of Framingham, Massachusetts developed a process for production of renewable LA using Biofine process [144]. The process involves pretreatment of LCF using dilute mineral acid. The cellulose fraction is then converted to LA with formic acid as a co-product. The hemicellulose fraction is converted to either furfural or upgraded to LA.

The production of hydrocarbon fuels or fuels additive from these platform chemicals involves series of reactions to eliminate oxygen heteroatoms (dehydration, hydrogenolysis, hydrogenation and decarbonylation/decarboxylation) and increase molecular weight by C–C bond forming reactions (aldol-condensation, ketonization and oligomerization) [142,145–150]. In 2010, Virent and Shell started production of bio-gasoline and gasoline blend components in the demonstration plant located at Virent's facilities in Madison, Wisconsin USA [151]. Virent's BioForming® technology is based on combination of aqueous phase reforming (APR) of carbohydrates with modified conventional catalytic processing. In 2014, the company successfully cleared registration from US Environmental Protection Agency for blending bio-gasoline with petro-gasoline to the extents of 45%. In 2014, Virent further announced that Coca-Cola company is making additional investments for commercialization of bio-based para-xylene, BioFormPX®.

3.6. Platform chemicals

Almost all organic chemicals and finished products manufactured in petrochemical industry are derived from a set of few building block chemicals [32]. The biorefinery in principle should also produce similar kinds of building block chemicals from biomass to meet societal needs of organic chemicals and polymers commonly known as platforms chemicals. In 2004, Pacific Northwest National Laboratory (PNNL) and NREL shortlisted thirty potential candidates from a list of more than three hundred candidates based on petrochemical model of building blocks, chemical data, known market data, properties and performance of the candidates [152]. These thirty chemicals were further reduced to twelve based on their potential markets as building blocks and technical complexity of synthetic pathways (Table 3) [152].

The bio-based products developments progressed significantly since 2004. Therefore, based on recent trends of bio-based products opportunities from carbohydrates, updated group of “Top 10 + 4” platform chemicals were identified based on similar criteria used in the 2004 report (Table 4) [153]. With exception of glycerol and isoprene, all other platform chemicals are essentially produced from sugars derived from various sources of carbohydrates by biological, chemical or enzymatic means [15,154–159] as shown in Fig. 8. These platform chemicals have tremendous potentials for conversion to several high-value bio-based chemicals and polymers [155,160–162]. The paradigm shift from hydrocarbons based building block chemicals in petrochemical industry to highly oxygen-functionalized bio-based platform chemicals will generate notable opportunities for chemical processing industry [163–164]. The use of oxygenated platform chemicals will eliminate needs of several capital-intensive oxidative processes used in petrochemical industry. The new chemistry based on these oxygen-functionalized platform chemicals is however unsuitable with existing petrochemical industry infrastructures.

The platform chemical, glycerol is however obtained as a by-product during the production of biodiesel that has enormous derivative potentials [43–45]. The biohydrocarbons are gradually gaining interests as platform chemical for wide ranges of applications as hydrocarbon fuels and building block chemicals [96,165–166]. The biohydrocarbons include long-chain alkanes and alkenes (ethylene, propylene, butylenes and butadienes), long-chain terminal alkenes (C₆–C₂₀) and isoprenoids (isoprene, farnesene, bisabolene and pinene). The biohydrocarbons can be synthesized either from sugars using genetically engineered microorganism (using host bacterium *E. coli* and the yeast *S. cerevisiae*) or directly using photosynthetic bacteria (cyanobacteria). The latter approach is quite attractive as it eliminates the need of sugars. The cyanobacteria synthesize hydrocarbons directly using CO₂ and sunlight as sole carbon and energy sources respectively. The isoprene is synthesized naturally in plants, animals and bacteria [135,167–168]. The isoprene units are recombined to produce large varieties of compounds with different molecular weights and degree of branching for applications as gasoline, diesel and jet fuel [169]. In 2008, Genencor announced collaborative research agreement with Goodyear to develop at industrial scale manufacture of isoprene using industrial biotechnology [170]. The isoprenoids especially farnesene (C₁₅ hydrocarbon) is gaining increasing interests in recent times for large-scale production of hydrocarbon fuels.

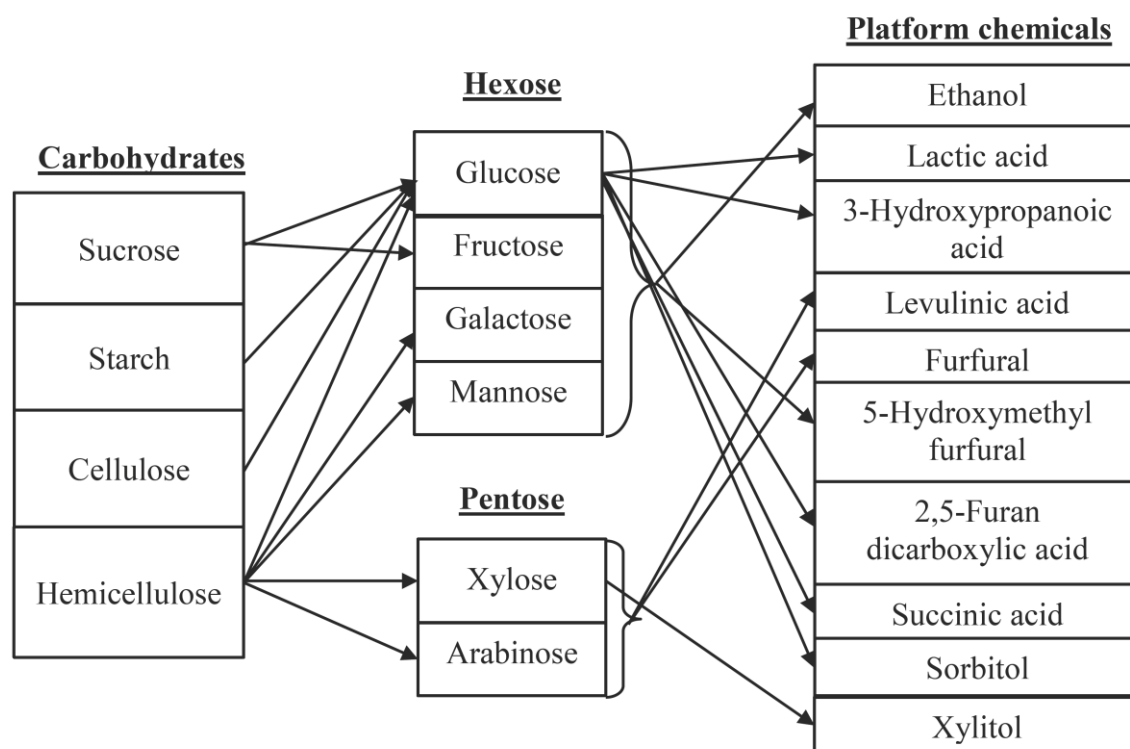


Fig. 8. Roadmap to platform chemicals from carbohydrates.

FDCA is another important platform chemical. It finds widespread applications as precursor for industrial plastics including bottles, textiles, food packaging, carpets, electronic materials and automotive applications. FDCA is currently considered as a substitute of terephthalic acid and polyethylene terephthalate (primarily used as a polyester precursor for cloths and plastic bottles) [143]. Avantium is currently operating pilot plant at Chemelot campus in Geleen, Netherlands to produce methyl levulinate, FDCA and polyethylene furanoate (PEF) [171]. PEF polyester offers plenty of opportunities as fibers, films and other applications. Together with the partners (Coca-Cola, Danone and ALPLA), the company is currently engaged to make PEF bottles as commercial success. The company also announced commercial scale manufacturing of 50,000 tons FDCA per year by 2016 using Avantium's YXY technology. The technology involves catalytic dehydration of carbohydrates in methanol to methoxymethyl furfural and methyl levulinate. The methoxymethyl furfural is subsequently transformed to FDCA by catalytic oxidation in acetic acid. FDCA is further polymerised with ethylene glycol to produce PEF.

Sugar alcohols (xylitol and sorbitol) are generally used in pharmaceuticals, oral and personal care products and as precursor for value-added chemicals [172-174]. The sugar alcohols are finding newer applications as intermediates for the production of hydrocarbons fuels through aqueous phase catalysis. The xylitol is also used as natural

sweetener for diabetics. The xylitol and sorbitol are currently produced commercially by catalytic hydrogenation of xylose and glucose respectively over nickel catalyst under high temperature and pressure (403–423 K and 4-12 MPa H₂). Sugar alcohols can also be produced through metabolic engineering using *E. coli* as an effective host organism [173-174].

Table 4
Revised list of platform chemicals.

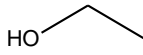
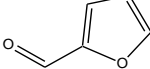
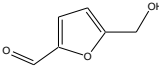
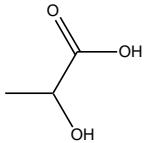
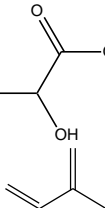
Ethanol		Biohydrocarbons
Furfural		Succinic acid
5-Hydroxymethyl furfural		Hydroxypropionic acid/aldehyde
Furan dicarboxylic acid	-	Levulinic acid
Glycerol and derivatives	-	Sorbitol
Lactic acid		Xylitol
Isoprene		

Table 5
Annual surplus availability of crop residues in India [185].

Feedstock		Surplus availability, MMT/annum
Sugar cane	Tops	79.5
	Bagasse	6.4
Oilseeds	Waste	17.3
Water hyacinth	Whole	14.0
Cotton	Stalks	11.4
Rice straw	Straw	8.5
	Husk	0.4
Wheat	Straw	9.1
Pulses	Waste	5.7
Maize	Stover	1.1
	Cob	1.7
Bamboo	Husk	1.1
	Top, Root, Leaves	3.3
Jowar	Stover	1.6
Pine	Needles	1.2
Bazra	Stalks	1.2
Ragi	Stalks	0.5
Chillies	Stalks	0.5
Total		164.5

3.7. Comparisons of biorefinery

3.7.1. Availability and cost of feedstock

The LCF is world's most abundant and inexpensive biomass. In general, LCF (\$3 per GJ) is fairly cheaper compared to edible biomass (5 \$ per GJ), crude oils (10–15 \$ per GJ) and vegetable oils (18–20 \$ per GJ) [175]. Therefore, LCB has immense potentials to meet societal needs of energy, fuels and organic chemicals. However, recalcitrant nature of LCF and excessive production costs of bio-fuels together with dearth of cost-competitive conversion technologies limits large-scale operation of LCB so far [176]. At present, the cost of cellulosic-ethanol is almost double compared to corn-ethanol [175].

3.7.2. Feedstock diversity

The chemical composition of TGF and SSF are fairly consistent irrespective of their sources and recovery processes [177]. Moreover, the carbohydrates are easily separated from SSF either intact or directly as sugars. Vegetable oils are also easily extracted from seeds. These characteristic features enable conversion of these biomass to bio-fuels and organic chemicals using unique processing technology globally. On the contrary, the chemical compositions and physicochemical properties of LCF vary considerably depending on types and sources of biomass. The diversity of LCF is considered as a key bottleneck of LCB. However, it is not quite unusual even in existing petroleum refinery where chemical nature of crudes from one well differ drastically from another well.

The development of flexible processing technology for processing of LCF of varying chemical composition/physiology is thus necessary for successful realization LCB. Alternatively, different types of LCF can be segregated into its constituent fractions (cellulose, hemicellulose and lignin) with reasonably consistent chemical composition. The individual fractions can be further processed using specific conversion technologies. Though latter approach sounds fairly promising; the success of this approach however depends entirely on cost of segregation of biomass. Recently, NREL developed a pretreatment process, called clean fractionation, to segregate LCF into three major fractions [178]. CIMV, France also developed a technology for manufacture of cellulose pulp, bio-lignin and C₅ sugars syrup from LCF [179].

3.7.3. Edible versus non-edible feedstock

As opposed to LCB, SSB and TGB use edible biomass as feedstock. The continuous and large-scale usage of expensive edible biomass is however not economically feasible and may lead to depletion of food supply and escalation of food price leading to economic imbalance especially in densely populated countries like India. The cultivation of vegetable oils and SSF in excess of food requirements could be an alternative to overcome this problem. However, large fractions of arable lands needs to be diverted for energy crops to achieve the goal making the proposition completely unacceptable. The usage of non-edible biomass such as non-edible oils, waste edible oils or microalgal oils could be an alternative approach to achieve the goals of biorefinery. The most abundant non-edible oils in India are karanja, mahua, neem, jatropha and castor etc. Additionally, Government of India promoted cultivation of jatropha in non-agricultural lands as a source of non-edible oils for biorefinery.

At present, most of the biorefinery technologies are in nascent stage and concepts are gradually nucleating with continuous flow of fresh ideas of feedstock and conversion strategies by numerous researchers and industries throughout the world. It is quite imperative to conclude at this stage which types of biorefinery will be predominately acceptable globally in near future. The LCB and microalgal biorefinery is expected to dominate if technological advancements results cost-competitive production of bio-fuels/organic chemicals from these biomass.

3.8. Availability of biomass

The annual production of dry woody biomass from terrestrial plants in the world is 1.3×10^{10} metric tons which is equivalent to 7×10^9 metric tons of coal or about two-thirds of the world's energy consumptions [180]. Additionally, ~180

Table 6
Comparison of jatropha with microalgae as source of biodiesel.

Potential jatropha plantation area ^a	Food grains area during 2011–12 ^a	Consumption of transportation fuels in 2009–10, tons	Biodiesel yield, toe /hectare	Area required to meet transportation fuels ^a	% of area required to meet transportation fuels			
					Jatropha area	Food grains area		
13.4 [211]	125.49 [212]	7.3765×10 ⁰⁷	Jatropha	1.29 ^b	57.2	426.7	45.6	
			Microalgae ^c					
			Photobioreactor	43.4	1.70	12.7	1.4	
			Raceway ponds	31.5	2.34	17.5	1.9	

^a Million hectares

^b Assumptions: annual yield of seeds = 7 tons/hectare, yield of biodiesel= 1 liter biodiesel/4 kg seeds, density=860 kg m⁻³, 1 ton biodiesel = 0.86 toe.

^c Assumptions: oil content=30 wt% of dry biomass, density=860 kg m⁻³ [213].

million tons of cellulosic biomass is available annually from agriculture and other sources [180]. Biomass Research & Development Technical Advisory Committee set a very challenging target of supply of US's 5% power, 20% transportation fuels and 25% chemicals from biomass by 2030 [181]. This will eventually reduce nation's 30% petroleum consumption. To achieve this goal, more than one billion tons of dry biomass is required annually—a five-fold increase over the current consumption. The US DOE survey in 2005 showed that annual availability of biomass was 1.3 billion tons [181]. This can potentially produce 130 billion gallons of transportation fuels (ethanol, mixed alcohols, green gasoline, biodiesel and green diesel) which corresponds to reduction of country's ~40% petroleum consumption [181]. Based on revised estimates in 2011, annual consumption of dry biomass in US was nearly 200 million tons with ~130 million tons being obtained from forests (fuel wood, mill residue, pulping liquors and MSW) [182]. This is equivalent to nation's 4% total primary energy consumption [182]. The dry biomass consumption was further projected to 329 million tons by 2030.

The accurate estimates of availability of surplus biomass are however very scarce in India. According to Ministry of New and Renewable Energy, ~120–150 million metric tons of surplus biomass (agricultural and forestry residues) are available annually in India which is equivalent to power generation potential of about 18,000 MW [183]. If entire surplus biomass is diverted to bio-fuels production, it can potentially produce 1.35×10⁷ tons of oils equivalent (toe) or 1.34×10⁷ tons of diesel or 1.29×10⁷ tons of petrol (assuming 1 toe =41.87 GJ; 1 ton diesel =1.01 toe; 1 ton petrol = 1.05 toe) [184]. The petroleum consumption in India during 2010–11 was 14.18×10⁷ metric tons with contributions of major transportation fuels were 1.42×10⁷, 5.08×10⁶ and 5.99×10⁷ metric tons for MoGas, ATF and HSDO respectively [7]. The

surplus biomass thus can potentially reduce consumption of nation's ~10% petroleum, ~90% petrol or ~22% diesel. Apart from this, ~5000 MW power could be generated through bagasse based cogeneration in the country's 550 sugar mills [183]. Pandey et al. also reported similar estimates of availability of surplus crop residues [185]. Their estimates showed that 164.5 MMT of surplus crop residues were available in India during 2007–2008 which was 26.4% of overall agricultural biomass generation (Table 5). The sugarcane tops are highest surplus crop residue followed by oilseed residue, cotton stalks, rice straw and wheat straw.

Additionally, India has estimated annual production potential of ~20 million tons of non-edible oil seeds which is equivalent to 3.69×10⁶ toe or ~2.5% of petroleum consumptions during 2010–2011 [184,186]. The planning commission of India identified ~13.4 million hectares non-agricultural lands for cultivation of jatropha that can potentially produce 1.73×10⁷ toe which is equivalent to consumption of ~12% petroleum or ~20% transportation fuels during 2010–2011 (Table 6). As observed from the table, to fulfill entire transportation fuels demands in India by biodiesel, 49.2 million hectares lands are required for cultivation of jatropha which is ~39% of county's crop area. Diverting such large fractions of arable lands for cultivation jatropha is completely unacceptable.

In recent times, microalgae as a source of TGF have gained huge attention throughout the globe due to its exorbitantly high productivity with high oils contents. The calculation showed that ~12–18% identified jatropha cultivation area or less than 2% of arable area is sufficient to produce biodiesel from microalgae to fulfill country's present transportation fuels requirements (Table 6). However, such high biodiesel productivity has been achieved by short-term trials. Average annual microalgal biomass productivity of about 20–22 g

$\text{m}^{-2}\text{d}^{-1}$ ($\cong 18.8\text{--}20.7$ toe biodiesel/hectares for 30 wt% oils contents) has been achieved so far in small scale trials in open raceway ponds [187]. Considering such realistic microalgal biomass productivity, the whole transportation fuels requirements of India can be realized by only $\sim 3\%$ of arable lands.

The planning commission of India set a challenging target of blending 10% ethanol in gasoline and 20% biodiesel in diesel by 2011–2012 [188]. The current availability of surplus biomass in India is sufficient to meet this target provided availability of suitable conversion technologies and biomass collection logistics. However, with exception of Godavari Biorefineries Ltd. and Praj Industries Ltd., the commercial initiatives are limited in India. If entire surplus biomass is diverted to bio-fuels, it can reduce country's $\sim 25\%$ petroleum consumption only. The cultivation of short rotation and fast growing energy crops (grasses and trees) or highly productive microalgae and their conversion technologies should be emphasized for complete replacement of petroleum or at least transportation fuels by biomass in near future.

3.9. Challenges of biorefinery

- Feedstock diversity: The physical properties, chemical compositions and cost of LCF vary considerably depending on the types, sources and collection logistics. This diversity creates challenges to develop replicable biomass supply systems and specialized conversion technologies to bio-power or bio-fuels for various types of LCF [189].
- Biomass collection and transportation logistics: The centralized integrated biorefinery, that needs huge quantities of biomass, is expected to be located far away from biomass source. The collection and transportation of biomass especially lighter ones (grass, straws, stovers etc.) from distant field to biorefinery is extremely expensive. It was estimated that cost of delivery of switchgrass (without farming cost and payment to farmers) to a biorefinery of capacity 1814 dry tons/day (2000 dry tons/day) were: \$44–\$47/dry tons for baling, \$37/dry tons for loafing, \$40/dry tons for chopping and piling and \$48/dry tons for chopping and ensiling [190]. The availability of cost-effective small-scale biorefining technologies is thus crucial to reduce expensive transportation of biomass. These decentralized technologies will enable conversion of the lighter biomass to easy-to-transport highly dense form of biomass (e.g. baling for grasses, crop residues and forest

trimmings) or intermediates within the field or nearby locality [191]. The dense biomass or intermediates can then be easily transported and processed in centralized biorefinery [164]. For example, fast pyrolysis, that is economical at small scale, can be established for densification of voluminous biomass to bio-oil for decentralized biorefinery. Alternatively, combined heat and power plants can be developed at community scale producing 1 to 30 MW [191]. These decentralized systems have the potentials to source biomass locally with minimum infrastructure costs. T.L. Richard proposed three different biomass supply chain models for biorefinery: (1) independent local suppliers for smaller bio-energy facilities located close to biomass source, (2) large contiguous plantations where the individual company cultivates plants in vast areas adjacent to the industry and (3) regional or global commodity markets where aggregators can gather large quantities of biomass, blend as needed to meet desired specifications and then sell at market prices to buyers [191]. The consistent quality biomass can be ensured in the third approach.

- Seasonal variation: The biomass (especially agricultural biomass) are in general perennials making operations of biorefinery in a seasonal time-frame [32]. The long-term storage of biomass is one alternative to overcome this problem. The requirements of hefty storage space together with continuous degradation of biomass with time are associated challenges with long term storage of biomass. Alternatively, native biomass can be converted to easy-to-store stable intermediates. For examples, vegetable oils are extracted from seeds or cellulosic biomass can be segregated into cellulose, hemicellulose and lignin that can be stored for longer time-frame without further degradation.
- Land usage: The huge quantities of biomass are required to fulfill long-term goal of complete replacement of petroleum-derived fuels, organic chemicals and polymers by biomass. The goal should be achieved with minimal sacrificing of arable lands [192]. The usage of surplus agricultural residue, forestry waste and residue and MSW should be encouraged to avoid adverse impact on food supply. The cultivation of fast growing and highly productive biomass, for examples, microalgae and energy crops should also be focused without extensive change in arable lands usages.
- Compatibility with refinery infrastructure: Today's complex petroleum processing

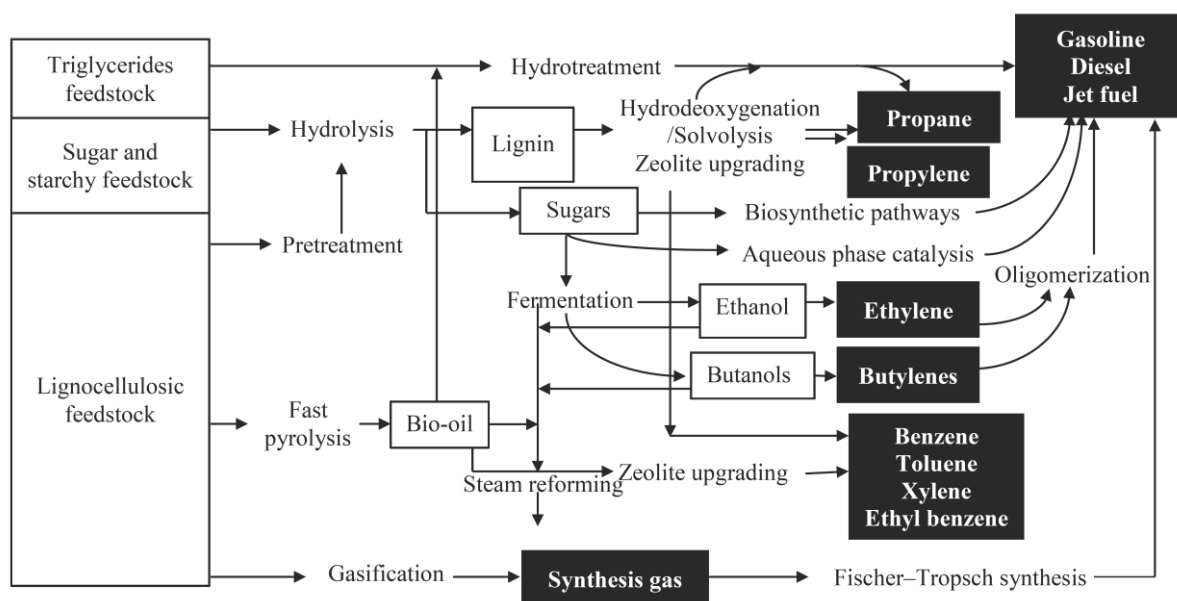


Fig. 9. Roadmap to hydrocarbons biorefinery.

technologies and associated infrastructures were developed with continuous efforts of last two century. The compatibility of biorefinery with existing petroleum refinery and petrochemical industry infrastructures is thus essential to eliminate the needs of capital-intensive new infrastructures. The compatibility will also facilitate rapid growths of biorefinery. Instead of oxygenated bio-fuels and platform chemicals, production of hydrocarbon fuels and building block chemicals (compatible with existing infrastructures) from biomass should be encouraged. In early concepts of biorefinery, the SG was thus considered as a potential platform chemical as existing gasification technology enables production of SG from biomass.

- Market and economic viability: Integrated biorefinery must optimize use of biomass to create products matched perfectly with market demands. These products should be economically competitive with fossil fuels. At present, ~85-90% petroleum refinery output goes for production of fuels with only ~10-15% being diverted to petrochemical industry for production of organic chemicals. The biorefinery in principal should also produce similar proportion of fuels and organic chemicals to match exactly with market demands.
- Sustainability: The life cycle analysis must be carefully modelled and monitored for various feedstock to understand economic, environmental and social impacts of biorefinery. Only a few lifecycle analysis were however reported so far using

agricultural residue, switchgrass as energy crops and wood residue [193-196].

- Consistent R&D investments: Government, academia and industry made significant contributions in developing feedstock and technologies to foster growth of nascent biorefinery. Many of these technologies remain in early stages of development. Therefore, on-going and consistent supports is essential for scientific understanding and technological developments of profitable manufacturing processes for biorefinery [189,192].

4. Hydrocarbon biorefinery

The oxygenated bio-fuels (biodiesel and ethanol) are not well accepted by consumers due to their lesser calorific value and hence lesser fuel mileage with almost same price as petroleum fuels. Additionally, these bio-fuels are incompatible with existing internal combustion engines that confines their applications for blending with petroleum derived fuels to limited extents only. On the other hand, new chemistry based on oxygen-functionalized platform chemicals needs developments of capital-intensive new infrastructures for their downstream conversion. Therefore, novel manufacturing concepts are nucleating for production of hydrocarbon fuels and building block chemicals from biomass analogous to petroleum refinery and petrochemical industry commonly known as hydrocarbon biorefinery (Fig. 9) [77,197].

The hydrocarbon biorefinery can be envisaged through thermochemical conversion processes such as gasification and fast pyrolysis. The SG produced by gasification of LCF or steam reforming of bio-

oils or alcoholic bio-fuels (ethanol and butanols) can be transformed to hydrocarbon fuels through FTS. The bio-oils produced by fast pyrolysis of LCF is upgraded to hydrocarbon fuels by hydrodeoxygenation and aromatic feedstock by zeolite upgrading [198-199]. The TGF is transformed to hydrocarbon fuels by hydrodeoxygenation with properties similar to petroleum diesel or jet fuel commonly known as green diesel and green jet fuel respectively [60,200-201]. The lignin can be transformed to fuels additives or phenolic building block chemicals through hydrodeoxygenation or aromatics by zeolite upgrading. The hydrocarbon biorefinery can also be envisaged through bio-ethanol and bio-butanols. The bio-ethanol and bio-butanols is dehydrated almost quantitatively using an acid catalyst to produce hydrocarbon building block chemicals, ethylene and butylenes respectively [202-205]. These olefins can be further transformed to hydrocarbon fuels through controlled oligomerization reaction [80,202-204,206]. The propane produced during hydrodeoxygenation of TGF and propylene obtained during zeolite upgrading of lignin as by-product could be a potential renewable feedstock for hydrocarbon biorefinery. The recent advancements of APD/H, APR, aqueous phase catalysis [77,87,145,147,207-208] and biosynthetic pathways [135-136,209] provides ample opportunities to wide range hydrocarbon fuels and building block chemicals. The carbohydrates of starchy biomass and LCF are converted to hydrocarbon fuels, mono-functional organic compounds and aromatics through a series of catalytic approaches. In 2013, Sapphire Energy, Inc. and Phillips 66 announced joint development agreement to produce highly branched and undecorated algae crude oil that can be processed in a refinery similar to crude oils to make all three major distillates – gasoline, jet fuel and diesel [210]. Sooner hydrocarbon bio-fuels and platform chemicals are going to be dominant over oxygenated bio-fuels and platform chemicals if technological advancements results competitive production cost [125].

5. Conclusions

The biorefinery provides potential avenues for production of heat, electricity, transportation fuels, organic chemicals and polymers from biomass through complex processing technologies. The biorefinery was classified into three broad categories based on the chemical nature of biomass: TGB, SSB and LCB. Consistent quality and easy to process feedstock for TGB and SSB leads technological realization relatively easy. Extensive usages of expensive edible-biomass for these biorefinery however pose serious threats of

food crisis, escalation of food prices and economic imbalance. LCB, that uses world's most abundant and inexpensive non-edible biomass, is most promising one. However, availability of huge quantities of biomass with consistent quality and cost-competitive processing technologies are key bottlenecks for its large-scale implementation. Cultivation of short rotation and fast growing energy crops or highly productive microalgae should be emphasized to fulfill long-term goal of complete replacement of fossil fuels with minimal sacrificing of arable lands. The small scale biomass processing technologies must be emphasized for decentralized biorefinery to avoid expensive transportation of biomass. The platform chemicals derived from carbohydrates of SSF and LCF provides notable opportunities to produce an array of derivatives to fulfill societal needs of organic chemicals and polymers. However, new chemistry and process based on these oxygen-functionalized platform chemicals are unsuitable with existing petrochemical industry infrastructures. New manufacturing concepts are thus evolving for production of hydrocarbon fuels and building block chemicals from biomass. The promise of utilization of existing petroleum refinery and petrochemical industry infrastructures are the advantages of hydrocarbon biorefinery.

Abbreviations

APD/H	aqueous phase dehydration/hydrogenation
APR	aqueous phase reforming
DOE	Department of Energy
FDCA	2,5-furandicarboxylic acid
FTS	Fischer-Tropsch synthesis
HMF	5-hydroxymethylfurfural
LA	levulinic acid
LCF	lignocellulosic feedstock
LCB	lignocellulosic biorefinery
MSW	municipal solid waste
NREL	National Renewable Energy Laboratory
PEF	polyethylene furanoate
1,3 PDO	1,3 propanediol
PLA	polylactic acid
PNNL	Pacific Northwest National Laboratory
SG	synthesis gas
SPB	sugar platform biorefinery
SSB	sugar and starchy biorefinery
SSF	sugar and starchy feedstock
TGB	triglycerides biorefinery
TGF	triglycerides feedstock
toe	tons of oil equivalent

References

- [1] Fernando S, Adhikari S, Chandrapal C, Murali N. Biorefineries: current status, challenges, and future direction. *Energy Fuels* 2006;20:1727–37.

- [2] International Energy Agency. Key world energy statistics. 2011. Available from: <http://www.iea.org/publications/freepublications/publication/key_world_energy_stats-1.pdf>.
- [3] Rostrup-Nielsen JR. Making fuels from biomass. *Science* 2005;308:1421–2.
- [4] Ohara H. Biorefinery. *Appl Microbiol Biotechnol* 2003;62:474–7.
- [5] Kamm B, Kamm M. Principles of biorefineries. *Appl Microbiol Biotechnol* 2004;64:137–45.
- [6] US Energy Information Administration, Annual Energy Outlook 2013. Available from: <<http://www.eia.gov/forecasts/aeo/er/pdf/tbla2.pdf>>.
- [7] Ministry of Petroleum & Natural gas, Government of India. Basic statistics on Indian petroleum & natural gas. 2010–11. Available from: <<http://petroleum.nic.in/welcome.html>>.
- [8] de Lasa H, Salaices E, Mazumder J, Lucky R. Catalytic steam gasification of biomass: catalysts, thermodynamics and kinetics. *Chem Rev* 2011;111:5404–33.
- [9] US Department of Energy, Biomass resources. Available from: <http://www.eere.energy.gov/basics/renewable_energy/biomass_resources.html>.
- [10] <<http://www.biowert.de/>>.
- [11] Sims REH, Hastings A, Schlamadinger B, Taylor G, Smith P. Energy crops: current status and future prospects. *Glob Chang Biol* 2006;12:2054–76.
- [12] Sánchez OJ, Cardona CA. Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresour Technol* 2008;99:5270–95.
- [13] Carriquiry MA, Du X, Timilsina GR. Second generation biofuels: economics and policies. *Energy Policy* 2011;39:4222–34.
- [14] Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. *Green Chem* 2010;12:1493–513.
- [15] Corma A, Iborra S, Velty A. Chemical routes for the transformation of biomass into chemicals. *Chem Rev* 2007;107:2411–502.
- [16] Kumar A, Sharma S. Potential non-edible oil resources as biodiesel feedstock: an Indian perspective. *Renew Sustain Energy Rev* 2011;15:1791–800.
- [17] Ghadge SV, Raheman H. Process optimization for biodiesel production from mahua (*Madhuca Indica*) oil using response surface methodology. *Bioresour Technol* 2006;97:379–84.
- [18] Yenumala SR, Maity SK. Thermodynamic evaluation of dry reforming of vegetable oils for production of synthesis gas. *J Renew Sustain Energy* 2012;4:043120.
- [19] Yenumala SR, Maity SK. Reforming of vegetable oil for production of hydrogen: a thermodynamic analysis. *Int J Hydrog Energy* 2011;36:11666–75.
- [20] Hoekman SK, Broch A, Robbins C, Cenicerros E, Natarajan M. Review of biodiesel composition, properties, and specifications. *Renew Sustain Energy Rev* 2012;16:143–69.
- [21] Hu Q, Sommerfeld M, Jarvis E, Ghirardi M, Posewitz M, Seibert M, et al. Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances. *Plant J* 2008;54:621–39.
- [22] Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Appl Energy* 2010;87:1083–95.
- [23] Atadashi IM, Aroua MK, Aziz ARA, Sulaiman NMN. Production of biodiesel using high free fatty acid feedstocks. *Renew Sustain Energy Rev* 2012;16:3275–85.
- [24] Parker R, Ring S. Aspects of the physical chemistry of starch. *J Cereal Sci* 2001;34:1–17.
- [25] Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind Eng Chem Res* 2009;48:3713–29.
- [26] US Department of Energy. Available from: <<http://www.oit.doe.gov/e3handbook>>.
- [27] Kim J, Yun S, Ounaies Z. Discovery of cellulose as a smart material. *Macromolecules* 2006;39:4202–6.
- [28] Hendriks ATWM, Zeeman G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour Technol* 2009;100:10–8.
- [29] Kuhad RC, Gupta R, Khasa YP, Singh A, Zhang Y-HP. Bioethanol production from pentose sugars: current status and future prospects. *Renew Sustain Energy Rev* 2011;15:4950–62.
- [30] Mäki-Arvela P, Salmi T, Holmbom B, Willför S, Murzin DY. Synthesis of sugars by hydrolysis of hemicelluloses - a review. *Chem Rev* 2011;111:5638–66.
- [31] Hu F, Ragauskas A. Pretreatment and lignocellulosic chemistry. *BioEnergy Res* 2012;5:1043–66.
- [32] Cherubini F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Convers Manag* 2010;51:1412–21.
- [33] Speight JG. The chemistry and technology of petroleum. fourth ed. CRC Press; 2007.
- [34] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass:

- chemistry, catalysts, and engineering. *Chem Rev* 2006;106:4044–98.
- [35] Lee S. Energy from biomass conversion. In Lee S, Speight JG, Loyalka SK, editors. *Handbook of alternative fuel technologies*. Taylor & Francis Group; 2007, p. 377–393.
- [36] Kamm B, Gruber PR, Kamm M. *Biorefineries—industrial processes and products*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; 2006.
- [37] Kamm B, Kamm M. Biorefinery – systems. *Chem Biochem Eng Q* 2004;18:1–6.
- [38] National Renewable Energy Laboratory (NREL). What is a biorefinery? Available from: <<http://www.nrel.gov/biomass/biorefinery.html>>.
- [39] Naik SN, Goud V V., Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. *Renew Sustain Energy Rev* 2010;14:578–97.
- [40] Nonato RV, Mantelatto PE, Rossell CEV. Integrated production of biodegradable plastic, sugar and ethanol. *Appl Microbiol Biotechnol* 2001;57:1–5.
- [41] Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Ree R Van, et al. Toward a common classification approach for biorefinery systems. *Biofuels, Bioprod Biorefin* 2009;3:534–46.
- [42] Octave S, Thomas D. Biorefinery: Toward an industrial metabolism. *Biochimie* 2009;91:659–64.
- [43] Zheng Y, Chen X, Shen Y. Commodity chemicals derived from glycerol, an important biorefinery feedstock. *Chem Rev* 2008;108:5253–77.
- [44] Zhou C-H, Beltramini JN, Fan Y-X, Lu G. Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem Soc Rev* 2008;37:527–49.
- [45] Vaidya PD, Rodrigues AE. Glycerol reforming for hydrogen production: a review. *Chem Eng Technol* 2009;32:1463–9.
- [46] Talebian-Kiakalaieh A, Amin NAS, Hezaveh H. Glycerol for renewable acrolein production by catalytic dehydration. *Renew Sustain Energy Rev* 2014;40:28–59.
- [47] Nakamura CE, Whited GM. Metabolic engineering for the microbial production of 1,3-propanediol. *Curr Opin Biotechnol* 2003;14:454–9.
- [48] <http://www.solvaychemicals.com/EN/Sustainability/Issues_Challenges/EPICEROL.aspx>
- [49] Boulos N, Caulier T. Polyglycerol esters demonstrate superior antifogging properties for films. *Plast Addit Compd* 2005:30–3.
- [50] Lancaster M. *Green chemistry: an introductory text*. The Royal Society of Chemistry; 2002.
- [51] Johansson I, Svensson M. Surfactants based on fatty acids and other natural hydrophobes. *Curr Opin Colloid Interface Sci* 2001;6:178–88.
- [52] Willing A. Lubricants based on renewable resources – an environmentally compatible alternative to mineral oil products. *Chemosphere* 2001;43:89–98.
- [53] Behr A, Westfechtel A, Gomes JP. Catalytic processes for the technical use of natural fats and oils. *Chem Eng Technol* 2008;31:700–14.
- [54] Hill K. Fats and oils as oleochemical raw materials. *Pure Appl Chem* 2000;72:1255–64.
- [55] Metzger JO, Bornscheuer U. Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification. *Appl Microbiol Biotechnol* 2006;71:13–22.
- [56] Snåre M, Kubičková I, Mäki-Arvela P, Eränen K, Murzin DY. Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel. *Ind Eng Chem Res* 2006;45:5708–15.
- [57] Maher KD, Bressler DC. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresour Technol* 2007;98:2351–68.
- [58] Al-Sabawi M, Chen J, Ng S. Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. *Energy Fuels* 2012;26:5355–72.
- [59] Taufiqurrahmi N, Bhatia S. Catalytic cracking of edible and non-edible oils for the production of biofuels. *Energy Env Sci* 2011;4:1087–112.
- [60] Kalnes TN, MarKer T, Shonnard DR, Koers KP. Green diesel production by hydrotreating renewable feedstocks. *Biofuels Technology* 2008:7–11.
- [61] Šimáček P, Kubička D, Šebor G, Pospíšil M. Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel. *Fuel* 2009;88:456–60.
- [62] Satyarthi JK, Chiranjeevi T, Gokak DT, Viswanathan PS. An overview of catalytic conversion of vegetable oils/fats into middle distillates. *Catal Sci Technol* 2013;3:70–80.
- [63] Khodakov AY, Chu W, Fongarland P. Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. *Chem Rev* 2007;107:1692–744.
- [64] Dalai AK, Davis BH. Fischer-Tropsch synthesis: a review of water effects on the

- performances of unsupported and supported Co catalysts. *Appl Catal A* 2008;348:1–15.
- [65] Klerk A de. Fischer–Tropsch fuels refinery design. *Energy Env Sci* 2011;4:1177–205.
- [66] Spivey JJ, Egbebi A. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chem Soc Rev* 2007;36:1514–28.
- [67] Subramani V, Gangwal SK. A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol. *Energy Fuels* 2008;22:814–39.
- [68] Chew TL, Bhatia S. Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. *Bioresour Technol* 2008;99:7911–22.
- [69] Luo G, Talebnia F, Karakashev D, Xie L, Zhou Q, Angelidaki I. Enhanced bioenergy recovery from rapeseed plant in a biorefinery concept. *Bioresour Technol* 2011;102:1433–9.
- [70] Ward AJ, Hobbs PJ, Holliman PJ, Jones DL. Optimisation of the anaerobic digestion of agricultural resources. *Bioresour Technol* 2008;99:7928–40.
- [71] Demirel B, Scherer P, Yenigun O, Onay TT. Production of methane and hydrogen from biomass through conventional and high-rate anaerobic digestion processes. *Crit Rev Env Sci Technol* 2010;40:116–46.
- [72] Shilton A, Guieysse B. Sustainable sunlight to biogas is via marginal organics. *Curr Opin Biotechnol* 2010;21:287–91.
- [73] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. *Renew Sustain Energy Rev* 2010;14:217–32.
- [74] Wijffels RH, Barbosa MJ, Eppink MHM. Microalgae for the production of bulk chemicals and biofuels. *Biofuels, Bioprod Biorefin* 2010;4:287–95.
- [75] Brennan L, Owende P. Biofuels from microalgae—a review of technologies for production, processing, and extractions of biofuels and co-products. *Renew Sustain Energy Rev* 2010;14:557–77.
- [76] Balat M, Balat H, Öz C. Progress in bioethanol processing. *Prog Energy Combust Sci* 2008;34:551–73.
- [77] Serrano-Ruiz JC, Dumesic JA. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. *Energy Env Sci* 2011;4:83–99.
- [78] Demirbas A. Competitive liquid biofuels from biomass. *Appl Energy* 2011;88:17–28.
- [79] Taarning E, Osmundsen CM, Yang X, Voss B, Andersen SI, Christensen CH. Zeolite-catalyzed biomass conversion to fuels and chemicals. *Energy Env Sci* 2011;4:793–804.
- [80] Gayubo AG, Alonso A, Valle B, Aguayo AT, Olazar M, Bilbao J. Hydrothermal stability of HZSM-5 catalysts modified with Ni for the transformation of bioethanol into hydrocarbons. *Fuel* 2010;89:3365–72.
- [81] Dürre P. Biobutanol: an attractive biofuel. *Biotechnol J* 2007;2:1525–34.
- [82] Dürre P. Fermentative production of butanol—the academic perspective. *Curr Opin Biotechnol* 2011;22:331–6.
- [83] Kumar M, Gayen K. Developments in biobutanol production: new insights. *Appl Energy* 2011;88:1999–2012.
- [84] Green EM. Fermentative production of butanol—the industrial perspective. *Curr Opin Biotechnol* 2011;22:337–43.
- [85] Connor MR, Liao JC. Microbial production of advanced transportation fuels in non-natural hosts. *Curr Opin Biotechnol* 2009;20:307–15.
- [86] Mascal M. Chemicals from biobutanol: technologies and markets. *Biofuels, Bioprod Biorefin* 2012;6:483–93.
- [87] Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA. Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels. *Science* 2010;327:1110–4.
- [88] McGuinness DS. Olefin oligomerization via metallacycles: dimerization, trimerization, tetramerization, and beyond. *Chem Rev* 2011;111:2321–41.
- [89] Ni M, Leung DY, Leung MKH. A review on reforming bio-ethanol for hydrogen production. *Int J Hydrog Energy* 2007;32:3238–47.
- [90] Haryanto A, Fernando S, Murali N, Adhikari S. Current status of hydrogen production techniques by steam reforming of ethanol: a review. *Energy Fuels* 2005;19:2098–106.
- [91] Navarro RM, Peña MA, Fierro JLG. Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass. *Chem Rev* 2007;107:3952–91.
- [92] Dhanala V, Maity SK, Shee D. Steam reforming of isobutanol for production of synthesis gas over Ni/ γ -Al₂O₃ catalysts. *RSC Adv* 2013;3:24521–24529.
- [93] Atsumi S, Hanai T, Liao JC. Non-fermentative pathways for synthesis of branched-chain higher alcohols as biofuels. *Nature* 2008;451:86–9.
- [94] Cann AF, Liao JC. Pentanol isomer synthesis in engineered microorganisms. *Appl Microbiol Biotechnol* 2010;85:893–9.
- [95] Machado HB, Dekishima Y, Luo H, Lan EI, Liao JC. A selection platform for carbon chain elongation using the CoA-dependent pathway to produce linear higher alcohols. *Metab Eng* 2012;14:504–11.

- [96] Rabinovitch-Deere CA, Oliver JWK, Rodriguez GMM, Atsumi S. Synthetic biology and metabolic engineering approaches to produce biofuels. *Chem Rev* 2013;113:4611–32.
- [97] Mäki-Arvela P, Simakova IL, Salmi T, Murzin DY. Production of lactic acid / lactates from biomass and their catalytic transformations to commodities. *Chem Rev* 2014;114:1909–71.
- [98] Nampoothiri KM, Nair NR, John RP. An overview of the recent developments in polylactide (PLA) research. *Bioresour Technol* 2010;101:8493–501.
- [99] <<http://www.mbi.org/technologies-3/succinic-acid/>>.
- [100] <<http://www.bio-amber.com>>.
- [101] Kumar V, Ashok S, Park S. Recent advances in biological production of 3-hydroxypropionic acid. *Biotechnol Adv* 2013;31:945–61.
- [102] Valdehuesa KNG, Liu H, Nisola GM, Chung W-J, Lee SH, Park SJ. Recent advances in the metabolic engineering of microorganisms for the production of 3-hydroxypropionic acid as C₃ platform chemical. *Appl Microbiol Biotechnol* 2013;97:3309–21.
- [103] <<http://www.chemicals-technology.com/projects/dupont-tate-lyle-biochemical-loudon-tennessee/>>.
- [104] Liu S, Lu H, Hu R, Shupe A, Lin L, Liang B. A sustainable woody biomass biorefinery. *Biotechnol Adv* 2012;30:785–810.
- [105] Amidon TE, Liu S. Water-based woody biorefinery. *Biotechnol Adv* 2009;27:542–50.
- [106] Menon V, Rao M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. *Prog Energy Combust Sci* 2012;38:522–50.
- [107] Stöcker M. Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials. *Angew Chem, Int Ed* 2008;47:9200–11.
- [108] Maghanki MM, Ghobadian B, Najafi G, Galogah RJ. Micro combined heat and power (MCHP) technologies and applications. *Renew Sustain Energy Rev* 2013;28:510–24.
- [109] Bridgewater A V. The technical and economic feasibility of biomass gasification for power generation. *Fuel* 1995;74:631–53.
- [110] Luque R, Osa AR de la, Campelo JM, Romero AA, Valverde JL, Sanchez P. Design and development of catalysts for biomass-to-liquid-Fischer–Tropsch (BTL-FT) processes for biofuels production. *Energy Env Sci* 2012;5:186–202.
- [111] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. *Fuel Process Technol* 2001;73:155–73.
- [112] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew Sustain Energy Rev* 2011;15:1615–24.
- [113] Demirbaş A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Manag* 2000;41:633–46.
- [114] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy* 2011;36:2328–42.
- [115] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 2006;20:848–89.
- [116] Mortensen PM, Grunwaldt J-D, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. *Appl Catal A* 2011;407:1–19.
- [117] Graça I, Lopes JM, Cerqueira HS, Ribeiro MF. Bio-oils upgrading for second generation biofuels. *Ind Eng Chem Res* 2013;52:275–87.
- [118] Jacobson K, Maheria KC, Dalai AK. Bio-oil valorization: a review. *Renew Sustain Energy Rev* 2013;23:91–106.
- [119] Ayalur Chattanathan S, Adhikari S, Abdoulmoumine N. A review on current status of hydrogen production from bio-oil. *Renew Sustain Energy Rev* 2012;16:2366–72.
- [120] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour Technol* 2005;96:673–86.
- [121] Zhou C-H, Xia X, Lin C-X, Tong D-S, Beltramini J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem Soc Rev* 2011;40:5588–617.
- [122] Rinaldi R, Schüth F. Acid hydrolysis of cellulose as the entry point into biorefinery schemes. *ChemSusChem* 2009;2:1096–107.
- [123] Chen Y. Development and application of co-culture for ethanol production by co-fermentation of glucose and xylose: a systematic review. *J Ind Microbiol Biotechnol* 2011;38:581–97.
- [124] Kim SR, Ha S-J, Wei N, Oh EJ, Jin Y-S. Simultaneous co-fermentation of mixed sugars: a promising strategy for producing cellulosic ethanol. *Trends Biotechnol* 2012;30:274–82.
- [125] Regalbuto JR. Cellulosic biofuels-got gasoline? *Science* 2009;325:822–4.

- [126] Olofsson K, Bertilsson M, Lidén G. A short review on SSF - an interesting process option for ethanol production from lignocellulosic feedstocks. *Biotechnol Biofuels* 2008;1:7:1–14.
- [127] Lynd LR, Weimer PJ, Zyl WH Van, Pretorius IS. Microbial cellulose utilization: fundamentals and biotechnology. *Microbiol Mol Biol Rev* 2002;66:506–77.
- [128] Lynd LR, van Zyl WH, McBride JE, Laser M. Consolidated bioprocessing of cellulosic biomass: an update. *Curr Opin Biotechnol* 2005;16:577–83.
- [129] Kaparaju P, Serrano M, Thomsen AB, Kongjan P, Angelidaki I. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. *Bioresour Technol* 2009;100:2562–8.
- [130] Kleinert M, Barth T. Phenols from lignin. *Chem Eng Technol* 2008;31:736–45.
- [131] Pandey MP, Kim CS. Lignin depolymerization and conversion: a review of thermochemical methods. *Chem Eng Technol* 2011;34:29–41.
- [132] Kleinert M, Barth T. Towards a lignocellulosic biorefinery: direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy Fuels* 2008;22:1371–9.
- [133] Kleinert M, Gasson JR, Barth T. Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. *J Anal Appl Pyrolysis* 2009;85:108–17.
- [134] Thring RW, Katikaneni SPR, Bakhshi NN. The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst. *Fuel Process Technol* 2000;62:17–30.
- [135] Ladygina N, Dedyukhina EG, Vainshtein MB. A review on microbial synthesis of hydrocarbons. *Process Biochem* 2006;41:1001–14.
- [136] <<http://www.amyris.com/>>.
- [137] Zhang F, Rodriguez S, Keasling JDD. Metabolic engineering of microbial pathways for advanced biofuels production. *Curr Opin Biotechnol* 2011;22:775–83.
- [138] Hu L, Zhao G, Hao W, Tang X, Sun Y, Lin L, et al. Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes. *RSC Adv* 2012;2:11184–206.
- [139] Lange J-P, van der Heide E, van Buijtenen J, Price R. Furfural-a promising platform for lignocellulosic biofuels. *ChemSusChem* 2012;5:150–66.
- [140] Yan K, Wu G, Lafleur T, Jarvis C. Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. *Renew Sustain Energy Rev* 2014;38:663–76.
- [141] Karinen R, Vilonen K, Niemelä M. Biorefining: heterogeneously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. *ChemSusChem* 2011;4:1002–16.
- [142] Climent MJ, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem* 2014;16:516–47.
- [143] Rackemann DW, Doherty WOS. The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioprod Biorefin* 2011;5:198–214.
- [144] <<http://biofinetechnology.com/>>.
- [145] Huber GW, Chheda JN, Barrett CJ, Dumesic JA. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* 2005;308:1446–50.
- [146] Huber GW, Dumesic JA. An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catal Today* 2006;111:119–32.
- [147] Huber GW, Cortright RD, Dumesic JA. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew Chem, Int Ed* 2004;43:1549–51.
- [148] Chheda JN, Huber GW, Dumesic JA. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew Chem, Int Ed* 2007;46:7164–83.
- [149] Cortright RD, Davda RR, Dumesic JA. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 2002;418:964–7.
- [150] Huber GW, Shabaker J. W, Dumesic JA. Raney Ni-Sn catalyst for H₂ production from biomass-derived hydrocarbons. *Science* 2003;300:2075–7.
- [151] <<http://www.virent.com/>>.
- [152] Wery T, Petersen G. Top value added chemicals from biomass. Volume I- results of screening for potential candidates from sugars and synthesis gas. US Department of Energy, 2004. Available from: <<http://www1.eere.energy.gov/bioenergy/pdfs/35523.pdf>>.
- [153] Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green Chem* 2010;12:539–54.
- [154] Dapsens PY, Mondelli C, Pérez-Ramírez J. Biobased chemicals from conception toward industrial reality: lessons learned and to be learned. *ACS Catal* 2012;2:1487–99.
- [155] Tong X, Ma Y, Li Y. Biomass into chemicals: conversion of sugars to furan

- derivatives by catalytic processes. *Appl Catal A* 2010;385:1–13.
- [156] Climent MJ, Corma A, Iborra S. Converting carbohydrates to bulk chemicals and fine chemicals over heterogeneous catalysts. *Green Chem* 2011;13:520–40.
- [157] Holm MS, Saravanamurugan S, Taarning E. Conversion of sugars to lactic acid derivatives using heterogeneous zeotype catalysts. *Science* 2010;328:602–5.
- [158] Román-Leshkov Y, Chheda JN, Dumesic JA. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* 2006;312:1933–7.
- [159] Cherubini F, Strømman AH. Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems. *Biofuels, Bioprod Biorefin* 2011;5:548–61.
- [160] Gallezot P. Conversion of biomass to selected chemical products. *Chem Soc Rev* 2012;41:1538–58.
- [161] Lee JW, Kim HU, Choi S, Yi J, Lee SY. Microbial production of building block chemicals and polymers. *Curr Opin Biotechnol* 2011;22:758–67.
- [162] James OO, Maity S, Usman LA, Ajanaku KO, Ajani OO, Siyanbola TO, et al. Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxymethylfurfural. *Energy Env Sci* 2010;3:1833–50.
- [163] Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, et al. The path forward for biofuels and biomaterials. *Science* 2006;311:484–9.
- [164] Sanders J, Scott E, Weusthuis R, Mooibroek H. Bio-refinery as the bio-inspired process to bulk chemicals. *Macromol Biosci* 2007;7:105–17.
- [165] de María PD. Recent developments in the biotechnological production of hydrocarbons : paving the way for bio-based platform chemicals. *ChemSusChem* 2011;4:327–9.
- [166] Straathof AJJ. Transformation of biomass into commodity chemicals using enzymes or cells. *Chem Rev* 2014;114:1871–908.
- [167] Fortman JL, Chhabra S, Mukhopadhyay A, Chou H, Lee TS, Steen E, et al. Biofuel alternatives to ethanol: pumping the microbial well. *Trends Biotechnol* 2008;26:375–81.
- [168] Peralta-yahya PP, Keasling JD. Advanced biofuel production in microbes. *Biotechnol J* 2010;5:147–62.
- [169] Serrano-Ruiz JC, Ramos-Fernández EV, Sepúlveda-Escribano A. From biodiesel and bioethanol to liquid hydrocarbon fuels: new hydrotreating and advanced microbial technologies. *Energy Env Sci* 2012;5:5638–52.
- [170] <<http://biosciences.dupont.com/about-us/collaborations/goodyear/>>.
- [171] <<http://www.avantium.com/>>.
- [172] Zhang J, Li J, Wu S, Liu Y. Advances in the catalytic production and utilization of sorbitol. *Ind Eng Chem Res* 2013;52:11799–815.
- [173] Akinterinwa O, Khankal R, Cirino PCC. Metabolic engineering for bioproduction of sugar alcohols. *Curr Opin Biotechnol* 2008;19:461–7.
- [174] Rafiqul ISMSM, Sakinah AMMM. Processes for the production of xylitol—a review. *Food Rev Int* 2013;29:127–56.
- [175] IEA Energy Technology Essentials. Biofuel production. 2007. Available from: <<http://www.iea.org/techno/essentials2.pdf>>.
- [176] Himmel ME, Ding S-Y, Johnson DK, Adney WS, Nimlos MR, Brady JW, et al. Biomass recalcitrance: engineering plants and enzymes for biofuels production. *Science* 2007;315:804–7.
- [177] Holladay JE, White JF, Bozell JJ, Johnson D. Top value-added chemicals from biomass. Volume II — results of screening for potential candidates from biorefinery lignin. 2007. Available from: <<http://www.cpconline.in/downloads/PNNL-16983.pdf>>.
- [178] National Renewable Energy Laboratory (NREL). Clean fractionation. 2008. Available from: <<http://www.nrel.gov/biomass/pdfs/43959.pdf>>.
- [179] <<http://www.cimv.fr/>>.
- [180] Demain AL, Newcomb M, Wu JHD. Cellulase, clostridia, and ethanol. *Microbiol Mol Biol Rev* 2005;69:124–54.
- [181] Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, Erbach DC. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. US Department of Energy 2005. Available from: <http://www1.eere.energy.gov/bioenergy/pdfs/final_billionton_vision_report2.pdf>.
- [182] Perlack RD, Stokes BJ. U.S. Billion-ton update: biomass supply for a bioenergy and bioproducts industry. US Department of Energy 2011. Available from: <http://www1.eere.energy.gov/biomass/pdfs/billion_ton_update.pdf>.
- [183] Ministry of New and Renewable Energy, Government of India. Biomass power and cogeneration programme. Available from: <<http://www.mnre.gov.in/schemes/grid-connected/biomass-powercogen/>>.

- [184] <http://en.wikipedia.org/wiki/Tonne_of_oil_equivalent>.
- [185] Pandey A, Biswas S, Sukumaran RK, Kaushik N. Study on availability of Indian biomass resources for exploitation: a report based on a nationwide survey. 2009.
- [186] Auto fuel policy report. Other alternative fuels and technologies. 2010. Available from: <www.it.iitb.ac.in/~kavi/CAR/tapanbasu2.pdf>.
- [187] Borowitzka MA, Moheimani NR. Sustainable biofuels from algae. *Mitig Adapt Strateg Glob Chang* 2013;18:13–25.
- [188] Planning Commission, Government of India. Report of the committee on development of biofuels, 2003. Available from: <http://planningcommission.nic.in/reports/genrep/cmtt_bio.pdf>.
- [189] US Department of Energy. Integrated biorefineries: biofuels, biopower, and bioproducts. 2013. Available from: <http://www1.eere.energy.gov/biomass/pdfs/ibr_portfolio_overview.pdf>.
- [190] Kumar A, Sokhansanj S. Switchgrass (*Panicum virgatum*, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model. *Bioresour Technol* 2007;98:1033–44.
- [191] Richard TL. Challenges in scaling up biofuels infrastructure. *Science* 2010;329:793–6.
- [192] Taylor G. Biofuels and the biorefinery concept. *Energy Policy* 2008;36:4406–9.
- [193] Cherubini F, Ulgiati S. Crop residues as raw materials for biorefinery systems – a LCA case study. *Appl Energy* 2010;87:47–57.
- [194] Cherubini F, Jungmeier G. LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. *Int J Life Cycle Assess* 2010;15:53–66.
- [195] Piemonte V. Wood residues as raw material for biorefinery systems: LCA case study on bioethanol and electricity production. *J Polym Env* 2012;20:299–304.
- [196] Uihlein A, Schebek L. Environmental impacts of a lignocellulose feedstock biorefinery system: an assessment. *Biomass Bioenergy* 2009;33:793–802.
- [197] Huber GW (Ed.). Breaking the chemical and engineering barriers to lignocellulosic biofuels: next generation hydrocarbon biorefineries. 2008. Available from: <<http://www.ecs.umass.edu/biofuels/Images/Roadmap2-08.pdf>>.
- [198] Carlson TR, Vispute TP, Huber GW. Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem* 2008;1:397–400.
- [199] Vispute TP, Huber GW. Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils. *Green Chem* 2009;11:1433–45.
- [200] <http://www.uop.com/processing-solutions/biofuels/green-diesel/#natural-oils-conversion>>.
- [201] <<http://www.uop.com/processing-solutions/biofuels/green-jet-fuel/>>.
- [202] West RM, Braden DJ, Dumesic JA. Dehydration of butanol to butene over solid acid catalysts in high water environments. *J Catal* 2009;262:134–43.
- [203] Zhang D, Al-Hajri R, Barri SAI, Chadwick D. One-step dehydration and isomerisation of n-butanol to iso-butene over zeolite catalysts. *Chem Commun* 2010;46:4088–90.
- [204] Jeong S, Kim H, Bae J, Kim DH, Peden CHF, Park Y-K, et al. Synthesis of butenes through 2-butanol dehydration over mesoporous materials produced from ferrierite. *Catal Today* 2012;185:191–7.
- [205] Schill SR. Braskem starts up ethanol-to-ethylene plant. *Ethanol Producer Magazine* 2010. Available from: <<http://www.ethanolproducer.com/articles/7022/braskem-starts-up-ethanol-to-ethylene-plant>>.
- [206] Gayubo AG, Alonso A, Valle B, Aguayo AT, Bilbao J. Selective production of olefins from bioethanol on HZSM-5 zeolite catalysts treated with NaOH. *Appl Catal B* 2010;97:299–306.
- [207] Kunkes EL, Simonetti DA, West RM, Serrano-ruiz JC, Gärtner CA, Dumesic JA. Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. *Science* 2008;322:417–21.
- [208] Xing R, Subrahmanyam AV, Olcay H, Qi W, van Walsum GP, Pendse H, et al. Production of jet and diesel fuel range alkanes from waste hemicellulose-derived aqueous solutions. *Green Chem* 2010;12:1933–46.
- [209] <<http://www.ls9.com/>>.
- [210] <<http://www.sapphireenergy.com/>>.
- [211] <<http://www.pcrabiofuels.org/Estimation%20of%20land.htm>>.
- [212] <<http://agricoop.nic.in/>>.
- [213] Chisti Y. Biodiesel from microalgae. *Biotechnol Adv* 2007;25:294–306.