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Review

Significance and Challenges of Biomass as a Suitable Feedstock for Bioenergy and Biochemical Production: A Review

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Abstract: Fossil fuels have been a major contributor to greenhouse gases, the amounts of which could be reduced if biofuels such as bioethanol and biodiesel were used for transportation. One of the most promising biofuels is ethyl alcohol. In 2015, the world production of ethanol was 25.6 billion gallons and the USA, Brazil, China, the European Union, and 28 other countries have set targets for blending ethanol with gasoline. The two major bio-source materials used for ethanol production are corn and sugarcane. For 1st generation biofuels, sugarcane and corn feedstocks are not able to fulfill the current demand for alcohol. Non-edible lignocellulosic biomass is an alternative bio-source for creating 2nd generation biofuels and algae biomass for 3rd and 4th generation biofuels. This review discusses the significance of biomass for the different generations of biofuels, and biochemical and thermochemical processes, and the significance of biorefinery products.

Keywords: biofuel; lignocellulosic biomass; biochemicals; ethanol; biorefinery

1. Introduction

The development of human society and the upsurge in population growth have generated a considerable demand for food and energy. In recent times, the world population has depended heavily on fossil fuels and their derivatives. The intensive use of fossil fuels and their derivatives has given rise to greenhouse gases (GHG), such as methane, carbon dioxide, and nitrous oxide [1,2]. Currently, the primary source of energy for the transport and production of materials in the world is oil. Approximately 84 million barrels of oil are used per day and this is projected to increase to about 116 million barrels by 2030. The transport sector, which has expanded considerably in Europe and the USA, accounts for about 60% of this demand [3]. The consumption of oil in China and India is on the rise and growing at a minimum of 3% per year. The production of chemicals and plastic materials is also heavily dependent on fossil resources, and constitutes about 4% of the world's refined oil [4].

It is evident that plant-based waste materials (lignocellulosic biomass) have the potential to be used instead of fossil resources as feedstocks for the production of biofuels and chemicals [5]. The use of biomass and bioenergy can significantly reduce greenhouse gas emissions. The carbon dioxide given off when is the plants are burned is counterbalanced by the amount absorbed when they were grown [6]. Thus, bioenergy produced from biomass is an essential substitute for fossil energy and has attracted widespread attention around the world. It currently contributes about 9% of the total global energy supply [7]. Climate change, energy security and food security are the most pressing issues that are driving the search for a substitute feedstock for the production of biofuels, biochemicals, and bioenergy at both regional and national levels. These issues can only be solved by specific governmental policies. However, the challenge of drafting policies is that if they are designed to target one issue, they may be detrimental to another [8]. Conflicts can be resolved by using solar, wind and hydro power as renewable sources for electricity and heat, and lignocellulosic biomass for transportation fuels and chemicals, since it is the only carbon-rich material source available on the earth other than fossils [9]. However, the sustainability of the biomass supply is a critical issue, particularly because fertile land needs to be used to cultivate energy crops rather than food.

According to the IEA [10], bioenergy usage can be divided into various categories: (1) traditional use; (2) modern building heat; (3) electricity and co-generation; (4) transport; (5) industry—heat; (6) commercial heat and (7) other uses. Of all these sectors, transport is the most heavily dependent on oil (about 90%) [10]. The increase in demand for transport in China rose from 5% in 1980 to 11% in 2005. In India, the transport sector currently consumes 27% of the total demand for primary oil, and this will increase to 47% by 2030 [3]. In this regard, liquid biofuel could be used to decarbonize the transport sector, and thus reduce GHG.

If a solution is to be found to the over-reliance on oil and climate change mitigated, the transport and chemical sectors need to be completely restructured. It has been acknowledged that there is no single-window solution to these problems and that combined actions aimed at changes in public behavior, the modernization and expansion of public transport, and advances in vehicular technologies are much desired [11].

This paper first gives an overview of the feedstock used in biofuel production and then goes on to discuss the emerging biorefinery of the two primary biofuels (bioethanol and biodiesel) with their accompanying biochemicals. For the sustainability of biofuel production, the emerging concept of biorefinery is linked to the idea of a holistic circular economy and discussed in the context of the EU, India and the USA. In this regard, critical analysis and evaluation focuses on: (i) the supply of lignocellulosic feedstocks and (ii) the markets for intermediate or end-products. The progress made in these indicators will assist in transitioning from a petroleum-based economy to a circular—economy.

2. Effects of Biochemical Composition on Biofuel Production

Biomass is composed of cellulose, hemicellulose, lignin and a small fraction of inorganic matter. The relative biochemical composition and the inorganic components vary in each plant. The composition of the pyrolyzed product largely depends on these compositional variations in biomass species. The degree of biomass decomposition and recalcitrance during pyrolysis and hydrolysis, respectively, depends on its composition. The ease with which the three significant components (cellulose, hemicellulose and lignin) decompose is attributed to their structural stability [12]. Pyrolysis of cellulose or hemicellulose produces greater oil yields than lignin. Yang et al. [13] reported the weight loss behavior of hemicellulose, cellulose, and lignin. Maximum weight loss was observed for cellulose (94.5%) and hemicellulose (80%) at 400 °C and 268 °C, respectively, while only 54.3% of lignin was volatilized at 900 °C. The temperature at which oil yield is maximum clearly depends on the biomass components. Lignin also contributes to the large portion of char residue during the pyrolysis of lignocellulose biomass. Other authors have reported similar observations for the pyrolysis of cellulose, lignin, bark, rice husk, and corn stalk [14]. The structural differences among significant biomass components cause compositional variability in the pyrolysis products [14]. The reactivity of biomass species during pyrolysis is also affected by the presence of oxygen contents and heteroatoms. In general, the greater the oxygen and heteroatom content, the better the reactivity of biomass is, although some studies have reported that oxygen content has a relatively small effect on the reactivity of biomass during pyrolysis [15]. The biochemical composition of biomass feedstock affects the efficiency of biofuel production and energy output. This is a major challenge for using biorefinery processes [16,17].

3. Biomass Types in Focus

According to the International Energy Agency biomass is defined as any organic matter that comes from biogenic sources and is available on a renewable basis. This includes animals and plants sourced by wood and agricultural crops, and organic waste from municipal and industrial sectors.

Biomass resources can be classified according to their origin (see Table 1). Various other crops have been scientifically tested and proposed for commercial energy farming. Energy crops include woody crops and grasses/herbaceous plants, starch and carbohydrate-containing crops and oilseeds. Ideal energy crops should have the following characteristics: (i) cultivation requires low energy input; (ii) yields must be high; (iii) processing requires low energy input; (iv) cellulose and hemicellulose content is high [18]. The biochemical content is dependent on local climate and soil conditions. Despite all the excitement associated with biofuel usage, the sustainability of biomass is critical. Issues such as (1) national, regional and local environmental policies; (2) types of bioenergy, feedstocks and processing technologies available in specific areas, and (3) the logistics of biomass transport to the refinery site can hinder the sustainability of biofuel production. The task of evaluating whether a bioenergy production process or the biomass feedstock used is sustainable is not inconsequential, especially when the above-mentioned concerns about the sustainability of biofuel production are considered. It cannot be claimed that the biomass resources reviewed in this study are sustainable in all aspects, as the final impacts of their use will depend on the local conditions of cultivation, harvest, transport, storage and, eventually, conversion technologies. However, all the assessed biomass resources have a low environmental impact [19]. In addition, they are residues from agricultural production, and are potentially sustainable when handled efficiently and with respect for nature and the environment.

Table 1. Biomass type according to origin.

Category		Representative Material
Agriculture	Sugars	Sugarcane, corn, sweet sorghum
	Starch	Maize, cassava, sweet potato
	Oil seed crops	Rapeseed, palm oil, *Jatropha*, Soybean, mustards, sunflower, coconut
Lignocellulosic plants short rotation coppice	Tropical grasses	Poplar, sycamore, switchgrass, *Miscanthus*, alfalfa, Altai wildrye, sweet clover
Organic residues and waste	Industrial residues and waste	Straw, bagasse, husks, shells, wood shaving, sawdust, fiber sludge, brewery by-products, oil extraction meal, cross-cut ends, plywood by-products
	Agriculture and forestry residue	Stumps, whole tree, bark, shrubs, slabs, logging by-products, dung, manure, poultry waste
	Municipal waste	Slaughterhouse byproducts, kitchen waste, biosludge

The table was compiled with reference to [10,20,21].

4. First-Generation Biofuels

First-generation biofuel production is heavily dependent on energy crops such as maize (corn) and sugarcane.

Maize or corn (*Zea mays*) is a grain that belongs to the *Grimanaceae* family [22]. The corn stover (cobs, stalks, and leaves) residues obtained from maize cultivation have various advantages over other energy crops [23]. The corn stover contains cellulose and hemicellulose which can be pretreated with hydrolysis techniques.

Sugarcane (*Saccharum*) is a semi-perennial plant (C6 group) belonging to the *Poaceae* family (grass family), typical of tropical and subtropical countries [24]. Unlike starchy biomass, the production of bioethanol from sucrose-based feedstocks does not require a saccharification step, as the sugars are readily available, which makes the production process simpler [25].

Global biofuel production is on the rise. Europe is the leader in biodiesel production while the USA is the leading producer of ethanol (see Figure 1). Ethanol and biodiesel are the two major fuels with the potential to replace gasoline and diesel, the major contributors to GHGs and particulate matter, respectively. Biohydrogen is also attracting some attention because of its eco-friendly by-product, H_2O. Ethanol produced from corn and sugar cane is referred to as ‘1st generation’ (1G) bioethanol. In 2015, 25.6 billion gallons of bioethanol was produced with the USA contributing 14.81 billion gallons and Brazil 7.09 billion gallons, (Figure 2). Between them, the USA and Brazil produced 85% of the worlds’ bioethanol. The USA depends heavily on corn for bioethanol production while Brazil tends to use sugar cane. While this seems to be a sign of progress, there are considerable reservations about the source of the starting material used in the production because it can have a negative impact on food security and biodiversity. The process of ethanol production depends on the raw materials used. Ethanol production can be simplified into three steps: (1) acquire or generate fermentable sugars; (2) convert sugars into ethanol by fermentation and (3) separate and purify, usually by distillation-rectification-dehydration [26] The simplified process for converting corn and sugarcane to ethanol shown in Figure 3 can be modified for different feedstocks and conversion technologies. Using a pretreatment, sugars are extracted or made more accessible (if corn is the feedstock) for further fermentation processes, during which the sugars available depend on the feedstock and pretreatment used. Fermentation can be carried out in any one of three different methods batch, fed-batch or continuous. In batch fermentation, the hydrolysate (liquid fraction containing sugar, yeasts, nutrients and other ingredients) is added to the medium at the beginning of the fermentation. In fed-batch fermentation, one or more inputs are added as fermentation progresses. In continuous fermentations, ingredients are constantly injected at a specific flow rate and products are removed from the fermentation reactors. The efficiency of the conversion process can be enhanced if the cell density is increased by immobilizing the yeast [27]. The vinasse obtained from the distillation column can be volatilized to generate co-products (see Figure 3). The chemical and physical make up of corn makes ethanol production from corn more complex than from sugarcane (sucrose is readily available). The volume of ethanol produced from corn is five times higher per ton of feedstock while the productivity of ethanol produced from sugar cane is greater per hectare. In this regard, cultivated sugarcane produces between 60 and 120 t per hectare while corn produces between 15 and 20 t per hectare, of which 50% is dry matter [25].

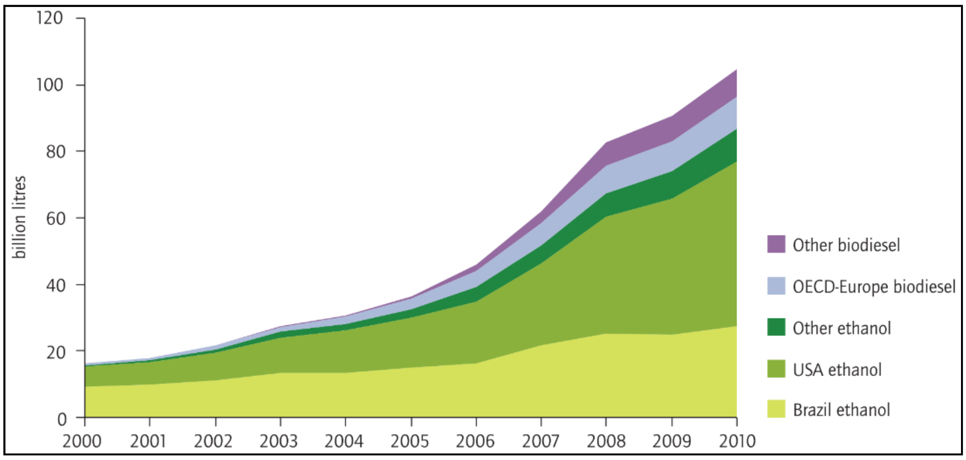

Figure 1. Global biofuel production (adapted from IEA 2011 [28]).

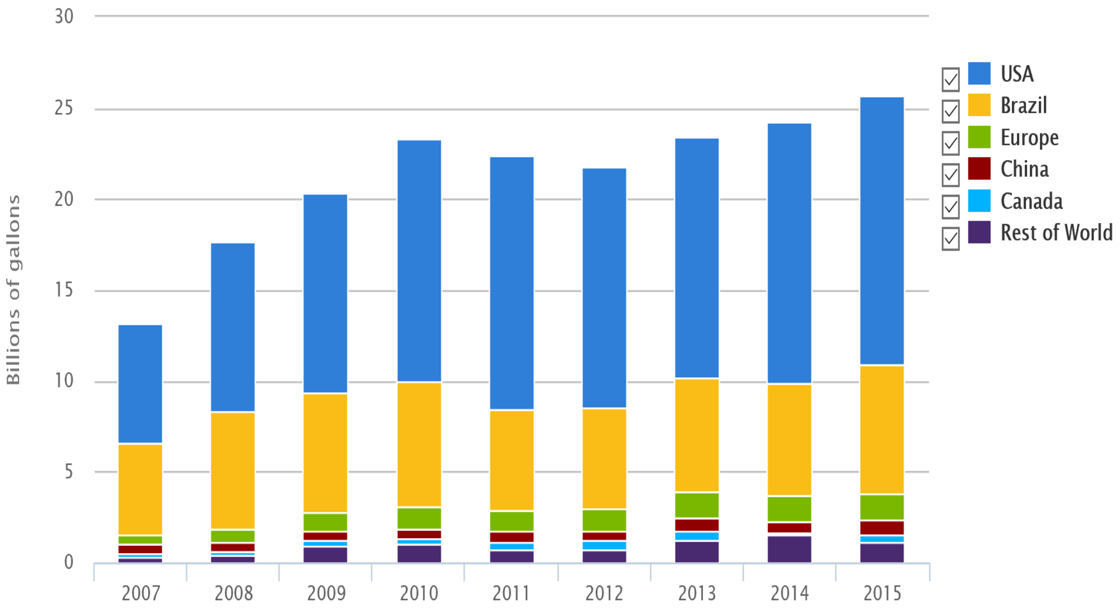

Figure 2. Global bioethanol production (source: www.afdc.energy.gov/data/).

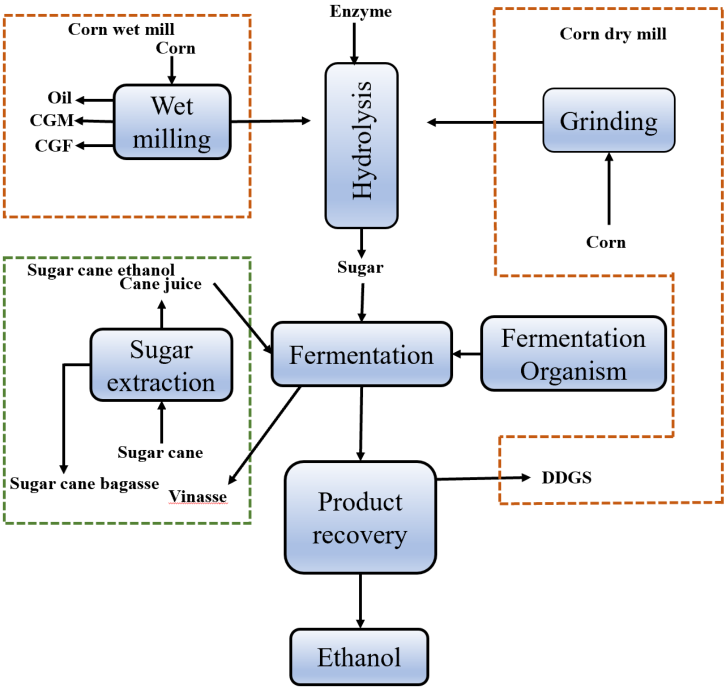

Figure 3. An abridged process flow diagram for the production of ethanol from sugarcane and corn. Adapted from [27]. They both have similar fermentation and ethanol recovery operations but use different approaches to release sugars and generate different co-products. Sugar can be directly extracted from sugarcane, and the residual bagasse is used as a boiler fuel to provide much of the energy for the extraction and ethanol production and recovery operations. In a corn dry mill, corn is ground, and enzymes and heat are added to hydrolyze starch to sugars for conversion to ethanol, while the oil, protein, and fiber in corn are recovered after fermentation as an animal feed known as DDGS. Wet mills first fractionate corn to separate corn oil, corn gluten meal (CGM), and corn gluten feed (CGF) to capture value for food and animal feed, and the starch can then be hydrolyzed to sugars for fermentation to ethanol.

Biodiesel is produced from raw vegetable oils derived from soybean, canola, palm oil or sunflower, as well as animal fats and used cooking oil, which are also known as 1st generation biodiesel. Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is derived from renewable resources. Burning biodiesel does not increase current net atmospheric levels of CO_2, a greenhouse gas [29]. It is safely biodegradable, offers scope for recycling waste oils, and produces less air pollution than fossil diesel [30]. Biodiesel is simple to manufacture and provides excellent engine performance. It has better lubricating properties than petrodiesel (for example, higher density, greater cetane number, low sulfur emission, and low flash point), which makes it the safest fuel to handle [31]. Renewable biodiesel is produced mainly from vegetable oils and animal fats, which are converted into fatty acid methyl esters. However, the current biodiesel production process has a number of problems. In particular, the process involves adding methanol from fossil fuels. It has been reported that up to 35% of the total primary energy requirement for biodiesel production comes from fossil fuels [32]. Methanol makes up about 10% of the feedstock input, so biodiesel is not completely renewable [33]. The three well-established processes for producing biodiesel are microemulsion, thermal cracking and transesterification [34]. Transesterification, the reaction of a fat or oil with an alcohol to form esters and glycerol, is the most popular and preferred route to biodiesel production (see Figure 4). The reaction may be facilitated by catalysts that use primary or secondary monohydric aliphatic alcohols with 1–8 carbon atoms [35].

Most current biofuel production processes follow so-called 1st generation conversion pathways, which use sugar, starch or the vegetable oil components of crops. Converting crops to biofuels usually requires fossil energy. In comparison with petroleum fuels the 1st generation pathway reduces GHGs from "well-to-wheels" by 20–70% [36]. The extensive use of biofuels requires the range of non-edible feedstock (lignocellulosic biomass) to be extended, and advanced conversion technologies to be used for bioethanol and biodiesel production.

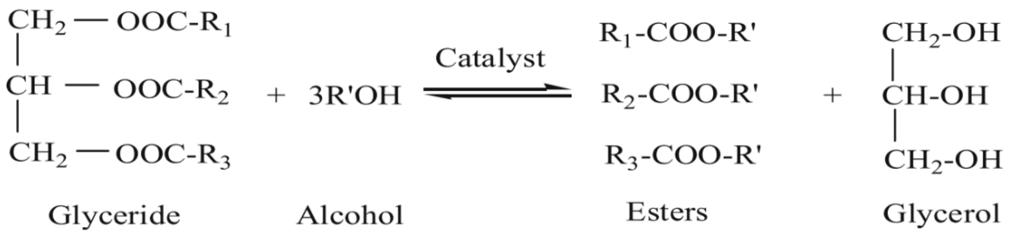

Figure 4. Biodiesel production by transesterification with short-chain alcohols (adapted from [29]).

5. Lignocellulosic Biomass as Feedstock for Biofuel Production

Second (2nd) generation biofuels are produced from cellulose, hemicellulose or lignin (Table 2). Lignocellulosic biomass is a significant alternative to sugarcane and maize because it solves the problems of food and energy security associated with using edible food for biofuel production. The lignocellulose feedstocks that have received most attention are corn stover, rice husk, wheat straw, and sugarcane baggase. Corn stover has an estimated cellulose, hemicellulose, lignin, protein and ash content of 33–43%, 20–34.5%, 8–14.1%, 5% and 4%, respectively [37]. Lim et al. [38] estimated rice husk composition to be cellulose (28.6%), hemicellulose (28.6%), lignin (24.4%) and extractive matter (18.4%). The biochemical composition of sugarcane bagasse is 40% cellulose, 25 % hemicellulose and 10 % of other extractives [39]. Wheat straw's cellulose, hemicellulose, and lignin content is estimated to be 33–40 w/w%, 20–25 w/w% and 15–20 w/w%, respectively [40]. The considerable cellulose and hemicellulose content of the lignocellulosic biomass serves as a vital source of sugars for the production of ethanol. Purpose-grown energy crops such as vegetative grasses and short-rotation forests have great potential for the production of 2nd generation biofuel [41] These vegetative grasses include switchgrass, *Miscanthus*, big bluestem, Altai wildrye, alfalfa and yellow sweet clover. Switchgrasses and miscanthus have also received a great deal of attention [42]. Switchgrasses provide higher yields and lower production costs. Switchgrass is highly tolerant to draught and can adapt to many soil and climate types. Miscanthus is a high yielding bioenergy crop. Both switchgrass and miscanthus are perennial so they do not need to be planted every year. They have a C_4 photosynthetic pathway with a high carbon-dioxide fixation rate. This allows for high rates of photosynthesis and plants grow faster [43]. These grasses can grow on marginal land and require minimum water for cultivation. Along with agricultural waste, they can be used as feedstock to produce biofuel, but factors such as geographical location and variability in their biochemical composition constitute a major challenge. For instance, low winter temperatures and short vegetation periods are major limitations to the growth of C_4 grasses in northern Europe [44]. Attack from insecticides is also a challenge to the cultivation and sustainability of energy crops. Recently, forests in Western Canada were infected by mountain pine beetle, which destroyed 725 million cubic meters of timber in British Columbia and has affected over 17 million ha to date [45].

2nd generation biofuels can be blended with gasoline, which can be combusted in combustion engines and distributed through existing infrastructure or engines that are slightly modified for internal combustion. One example of 2ndgeneration biofuel is cellulosic ethanol, which is produced via a biochemical route, in which enzymes and other microorganisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars before they are fermented to produce ethanol. On the other hand, the thermo-chemical route of biofuel production (also known as biomass-to-liquids, BTL) is pyrolysis/gasification, which produces a synthesis gas ($CO + H_2$). These gases can assist in the production of a wide range of long carbon chain biofuels, such as synthetic diesel, aviation fuel, or ethanol based on the Fischer-Tropsch conversion [46]. Biochemical processes (fermentation) for ethanol production occur at lower temperatures with lower reaction rates (see Figure 5). The fermentation processes rely on microorganisms to convert sugars available in liquid medium into products that are recoverable (usually ethanol or organic acids). Ethanol is the major product expected during fermentation processes, but other desirable compounds are often produced in the process. Hexose and pentose sugars from cellulose and hemicellulose, respectively, require microorganisms if they are to be converted to ethanol [17]. Anaerobic digestion is initiated when bacteria consume the organic substrate under an oxygen-starved environment at temperature ranges between 30 and 65 °C. Even though higher ethanol yields are always desired during biochemical processes, other factors affect full ethanol production from the lignocellulosic biomass. The pre-treatment stage is perhaps the most critical step: it aims to depolymerize cellulose and hemicellulose into glucose and xylose, respectively, and may encounter incomplete depolymerization or over-depolymerization depending on the pre-treatment technique used. Incomplete depolymerization of cellulose and hemicellulose in lignocellulosic biomass gives oligosaccharides such as cellobiose and xylo-oligosaccharides, respectively. Harsh pretreatment could trigger over-depolymerization, which chemically transforms glucose and xylose to 5-hydroxymethylfurfural (HMF) and furfural, respectively. HMF and furfural formation in the fermentation medium can inhibit bacterial growth and lead to low yields of ethanol [47]. The hydrolysis yield can vary the efficiency of this conversion by between 40 and 98%. The conversion efficiency is affected by the feedstock and the pre-treatment adopted during hydrolysis [48–53]. The enzymatic hydrolysis of lignocellulose is not efficient since it is also affected by the crystallinity of cellulose, the degree of polymerization, moisture content, available surface area and lignin content [54–58]. Grous et al. [59] and other authors [60,61] contend that the pore size of the substrate as a function to the size of the enzymes is the main limiting factor in the enzymatic hydrolysis of (lignocellulosic) biomass. Due to the variability of the lignocellulosic biomass, the pretreatment technique should be thoroughly assessed before commercial scale production is initiated [62]. All the above limitations associated with pretreatment techniques and the cost of lignocellulosic biomass has made 2nd-generation bioethanol more expensive than 1st-generation bioethanol [63]. Improving current hydrolysis techniques could lower the cost of production in the future [64].

Table 2. Classification of second-generation biofuels from lignocellulosic feedstocks.

Biofuel Group	Specific Biofuel	Production Process	Technology (Route)
Bioethanol	Cellulosic ethanol	Advanced enzymatic hydrolysis and fermentation	Biochemical
	Biomass-to-liquid (BTL)		
Synthetic Biofuels	Fischer-Tropsch (FT) diesel	Gasification and synthesis	Thermochemical
	Synthetic diesel		
	Biomethanol		
	Heavier alcohols (butanol and mixed)		
	Dimethyl ether		
Methane	Bio-synthetic natural gas (SNG)	Gasification and synthesis	Thermochemical
Bio-hydrogen	Hydrogen	Gasification and synthesis/Biological processes	Thermochemical/Biochemical

Adapted from [65].

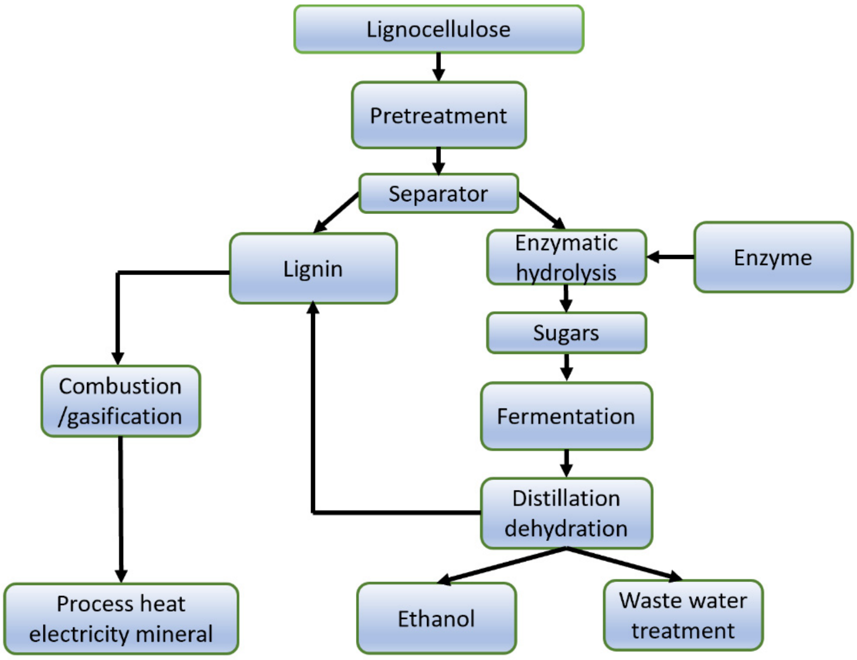

Figure 5. Biochemical process for conversion of lignocellulosic waste to ethanol (adapted from [27]).

Thermochemical processes can transform lignocellulosic biomass into energy and chemical products by two routes. The first of these processes is gasification in which the biomass is kept at high temperature (>700 °C) with limited oxygen levels to produce syngas, a mixture of H_2, CO, CO_2 and CH_4 [66]. Syngas can be used as a stationary biofuel or can be a chemical platform for the production of fuels such as dimethyl ether, ethanol, isobutene or chemicals. Pyrolysis is the second thermochemical route for converting biomass into biofuel. During pyrolysis, an intermediate temperature of 300–600 °C is applied to the biomass without the presence of oxygen to transform the feedstock into liquid pyrolytic oil, solid char and light gases that are similar to syngas [67]. Char-generated bio-oil can be used for stationary electric power or thermal energy plants. Direct combustion is also another pathway to generating heat through thermochemical processes. This is the oldest and probably the most common form of biomass conversion. Biomass is burnt in an oxygen-rich atmosphere mainly for the production of heat [68]. BTL-diesel and lignocellulosic ethanol are the 2nd generation biofuel options that have most been discussed. Both fuels can be blended with conventional diesel and gasoline, or be used pure. Some countries have established the blending of biofuel with petroleum-based fuels as national policy (see Table 3). Another promising 2ndgeneration biofuel is bio-SNG, a synthetic gas similar to natural gas. The biofuel yields in terms of fuel equivalence are higher for this conversion route than lignocellulosic ethanol and BTL-diesel [65].

Lignin, which is primarily made up of phenylpropane units is the natural polymer considered to be the second most abundant in lignocellulosic biomass [69]. The macromolecular structure gives it a highly energetic chemistry and it can easily be used to cogenerate power and as a fuel [70] by other industries including the pulp and paper industry. Lignin can be used as a raw material for generating hydrogen in a biorefinery process. The aromatic phenol monomers from lignin are a suitable source for generating high value-added chemical compounds that can be used for the manufacturing of bioplastic and bioadhesives. The production of these aromatic phenol monomers from biomass create a new market for bioplastics and bioadhesives. Beauchet et al. [71] have managed to convert lignin (10–20% weight) into cathecol, guaiacol, and phenol.

Table 3. Fuel ethanol blends in some countries.

Country	Current Mandate/Target	Future Mandate/Target	Current Status
Argentina	E5, B7	n.a	M
Australia NSW, QL	E4, B2	NSW; E6 (2011), B5 (2012); QL: E5	M
Brazil	E20-25, B5	n.a	M
Canada	E5 (up E8.5 in 4Prov), B2-B3 (in 3Prov)	B2 (nationwide) (2012)	M
China	E10 (9 Prov)	n.a	M
European Union	5.75% biofuels *	10% RET **	T
India	E5	E20, B20 (2017)	M
Japan	500 MI/y (oil equ)	800 MI/y (2018)	T
Malaysia	B5	n.a	M
Norway	3.5% biofuels	5% proposed for 2011; possible alignment with EU mandate	M
South Africa	n.a	2% (2013)	n.a
United States	48 billion liters, of which 0.02 bln. Cellulosic-ethanol	136 billion litres, of which 60 bln cellulosic-ethanol	M

E2 = Ethanol blend in %, B2 = Biodiesel blend, MI/y = Million liters per year, Prov = province, NSW = New South Wales. QL = Queensland. * Currently, each member state has set different targets and mandates. RET = Renewable in transport (** Lignocellulosic-biofuels, as well as biofuels made from wastes and residues, count twice and renewable electricity 2.5-times towards the target). M = Mandatory, T = Target, na = not available. Source OECD/IEA 2011.

However, converting woody biomass into fermentable sugars requires costly technologies involving pretreatment with special enzymes or physico-chemical treatment, so at present 2ndgeneration biofuels cannot be produced economically on a large scale [72]. Other chemical treatments (for example, heterogeneous catalysis) can be used to hydrolyse lignocelluloses, thus avoiding the enzymatic step. Further, microorganisms can ferment the sugars resulting from hydrolysis to obtain biofuels. Depending on the microorganism, ethanol [73] or biohydrogen [74] can be produced (Figure 6). Moreover, the microwave-assisted chemical reaction significantly reduces reaction time. Microwave-assisted hydrolysis generates hot spots on cellulose which break up its crystalline structure under mild conditions [75]. Hence, any technology that provides an efficient heating process is more likely to minimize the overall production cost of biofuel. Unlike conventional methods, which have a much slower heating rate, heating by microwave radiation involves rapid heating and generates a uniform distribution of heat within the biomass.

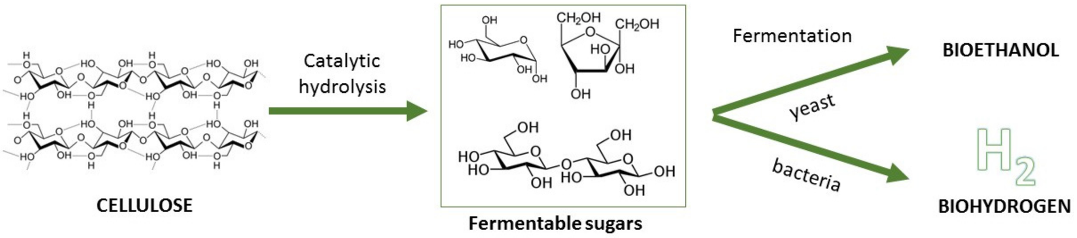

Figure 6. Conversion of biomass to biofuels by combined catalytic and biological processes (Adapted from [76]).

6. Third-and Fourth-Generation Biofuels

Third (3rd) generation biofuels are fuels that come from algal biomass. Generating biofuel from algae usually depends on the lipid content. Algae have received considerable attention for biodiesel production because they: (i) have a high lipid content (20–50%) and high growth rates; (ii) can grow in severe conditions; (iii) sequester CO_2 from the flue gases and (iv) are economical [77–80]. Several species of algae have been investigated including fast growing species: *Chlamydomonas reinhardtii*, *Dunaliella salina* and various *chlorella* species. Species of *Botryococcus braunii*, which grow slowly can accumulate large quantities of lipids [81]. The correlation between biomass productivity and lipid accumulation is not necessarily absolute because lipid accumulation accounts for the increase in the concentration of lipids within the microalgae cells but does not consider overall biomass production. Lipid productivity accounts for both the lipid concentration within cells and the biomass produced by these cells. Biomass productivity is a much more relevant indicator for accessing the potential costs of liquid biofuel production [82]. *Chlorella* species have been subject to intense investigation because of their high lipid content (approximately 60 to 70%) [83]. *Chlorella protothecoides* has the highest productivity of 7.4 g/L/day [84]. Algal biomass presents some geographical and technical issues. The high water content of algal biomass is a problem when lipids have to be extracted, so it has to be dewatered by either centrifugation or filtration. Culturing and dewatering processes consume a great deal of energy [85]. Ríos et al. [85] suggested that a balance needs to be found between all stages in microalgae transformation to optimize the general process. The lipids obtained from algae can be processed by a transesterification process or subjected to hydrogenolysis to produce drop-in aviation fuel (a derivative of kerosene grade alkane) [86]. 3rdgeneration biofuel can be made economical by using the microwave process. Most thermochemical routes involve applying heat during pyrolysis and transesterification by heating biomass to produce biofuel. Hence, conversions and yields can be higher in shorter reaction times [87]. Although moisture and mineral content can benefit the microwave-assisted pyrolysis process, high moisture content can increase the aqueous fractions and degrade the bio-oil quality whereas high inorganic content can reduce the bio-oil yield. Although organic content can improve the bio-oil yield, microwave absorbers are usually required to improve heating. The microwave-assisted approach significantly improves extractions of algae, are more efficient, reduce extractive-transesterification time and increase yield [88]. Cost-competitive algae fuels can be achieved by genetic modification to overcome the cultivation, harvesting and processing problems [89].

1st, 2nd and 3rdgeneration biofuels are classified according to the raw material used that is either of biomass by origin or determined as waste. Classifications of biofuels has always been problematic thereby limiting their application on a global scale.

In 4thgeneration biofuels, raw materials that are inexhaustible, cheap and widely available are used to convert solar energy to solar biofuels. The production of photobiological solar biofuel or electrofuel exploits the synthetic biology of algae and cyanobacteria [90–92]. Synthetic biology involves designing and creating new biological parts, and redesigning existing ones, devices and natural biological systems for useful purposes. 4th-generation biofuels are produced: (i) by designing photosynthetic microorganisms to produce photobiological solar fuels; (ii) by combining photovoltaics and microbial fuel production (electro-biofuels) or (iii) by synthetic cell factories or synthetic organelles tailored explicitly to produce the desired high-value chemicals (the production of which is currently based on fossil fuels) and biofuels [93]. This research area is in its initial stages and receiving a great deal of attention.

7. Oil Refinery Versus Biorefinery

In recent times there has been a focus on circular bio-based economies. Biorefineries are regarded as the cornerstone of a bioeconomy in which a range of thermochemical and biochemical routes including non-catalytic and catalytic technologies can be deployed and integrated to transform biomass organic molecules to many other bio-products [94]. The principle of the circular economy thus complements the renewable character of the bioeconomy and must facilitate the recycling of carbon after efficient uses. In this regard, the lignocellulosic biomass needs to be valorized as a platform chemical by using carbon from the biomass to produce commodities of interest for the industry.

Environmental impact is another factor underpinning the sustainable development of biorefinery systems [95]. As well as its environmental and economic aspects, biorefinery can help to reduce poverty in rural areas by creating jobs and increasing income for small farmers [96]. The EU has passed regulations to enhance the circular economy and also to break away from the linear economy characterized by "make, use, dispose" in favour of a more circular model based on "reuse, recycle or biodegrade" [97]. A private-public partnership between the EU and a consortium of bio-based industries have enjoyed considerable success with the policy of the circular economy [97].

Conventional oil refinery depends on crude oil from which naphtha is made. Naphtha is used as the feedstock for the production of platform chemicals (ethylene, propylene, C_4-olefins, benzene, toluene and xylene (BTX)), which, in turn, are used to produce other important industrial chemicals. In biorefinery, biomass polysaccharides that are depolymerized to monosaccharides (e.g., glucose, fructose, arabinose and xylose) can be converted via fermentation or chemical synthesis to various bio-platform molecules (BPM) which are analogous to the petroleum-platform molecules of current oil refinery. The US Department of Energy has identified the most promising BPMs so that scientists can streamline and focus their research. Chemicals such as ethanol, lactic acid and citric acid were not included on the list of possible research areas because it was considered that research in these areas was already at the advanced stage. Several other chemicals with promising functionalities are on the list [98]. Lactic acid is crucial to solving the environmental problems that polyethylene materials have unleashed on the world. Currently, lactic acid generated from starch and cellulose is a greener choice. Lactic acid is the monomer of polylactic acid (PLA), which is used in the production of biodegradable plastics [75]. BPMs have a higher oxygen content than oil-refined (benzene, ethylene) platform chemicals. By using BPMs, the chemistries of environmentally damaging oxidation mechanisms can often be changed to much greener reduction reaction mechanisms. The products from biorefinery systems can be categorized into two main groups; (1) material products and (2) energy products [99]. Energy products give electricity, heat and energy to transportation. Material products are used for their chemical functionalities and physical properties. The products of a biorefinery must be able to substitute all the fossil fuel-based products from petroleum refineries. Platform chemicals can be refined by producing the chemical with the same functionality from biomass instead of from fossils or producing a molecule with a different structure but an equivalent function. The most valuable energy products that can be produced in biorefineries are solid biofuels (char, lignin), gaseous biofuels (biogas, syngas, biohydrogen, biomethane) and biofuels for transportation (bio-alcohol, FT-fuels, biodiesel, bio-oil). Some valuable chemicals and materials produced by biorefinery are (1) organic acids such as lactic, succinic and itaconic acids and other sugar derivatives; (2) resins and polymers (furan-based resins, starch-based plastics, phenol-based resins) and (3) biomaterials such as wood panels, paper, pulp, cellulose, and fertilizers [8].

7.1. Lignocellulosic Feedstock in Biorefinery

The sustainability and expansion of the circular economy requires a sufficient supply of lignocellulosic biomass. To ensure this supply, high yield, high quality and low cost biomass needs to be produced urgently and, to this end, plants and animals have been genetically engineered. The intense cultivation of bio-engineered energy crops has significantly increased the presence of lignocellulosic biomass in the U.S bioeconomy [100]. New varieties of dedicated energy crops have been developed and their features enhanced through genetic engineering technologies, in an attempt to increase cellulose content, reduce lignin content, decrease biomass recalcitrance and promote in-plant production of cellulases and other hydrolytic enzymes [101,102]. Fu et al. [103] have demonstrated that manipulating the lignin structure of switchgrass reduced thermal-chemical, enzymatic and microbial recalcitrance. Biotechnological advances suggest that the USA could produce 1.3 billion dry tons of biomass annually at a cost $60 (farmgate price, 2014) for bioenergy and bioproduct with no compromise in food security [103,104]. In the European Union (EU), 1 billion tons of lignocellulosic biomass will be produced on an annual basis by 2030 [105]. The EU has initiated many lignocellulosic biomass production projects (see Table 4).

Table 4. Projects funded by the EU for using lignocellulosic feedstocks in the biorefinery industry. Adapted from [106].

Project Name	Biorefinery Feedstock	Coordinating Country	Period	Total Cost €
AgriChemwhey	Byproducts from dairy processing	Ireland	2018–2021	29,949,323
GRACE	Miscanthus or hemp varieties from marginal lands Kraft	Germany	2017–2022	1,500,085,121
SmartLi	Kraftlignins lignosulfonates and bleaching effluent	Finland	2015–2019	240,746,125
BIOSKOH	Lignocellulosic feedstock	Italy	2016–2012	30,122,313,773
BARBARA	Agri and food waste	Spain	2017–2020	2,711,375
AgriMax	Agri and food waste	Spain	2016–2020	1,554,349,456
PULP2VALUE	Sugarbeet pulp	Netherlands	2015–2019	1,142,384,750
GreenSoIRES	Lignocellulosic residues or wastes	Netherlands	2016–2020	1,060,963,701
Dendromass4Europe	Dendromass on marginal land	Germany	2017–2022	2,044,231,8750
SYLEED	Wood residues	France	2017–2020	14,976,590
GreenProtein	Vegetable residues from packed salad processing	Netherlands	2016–2020	554,651,999
PROMINENT	Cereal processing side streams	Finland	2015–2018	14,976,590
FIRST2RUN	Cardoon from marginal lands	Italy	2015–2019	310,389,750
Zelcor	Lignocellulosic residues from ethanol production, lignins dissolved during pulping process, and lignin-like humins formed by sugar conversion	France	2016–2020	671,001,250
STAR4BBI	Lignocellulosic feedstock from forests and agriculture	Netherlands	2016–2019	99,587,750
BIOrescue	Wheat straw and agroindustrial waste	Spain	2016–2219	376,758,750
OPTISOCHEM	Residual wheat straw	France	2017–2021	1,637,681,683
US4GREENCHEM	Lignocellulosic feedstock	Germany	2015–2019	3,803,925
FUNGUSCHAIN	Mushroom (*Agaricus bisporus*) farming residues	Netherlands	2016–2020	814,366,125
POLYBIOSKIN	Food waste	Spain	2017–2020	405,835,938
Valchem	Woody feedstock	Finland	2015–2019	1,850,270,325
LIBBIO	Andes lupin from marginal lands	Iceland	2016–2020	4,923,750
LIGNOFLAG	Straw	Germany	2017–2020	34,696,215

The EU has hoped to respond to such an ambitious challenge by funding 23 different projects at a total cost of €61 billion between 2016 and 2022. In 2017, there were about 224 biorefineries operating in the EU zone. Of these, 181 used sugars, starch, oils and fats to produce biofuels. However, only 43 biorefineries in Europe depended on lignocellulosic feedstock [107]. In the near future, the success of projects initiated by the EU and EU directive 2015/1513 [108] may increase the number of biorefineries using lignocellulosic biomass. On the other hand, in India, which has a population of about 1.5 billion, fossil fuels provide 70% of the energy demand [109]. For this reason, reducing the dependence on fossil fuels and focusing on the development of renewable energy sources has been a national biofuel policy since 2008 [110]. India is well known for having an agriculture-based economy and currently generates about 600 metric tons of agricultural waste annually. The country has made huge strides in the biotechnology sector but the focus is heavily on the pharmaceutical industries [111]. The bioeconomy in India is expected to expand by 2025. For example, in Kashipur (Uttarakhand) a multi-feedstock biorefinery was set up to convert lignocellulosic biomass into bioethanol [112]. The enormous progress made by the EU, the USA and India is a step in the right direction to catalyze a shift from a fossil-fuel economy to a circular economy. The circular economy not only helps to reduce GHG but also promotes employment. It is also important to mention that Canada, Australia and South Africa have passed laws to curb their usage of fossil fuels. These countries have taken steps to increase the integration of biofuels into their energy mix (Table 3).

Barriers to the Sustainability of Lignocellulosic Feedstock.

Even though research into genetic engineering has been intense in an attempt to find a way to reduce the recalcitrance of lignin structure and make cellulose and hemicellulose more accessible, there are numerous lignocellulosic biomasses that have yet to be investigated. So the recalcitrance of lignocellulosic biomass is still a limitation for the production of biofuels on a large scale. An efficient pretreatment method will be required to free all sugars for conversion into biofuels and biomaterials. Over the years, various pretreatment methods have been used for the depolymerization of lignocellulose [113–116]. Recently, the combination of conventional pretreatments with microwaves has improved the hydrolysis of lignocellulosic material. Likewise, sustainable and viable biorefinery is the only solution to the logistical bottleneck surrounding the lignocellulosic feedstock supply chain, which includes transportation, drying, storage and packaging. These processes are not stringent but may vary according to biomass source and type. The degree of lignocellulosic biomass quality and variability has an impact on the efficiency of subsequent pretreatment processes. The storing of biomass is a challenge in the supply chain [117]. Moisture content affects the supply cost because it increases the volume of the lignocellulose biomass and, therefore, the number of truckloads required to distribute it [118]. The proximity of biorefineries to sources of lignocellulose affects the overall costing of biofuels and biochemicals, and if sources are far away the cost of producing biofuels and biochemical can escalate.

7.2. Bio-Markets

Bio-based products include biofuels such as bioethanol, biodiesel and biogas, biochemicals and biomaterials (see Table 5). Currently, the target of EU directive (EU) 2015/1513 is that 2nd-generation biofuels will provide 25% of European transportation by 2030. It is also expected that by this date the EU will have reduced its dependency on oil-based chemicals by 30% by promoting bio-based chemicals. As far as the USA is concerned, the market value of its bio-economy reached $415 billion in 2015, which accounted for 2.3% of its gross domestic product (GDP) [119]. Every year, the USA has the capacity to supply 189 billion liters of transportation fuels, 23 million tons of bioproducts, and bio-power.

Table 5. Bio-based platform chemicals and derivatives (adapted from [120]).

Platform-Biobased Chemical	Market Demand (Million Metric Tons/Year)	Conversion Pathway	Derivatives	Applications
Ethanol	86.0	-	-	Fuels
		Polymerization	Polyethylene	Plastic industries
			Polypropylene	
		Oxidation	Polyethylene terephthalate	
			Ethylene glycol	Plastic industries
				Textile fibers
				Antifreezes, coolant, solvents
Furans (furfural, 5-hydroxymethylfurfural)	0.3	Polymerization Oxidation Hydrogenation	Biopolymers Fumaric acid Furoic acid Furandicarboxylic acid Furfurylalcohol	Plastic industries Chemical industries
Glycerol	2.0	Hydrogenolysis Oxidative dehydration	Diols (ethylene/propylene glycol) Acrylic acid	Chemical industries Plastic industries Coating
Biohydrogen	NA	-	-	Fuels (jet fuels, diesel, gasoline)
Lactic acid	0.4	Polymerization	Polylactic acid	Plastic industries
Succinic acid	0.05	Dehydration	Acrylic acid	Plastic industries coating
		Hydrogenation	Diol (propanediol, butanediol) Butyrolactone	Chemical and plastic industries
Hydroxypropionic acid	NA	Oxidation	Maleic acid Fumaric acid	Chemical industries
		Polymerization	Polyester polyols	Adhesives Coating
		Dehydration	Acrylic acid	Plastic industries Coatings
Levulinic acid	NA	Hydrogenation	y-Valerolactone	Fuel additives
Sorbitol	1.7	Oxidation	Succinic Acetyl acrylic acid	Chemical industries
		Hydrogenolysis	Diols (ethylene/propylene glycols)	Chemical industries
Xylitol	0.1	Hydrogenolysis	Diols (ethylene/propylene glycols)	Chemical industries

8. Conclusions and Future Perspectives

Ethanol is now used on a massive scale the world over so it needs to be produced in a cost-effective and environmentally sustainable way. One major advantage of biomass as a suitable feedstock in biorefinery processes is its availability. It is a cheaper feedstock for the production of biofuels and platform chemicals. It is also important to recognize the difficulties associated with the depolymerization of biomass into fermentable sugars. Current pretreatment techniques need to be improved to make 2ndgeneration biofuels economical. It should be noted that the hydrolysis of biomass requires energy. However, when chemical processes are assisted by microwave reactors, the length of the reactions and the energy consumption are reduced. Other factors such as the transportation of lignocellulosic biomass, pests, diseases, and land use have made the production of 2nd-generation biofuels more expensive. Nevertheless, the absorption of CO_2 by some grasses has greater environmental advantages in climate change. The value of biofuels goes beyond their use as transportation fuels, and attention should be given to the economic and environmental benefits of the co-products of biofuels. The success of material products could save our fragile earth from further environmental degradation. The various generations of biofuel significantly reduce GHG emissions and our reliance on crude oil, encourage energy diversity, and create a large number of rural jobs. Today, the blending limits established in the United States, Brazil, China, India and other countries (see Table 3) will reduce both gasoline prices and GHG. At present, the long-term success of biofuels requires streamlined and aggressive research, and research data should be consolidated and made known to all stakeholders. Financial incentives and supportive regulations, which are instrumental in driving the commercial production and adoption of advanced biofuels should be encouraged.

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