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Coproducts of Biofuel Industries in Value-Added Biomaterials Uses: A Move Towards a Sustainable Bioeconomy

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1. Introduction

World population is expected to grow nearly 9 billion in 2040 and eventually increases the global energy demand by 30% compared to current conception [1]. The issues related to increasing trend of crude oil cost, depleting source of fossil fuels and emerging threat on greenhouse gas emissions are leading the global energy sector to undergo a fundamental transformation towards renewable energy sources [1-2]. As the result, a main focus is motivated on renewable energy technologies that are based on solar, wind and biofuels. In transportation point of view, biofuels receive extensive attention due to their versatility in storage and refilling. Both bioethanol and biodiesel come together as biofuel currently produced from renewable resources through two different pathways. In some countries like Brazil, biofuels are produced and marketed at competitive cost compared to petroleum-based fuels employing existing technology [3-4]. They also carry following advantages comparing to petro fuels; (i) create significantly less pollutants (SO_x and NO_x), which also mitigates CO_2 emission, (ii) biodegradable nature lead to the less environmental leak risk and (iii) provides better lubricant effect, which enhances the engine life [5]. In addition, these emerging biofuel technologies will be expected to create more economic benefits to agriculture sectors and new rural job opportunities. Moreover, biofuels are attractive options for future energy demand since they can be produced domestically by many countries while the respective retail and consumer infrastructure needs minimum modification; so does the existing engine and fueling technology [6].

However, biofuel foresees a challenging journey to benefit from its highest potentials and to guarantee a viable future. Primarily, it needs policy support and commercialization. At the

same time, research and development is crucial to conquer the challenges and bring sustainability to biorefinery facilities [7]. Major motivation for biofuels usage arises from the execution of biofuel policies by many countries, which mandates the incorporation of bio-counterpart into traditional fuels. United Kingdom introduced the Renewable Transport Fuels Obligation (RTFO) and encouraged the oil suppliers to incorporate biofuel into transport fuel between 2.5 and 5% during 2008-2010. RTFO's ultimate aim is to increase this 5% upto 10% by 2020, which will reflect in the demand of minimum 5 million tonnes [8]. Renewable fuel blending mandates in Canada was implemented through Canadian Environmental Protection Act, which recommends 5% ethanol with gasoline (in 2010) and 2% biodiesel with diesel (in 2012) [9]. In South Africa, the National Biofuels Industrial Strategy was introduced by the government in 2007, which recommends the implementation of 2% biofuels into liquid road transport fuels by 2013 [10]. Currently India's ~80% crude oil demand is satisfied by foreign suppliers, which is projected to rise 90% in 2025. In order to reduce this foreign dependency, India has announced the target of ethanol blending with gasoline 20% by 2017 [11]. In biofuel production, China has clear production goals to meet emerging demand in near future. China's integrated biofuel policies (rural welfare, improved energy security, reduced fossil fuel dependence, and CO₂ emissions) aimed to meet ~ 15% of the total transportation fuel demand by 2020 [12]. In Malaysia, the National Biofuel Policy initially planned to proceed with 5% biodiesel blend with 95% petroleum diesel, which is similar to Europe's B5, which has been started from 2009. This will be implemented through short, medium and long term strategies aiming to reduce their petroleum imports [13]. In addition to that, many countries have already designed various incentive programs for the effective promotion of biofuel production including bioethanol and biodiesel. This implements 5-20% biofuel supplement into traditional fuels [14].

Such blending mandates of biofuels adopted by the E.U. and U.S. created a dispute of increased food prices. Besides, the contribution of corn bioethanol in addressing the global warming issues is very modest while having a small positive net energy balance; i.e. the energy return on investment (EROI) of corn bioethanol is low (=1.2-1.6) compared to oil (=9) [6]. The emerging challenges for 1st generation of biofuel industries that utilizes corn and soybean as a major feed stock for biofuel production motivated the search for non-food and more efficient energy feedstocks like jatropha, lignocellulosic biomass and algae. Among them, cellulosic matter will be the major feedstock for second generation biofuel, since it exhibits much higher yield per hectare in comparison with sugar or starch crops [6]. As a result, cellulosic biomass can potentially yield higher land fuel (135 GJ/ha) than corn kernel (85 GJ/ha) and soy (18 GJ/ha) [15]. Moreover, significantly higher carbon sequestration is another advantage of the use of cellulosic biomass in biofuel production compared to the first generation biofuel crops [6].

This biomass-biofuel conversion can be performed under three major classes and they are (i) conversion of renewable polysaccharides into sugar molecules and their effective fermentation into ethanol, (ii) syngas production and their bio/chemical conversion into alcohols and (iii) production of bio-oil though fast-pyrolysis and their upgrade into transportation fuels. Considering the lignocellulosic feedstock as the biofuel precursor, it is crucial to create the necessary infrastructure in many levels from biomass to biofuel production; agriculture-technology-policy. The new utilization of biomass would largely affect the agriculture sector and necessitates effective actions to ease the adaptation process. Biofuel production uses land which keeps it from food production and environmental preservation. Other issues might be

considered; soil erosion may worsen by expanding the biomass production, reduction of environmental land affects biodiversity and more pesticides and fertilizers may be used. Thus, the sustainability of biofuel is not achieved solely by a positive net energy balance [6]. In spite of all raised issues, it is important to bear in mind that biofuel still offers its advantages even if it has a small contribution compared to fossil fuels. In this regard, the two main challenges in biomass production can be (a) developing crops with suitable physical and chemical traits for biofuel production and (b) increasing biomass yields (double or more) [7]. How to put these two different strands into an integrated production strategy is important and brings new research topics into the whole agriculture picture. The outcome of such productivity-enhancing innovations, research and development motivated by biofuel can be such that by 2050, the whole world population could be supplied enough diet while less cropland is used than today [6]. The respective biorefinery operation also needs improvements so that sugars can be produced from cellulosic biomass and fermented economically feasible and able to compete with production from corn and sugar. These include improvement in lignocellulosic pretreatment, reduction in enzyme (cellulase) cost, both cellulase production and ethanol fermentation by using modified microorganisms [7].

In general, the growth of biofuel industry consists of (i) increased production capacity and (ii) successful transformation of industrial technology from discrete batch method (small-scale) into continuous flow method (larger-scale) [16]. In most of the small scale manufacturing, the industries do not have the practice of collecting coproducts, thus they run with increased operating costs. Hence, larger-scale industries are keen in capturing their coproducts in order to reuse them in the production process, which results in the reduction of operating cost significantly. Thus, value-added processing may serve as a viable alternative that not only reduces the impact on the environment, but also generates additional revenue source for biofuel plants [17]. Sustainable bioeconomy road map that integrates renewable resources, biofuel production/ utilization and the value-addition to the respective coproducts is shown schematically in Figure 1. In recent years, biofuel coproducts have been utilised for the fabrication of various chemicals for diversified applications and used as the filler/reinforcement for polymer blends as well as composites. The emerging opportunities for the biofuel coproducts in biomaterials (polymers/ composites) applications make successive transformation of coproducts to renewable feedstock with economic benefits. Capitalizing this transformation enhances the economic viability and also the sustainability of biofuel industries. Thus, this chapter summarizes the various aspects in biomaterial applications of the biofuel coproducts and their role in sustainable bioeconomy.

2. Current status of coproducts from biofuel industries

2.1. The global biofuel industry status

The biofuel industry has been growing rapidly during recent years and continues to expand for the next decade. Such expansion is basically driven by renewable energy goals and different policy supports as for example use mandates, tax relief, fuel quality specifications and investment capacities in leading producing countries [18]. Based on the projection reported by

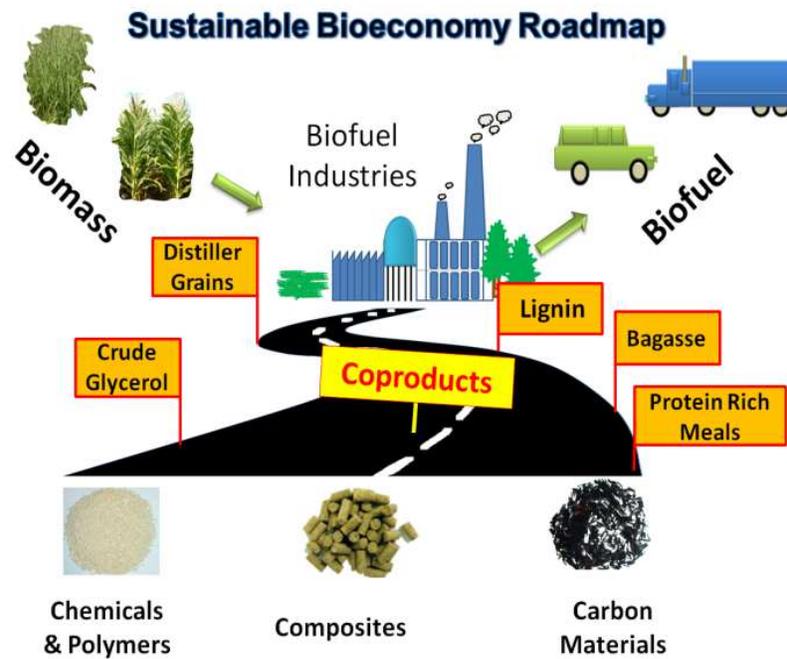


Figure 1. Sustainable bioeconomy roadmap.

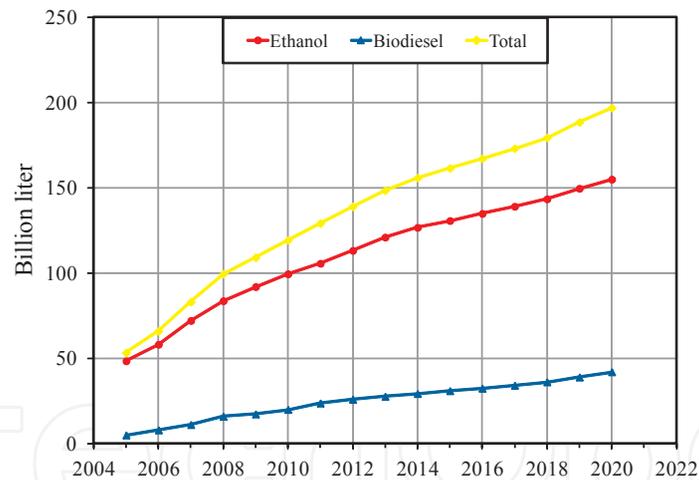


Figure 2. Development of global biofuel industry (drawn from data reported in [19, 21]).

the OECD (organization for economic co-operation and development) – FAO (food and agriculture organization of the united nations) Agricultural Outlook for the 2011-2020 period, the global bioethanol industry will be growing almost 68% from an average of 92 billion liter in the 2008-2010 period to 155 billion liter in 2020 (Figure 2) [19]. In this regard, coarse grains and sugarcane are going to remain the major precursors in bioethanol production and in 2020 they are expected to account for 78% of bioethanol feedstock (Figure 3) although this value was 81% on average during the 2008-2010 period [20]. The large scale production of cellulosic ethanol is still not achieved and under research and development. Therefore, it is expected to

expand in the latter projected years reaching up to more than 4 billion liter in 2020. This is far less than the respective value for the first generation ethanol. The rest feedstocks include wheat (3.9%), molasse (3.2%), non-agricultural feedstock (2.6%), sugar beet (2%) and other (5.8%) [20].

Similar trend has been presented for biodiesel as illustrated in Figure 2 [21]. The growth in this industry in 2020 is projected to be almost 138% compared to 2008-2010 period on average; an increase from 17.6 to 41.9 billion liter. Vegetable oils will contribute more than 78% as the main feedstocks for biodiesel production. The application of non-food oils such as jatropha in biodiesel production still remains very less as compared with the contribution of vegetable oils such as soybean and palm oil. Feedstocks other than edible oils in biodiesel production include non-agriculture feeds (12.3%), biomass-based (6%) and jatropha oil (3.2%) (Figure 3) [22]. The huge impact of such expansion in biofuel industry on the respective coproducts is incontestable. Based on the feedstock share in the biofuel production by 2020, the major coproducts of different sectors of the biofuel industry can be listed as dried distillers' grains with solubles (DDGS) from dry mill corn ethanol, corn gluten meal and corn gluten feed from wet mill corn ethanol, bagasse from sugarcane ethanol, lignin from second generation lignocellulosic ethanol, and soy meal and crude glycerol from biodiesel. More focus on these coproducts will be dedicated in the following sections.

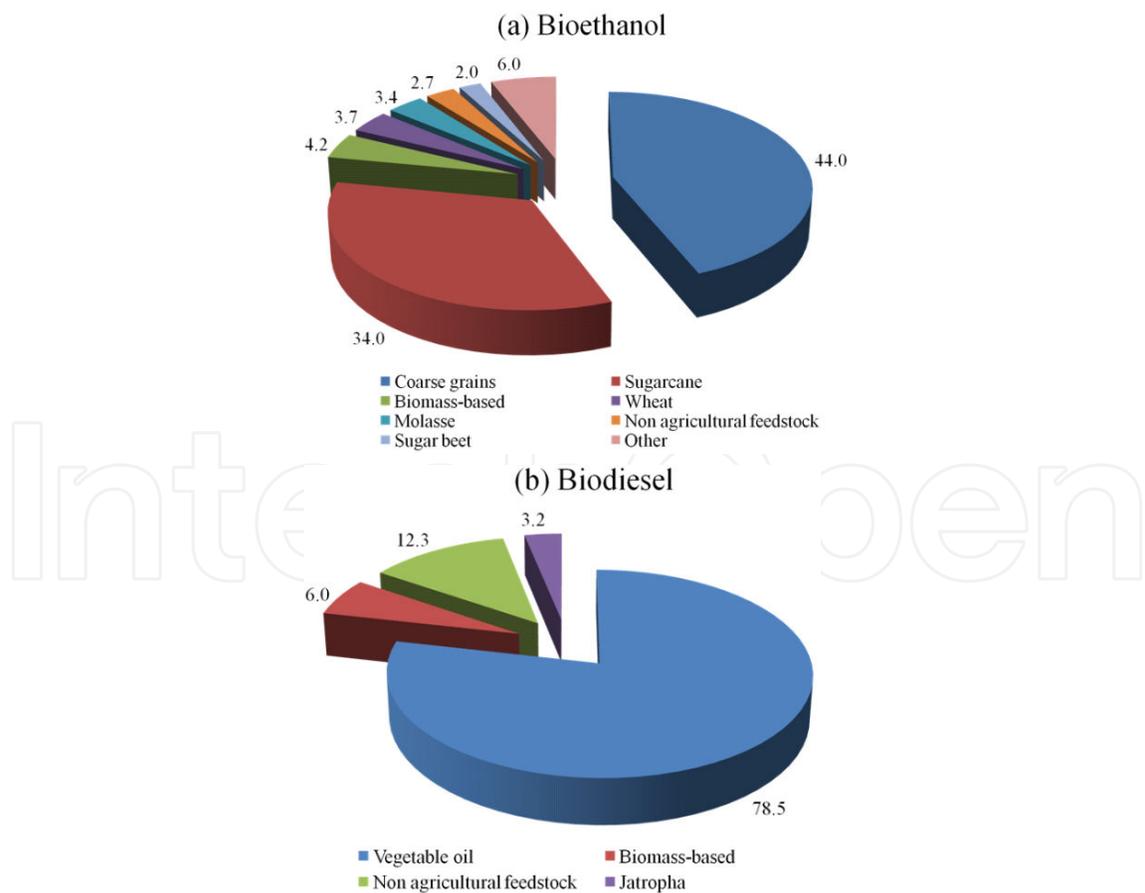


Figure 3. The global biofuel production by feedstocks contribution (%) in 2020 (redrawn from data reported in [20, 22]).

2.2. Biofuel coproducts

2.2.1. Corn bioethanol

Starch-based ethanol can be obtained from corn, wheat, barley, sorghum or any other starchy grain by fermentation. However, due to highly fermentable starch content, corn is the main feedstock for ethanol production by fermentation and accounts for 98% of all starch-based ethanol feedstocks [1]. Bioethanol from corn is produced in both dry mill and wet mill plants each of which producing specific coproducts as described below.

2.2.1.1. Dry mill

In a dry mill, ethanol is produced from corn after several steps including grinding, slurring, cooking, liquefaction, saccharification, fermentation and distillation. Further steps are implemented to separate coproducts such as centrifugation, evaporation and drying. From the original corn mass before processing, approximately one third results in carbon dioxide during fermentation, one third is converted into ethanol and the residue are nonfermentable components in the form of different coproducts namely dried distillers' grains with solubles (DDGS), dried distillers' grains (DDG), wet distillers' grains (WDG) and condensed distillers' solubles (CDS). The coproducts are mainly dried and sold as dried distillers' grains with solubles (DDGS). This way, it is possible to store the coproduct for a longer time or ship it to far distances with less probability of fungi attack. A smaller part of the coproducts are shipped wet locally for immediate usage [23-24]. Distillers' grains have been traditionally using as animal feed due to its nutritious value as shown in Table 1 [25-31]. At the end of ethanol production process, when most of the grain's starch portion is fermented, there is an increase of 3 to 4 times in other components of the grain including protein, lipid and fibre over that contained in the unconverted whole grains [27].

Several attempts and studies have been published on distillers' grains application as animal feed in many different species such as dairy cattle [32], beef cattle [33], swine [34], broiler [35], laying hen [36], turkey [37], lamb [38], catfish [39], tilapia [40], trout [41] and prawn [42]. However, four major livestock species to which distillers' grains is practically fed are beef cattle, dairy cattle, swine and poultry [43-45]. Renewable Fuel Association (RFA) reports the distillers' grains consumption in 2009 in different species at approximately 39% for dairy cattle, 38% for beef cattle, 15% for swine, 7% for poultry and 1% for other species [24]. The important question here is whether the increasing supply of distillers' grains can be totally consumed by animals or the supply far exceeds its demand as feed. According to Hoffman and Baker [44] and Tokgoz et al. [46] the potential domestic and export use of distillers' grains in U.S. exceeds its production and the U.S. beef sector is the dominant user of distillers' grains. However, such opinions need precise consideration with respect to the fact that incorporation of distillers' grains within animal diets exhibits some limitations. Since distillers' grains are highly concentrated in terms of nutritious content, it should be included as a part of animal feed. In this regard, Canadian Food Inspection Agency (CFIA) has set out the policy for the maximum inclusion rates of distillers' grains in the feed of different species [47]. For example, the inclusion rates of distillers' grains in the diet of beef cattle and swine must not exceed 50% on a dry basis. This suggests that continuing the use of distillers' grains in animal diet in order to

keep the track with its increasing supply from ethanol production can only come true if the number of consumer animals is also increasing. In other words, finding new value-added usages for distillers' grains within feed sector should also be considered in the future.

	DDGS [25-27]	CGM [28]	CGF [28]	SM [29]	CM [29-30]	JM [31]
Dry Matter (%)	88.8-91.1	90	87-90	NA	91.5	NA
Protein (% DM)	24.7-32.8	60	18-22	53.5-54.1	38.3	55.7-63.8
Fat (% DM)	11.0-16.3	2.5	2-5	1.4-2.3	3.6	0.8-1.5
Acid Detergent Fiber (ADF) (% DM)	12.4-15.2	5	13	7.2-10.2	17.5	5.6-7.0
Neutral Detergent Fiber (NDF) (% DM)	46.1-51.6	NA	35	9.6-13.8	21.5	8.1-9.1
Ash (% DM)	4.2-12.0	1.8	6.5-7.5	7.2-8.1	8.1-8.6	9.6-10.4

DDGS: dried distillers' grains with solubles, CGM: corn gluten meal, CGF: corn gluten feed, SM: soybean meal, CM: canola meal, JM: jatropha meal, NA: not available

Table 1. Composition of different biofuel coproducts

It is worth to note that the U.S. dried distillers' grains with solubles (DDGS) exports already doubled in 2009 compared to 2008 and U.S. has managed to increase its export of DDGS in 2010 by 60% compared to 2009 [48]. This may suggest that there is an excess of DDGS supply over its consumption in animal feed sector in the United States. Moreover, it should be carefully examined how the revenue from distillers' grains sale as feed, returning to the biofuel industry will economically help the ethanol industry. For corn biofuel industry to stay viable, the applications of its coproduct, distillers' grains, need to be expanded [23]. Consequently, the new outlets of distillers' grains may add value to it and create revenue for the corn ethanol biofuel. Such new usages can be value-added animal [23, 49] and human food [50], burning [51-52], extraction of zein [53], cellulose [54] and oil [55-56] from distillers' grains, and biobased filler for polymer composites, which is going to be discussed more later on.

2.2.1.2. Wet mill

Wet milling is a corn processing process in which the produced corn starch can be fermented into ethanol. Thus, ethanol is not the only product of a wet mill. In the beginning, the feedstock goes through a steeping step that soaks it in warm water containing small quantities of dissolved sulfur dioxide for almost 40 hours. This step facilitates the separation of the grain components. The different processes will be then applied such as grinding, screening, germ separation, oil refining, starch-gluten separation, drying, fermentation and syrup refining. Other products of a wet mill plant produced along with ethanol in these processes include starch, corn oil, high fructose corn syrup (HFCS) and glucose/dextrose. The coproducts of

different steps are corn gluten feed, corn gluten meal, corn germ meal and corn steep liquor [28]. Corn gluten feed and corn gluten meal are the major feeds for livestock produced in a wet mill. As compared to the produced ethanol in a wet mill, corn gluten feed and corn gluten meal are produced almost as much as 70% and 17% of the mass of the produced ethanol, respectively [44]. The composition of the wet mill coproducts are presented in Table 1. Similar to distillers' grains, these coproducts account for a good source of nutritious components such as protein and fiber for feed applications. The value of these coproducts for animal feed has been realized for many years now and they are used as the feed for a wide range of animals including beef cattle [57], calf and lamb [58], dairy cattle [59], poultry [60], swine [61], pet [62] and fish [63]. Also, it has been reported that corn gluten meal can be used as the pre-emergence weed control (to control weeds before the weed seeds germinate) [64] and has been regulated by US Environmental Protection Agency (EPA) [65].

2.2.1.3. Corn ethanol coproducts production

Although there is a lack of comprehensive statistics on global production of corn bioethanol coproducts, a general insight can be obtained considering the production of these coproducts in the United States during last 10 years. This may be reasonable since U.S. is the largest ethanol producer globally with more than 50% contribution in 2007 and 2008 [8]. As reported by the Renewable Fuels Association (RFA) (Figure 4), the production of distillers' grains, corn gluten feed and corn gluten meal in the U.S. have shifted totally more than 10 times from 3.1 million tonnes in 2001 to 32.5 million tonnes in 2010 [24].

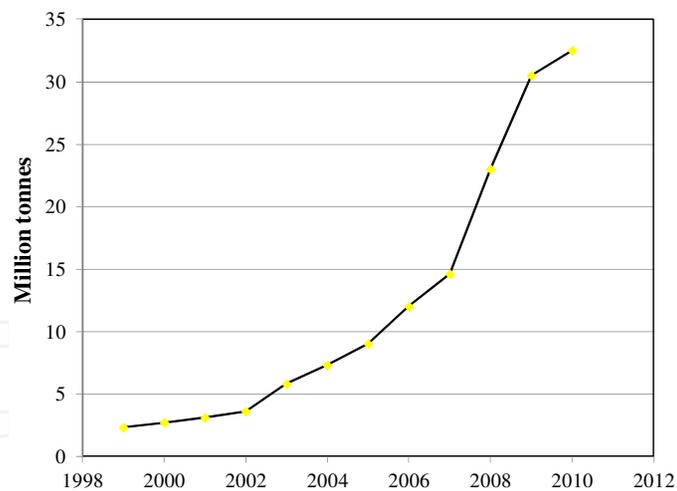


Figure 4. Production of ethanol biorefineries coproducts in US including distillers grains, corn gluten feed and corn gluten meal (drawn from data reported in [24]).

2.2.2. Sugarcane bioethanol

In a sugar mill, the crushed sugarcane is washed to go for juice extraction. The resulted juice can be used for sugar as well as ethanol production. Bagasse is the lignocellulosic coproduct after the sugarcane is crushed for juice extraction [66]. Approximately, it consists of 50%

cellulose, 25% hemicellulose and 25% lignin [67]. Bagasse has been widely used as the fuel for generating electricity. One metric ton of bagasse containing 50% moisture will produce heat equivalent to that from 0.333 tons of fuel oil [68]. This coproduct has been considered for such purpose in different countries such as Zimbabwe [69], Nicaragua [70] and Brazil [71]. Another large utilization of bagasse is in paper and pulp industry. This was patented in 1981 [72] and found huge application in many places such as India as early as 1990 [73]. The particleboard production is another industrial utilization of this biomass [74]. Bagasse has been also used in composting to a limited extent [68] and use of fungal strains on bagasse has been reported to produce compost with low pH and high soluble phosphorus [75]. Fermentation of bagasse using mold cultures was also considered to produce animal feed [76].

As a lignocellulosic material, bagasse has the potential of a feedstock for biofuel production either by gasification or hydrolysis method. In this context, still the biofuel production from bagasse via gasification has not been reported. However, as an alternative method competitive to the direct combustion of bagasse, gasification using a two-stage reactor has been proposed to be economically viable and more efficient [77]. Also, studies have been conducted in order to improve the bagasse gasification as far as retention and separation of alkali compound is concerned during the process. Considering the lignocellulosic ethanol production from bagasse, several investigations has been published on liquid hot water, steam pretreatment [78] and acid hydrolysis of it [79] as well as simultaneous saccharification and co-fermentation (SSCF) method [80]. As published in 2004, about 180 MT of dry sugarcane bagasse is produced globally and can be utilized to produce about 51 GL of bioethanol [81].

The expansion in production of the sugar-based ethanol is one of the key factors affecting the bagasse production. The sugarcane harvest of Brazil, the global leader of sugar-based ethanol, has shifted upward approximately 45% during recent five years from 425.4 MT in 2006-07 to 620.4 MT in 2010-11 (Figure 5) [82]. The ethanol production in Brazil generally shows a similar trend. To produce one liter of ethanol, 12.5 Kg of sugarcane is required. The weight of the produced bagasse is about 30% of the weight of sugarcane used for sugar or ethanol production [66]. Therefore, the bagasse production of Brazil in 2010-11 can be estimated as more than 180 MT, almost equal to global bagasse production before 2004.

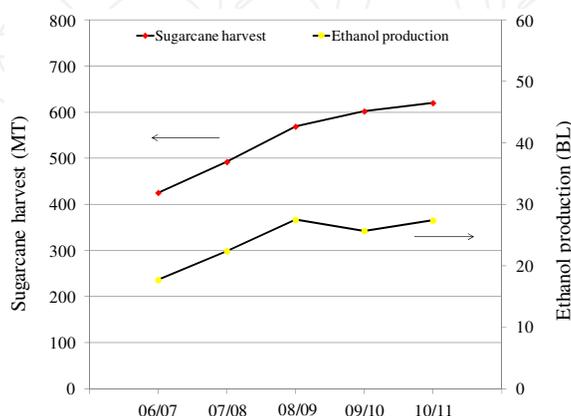


Figure 5. Brazilian sugarcane harvest and ethanol production (drawn from data reported in [82]).

2.2.3. Lignocellulosic bioethanol

In a second generation bioethanol plant, lignocellulosic polysaccharides (cellulose and hemicellulose) are broken down into monosaccharides (hexose and pentose) to be further fermented into ethanol. This includes a sequence of processes such as pretreatment, hydrolysis (enzymatically or chemically), fermentation and purification. At the end, the residual from the original lignocellulosic biomass is the coproduct mainly in the form of lignin [83]. The amount and quality of the produced lignin depends on the original lignocellulosic matter and the process. Typically, lignocelluloses contain 10–30 % lignin, which depends on various factors such as nature of biomasses, growth as well as isolation process [84]. As we know, lignin is a polymer that exists in the cell walls of plants, which is available in nature next to cellulose. The role of lignin in plant is to save them from compression, impact and bending. In addition to that, the major role of lignin extends to prevent the plant tissues from various kinds of naturally occurring microorganisms [85].

Chemically the polymeric structure of lignin is highly complicated and consists of three different monomer units (Figure 6) and they are called as p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [86-87]. In addition to plant varieties, the lignin extraction process (known to be delignification) play a major role in the determination of local structure. Thus, the chemical structure of lignin extracted from plant biomass is never similar as exist in plant. There is a possibility for the alteration of monomer arrangement in the lignin structure. Hence, the lignin in plants, called as “natural lignin”, is termed as “technical lignin” after isolation. These technical lignins can be further classified into three classes based on the domination of monomer units and they are [88]: (i) Softwood lignin: dominated with coniferyl monomer units, (ii) Hard wood lignin: combinations of equal quantities of guaiacyl and syringyl monomer units and (iii) Grass lignin: equally formulated with all three monomers of coniferyl, sinapyl and p-coumaryl.

The sources for lignin production can be divided into two major categories and they are (i) paper and (ii) bioethanol industries. They use different types of de-lignification process thus the lignin from paper industries and the lignin from bioethanol industries are not similar. Paper industries adopt Kraft, Sulphite, and Soda pulping processes to remove lignin from biomass, where as lignocellulosic ethanol industries, prefer to go with organosolv, steam explosion, dilute acid as well as ammonia fibre explosion for the removal of lignin [89]. Due to the tough food-versus-fuel concerns, non-food crops such as switchgrass, miscanthus and sugarcane bagasse become an effective feedstock for ethanol production and those related biofuel are named as second generation biofuels [90]. As the global demand for biofuel continues to grow, there will be emerging opportunities for lignocellulosic ethanol industries, which is expected to create a huge amount of lignin and it is predicted to be ~225 million tons by 2030 [85]. The challenge is to dispose them effectively that includes using them as a feedstock for energy products as well as for the fabrication of various chemicals and materials [91]. In common practice, lignin has been used for energy fuel, which is also the easiest way of disposal. In other hand, value-added uses of lignin can give economic return to the lignocellulosic ethanol industries and can improve their sustainability.

Only 2% of the lignin, which is produced from various sources, has been used as the feedstock for various chemicals including phenol, terephthalic acid, benzene, xylene, toluene, etc. [89]. In addition to these, lignin has also been used in fertilizer, wood adhesives, surfactants, and also some kind of coloring agents [89]. Recently, lignin has been included as filler/reinforcing agent for blends and composites in both thermoplastic as well as thermoset platforms [85, 92-94]. In addition to that, lignin is found to be a suitable renewable carbon source for the synthesis of carbon materials [95]. Lignin has been widely exploited for the fabrication of activated carbon for various purposes including hydrogen storage, waste water removal and energy storage/conversion. Especially synthesizing nanostructured carbon materials from renewable resource-based lignin receives a great scientific interest due to the unique morphology as well as their physicochemical properties. As the global demand grows for the carbon fibre composites, there is a huge demand for the low cost carbon fibres. Lignin-based carbon fibres can substitute polyacrylonitrile (PAN)-based carbon fibre, hence the opportunity for lignin as a successful feedstock for carbon fibre is in near future [96]. This will be possible by understanding the basics of lignin chemistry and their application for fibre fabrication.

2.2.4. Biodiesel

2.2.4.1. Proteineous meal

The major biodiesel feedstocks are vegetable oils which are generally produced by crushing oil seeds, leaving significant quantity of proteineous meals as coproducts. The global consumption of proteineous meal in 2011/12 as reported by USDA Economic Research Services [97] is depicted in Figure 7 indicating soybean as the predominant crop producing proteineous meal with 67 % contribution. According to the FAOSTAT database [98], US, Brazil and Argentina were the global premiers of soybean production in 2010 with 35, 26 and 20% contribution, respectively. The next largest producer is China with almost 6% share in the global soybean production. In this context, biodiesel production of the US, as for example, has increased, during 2006-11 period, 340% from 250 to 1100 millions of gallons [99], which promoted the proteineous meal production. Soybean meal is traditionally used as a filler in animal feed including poultry, swine, beef, dairy, pet and other animals due to its concentrated protein content (Table 1).

Other examples of plant-based feedstock potentially suitable for oil extraction and biodiesel production can be listed as canola and linseed [100], palm [101], karanja [102] and jatropha [103]. Jatropha is a non-edible seed from a large shrub commonly found throughout most of the tropical and subtropical regions of the world. As shown previously in section 2.1, jatropha is projected to have a 3.2 % contribution in biodiesel production by 2020. The growing utilization of plant-based feedstocks other than soybean meal in biodiesel production also brings new streams of proteineous meal as coproducts.

2.2.4.2. Crude glycerol

Biodiesel is chemically known as methyl esters, which is produced through transesterification reaction by reacting a vegetable oil or animal fat with an alcohol under a strong base catalysis environment [104]. Along with biodiesel, such transesterification reaction produces significant

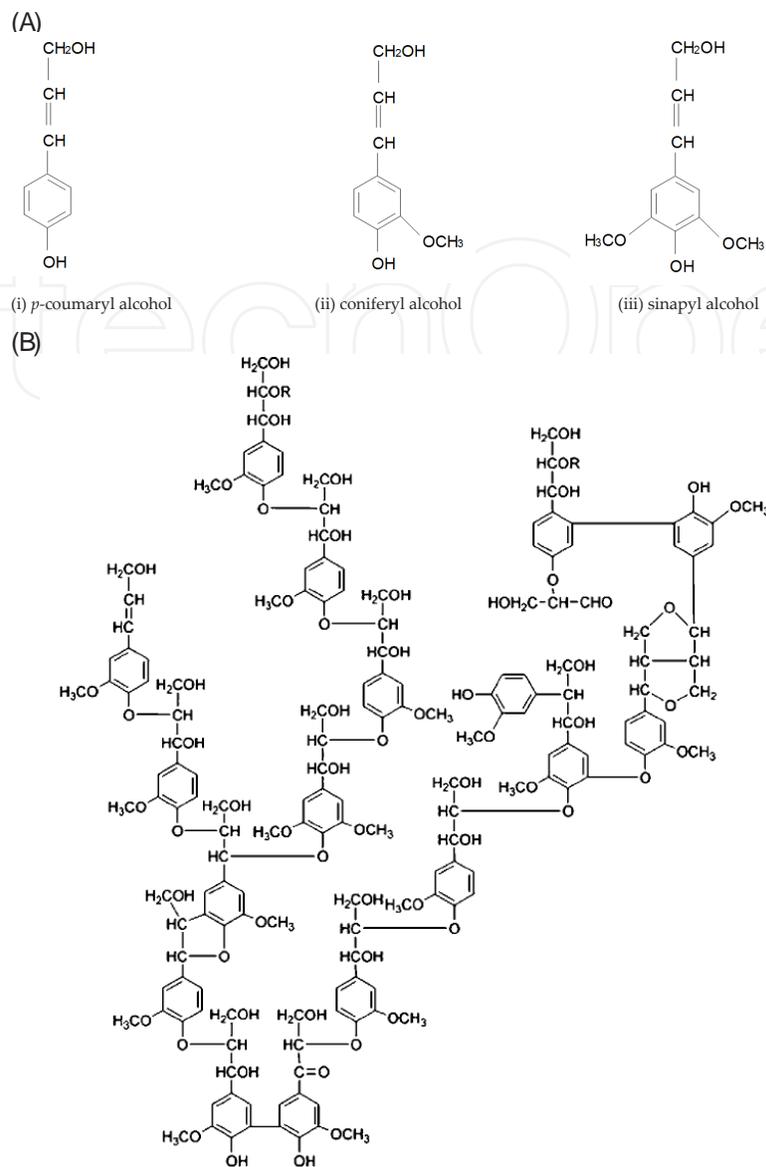


Figure 6. (A) Phenolic precursors that form the lignin and (B) Chemical structure of lignin (reprinted the figure with permission) [87].

quantity of glycerol (also called as glycerin), which is normally collected with other ingredients such as catalysis, water and unreacted alcohol and it is termed as crude glycerol [105]. Normally biodiesel industries utilize excess amount of methanol as required for the completion of reaction, which leaves unreacted methanol to the glycerol after the reaction. With every 3 gallons of biodiesel, 1kg of crude glycerol is produced and it shows very low value because of its impurity [106]. As the global biodiesel production increases exponentially, the resulting crude glycerol is extensively high and become issues due to their disposal or effective utilization. On the other hand, pure glycerol has found a wide range of applications that includes food, cosmetics, and drugs. In order to upgrade the crude glycerol to those high end applications, it should undergo various purification stages such as bleaching, deodorizing, and ion exchange. Normally, this is not affordable nor economically feasible for most of the small/

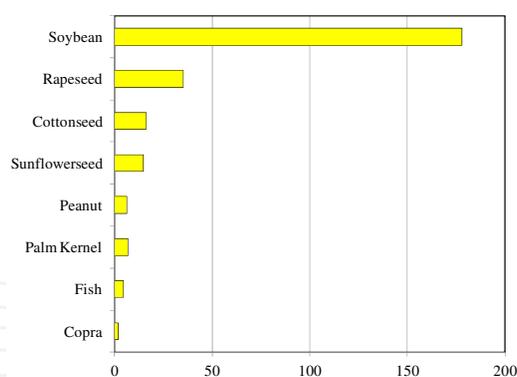


Figure 7. World protein meal consumption (million tonnes) in 2011 (drawn from data reported in [97]).

medium ranged industries. Hence, it is necessary to investigate the value-added uses of crude glycerol in various applications.

Prior to that, it is necessary to understand the relationship between the oil feedstock and the crude glycerol. Thompson and He [105] performed a research on the characterization of crude glycerol samples from various feedstocks. Their research shows that the compositions of different crude glycerol are highly varying with their feedstocks. This creates the challenge to adopt a universal protocol to fabricate value-added products from crude glycerol from various feedstocks. Crude glycerol has been used to produce various products including 1,3/1,2-propanediol, dihydroxyacetones, polyesters and hydrogen [107]. Mu et al. [108] reported the synthesis of 1,3-propanediol using crude glycerol produced during biodiesel preparation through fermentation process using *Klebsiella pneumonia*. They used the crude glycerol obtained during soybean oil-based biodiesel production employing alkali catalysis. They ultimately compared the product of 1,3-propanediol obtained from pure glycerol and found that they are similar to each other [108]. Soares et al. [109] demonstrated the generation of synthesis gas or syngas (hydrogen and carbon monoxide) from glycerol at very low temperature between 225-300 °C employing a Pd-based catalyst. Further it can be converted into fuels/chemicals by Fischer–Tropsch methanol synthesis. They also suggest this process for the effective utilization of various crude glycerol feedstocks for the fabrication of high value fuels/chemicals. Mothes et al. [110] reported the synthesis of poly (3-hydroxybutyrate), PHB, using crude glycerol (rape seed oil-based) as the feedstock via biotechnological process employing *Paracoccus denitrificans* and *Cupriavidus necator* microbes. They compared the properties of the synthesized PHBs from two different feedstocks and found that the properties are very similar. Zhou et al. [111] reviewed the chemo-selective oxidation of crude glycerol into various products such as glyceric acid, hydroxypyruvic acid and meso-oxalic acid which can be used as precursor for various fine chemicals and polymeric materials. These reports indicate the emerging opportunities for crude glycerol for various applications including chemical, fuel and materials.

2.3. Sustainability through value addition

Due to the uncertainty in long term availability of fossil fuels and their continuous threat to environment through greenhouse gas emission, there is a drive across the globe towards the

exploration of various biorefinery systems. Production of biofuel creates impact in utilization of biomass, replacement of possible extend of gasoline, reduction of greenhouse gas emission and the creation of significant amount of coproducts [112]. Biofuel production from biomass tends to strengthen the entire value chain (farming community-biofuel industries-consumers) and claims as the probable sustainable alternate for the conventional fossil fuel systems. Biomass is the sustainable feedstock for biofuel industries and biofuel provides ecological safety towards sustainable transportation, however the emerging concern is about the co/by-products. If they create challenging environmental issues in disposal, sustainability of this technology is challenged. Thus, value addition to these biofuel coproducts plays key role for the sustainability of biofuel technology in long term perspective [113]. With this understanding, the ultimate aim of biorefinery is focused to satisfy the conceptual "triple bottom line" of sustainability that includes (i) economic development; commercial value for biomasses, biofuels and coproducts, (ii) social development; appearance of new manufacturing sectors as well as creation of rural job opportunities, and (iii) environmental/resource sustainability; greenhouse gas reduction and eco-friendly green products [114]. In order to ensure the sustainability of biofuel technology it is essential to address various issues including (i) "food vs. fuel" due to the usage of edible resource for biofuel production, (ii) resource availability/management; effective utilization of land/water resources, (iii) environmental impact; issues related to land/water quality retention, conversion of grasslands/forests to agricultural fields and the efficient disposal/utilization of biofuel coproducts and (iv) validated measures: policy making and certification/standardization [115]. Scale-up activities of biofuel production is essential due to the increasing demand for the substitution of fossil fuel. However, it is significantly controlled by various factors such as effective land usage for the larger biomass generation, water availability for agricultural forming, retention of soil quality, environmental impact of biofuel coproducts and labor market shift towards biorefinery [116-117]. The successive transformation of biofuel production from conventional to second generation effectively addresses the issues related to water consumption. Lignocellulosic ethanol industries utilise perennial crops such as miscanthus and switchgrass, which grows on marginal land and consume very less water. The challenge is towards biofuel coproducts. Failure of handling these large quantity coproducts will ultimately create serious environmental issues. These emerging technologies related to the effective utilization of biofuel coproducts that holds significant quantity of renewable content significantly substitute/replace petroleum-based products and helps in reduction of greenhouse gas emission.

3. Value-added biomaterials from biofuel coproducts

3.1. Distillers' grains

3.1.1. As biofiller in producing polymeric biocomposites

The low cost of distillers' grains (DDG and DDGS) is a key incentive for researchers to utilize them as biobased fillers in manufacturing polymer composites. Also, addition of DDG(S) to the polymer matrix can result in improved stiffness as long as proper treatments and proc-

essing aspects are taken into account. It is less than ten years that DDGS-containing biocomposites has been reported in the literature. In this regard, the very first produced DDGS-containing composites exhibited low mechanical properties so that the utilization of DDG(S) as a biofiller in composite materials seemed to be not worthy in the beginning. However, recent works project a better future for DDG(S)-based biocomposites.

3.1.1.1. DDGS-polyolefin biocomposites

Polyolefins such as polypropylene (PP) and polyethylene (PE) were the first polymers compounded with DDGS up to 30 wt% [118]. The mentioned work included a comparison of four types of biofiller such as big blue stem (BBS) grass, soybean hull, pinewood and DDGS in terms of the mechanical performance of the their biocomposites with PP and PE. The composite processing was performed in a twin screw extruder and mechanical properties tests were conducted. Generally, the studied biofillers increased the flexural and tensile moduli. However, DDGS increased the modulus not significantly in comparison with neat PE and PP. Moreover, the tensile and flexural strengths decreased drastically as a result of compounding with DDGS. In general, the authors of [118] came to a conclusion that DDGS is not a suitable biofiller because of the decreased mechanical properties of the studied DDGS/polyolefin composites. In another work, the composite of high density PE with DDGS has been produced via extrusion and injection molding technique with DDGS content of 25 wt% [119]. The effect of maleated polyethylene (MAPE) as the compatibilizer was studied. Moreover, DDGS was solvent-treated to remove its oil and polar extractables. It has been reported that the application of the MAPP with solvent-treated DDGS resulted in better tensile and flexural properties of the composite compared to the respective properties of the neat HDPE.

3.1.1.2. DDGS-polyurethane biocomposites

This is another attempt of biomaterial application of DDGS. The overall idea of such work was to utilize a tough binder between rigid particles of DDGS to create an acceptable flexible material. Thus, polyurethane prepolymer (PUP) from castor oil was used as a binder with different compositions of DDGS and the biocomposites were prepared in a two-step process; PUP and DDGS were premixed in a micro-extruder and then compression molded to the shape of sheet. The mechanical and dynamic mechanical properties characterizations showed that the produced PUP/DDGS sheet was more flexible compared to the brittle DDGS material, thus polyurethane enhanced the properties of DDGS [120].

3.1.1.3. DDGS-phenolic resin biocomposites

Tatara et al. [121-122] bonded DDGS particles, from 0 to 90 wt%, with phenolic resin via compression molding process. Mechanical properties of the blends showed a reduction in modulus, tensile strength and elongation at yield by increasing the DDGS amount. However, the researchers believed that the cost saving resulted from the addition of low-cost DDGS filler in a reasonable quantity may offset the reduction in property performance; i.e. a cost-performance balance is achieved. In this context, inclusion of 25 and 50 wt% of DDGS maintained the mechanical strength to an acceptable value. In another work, the effect of DDGS particle

size and content (25 and 50%) was studied when phenolic resin-based glue and wood glue were used to produce DDGS composites [123]. Overall, the DDGS composite with resin glue showed better mechanical properties and curing uniformity compared to wood glue/DDGS composites. Also, DDGS enhanced the flexural properties such as modulus and maximum stress. Also, composites of DDGS with smaller particle size (0.7 mm) had higher mechanical properties compared to those with higher particle size (0.34 mm).

3.1.1.4. DDGS biopolymer biocomposites

During recent years, biopolymer thermoplastics such as poly(lactic acid), PLA [124], poly(butylene succinate), PBS [125], polyhydroxy(butyrate-co-valerate)/poly(butylene succinate), PHBV/PBS, blend [126] and poly(butylene adipate-co-terephthalate), PBAT [127] have been utilized to produce DDGS composites. The influence of DDGS amount from 20 to 50 wt% as well as compatibilizer in PLA/DDGS composites were investigated [124]. Drastic decrease in tensile modulus and strength was observed by increasing the wt% of DDGS when no compatibilizer was used. On the other hand, after using isocyanate type of compatibilizer, a huge improvement in tensile modulus and strength was observed in the PLA/20% DDGS composite (Figure 8). In comparison with pure PLA, the compatibilized formulation showed higher modulus and almost equal strength. In another work, the thermal degradation of DDGS was studied with considerations for biocomposite processing and it was reported that water-washing of DDGS improved the thermal stability of DDGS to the extent that its thermal decomposition was highly prevented at typical temperatures of polymer melt processing. Such improvement in thermal stability of DDGS resulted in better strength and modulus of the PBS/DDGS biocomposite with 30 wt% DDGS [125]. The effect of compatibilizer was studied in a composite of 30 wt% DDGS and PHBV/PBS blend processed in a micro-extruder/micro-injection molding machine [126]. The DDGS used in this biocomposite had a water-washing step prior to compounding with bioplastics. Using a compatibilizer (isocyanate type), the interfacial adhesion was enhanced. The optimized biopolymer/DDGS composite exhibited improved tensile modulus compared to the biopolymer matrix while having almost equal strength. The influence of DDGS on the biodegradability properties of PBAT/DDGS biocomposites has been evaluated [127]. It was observed that PBAT/DDGS biocomposite was found to be more bio-susceptible material compared to virgin PBAT and was totally biodegraded. During the biodegradation experiment DDGS domains were preferentially attacked by microorganisms and influenced the biodegradability of the PBAT matrix. The produced biocomposite showed a degree of biodegradation similar to the biodegradation rate of natural materials such as DDGS and cellulose.

3.1.2. Other biomaterial applications

DDGS as a source of protein, fiber and fat has been used to isolate these components. Xu et al. [53] implemented a novel acidic method to extract zein from DDGS which is the main protein in corn and corn coproducts such as DDGS. The resulted zein has the potential for uses in fibers, films, binders and paints applications. Their method also isolated DDGS oil during protein extraction. Other researchers have also investigated the extraction of oil from DDGS

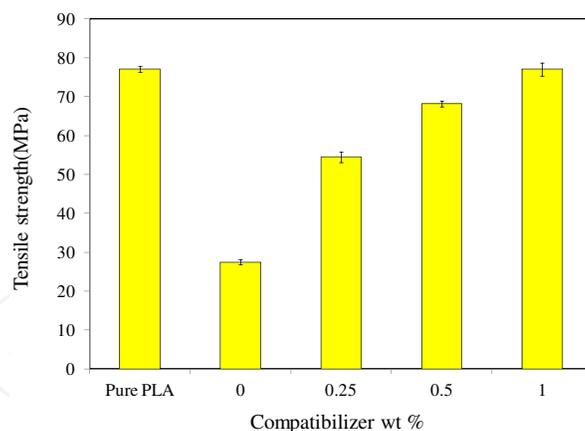


Figure 8. The effect of compatibilizer on tensile strength of the biocomposite PLA-20wt% DDGS (drawn from the data table with permission) [124].

[55, 128]. The obtained oil can be used as precursor for biodiesel production. It has been also tried to extract fiber from DDGS with physical methods such as sieving and elutriation [129] or extract cellulose chemically by sodium hydroxide solution [54]. The obtained cellulose had properties suitable for films and absorbents. The bioadhesive formulation obtained from DDGS is another biomaterial application of this coproduct [130-131]. This glue is prepared by reaction with an aqueous base solution. Urea can be also included with the base. The obtained bioadhesive is particularly useful as boxboard glue.

Recently, it has been tried to produce thermoplastics from DDGS by chemical methods such as acetylation [132] or cyanoethylation [133] with almost similar approaches. Hu et al. [133] were successful in producing highly flexible thermoplastic films from DDGS. The oil and zein protein of the DDGS were extracted first and the resultant underwent cyanoethylation using acrylonitrile. A compression molding machine was implemented to produce oil-and-zein-free DDGS films. It was observed that the produced films had much higher strength even at high elongations compared to films developed from other various biopolymers. Therefore, cyanoethylation could be a viable approach to develop bio-thermoplastics from biopolymers for applications such as packing films, extrudates and resins for composites. It has been also tried to find a novel use of dried distillers' grains (DDG) as a feedstock for bio-polyurethane preparation [134]. The procedure consist of, first, liquefaction of DDG in acidic conditions at atmospheric pressure and then reaction of hydroxyl-rich biopolyols in the liquefied DDG with methylene diphenyl diisocyanate (MDI) to form networks of cross-linked polyurethane. Thus, DDG-based bio-polyols were the precursor in this way to synthesize flexible and rigid polyurethane foams. The biodegradation tests showed that the degradation of these polyurethane foams in a 10-month period was about 12.6% most probably because of natural extracts such as proteins and fats in DDG and partially cross-linked or uncross-linked residue in the foam [134].

3.2. Bagasse

Bagasse has been used in biomaterial applications since a very long time ago. It has been used for interior panels and particleboard production. The first bagasse composition panel plant in Americas was built by Celotex, Louisiana, in 1920. Since then, more than 20 bagasse particleboard plants have been built throughout the world [135]. However, recent characterization of bagasse fiber for its chemical, physical and mechanical properties indicates that the potential of this coproduct of sugar and biofuel industries is much more than its applications in interior and structural components [136]. Bagasse is mostly burnt to generate energy for the sugar industry itself. Considering the fact that for such purpose almost 50% of the bagasse's production is enough [137], it is necessary to develop new uses for these fibers to implement the rest 50 % and reduce their environmental impact. Moreover, the burning of bagasse fiber is also a matter of concern as far as atmospheric pollution because of smoke, soot and ash is concerned [138]. Chemical composition as well as physical and mechanical properties of bagasse fiber are presented in Table 2 [136, 139-142]. Bagasse fiber consists of structural components such as cellulose and hemicellulose that can provide stiffness and rigidity to the polymers and enhance their engineering applications. Besides, bagasse exhibits a porous cellular structure with a hollow cavity called lumen existing in unit cell of the fibers. Therefore, the bulk density of bagasse fiber is lower than other natural fibers and bagasse fibers can act more effectively as thermal and acoustic insulators [142]. For example, the densities of kenaf and banana fibers are 749 kg m^{-3} [140] and $1350\text{-}1500 \text{ kg m}^{-3}$ [139], respectively, which are higher than that of bagasse ($344\text{-}492 \text{ kg m}^{-3}$ [139-140]). Also, cellulosic fibers such as bagasse with low Young's modulus can act as useful crack growth inhibitors [143].

	Properties	Ref.
Chemical composition	Cellulose (%)	32.0-55.2 [139]
	Hemicellulose (%)	16.8-32.0 [139]
	Lignin (%)	19.0-25.3 [139]
	Ash (%)	1.1-4.3 [139]
	Extracts (%)	0.7-3.5 [139]
Physical properties	Density (kg m^{-3})	344-492 [139-140]
	Diameter (μm)	394-490 [136, 140-141]
	Moisture content (%)	52.2 [136]
	Water absorption (%)	235 [136]
Mechanical properties	Tensile strength (MPa)	29.6-96.2 [136, 141-142]
	Tensile modulus (GPa)	4.5-6.4 [140, 142]
	Elongation at break (%)	4.0 [142]

Table 2. Chemical composition, physical and mechanical properties of bagasse fiber

3.2.1. *Bagasse particleboards*

Bagasse particleboards generally consist of bagasse fibers bound together with either an organic or inorganic binder. The organic binders are mostly a phenolic or polyester thermoset resins and the board is produced by compression molding under high pressure and temperature. Different inorganic binders such as cement, gypsum and calcined magnesite can also be used to produce bagasse boards [144-146]. Besides, binderless bagasse particleboards have been produced and patented in 1986 which can simplify the manufacturing process and reduce production cost since the blending operation and equipment are eliminated [147]. In this regards, different processing techniques such as hot pressing [148] and steam-injection pressing [74] have been conducted.

3.2.2. *Bagasse-thermoset biocomposites*

Phenolic resins are the major thermosets used for bagasse particleboards and several studies have been published on using resol [137], Novolac [149], lignophenolic [150] and other phenolic resins [143, 151] with bagasse fiber. Zárate et al. [137] studied the effect of fiber volume fraction on the density and flexural properties of composites from resol and several fibers including bagasse. They compared the efficiency criterion for mechanical performance, which relates the strength and stiffness with density, of the composites with those of typical structural materials including aluminum, magnesium, polyethylene and steel. Based on this comparison, it was concluded that the stiff composite materials produced from bagasse fibers and resol matrix are better compared to typical structural materials such as steel [137]. The effect of maleic anhydride (MA) treatment of bagasse fiber on properties of its composite with Novolac has been studied [149]. It has been reported that the composites with MA treated fibers had a hardness of 2–3 times more than that of the untreated bagasse composite and MA treatment reduced water and steam absorption of the fibers. Paiva and Frollini [150] extracted lignin from sugarcane bagasse by the organosolv process and used it as a partial substitute of phenol in resol phenolic matrices to produce bagasse-lignophenolic composite by compression molding. They observed improvement in the impact strength when sugarcane bagasse was used, but no improvement was found as a result of fiber treatments such as mercerization and esterification.

Unsaturated polyesters are another family of thermoset resins used for bagasse-based composite purposes. The effect of fiber size, its surface quality and the compression molding parameters on the flexural properties of composites from polyester and chopped bagasse fiber has been investigated. It was found that composites produced with bagasse particle size of less than 2 mm, and pre-treated for the extraction of sugar and alcohol exhibited the highest mechanical performance [138]. The effect of chemical treatments using sodium hydroxide and acrylic acid on the properties of bagasse-polyester composites has been studied. The treatments resulted in the better interaction between fiber and matrix as well as lower water absorption than composites with untreated fiber [142].

3.2.3. Bagasse-thermoplastic biocomposites

Bagasse has been used as reinforcing filler in different thermoplastic matrices such as poly(ethylene-co-vinyl acetate) (or EVA) [152-153], polyolefins [154-155] and starch-based biodegradable polyester [140-141, 156-157]. The effect of cultivar type and surface cleaning of the bagasse fiber on the tensile properties of the bagasse-EVA composites have been investigated [152]. The results suggested that blends of bagasse from various cultivars can be used for commercial applications of these composites. Also, the surface cleaning of the bagasse obtained from sugar mill was good enough to use the bagasse without further surface treatment. Another study on the impact behavior of the bagasse-EVA composites showed that the mechanical performance of this type of composites could be tailored by varying the bagasse volume fraction in order to reproduce the behavior of wood-based particleboards [153]. Luz et al. [154] explored the efficiency of two different processing methods, injection molding and compression molding, to produce bagasse-polypropylene (PP) composite. They found that the injection molding under vacuum process was more efficient and created homogeneous distribution of fibers without blisters. It was observed that bagasse incorporation into PP improved the flexural modulus. High density polyethylene (HDPE) was used as the matrix for incorporation of cellulose obtained from bagasse [155]. It has been reported that modification of bagasse cellulose with zirconium oxychloride helped in improving the tensile strength of the biocomposite.

Bagasse fibers have been used to produce biocomposites from bagasse and biodegradable corn starch-based polyester which is reported as a blend of starch and polycaprolactone (PCL). The effects of volume fraction and fiber length were investigated and an optimum value for both factor were reported beyond which the decrease in mechanical performance was observed [140]. Also, it was reported that after alkali treatment of the bagasse fibers the improvement in fibre-matrix adhesion occurred that resulted in enhancement of mechanical properties [141]. Moreover, incorporation of bagasse fiber into the polyester matrix improved tensile as well as impact strength. Acetylated starch has been reinforced with bagasse fiber [156-157]. The matrix in that case was a blend of starch, PCL and glycerol. It was observed that incorporation of alkali-treated bagasse fiber up to 15 wt% increased the tensile strength while it decreased when bagasse content was more than this value. Also, the water absorption of the composite was improved as the bagasse content increased due to hydrophobic nature of bagasse compared to acetylated starch.

3.2.4. Other biomaterial applications

It has been also tried to convert bagasse fibers into a thermo-formable material through esterification [158-159]. This has been done without any solvent using succinic anhydride followed by hot-pressing to produce the test samples. The thermoplasticization of the esterified fibers was proven to occur by scanning electron microscopy. By studying the effect of pressing parameters, it has been found that that de-esterification and hemicellulose degradation could occur on certain pressing conditions. It has been claimed that the mechanical properties of the produced composite could be superior to the standard properties of conventional high density wood particleboards.

3.3. Lignin

Biomaterials applications of lignin for the fabrication of polymers, blends and their reinforced composites are highly motivated due to the following reasons (i) abundance/occurrence in nature, (ii) phenolic chemical structure and the possibility of chemical modification and (iii) eco friendliness and reduced carbon footprint [160]. The challenge to use lignin as the materials feedstock is their complicated chemical structure as well as molecular weight, which are highly dependent on the lignin extracting process and also their sources [161]. The biomaterials application of lignin is vast and it has been blended/ reinforced with a wide range of polymeric systems such as thermoplastics, thermosets and elastomers as a renewable low cost filler [162]. Utilization of lignin as the raw material for the fabrication carbonaceous materials such as activated carbon and carbon fibres has a long history, however the creation of nanostructured materials such as carbon nanoparticles/nanofibres are quite new, which has a huge commercial potential [95, 163]. The emerging opportunities for lignin in these areas are summarized in this section.

3.3.1. Polymeric blends and composites from lignin

3.3.1.1. Lignin in thermoplastics

In polymers, lignins have been used as low-cost fillers aiming to retain their mechanical properties. Nitz et al. [164] reported the influence of various types of lignin reinforcement with the thermoplastics on their mechanical properties. Their results indicate that they are able to incorporate ~40 wt% lignin in to polyamide 11 (PA11), polyester (Ecoflex®) and polyestera-mide (BAK®) systems without impairing their mechanical properties [164]. Generally lignin shows high cross-linking/intramolecular interactions, which limits their application in solid material systems. This can be overcome through polymer blending; however, achieving miscibility is very essential to develop a material system with superior properties [165]. This is possible in lignin-based blends by manipulating the chemistry of hydrogen bonding between the OH groups and interacting sites of polymers, either polar or semi polar [165]. Moreover, the hydrogen bond with a polymer varies with lignin to lignin since the monomer combinations of the lignins are unique [166].

Lignin–thermoplastic blends can be classified into two categories and they are (i) lignin – petro-based polymer blends and (ii) lignin–renewable resources based polymer blends. Blending the lignin with polyethylene and polypropylene is well known [166-169]. Alexy et al. [166] reported the effect of lignin concentration in the fabrication of polymeric blend with PP and PE. They measured the tensile strength as the measure of mechanical properties over the various lignin compositions. For both the polymer systems they identified that the mechanical properties decrease with increasing lignin content [166]. In addition to mechanical properties, Canetti et al. [169] and Mikulášová et al. [170] reported the fabrication of lignin/PP blends and investigated their thermal and biodegradable properties respectively. Poly(vinyl chloride) (PVC) is the next popular thermoplastic, which has been produced globally and exhibits a wide range of applications [171]. Raghi and coworkers [171] reported the fabrication of lignin/PVC blend and studied their mechanical/weathering properties. Their research investigation

confirmed that the addition of lignin to PVC enhanced their tensile strength and not influenced their weathering behavior. Banu et al. [172] reported the fabrication of PVC/lignin blends and investigated the effect of plasticizer in their formulations. They concluded that the specific thermal and mechanical properties are feasible in some formulations with the addition of plasticizer. In addition to that, lignin/ poly(vinyl alcohol) (PVA) and lignin/ poly(ethylene oxide) (PEO) blend systems with various types of lignins are also investigated for the effective electrospinning performance [173-176]. Sahoo et al., [92] reported the fabrication of polybutylene succinate (PBS) reinforced with renewable resource-based lignin employing a melt extrusion process. They found that lignin reinforcement in PBS enhances their properties synergistically and also achieved the incorporation of high fraction of lignin of about 65%. In addition to that, they also reported the fabrication of PBS-based composite materials with the hybrid reinforcement of lignin and other natural fibre [93]. They found that the hybrid reinforcement is more beneficial over individual reinforcement for the better flexural strength.

The research on lignin-based polymer blends with renewable resource-based biopolymer is very limited. Only few publications are available in this content. Camargo et al. [177] reported the melt processing of poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) with lignin, in which they used the lignin isolated from sugarcane bagasse. They found that the addition of lignin to PHBV caused a reduction in their mechanical properties, which is due to the zero integration of lignin and PHBV [177]. Mousavioun et al. [178] performed the processing of poly(hydroxybutyrate) (PHB)-soda lignin blend and studied its thermal behavior. They found that the addition of soda lignin formed the miscible blend and improved their overall thermal stability. However, they have not reported their mechanical properties [178]. Vengal et al. [179] investigated the blending effect of lignin with starch and gelatin for the fabrication of biodegradable polymeric films. They found that the addition of lignin into starch can create better film with the composition of 90:10 (lignin: starch) and further increment of lignin content decreases their properties. Casetta et al. [180] fabricated the PLA and lignin blend and investigated their flame retardant behavior. They observed that the addition of lignin to PLA enhanced their flame retardant property compared to virgin PLA.

3.3.1.2. Lignin in thermosets

The lignins of different resources have been incorporated into various thermoset resins. Amorphous/heterogeneous nature and the complex structural composition of lignin result their behavior as either like a filler or like a reactive macromonomer in epoxy resin systems. Mansouri et al. [181] characterized the alkaline lignin and suggested their possible use for phenol-formaldehyde resin due to the availability of huge OH groups. Peng et al. [182] reported the fabrication of phenol-formaldehyde thermoset resin with lignin fillers and investigated their chemo-rheological properties. They found that the curing rate of the resin system decreased with increasing lignin content. Guigo et al. [183] fabricated the poly(furfuryl alcohol)/lignin composites and reported their monophasic behavior. This indicates the reactive monomer behavior of lignin in this thermoset system. Thielemans et al. [184] investigated the effect of kraft lignin on unsaturated thermosetting resin, which was a mixture of epoxidized soybean oil and styrene, for the fabrication of natural fibre reinforced thermoset composites. They found the complete

solubility of lignin into the resin system and their result on natural fibre composites indicated the compatibilizing effect of lignin. Nonaka et al. [185] reported the fabrication of a new resin system by aqueous mixing of alkaline kraft lignin with polyethylene glycol diglycidyl ether (PEGDGE), and a curing reagent. They identified the complete compatibility between lignin and PEGDGE through the studies on dynamic mechanical analysis.

3.3.1.3. Ligninin rubber blends

Although the history of lignin/rubber blend started in 1949, a very little work has been performed till date [186]. The role of lignin in rubber is identified as reinforcing filler and stabilizer or antioxidant. Kumaran et al. [186] performed an extensive research on the utilization of lignins in rubber compounding and identified the improvement of many properties. They reported that the addition of lignin into rubber improved their tear, abrasion and flexural crack resistances. Košíková et al. [167] investigated the reinforcement effect of sulfur-free lignin with styrene butadiene rubber (SBR). They identified that the lignin blending with SBR influenced their vulcanizing behavior and enhanced the various physicommechanical properties significantly. In addition to that, Wang et al. [187] investigated the fabrication of latex/modified lignin blend and identified their effective water barrier properties. Processing condition of the lignin/rubber is critical for the achievement of better properties. Tibenham et al. [188] reported the hot-milling of lignin/rubber precursors with hexamethylenetetramine, which yields a vulcanizate. They also found that the modulus, tensile strength, and hardness properties were in the same order as the rubber reinforced with carbon blacks.

3.3.1.4. Lignin in polyurethane

Polyurethanes are made of diisocyanate and polyol precursors, which have been used for the highly diversified applications. Traditionally, they were made from petroleum-based synthetic polyols and nowadays soy-based polyols are also widely used as the renewable feedstock. Nakamura and his co-researchers [189] investigated the lignin-based polyurethane (PU) films using polyethylene glycol (PEG) and diphenylmethane diisocyanate (MDI). They reported the thermal behavior of new polyurethane system, which indicates that the addition of lignin to PEG enhances their T_g proportionally. The combination of lignin and PEG for the formation of polyurethane resulted in various types of microstructure such as soft and flexible and hard. Their mechanical properties were highly dependent on their distribution as well as cross-linking ability between lignin-PEG-MDI segments [190]. Sarkar et al. [191] reported the synthesis of lignin-hydroxyl terminated polybutadiene (HTPB) co-polyurethanes using toluene diisocyanate as initiator. Their characterizations showed the better properties up to 3% lignin incorporation and further increment of lignin caused the reduction in their properties [191]. Saraf et al. [192-194] made an extensive research on various aspects of lignin-based polyurethane and suggested their suitable formulations for the enhanced performance. In addition to that, various types of lignin also investigated for the fabrication of polyurethane systems [195-196]. Thring et al. [195] reported the fabrication of polyurethanes from Alcell®. They found that the increasing lignin content decreases the degree of swelling and cross-

linking and causes the formation of brittle and hard structures. Yoshida et al. [196] utilized the kraft lignin for the fabrication of polyurethanes. They reported that the increasing lignin content increases the cross-link density and generally causes a hard and brittle nature. They also fabricated the polyurethane from various kraft lignins with different molecular weight and found that the cross-link density has increased with increasing molecular weight [197]. These studies conclude that the higher loadings of lignin in polyurethane caused the formation of rigid structure due to higher cross-link density and resulted in poor mechanical properties. This can be overcome by employing suitable chemistry in controlling the order of cross-linking.

3.3.2. Lignin in adhesives

Phenolic structure of lignin offers possible substitution with phenol-formaldehyde (PF) resin, which exhibits a wide range of applications as adhesives. Lignin substitute in phenol-formaldehyde (PF) formulation can vary from 30 to 50%, which exhibits similar or better performance compared to virgin PF resin. Haars et al. [198] reported the fabrication of room-temperature curing adhesives using lignin and phenoloxidasas as precursor chemicals. They reported the possible use of this new bioadhesive as thermosetting glue. They also indentified the increment of water resistance during the usage in particleboard production. Mansouri et al. [199] demonstrated the fabrication of lignin adhesives without formaldehyde for wood panel. Their synthesized lignin adhesives showed better internal bond strength, which also passed required international standard specifications. They found that the newly bioadhesive from lignin exhibits many properties comparable to formaldehyde-based commercial adhesives. Schneider et al. [200] patented the new technology for the fabrication of new kind of adhesives using furfuryl alcohol and lignin employing zinc chloride-based catalyst. Lignin isolated from bagasse was also experimented for the fabrication of biobased cost effective adhesives [201-202]. The obtained adhesives were used for the purpose of particleboard and wood adhesives.

3.3.3. Lignin based carbon nanostructures

Recently, carbonaceous nanomaterials that include carbon nanotubes, carbon nanofibres, graphene/graphite nanosheets and also particulate carbon nanostructures have received an extensive importance due to their possible commercial values in diversified areas like polymeric composites, sensors, energy storage/ conversion, catalysis, filters and biology [203-208]. Traditionally, carbonaceous materials were prepared from petroleum-based precursors (liquid/gaseous hydrocarbons and carbon rich polymers such as polyacrylonitrile-PAN). As the global demand for carbon materials (nano/micro) grows continually and also the conventional sources are finite there is a need to investigate for the alternate carbon source. Thus, renewable resource-based biomaterials such as seed, oil, dried fibres as well as stem have been explored for the development of various carbon materials [209-212]. The challenge in using plant-based materials as carbon feedstock is to control the carbonizing process as well as the usage of suitable catalysis in order to achieve nanostructured materials. In addition to the larger availability of biobased feedstocks for the carbonaceous materials, it also provides eco-

friendliness with the reduced carbon footprint. The biofeedstock exhibits a diversified morphology with the various combination of chemical structures, which can result in the formation of varieties of carbon nanostructures. Lignin has been widely used for the fabrication of activated carbon, however synthesizing carbon nanostructures such as particles/fibres are very new, thus next section summaries the effective uses of lignin as precursor for the fabrication of carbon nanostructures and their emerging applications [213-214].

3.3.3.1. Carbon nanoparticles

Lignin can be used as an efficient precursor in synthesizing carbonaceous nanomaterials with different morphology not only due to their carbon rich phenolic structure, but also for their capable chemical modification. Synthesizing the carbon nanoparticles with different morphology is possible by adopting various order of chemical modification as well as the processing conditions. The challenge is to inhibit the nucleation of carbon structures during the carbonization process to avoid larger particles, which normally occurs at elevated temperatures. Chemical modification can result in the formation of cross-linked structure, which normally alters the carbonization mechanism and can cause the formation of carbon nanostructures with different morphology. Babel et al. [215] reported the synthesis of KOH activated lignin-based carbon nanoparticles and their effective hydrogen storage capability. Recently, Gonugunta et al. reported the fabrication of carbon nanoparticels from lignin by adopting freeze drying process [216-217].

3.3.3.2. Lignin-based carbon nanofibres

One dimensional (1D) nanostructures such as fibrous materials receives recent attention due to their unique physicochemical properties. A wide range of fabrication techniques have been used for the fabrication of fibrous nanomaterials, among them electrospinning has been found to be an efficient technique for the fabrication of various types of fibre nanostructures using polymeric solutions as precursors [218]. The fabrication of carbon nanofibres from lignin through electrospinning has three steps and they are (i) electrospinning of lignin fibres, (ii) thermal stabilization of lignin fibres and (iii) carbonization of thermo-stabilized lignin fibres [219]. Normally, lignin exhibits poor viscoelastic properties, which creates a lot of challenges during the electrospinning process. This can be overcome by blending the lignin with other kind of synthetic polymers such poly(ethylene oxide) [220]. Figure 9 shows the electrospun lignin fibre as the precursor for the fabrication of carbon nanofibres. Dallmeyer et al. [221] investigated seven different technical lignins (isolated lignin) for the fabrication of fibrous network. None of the lignins were able to be spun into fibres without a binding polymer such as PEO. In addition to PEO, utilization of polyacrylonitrile (PAN) as binding polymer was reported by Seo et al. for the fabrication of lignin-based carbon fibres [222]. The physicochemical properties and the morphology of lignin-based carbon nanofibres can be varied by manipulating the experimental parameters. Lallave et al. [219] reported the fabrication of various types of (filled and hollow) carbon nanofibers from Alcell lignins by coaxial electrospinning. Uniqueness of their process is the successful electrospinning of lignin without binder

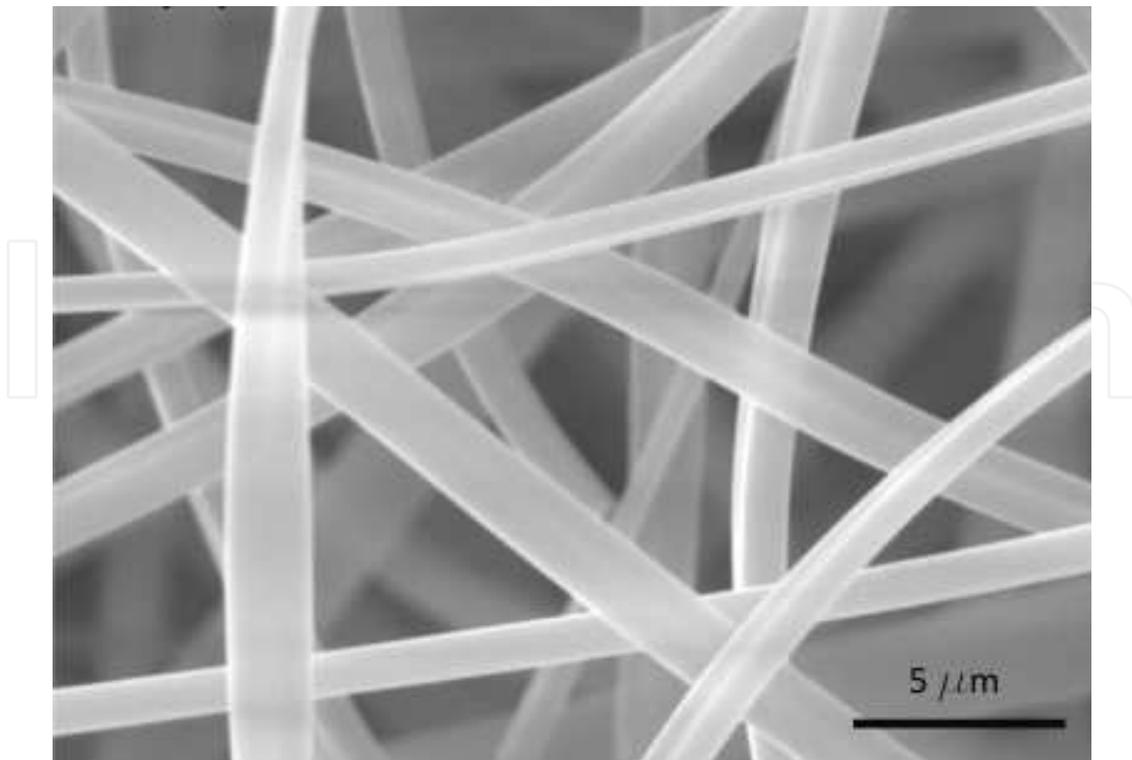


Figure 9. Electrospun lignin fibres (reprinted the figure with permission) [219].

polymer. Recently, Spender et al. [223] reported the rapid freezing process for the fabrication of lignin fibres with nano dimension.

3.4. Proteineous meals

As discussed in the previous sections, the major proteineous meal coproducts of biofuel industry are corn gluten meal from wet mill bioethanol and soybean meal from biodiesel industries. Different types of soy protein including soy flour (48% protein), soy protein concentrate (64% protein) and soy protein isolate (92% protein) can be extracted from soybean meal after oil extraction of soybean powder with hexane [224]. Similarly, corn gluten meal can be used to extract zein, the major protein in corn [225]. These proteins can be plasticized to produce films and formable thermoplastics. The biomaterial application of the these proteins has been investigated and reviewed extensively [225-226]. Recently, the biomaterial application of the meals themselves has attracted attentions and been studied in the form of plasticized meals as well as reinforcing fillers used in polymeric biocomposites.

3.4.1. Corn gluten meal

Corn gluten meal (CGM) is much cheaper than zein protein, thus creating more attraction compared to zein in producing thermoplastic materials. In this context, several plasticizers have been tried by many researchers for plasticization of CGM. Lawton and coworkers [227] studied the effect plasticizers such as glycerol, triethylene glycol (TEG), dibutyl tartrate, and

octanoic acid on melt processing and tensile properties of CGM. In another work, di Gioia et al. [228] plasticized CGM with different plasticizers including water, glycerol, polyethylene glycols (PEG), glucose, urea, diethanolamine, and triethanolamine, at concentrations of 10–30% (dwb). They implemented dynamic mechanical thermal analysis (DMTA) to investigate the change in glass transition temperature and rheological moduli of CGM. Similarly, the effect of “polar” plasticizers (such as water, glycerol) or “amphiphilic” plasticizers (such as octanoic and palmitic acids, dibutyl tartrate and phthalate, and diacetyl tartaric acid ester of mono-diglycerides) on the glass transition temperature of the CGM/plasticizer blends have been reported [229].

Plasticized CGM has been blended with several polymers. Corradini et al. [230] blended CGM with different plastics such as starch, polyvinyl alcohol (PVA) and poly(hydroxybutyrate-co-hydroxyvalerate), PHBV, using glycerol as plasticizer. After studying the glass transition temperature of the blends, they found that these blends are immiscible in the studied compositional range. Also in terms of mechanical properties, PVA improved the flexibility while PHBV enhanced the rigidity and starch caused slight changes in mechanical properties. CGM has also been blended with poly(ϵ -caprolactone), PCL [231]. In this work, CGM was first plasticized using glycerol/ethanol mixture, denatured by the addition of guanidine hydrochloride (GHCl), and then blended with PCL. They used twin screw extruder and injection molding for the processing. Their results showed that chemical modification of plasticized CGM with GHCl resulted in a high percent elongation. In another work CGM was blended with poly(lactic acid), PLA, plasticized with glycerol, water and ethanol using a single screw extruder followed by compression molding [212]. Their results showed that PLA enhanced the rigidity and improved the water resistance. CGM-wood fiber biocomposites have been the point of interest in several publications. CGM in these works has been used in the form of plasticized meal. Wu et al. [232] produced pellets of CGM-wood fiber, plasticized by glycerol, water and ethanol, to manufacture injection-molded plant pots for developing low cost, biodegradable containers used in agriculture. In another study, CGM plasticized with propylene glycol was blended with a biopolymer, poly(butylene succinate) (PBS), and wood fiber to produce a biodegradable material for plastic packaging applications [233]. The CGM content varied between 10–80 wt% and it was found that the produced biomaterial exhibited relatively high tensile strength, elongation at break and water resistance as long as the CGM content was less than 30 wt%. Similarly, CGM has been plasticized with different plasticizers such as glycerol, octanoic acid, polyethylene glycol and water, and reinforced with wood fiber using a twin screw extruder [234]. The best mechanical performance was achieved when a combination of 10 wt% octanoic acid and 30 wt% water was used as plasticizer with 20 wt% wood fibre as reinforcement. The mechanical properties were improved more when the CGM matrix was blended with polypropylene, coupling agent (maleated polypropylene) and cross-linking agent (benzoyl peroxide) with 50 wt% wood fibre [234].

3.4.2. Soybean meal

Soybean meal (SM) is still finding its way within scientific researches towards biobased material (biomaterial) applications. The number of publications on this topic is limited

compared to corn gluten meal. SM has been characterized for its chemical composition, moisture content, thermal behavior and infrared spectrum and its potential as a particulate filler in value-added biocomposites was evaluated by compounding with polycaprolactone (PCL) [235]. The composite of PCL/SM (70/30) was prepared by extrusion and injection molding and then tested for mechanical properties such as tensile, flexural and impact. It has been observed that PCL/SM composite exhibited higher tensile/flexural modulus, but lower strength, elongation and impact strength compared to PCL. At the same time, the resulted biocomposite had relatively less cost than PCL itself. Thus, addition of SM to PCL increases the rigidity, but the particle-matrix adhesion needs to be improved.

SM has been plasticized and blended with other polymers such as polycaprolactone (PCL), poly(butylenes succinate) (PBS), poly(butylene adipate terephthalate) (PBAT) [236-237], and natural rubber [238-239]. SM was plasticized and deconstructurized successfully using glycerol and urea in a twin screw extruder and then blended with biodegradable polyesters, PCL and PBS [236]. As a result of deconstructurization phenomenon, improvement occurred in mechanical properties of the protein-based blends. In another work, SM was plasticized using glycerol in presence of two different denaturants (deconstructurizers), and the resulted thermoplastic SM was blended with different polyesters, PBS, PCL and PBAT [237]. Taguchi experimental design was adopted to investigate the effect of each constituent on the tensile properties of the final blend. Wu et al. [238] produced vulcanized blend of natural rubber and 50 wt% SM. The rubber phase was embedded by the SM matrix suggesting the interaction between phases, also approved by the increase in the glass transition temperature of the rubber phase. The produced blend exhibited good elasticity and water resistance.

Another area of research conducted on SM is producing edible films from defatted SM for food packaging applications [240-241]. For this purpose, SM was fermented in a soybean meal solution (15 g/100 ml of water) by inoculation with *Bacillus subtilis* bacteria fermented under optimum conditions of 33°C and pH 7.0-7.5 for 33 h. Then, the fermented soybean solution was heated for 20 min at 75°C with 2-3 ml glycerol added to the solution to overcome film brittleness. The filtered solution was finally casted in a petri dish to produce films. Increasing amount of plasticizer in the fermented film led to a decrease in tensile strength and an increase in % elongation of the film compared to the ordinary soybean film. Moreover, the SM-based film exhibited higher water vapor permeability. On the other hand, experiments showed that growth inhibition of the produced SM-based film in the agar media containing *E. coli* was much higher than the ordinary soy protein film. These results indicated that the fermented SM-based films can be used as a new packaging material to extend the shelf-life of foods; however mechanical and physical properties need to be improved for more industrial applications.

3.5. Crude glycerol

Value-added uses of crude glycerol from biodiesel industries are highly diversified and it can be classified in to following categories, (i) chemicals/monomers: extraction and chemical/biological conversion approach for the synthesis of various precursors, (ii) plasticizer: use as low cost plasticizing agent in various biomaterials applications, (iii) hydrogen generation: as

the source for the generation of green hydrogen for energy applications, (iv) carbon source: carbon sole source for bacterial growth, which effectively used for the generation of bioplastics and (v) polyesters: combine with suitable organic acids and forms polyesters for various materials applications. In materials point of view, crude glycerol's application in plasticising as well as polyesters formation receives an immense attention and is discussed in this section.

As the global demand increases for the development of biodegradable materials, starch-based plastics receives an immense attention. The challenge is their unusual inter and intra molecular hydrogen bonds, which reduces their plastic performance [242]. This can be improved by incorporating plasticizers and manipulating processing conditions. Various plasticizers have been used on thermoplastic starch such as glycerol [243], glycol [244], sorbitol [245] and sugar [246]. Among them glycerol has been extensively used for the plasticization of starch-based materials. In addition to that, glycerol has also been used as an effective plasticizer in various other natural materials such as cellulose [247], chitosan [248], gelatin [249], DDG [250] and protein [233]. When these materials are plasticised with glycerol, their elasticity and toughness have been increased significantly with decreased brittleness. Numerous literatures are available for the glycerol plasticized natural products and most of the researchers have practiced pure glycerol as the precursor [233, 247-251]. Increasing trend of crude glycerol as plasticizer can be found in the literature for the development of various types of biomaterials [252-259].

Glycerol can be used to create polymeric materials by exploring their polyfunctional reactivity and the obtained polymers can have various applications as polyols substitutes, lubricant, raw materials to produce resins, polyesters and polyurethanes [260]. Among them, polyesters and polyurethanes receive more importance for their large volume biomaterial applications. The glycerol can easily react with carboxylic organic acids and forms polyesters, which can be used for various materials applications [260-261]. Carnahan et al. [262] demonstrated the synthesis of glycerol-based polyesters using succinic and adipic acids. Likewise, Tang et al. [263] synthesized the aliphatic polyesters from glycerol using sebacic acid with elastic properties. In both the cases they were using pure glycerol as a precursor and more publications are also available for fabrication of various other types of polyesters [264-265]. However, very few research works have been published based on the crude glycerol as feedstock for polyester synthesis. Brioude et al. [261] reported the fabrication of new polyester from crude glycerol and adipic acid through the bulk polymerization. They found that the newly developed crude glycerol-based polyester was amorphous in nature and has good mechanical and thermal stability. Similarly de Moura et al. [260] reported the polymerization between the glycerol and mono/bi-functional organic groups for the fabrication of new class of polyesters. They were able to synthesise two different classes of polymers with variable thermal stability. Their ultimate aim was to utilize these newly developed polyesters as matrix for the fabrication of natural fibre-reinforced composite materials. The obtained features (physicochemical) of these newly synthesised polyesters can also be used as modifiers for various types of thermosets (epoxy resins) as well as polyurethanes. Urea-formaldehyde (UF) has been widely known as an excellent adhesive used in wood panel fabrication. The challenge is to overcome their limited moisture resistance. The polyols made from glycerol can be used to enhance their moisture resistance properties. Recently, fungi-based

biological transformation of crude glycerol into various value-added products receives significant attention. Fungus exhibits more tolerance against the various impurities that exist in crude glycerol and found to be a suitable candidate for the biotransformations. Nicol et al. [266] reviewed the various research work on effective bioconversion of crude glycerol into many value added chemicals/materials employing fungus. They conclude that these techniques need to be further investigated for the extended applications. It is visible that glycerol will become as a high potential feedstock for various chemicals and tends to replace various existing petroleum derived products [267].

4. Conclusions

Growing energy demand for transportation, necessity of reducing the dependency on fossil fuel and the emerging environmental concerns about greenhouse gas emission have enhanced the growth of biofuel industries enormously and created new policy mandates by many countries. This caused the generation of a huge amount of under-valued coproducts of different types including distillers' grains, bagasse, lignin, protein-rich meals and crude glycerol. In order to claim biofuel production as the sustainable technology of future, it is necessary to create value-addition to these coproducts. This also provides solution to the emerging issues on the environmental impact of the accumulation of these coproducts. Moreover, the technological development related to the value-added uses of biofuel coproducts in biomaterials applications, is expected to (i) create new ecofriendly products, (ii) strengthen the bioeconomy and (iii) generate more rural job opportunity.

Among these coproducts, dried distillers' grains with solubles (DDGS), from dry mill ethanol industry, and the protein-rich meals such as corn gluten meal (CGM) and soybean meal (SM), respectively from wet mill ethanol and biodiesel industries, are traditionally used for animal feed applications. However, recent researches show the huge potential of these coproducts for biomaterial applications. DDGS can be used as filler or even as reinforcing phase in polymeric biocomposites by integrating pre-treatment, compatibilization and proper processing techniques. Moreover, it can be converted into a thermoplastic by chemical modifications such as acetylation and cyanoethylation. Also, it can be used for producing bioadhesive or extraction of fiber, oil and protein to be used for biomaterial usages.

Due to their high content of protein, CGM and SM can be plasticized using several plasticizers. Such plasticized meals have been blended successfully with several thermoplastics or been reinforced with wood fiber to create biomaterials with balanced properties. Besides, fermentation of these proteinoous coproducts can provide new opportunities for the development of biobased films for food packaging applications.

It has been a long time since bagasse, the sugarcane ethanol coproduct, has been used in thermoset-fiber composites for particleboard production. In addition to that, bagasse is recently considered as the reinforcing filler compounded with different thermoplastics. Also, it has been shown that bagasse can turn into a thermo-formable material through esterification.

Lignin, the major coproduct of lignocellulosic ethanol, is being upgraded from its traditional utilization, i.e. burning, into various value-added commercial products such as polymer blends/composites, adhesives, and carbon fibres.

The industrial applications of pure glycerol in different sections are well established. Consequently, crude glycerol coproduced in biodiesel industry has huge opportunities in biomaterial applications including chemicals/monomers, plasticizer, hydrogen generation, carbon source for bacterial growth and polyesters production.

Novel innovative research in utilizing biofuel coproducts for biomaterials applications (biopolymers and biocomposites) impends the value-added high-end uses in the automotive, packaging and other structural/durable sectors. This is expected to create a fundamental change in materials point of view by utilizing renewable resources as feedstocks. In addition to that, these biofuel coproducts also create opportunity for the fabrication of various nanostructured materials for the high value applications.

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