GREEN COMPOSITES FROM CO-PRODUCTS OF BIOFUEL INDUSTRIES: A NEW PARADIGM TOWARDS VALUE-ADDED INDUSTRIAL USES

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Introduction

Use of residues and undervalued co-products from biofuel industries as the raw materials for industrial manufacturing is the wave of the future. Lignin, hemicellulose, distillers’ grains and crude glycerol from biofuel production need to find value-added industrial uses.

At present, about 100 billion litres of first generation liquid biofuels (bioethanol and biodiesel) are commercialized globally. This provides around three percent of the world’s fuel needs. Food-versus-fuel concerns have stirred greater interest in biofuels from non-food crops like corn cobs, corn stovers, grasses, sugarcane bagasse, algae and jatropha etc.

The biofuels derived from plant and forest resources are getting accelerated momentum across the world. Both biofuel and related co-products should be used sustainably for a well-balanced bioeconomy. The downstream co-products and byproducts from the emerging alternative fuel industries are now under criticism in disturbing the main focus of environmental sustainability. A major concern that has been realized is to find value-added industrial products from these undervalued products. Biorefinery concept is a key pathway in moving in this direction [1].

Biofuels, biochemicals and biobased materials from renewable resources are receiving interest as potential substitutes as well as supplements to the petroleum-based counterparts.

The sky-rocketing price of petroleum along with its dwindling nature coupled with climate change concern and continued population growth have drawn the urgency for sustainability in all sectors from energy to materials.

The government’s push for green products, consumers’ desire and energy conservation are some of the key factors that drive research towards the development of renewable resource-based polymeric biomaterials. The use of bio- or renewable carbon unlike petro-carbon for manufacturing bioplastics and biobased materials is moving forward for a reduced carbon footprint. The goal is to use biobased materials containing the maximum possible amount of renewable biomass-based derivatives with a well-balanced cost-performance attributes with added advantages of eco-friendliness thus to have a sustainable future.

Researchers at the Bioproducts Discovery and Development Center (BDDC), University of Guelph have been constantly developing novel value-added biomaterials including novel bioplastics and green composites from biofuel co-products.

Co-products from Corn Ethanol Industries

Bioethanol production from corn consists of two different processes, dry milling and wet milling. In the dry-milling industry, the processing of one bushel of corn yields approximately 1/3rd as ethanol, 1/3rd as Distillers’ Dried Grains with Solubles (DDGS) and 1/3rd as carbon dioxide (CO2). Currently DDGS is used mainly as an inexpensive animal feed.

Globally, ethanol production has increased more than five times from 2000 to 2009 and the Global Renewable Fuels Alliance (GRFA) predicts a growth of 21.5 percent in the worldwide ethanol
production from 73.0 billion liters in 2009 to 88.7 billion liters in 2011. As a result, the distiller’s grains production of the largest producer of ethanol in the world, the US, has increased more than ten times during the 2000 – 2010 period from 2.7 to 32.5 million metric tons (Table 1) [2].

Table 1. Historic Distillers Grains Production from U.S. Ethanol Biorefineries [2]

<table>
<thead>
<tr>
<th>Year</th>
<th>Million Metric Tons</th>
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<tbody>
<tr>
<td>2000</td>
<td>2.7</td>
</tr>
<tr>
<td>2001</td>
<td>3.1</td>
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<td>2002</td>
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<td>2003</td>
<td>5.8</td>
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<td>2004</td>
<td>7.3</td>
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<td>2005</td>
<td>9.0</td>
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<td>2006</td>
<td>12</td>
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<td>2007</td>
<td>14.6</td>
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<td>2008</td>
<td>23</td>
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<tr>
<td>2009</td>
<td>30.5</td>
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<tr>
<td>2010</td>
<td>32.5</td>
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Such an increase in distillers' grains production suggests that the amount of the downstream products (DDGS) generated is enormous and it is of obvious benefit to use these co-products in value-added industrial products (Fig. 1).

Distillers’ dried grains with solubles (DDGS) have been studied in biocomposites and green composites use [3-9]. One of the very first studies reports the incorporation of DDGS, up to 30 wt%, into polyolefin polymers, e.g. polypropylene (PP) and polyethylene (PE) [3]. Wu and Mohanty [4] investigated the DDGS incorporation into polymerized polyurethane. They have reported the production of PU/DDGS compositions having 20 to 90% by weight of DDGS. Also, biopolymer blends have been used as the polymeric matrix in DDGS composites [5]. Polylactide (PLA) and DDGS-based composites have also been studied by Li and Sun [6]. There are reports on using phenolic resin as a binder between DDGS particles [7-9].

The incorporation of biomass-derived biofiber and crop-derived bioplastics into the composite materials in designing green composites poses immense opportunities in transportation parts, construction panels and packaging uses [10].

The scientific challenges in designing high strength DDGS-based green composites are in the uniform distribution of DDGS in the polymer matrix, improved compatibility between DDGS and the bioplastic and technological innovations in incorporating a high content of DDGS into the composite structures.

Co-products from Cellulosic Ethanol Industries and Paper and Pulp Industries

Lignin is the second most abundant renewable-resource biomass, after cellulose in nature, which generally exists in the plant cell walls. Lignin along with hemicelluloses and polysaccharide act as the matrix reinforced with cellulose fibres to prevent the plants from compression, impact, bending and strengthen the tissues against microorganisms [1, 11, 12]. The lignin content of plant can vary from 15–30% depending on the type of the plant. Lignin is formed by the polymerization of three different basic units, (i) p-coumaryl alcohol (ii) coniferyl alcohol and (iii) sinapyl alcohol with very complicated structure.

Lignin has diverse structures with a general poly-aromatic structure. Lignin structure varies with the chosen biomass, from wide varieties like grass, corn stovers or wood etc. and again with the pre-treatment chosen like acid-base reaction, steam explosion, etc. in isolating lignin from these biomasses. Thus lignin from cellulosic ethanol will have different structures and characteristics than pulp and paper industries based lignin.

Lignin is a random amorphous polymer and structurally has several different chemical functional
groups including hydroxyl, methoxyl, carboxyl and carbonyl groups. The free hydroxyl groups in the aromatic ring, are the most important characteristic function of lignin.

Lignin is the undervalued co-product obtained from delignification process in pulp and paper industry as well as cellulosic ethanol industry [12].

Considering the current production of lignin from pulp and paper industries as well as potential future production from lingo-cellulosic ethanol industries, it is estimated that around 300 M ton/year of lignin will be produced in North America. Lignin is now considered as an inexpensive by-product and is mainly used as a boiler fuel. The value of lignin can be better realized as a good source for new outlets such as renewable polymeric materials (Fig. 2), which will support the lignin industries.

Lignin can potentially find new usages in different areas. One application can be considered as the conversion of lignin into aromatic chemicals such as phenol, terephthalic acid, benzene, xylene, toluene, etc. which imposes technical challenges in producing high volume aromatic chemicals. Other uses of lignin in fertilizer, wood adhesives, surfactants, UV stabilizer and coloring agents are under practice. However, all these new uses account for only 2% of the generated lignin and the remaining is mostly burnt for energy [13], which poses the energy efficiency debate due to the fact that the energy obtained from lignin burning is found to be one fourth of the energy from regular fossil fuels [12]. Lignin and its applications with polymers have been recently reviewed [12]. There seem immense opportunities in finding value-added uses of lignin through polymeric materials uses. Lignin with its potential lower cost, lower density e.g. about half to that of talc, calcium carbonate (the usual fillers in plastics), biodegradability and superior water resistance provide many such attractions in polymeric materials applications.

Lignin has been widely used as an excellent low-cost blending material in various polymers in the development of different polymeric commercial products. Many researchers have been motivated in the area of lignin-based polymer blends with poly(ethylene oxide) (PEO), polyethylene terephthalate (PET), polyvinyl alcohol (PVA) as well as polypropylene (PP) and their uses in structural composites [12,14]. Polymer blends take attraction of polymer society due to the optimization of properties and lowering the cost of the polymers. Polyethylene terephthalate (PET) and polyethylene oxide (PEO) form miscible blends with lignin [15]. Moreover, it has been reported that lignin forms hydrogen bonding with poly(vinyl 4-pyridine) (PVP) which increased the mechanical properties of the PVP [16]. Recently we have reported the incorporation of lignin into a polybutylene succinate (PBS) bioplastic in engineering biobased composite materials [17]. One of the approaches is the utilization of hybrid reinforcement using lignin with other natural fibers in binding effectively with the polymer matrix in engineering hybrid composite materials. Researches on lignin-based thermoplastics and thermosetting polymer composites, including hybrid composite structures, are being constantly under development and progress at the Bioproducts Discovery and Development Centre, University of Guelph in finding diverse uses in automotive parts, building structures, consumer products and packaging materials matrix system thus engineering a new class of hybrid biocomposite materials.

In addition to all mentioned, as a rich source of carbon, lignin is found to be a suitable renewable source for the synthesis of carbonaceous materials. Lignin was successfully employed for the synthesis of carbon nanofibres using electrospinning techniques [18]. The use of lignin in developing carbon fibre has attracted more attraction recently. The report on lignin-based carbon fibre is being reported since 1969 [19]. The importance of lignin-based carbon fibres for composite uses has been reported [20].

![Fig. 2. Potential value-added industrial products from lignin.](image)
Conclusions

The value-added uses of co-products from biofuel industries will not only help in providing more economic advantages to these alternative fuel industries, but also will help in substituting the petroleum based counterparts thus helping to reduce our dependency on petroleum. The distillers’ dried grains with soluble (DDGS), the co-products from corn ethanol industries show immense opportunities in engineering new green composites when integrated with renewable resource-based bioplastics. Similarly lignin and bio-resin are looked into to engineering both thermoplastic and thermoset type green composites. The material chemistry and process engineering are key strategies in creating green composites of superior performance to compete with traditional plastic and mineral filler-based polymeric materials as well as glass fibre reinforced plastics.

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