

The application of lignin as renewable raw material in chemical industry

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The overutilization of fossil fuels will inevitably cause the global environmental problems and dwindling of available resources. For that reason, identifying renewable sustainable alternatives has attracted an increasing attention. Ligno-cellulosic biomass has been considered to be one of the most logical feedstocks to replace traditional fossil resources as one of the most accessible renewable forms of carbon. One of the primary components of lignocellulosic biomass, next to hemicellulose and cellulose is lignin. It is a by-product in paper and pulp industry. Lignin is mainly used as fuel directly, without further utilization which is suggested to be a waste of natural resources. With this purpose, the valorisation of lignin into value-added products needs attention of researchers. This review article focuses on chosen possible applications of lignin in chemical industry.

1. INTRODUCTION

In recent years there has been observed significant intensification of research regarding biodegradable polymers that is inextricably bound with gradual depletion of oil fields and problems with the management of non-biodegradable plastics [1-4]. There are

more and more people seeking not only new biodegradable polymers, but also alternative sources, which will allow to obtain environmentally friendly, and at the same time functional biomaterials [5-8]. Therefore, the attention of scientists is focused on waste lignocellulose mass, which is a large tonnage and nuisance waste from pulp and paper industry [9-11]. As the storage of huge amounts of this material is a big problem, most of the lignocellulose mass is subjected to combustion in order to obtain energy. However, the fact that this mass consists mainly of lignin and cellulose promoted attempts of its management in a more sophisticated and effective way.

Lignin is an amorphous phenolic polymer with a complicated and not completely investigated chemical structure. However, the latest developments in the field of analytical chemistry and spectroscopy improved significantly the knowledge of this biopolymer [12,13]. The structure of lignin is highly branched by carbon-carbon and ether bonds formed with three phenylpropionic monomers: coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol. In plants lignin is a linker between the cellulose bundles [14]. It gives strength and rigidity to the cell walls, resist microorganisms attack and conduct water in plant stems [15]. For many years, lignin was considered a substance unsuitable for commercial applications. Recently, this view has changed and now it is believed that soon lignin can become a main and in addition renewable source of aromatic compounds for the chemical industry [16,17]. Some progress has been achieved to convert lignin into value-added products, including carbon fiber, liquid fuels and chemicals [17-19]. Lignin is depolymerized to phenol that makes further production of good quality polymers possible [20]. There was developed the technology of DMSO, vanillin and polyols production that could be used in the synthesis of highly advanced materials [21-23]. However, the actual limitations in the development of the use of lignin materials are the following factors: the diversity of its structure, which strongly depends on the source of natural raw material, high polydispersity of molar mass, highly branched structure. The other problem is insufficient purity of the obtained raw material, which is of great importance in the context of its further processing [24]. Nevertheless, the structure and lignin unique properties gain increasing attention of scientists and result in many studies on overcoming the existing limitations and effective use of lignin.

2. PHENOLS

As far as the potential for phenol production from lignin is concerned, various factors need to be considered. First of all, the evaluation of new process economy, where the costs of energy, manpower, chemicals and equipment have to be balanced against the final market value of the product. Some factors connected with lignin conversion to phenols have already been solved. A large amount of these materials is produced and there are no competitive applications. This amount is also predicted to increase with the increasing lignocellulosic ethanol production. Additionally, the value of phenols produced from the coal feedstock and petroleum is expected to rise as a result of increasing restrictions on fossil fuels use and increasing oil prices [20].

Mante et al. studied selective defunctionalization by TiO_2 of monomeric phenolics from lignin pyrolysis into simple phenols [25]. The obtained results show that anatase TiO_2 is a very active catalyst for this process. Defunctionalization of phenolics can be promoted by TiO_2 without the use of hydrogen pressure. Yerrayya et al. described the selective production of phenols from lignin via microwave pyrolysis using various carbonaceous susceptors [26]. The authors stated that the type of carbonaceous material and the presence of moisture in the susceptor are very important and affect the feedstock heating pattern, selectivity of phenols from lignin and yield of bio-oil. The susceptor mass increasing to that of lignin enhanced the selectivity and yield of phenols over syringols and guaiacols in bio-oil. Ma et al. examined the catalytic conversion of lignin over a tungsten phosphide catalyst in a hot compressed water-ethanol mixed solvent [27]. The activity of the tungsten phosphide catalysts is comparable to the performances of noble metal catalysts. Fe and Ni doping of the tungsten phosphide improves selectivity of phenols but reduces the overall phenols yield. Longer reaction time leads to the re-polymerization reactions. Therefore, the increase of the reaction time decreases the yield of the monophenols. Yoshikawa et al. investigated the production of phenols from lignin via depolymerisation and catalytic cracking [28]. In the first step, lignin was depolymerized in an autoclave reactor using a silica-alumina catalyst in a water/butanol solution. Then the liquid products from the first step were catalytically cracked by using a fixed-bed flow reactor over an

iron oxide catalyst. Naron et al. studied the production of phenols pyrolysis of sugarcane bagasse lignin with impregnated catalysts [29]. The enhancement of depolymerisation at relatively low temperatures resulted in the increase of syringol, guaiacol, and vinylguaiacol production. The increases in the produced phenol amounts with a low catalyst content indicate the impregnation method effectiveness.

The presented examples demonstrate the huge potential of lignin for the phenols production.

3. VANILLIN

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the main flavour constituent of vanilla. In the past it was produced by direct extraction from vanilla beans. Nowadays it is produced mainly from guaiacol and is fully dependent on petroleum-derived compounds [30]. Synthesis of vanillin from renewable resources should result in a more sustainable process.

One of the possible routes of vanillin production based on biomass is controlled oxidation of lignin in a batch reactor described by Araújo et al. [22]. The obtained results indicate that a low-molecular weight lignin from softwoods is preferred to obtain a better vanillin yield than the high-molecular weight one. Additionally, at lower values of pH the vanillin degrades at a considerable rate which results in reducing its yield. Oxygen pressure and temperature should be adjusted for different cases considering that the final value should result from a trade-off between minimizing the vanillin oxidation and enhancing its conversion. Wang et al. [31] investigated the relationship between the β -O-4 linkages and vanillin yield in the vanillin production from lignin. The obtained results show that the interunit linkages of the lignin have significant influence on the vanillin yield. The more β -O-4 linkages in lignin, the higher yield of corresponding aldehydes was obtained. Wu et al. described the improved alkaline oxidation process for the production of vanillin and syringaldehyde from the steam-explosion hardwood lignin [32]. The high yields of aldehydes observed in this paper exceed largely those obtained in the conventional alkaline air oxidation of spent sulphite liquors. Isola et al. [33] demonstrated the hydrothermal liquefaction of lignin as a successful process for vanillin

synthesis. The obtained results show that catalyst choice and energy use are the most important environmental factors regarding vanillin production from lignin.

In fact, vanillin could provide a solution of finding aromatic, bio-based monomers which are able to replace traditional aromatic monomers derived from petroleum. The amount of research increasingly generated on the topic of vanillin production from lignin indicates the industrial interest in this technique. The rising price of petroleum and the fact that the raw material is bio-based make this vanillin production path more and more attractive from both economic and green chemistry points of view.

4. CARBON FIBRE

According to the definition carbon fibre contains at least 90% carbon. This lightweight material is characterized by stiffness, strength and high corrosion as well as heat resistance. Carbon fibre finds various applications, among others, in space industry, sport applications and aircraft. Its main disadvantage is high production cost which results in its limited supply. Nowadays the main precursors for carbon fibre manufacturing are polyacrylonitrile, petroleum pitch and regenerated cellulose (rayon) [34]. In contrast to polyacrylonitrile and petroleum pitch, lignin is a renewable raw material. Its carbon content is more than 60%. Additionally, it is possible to isolate, available in large amounts and cost-competitive compared with polyacrylonitrile. [35].

There are a lot of papers on carbon fibre preparation from lignins. For example, Sevastyanova et al. [36] used lignin nanocomposite fibers, obtained through the incorporation of montmorillonite organoclays after modification into the organosolv lignin. The extrusion properties of composites at different levels of inclusion were reported. The addition of materials resulted in improvement of fibre spinning efficacy and doubling of resulting lignin fibre strength. Bakter et al. [37] used carbon nanotubes to enhance the modulus, strength, thermal and electrical conductivity of different lignins applied for carbon fibre manufacturing. The nanotubes enhanced the fiber spinning process by increasing the composite heat capacity which results in fiber remaining molten a greater distance on the spin-line and better stretching properties.

Additionally, lignin composite fibers were stronger than those obtained by lignin alone [38]. Brodin et al. [39] investigated the oxidative stabilization of different kraft lignins (spruce, eucalyptus and birch). The authors studied the effect of different parameters on stabilization and carbonization yields. For eucalyptus and birch lignin, the increase of carbon yield with severe oxidative thermostabilization conditions was observed, in contrast to pine lignin that exhibited an optimum condition [38].

In combination with the increasing interest to replace petrochemical materials with renewable resources, carbon fibres from lignin are one of the most promising applications of lignin, but more research in this area needs to be done.

5. POLYMERS

Lignin finds application also in polymer composites and hybrid materials [39-43], blends [44-48], microspheres [49-53], polyurethanes [54-58], hydrogels [59-63], aerogels [64-65] and many others.

Due to its chemical structure lignin could provide additional functionalities in the polymer materials. For example, Setua et al. [66] investigated lignin reinforced rubber composites. Lignin modified with benzoyl peroxide produced superior hardness, elongation and compression set properties in comparison to the phenolic resin, the conventional filler. Thielemans and Wool [67] described the use of butyrate kraft lignin as compatibilizing agent for natural fiber reinforced thermoset composites. Butyrate kraft lignin improved the interface between the reinforcing flax fibers and the resin, consisting of styrene and an acrylated epoxidized soybean oil mixture. Additionally, the improved adhesion of the resin to the fibers was observed. Bula et al. [68] investigated a novel functional silica/lignin hybrid material as a potential bio-based polypropylene filler. The obtained material was characterized by high thermal and electrokinetic stability. The authors claimed that the incorporation of silica/lignin hybrid filler into polypropylene might significantly influence its notched impact strength and elongation at break. Gordobil et al. [46] studied physicochemical properties of poly(lactic acid) lignin blends obtained by the extrusion method. Lignins were acetylated in order to improve their compatibility with poly(lactic

acid). Blends with the acetylated lignin were characterized by better mechanical properties than with the original ones. The addition of lignin into the structure of polymeric microspheres results in better sorption capabilities due to the presence of functional groups from lignin as reported by Goliszek et al. [52]. Lee and Deng [69] described the synthesis of non-isocyanate polyurethane elastomer with lignin. The increase of lignin content resulted in the increasing tensile strength. Ciolacu et al. [60] prepared novel super absorbent hydrogels based on cellulose and lignin and evaluated their application in the polyphenols controlled release. The increase in release was directly connected with the lignin content increase in hydrogels. Quraishi et al. [70] presented the synthesis of hybrid alginate-lignin aerogels. The obtained materials were characterized as non-cytotoxic and featured good cell adhesion which might result in their future applications in regenerative medicine and tissue engineering.

Due to the environmental pollution and problems with plastics utilization, more environmentally friendly biomaterials are in demand. Even partial replacement of artificial plastic with a biomaterial increases its biodegradation properties. If the biomaterial provides additional functionalities it also improves the resulting material properties. The aim of scientists is to synthesize materials which are characterized by better physicochemical properties and are safer for the environment using renewable sources, for example lignocellulosic biomass.

6. CONCLUSIONS

In summary, due to the prevalence of lignin and the fact that it is a renewable compound, research on its use in synthesis as well as in preparation of new, advanced materials and/or biomaterials is very perspective. Due to the increasing demands for lowering the CO₂ emissions and the inevitable rise in petroleum and oil-based chemicals cost, it is obvious that biomass will play a prominent role in providing for future economic prosperity. Lignin which is already available in huge amounts as a by-product from paper and pulp industry can fill a part of this function, as it is potential for utilization in future high-value products.

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