

Catalytic Conversion of Lignins for Valuable Chemicals

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Modern civilization is moving from fossil sources of raw materials and, consequently, energy to renewable resources: plant raw materials and solar and wind energy. Emerging environmental requirements and recommendations, including carbon-neutral fuels, accelerate the development of transport biofuels produced from plant raw materials.

Plant raw materials contain cellulose, hemicellulose, and lignin as some of the main components (20–30% by weight). The history of chemical processing of wood shows that, among these three components, the utilization of lignin is the most difficult problem, and it is currently being developed rather actively. For example, MDPI has published three Special Issues of journals on this problem in recent years.

The structure of lignin consists of methoxylated phenolpropane groups, and this determines the possibility of its processing primarily into substitutes, including unsaturated, methoxylated phenols. However, the existing requirements for engine fuels limit the use of both aromatic and unsaturated compounds. In addition, the processing of lignins into the fuels is the most difficult problem compared to the processing of carbohydrates into ethanol and vegetable oils into biodiesel.

The properties of native and technical lignins differ greatly: the latter, as a general rule, are highly condensed under harsh conditions of chemical processing wood. For this reason, native lignins are more suitable than technical ones for the production of monomeric phenols, and this conclusion is formulated in two words “Lignin first” [1], which determine the current trends in the development of lignin processing processes [2,3]. Native wood lignins, however, are more expensive compared to lignosulfonates or Kraft lignins, and in some cases, this balances the disadvantages of native and technical lignins. Agrotechnical waste from processing herbaceous plants, such as wheat and rice straw, sugar cane bagasse, and others, are relatively cheap, and they contain up to 20–30% of native lignins. This kind of raw material combines the advantages of native and technical lignins: the possibility of obtaining low-molecular products with high yields and a low price.

Three groups of lignin destruction processes can be distinguished: hydrogenation, oxidation, and pyrolysis. As practice shows, hydrogenation has been developing most actively in recent years. In the middle of the twentieth century, such processes for obtaining phenols were brought to the scale of pilot plants but did not reach the industrial level. The development of modern effective catalysts has made it possible to double, up to theoretical limits, to increase the yields of such compounds as syringylpropane and syringylpropanol [4].

Industrial oxidation of lignosulfonates into vanillin existed in the 1950s–1970s. Vanillin is still produced from pulp waste on a relatively small scale (5–7% of world production). Probably, this is the only example of the production of an individual compound from lignins on an industrial scale. The number of research papers in the field of oxidation of lignins to vanillin has increased 10-fold over the past 20 years, and their citation has increased 20-fold. The selectivity of the catalytic oxidation of native lignins to vanillin has come close to the theoretical limit, i.e., the selectivity of nitrobenzene oxidation [2,3]. Thus, the “Lignin first” approach [1] becomes quite productive to obtain the individual compounds by both hydrogenation and oxidation methods.



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Pyrolysis of lignins and further hydrogenation of the resulting bio-oil gives the wide range of low-molecular-weight volatile products and is being actively investigated. Lignin pyrolysis tars (bio-oil) can contain up to 90% alkyl guaiacols, including 25–35% guaiacol [5]. Catalysts are able to increase the yield of bio-oil, but they do not permit to orient pyrolysis to the highly selective formation of individual phenols [6,7].

The original research papers published in this Special Issue solve the problems of catalytic conversion of lignins for valuable chemicals.

Two articles of the Issue are devoted to the study of processing agricultural waste, flax shives, by hydrogenation methods [8,9]. Thermal conversion of flax shives in ethanol with and without molecular hydrogen was studied in the presence of the bifunctional ruthenium catalyst on carbon support. This catalyst is highly efficient at 225–250 °C. The temperature elevation and addition of the catalyst improves the efficiency of thermal conversion of flax shives in ethanol. The maximum conversion (up to 77–79%) and the yield of the liquid products and monomeric methoxyphenols (9.9% based on lignin) are attained under supercritical conditions at 250 °C. The simplest compounds, such as guaiacol, are formed in the absence of catalysts, while propane derivatives are mainly formed under the action of the catalyst.

A comparison of the obtained results show that the use of hydrogen leads to an increase in the conversion and in the degree of delignification of flax shives, as well as to a decrease in the yield of cellulose both in catalytic and non-catalytic processes. In the hydrogen-free process under study, guaiacyl- and syringylpropenes are only reduced to the corresponding propanes at 250 °C, but hydrogenation of these propenes with molecular hydrogen gives the propanes even at a lower temperature (225 °C).

It was shown that the maximum total yield of methoxyphenols upon thermal conversion of flax shives in the absence of molecular hydrogen can exceed those in the hydrogenation process with H₂. Analysis of the molecular weight distribution of liquid products showed that using the catalyst, as well as molecular hydrogen, leads to shifting the molecular weight distribution towards low molecular weight products. The most promising individual compound of the process is guaiacylpropane [8,9].

Another kind of catalyst, various zeolites types with different acidity, with fin-like and worm-like mesoporous structures were applied to depolymerized Kraft lignin in supercritical ethanol [10]. Despite the reaction complexity of lignin depolymerization and its greatly diversified products, similar lignin conversion (60–75%) and comparable aromatics selectivity (30–40%) were attained for different zeolites used. The zeolites acidity and hierarchically porous structure were shown to be important to promote the process of lignin ethanolysis.

The obtained results provide important insights on the selection and design of zeolites with appropriate acidity and pore structure to facilitate lignin depolymerization in supercritical ethanol, and it will help not only to eliminate this high-volume farm waste and environmental hazard of paper and pulp plants, but also promote the utilization efforts on converting its rich aromatic units into important chemicals and fuels. The same knowledge may also benefit other catalytic cracking processes using a variety of heating and/or solvent assistance to improve the conversion, yield, and selectivity of bulky hydrocarbons [10].

The authors of the paper [11] showed that anaerobic digestion of biomass can be greatly facilitated by the products of lignin photocatalytic oxidation on the TiO₂–ZnO nanoparticle photocatalyst. The main detectable products of lignin photooxidation were vanillic, ferulic, benzoic, and p-coumaric acids. An excellent yield of methane of 39% was attained due to addition of the acids in the digesting biomass. Very interesting and promising research [12] revealed that an ionic liquid, EmimOAc (1-ethyl-3-methylimidazolium acetate), catalyzes the acetylation of both R–OH and ArOH groups with isopropenyl acetate (IPAc) as an acyl donor and the selective deacetylation of Ar–OAc groups. Such selective modification of R–OH groups in Kraft lignin and resulting solubility, thermal stability, and heat-meltability warrant further functionalization, such as polymerization via the rich Ar–OH groups for lignin-derived polymer applications. Therefore, this facile and

sustainable method for selective R–OH modification paves the way for the valorization of Kraft lignin as a functional polymeric material.

Assessing the prospects of lignin processing, it may be noted that obtaining relatively expensive low-tonnage products, the production of which from fossil fuel raw materials is much more expensive or even impossible (such as furfural from pentose carbohydrates), is the most attractive direction of lignin processing. An obvious and broad class of such products is methoxylated phenols. The production of substituted 2,6-dimethoxyphenols from lignins of hardwoods, for example, birch, with the emergence of large-scale sales markets, can be more economical than obtaining them from fossil raw materials, as compared to vanillin manufacturing. To conclude, note once more that agrotechnical wastes combine the advantages of native and technical lignins: the possibility to obtain low-molecular products with high yields and low price.

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