Demirel, J Biochem Eng Bioprocess Technol 2017, 1:1

Journal of Biochemical Engineering & Bioprocess Technology

Editorial

A SCITECHNOL JOURNAL

Lignin for Sustainable Bioproducts and Biofuels

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Keywords

Lignin; Bioproducts; Biofuel; Sustainable energy

Introduction

To meet the goal of replacing 30% of fossil fuel by biofuels around 2030, approximately 225 million tons of lignin will soon be produced beside the current production of between 40 and 50 million tons per year in the paper and pulp industry in the U.S. Yet only about 2% of the waste lignin is currently recycled into new products [1]. This is also the case for the rest of the world. One of the efficient routes of upgrading lignin is the fast pyrolysis, in which lignin molecules are decomposed to short chain molecules in the absence of oxygen producing vapor and char. After condensing the vapor bio-oil is formed. Depending on the type of biomass and pyrolysis conditions, bio-oil contains innumerous compounds including hydrocarbons of aromatics, aliphatic, and cyclic that includes phenols, ethers, aldehydes, ketones, carboxylic acids, pyridines, amines, and esters. Separation of phenols from lignin with polyaromatic nature can help achieve renewable, sustainable, and economical phenols, other chemicals, and fuels from lignin [2]. Since approximately 99 % of current phenol production originates from petroleum-based Cumene oxidation with rather low yield, lignin pyrolysis bio-oil can help reduce the dependence to fossil fuels for producing chemicals and fuels [2-4].

Bio-oil from fast pyrolysis of lignin

Compositions of lignocellulosic biomass vary considerably; the ranges of ash and fixed carbon in wt% on dry base (db) are 0.2-22.6 and 10.9-21.9, respectively, while ultimate analyses show the ranges of oxygen and hydrogen as 35.5-47.0 and 4.0-6.2, respectively [5]. Lignocellulosic biomass content in wt% db consists of 12.7-42.4 hemicellulose, 11.0-50.7 cellulose, 11.0-52.3 lignin, and 0.8-12.6 extractives. Lignin is a low grade fuel; however, it is the largest source of aromatic/phenolic compounds such as phenol, guaiacol, catechol, syringol, p-cresol, and o-cresol, and xylenol [1,6]. Formate (calcium formate $Ca(HCO_2)_2$)-assisted fast pyrolysis of lignin can produce bio-oil with more alkylated phenolic compounds that are suitable for phenol/formaldehyde resins, mainly due to deoxyhydrogenation during the pyrolysis. The formate salts decomposes within the range of lignin pyrolysis and provides in situ source of reactive hydrogen. This approach can produce renewable phenol-formaldehyde resin using useful aromatic monomer mixture predominated by phenol and substituted phenols as opposed to methoxy-phenols [7,8]. Type of particle size of biomass, pyrolysis temperature, reactor type (fluidized bed, ablative, vacuum, and auger), type of condensers (direct and indirect contact) can affect the composition of bio-oil [2,5]. Water soluble and organic phases are separated as two main streams out of condenser [9]. After condensing the vapor bio-oil is produced with a yield of up to 65 to 75% on a dry basis. Typical bio-oil consists of (wt% db, except water) acids (3-7), alcohols (1<), aldehydes, ketones, and furans (22-27), sugars (3-6), phenols (2-6), lignin derived fraction (15-25), and extractives (4-6) [5]. Feedstocks with high extractives content and/or high ash content commonly produce an aqueous phase, an upper layer, and a decanted heavy oily phase. Bio-oil can be considered a micro emulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products and small molecules from lignin decomposition. The continuous liquid phase stabilizes a discontinuous phase that contains of pyrolytic lignin macromolecules [2].

Valorization of lignin pyrolysis bio-oil

It is a challenge to valorize lignin pyrolysis bio-oil since it is corrosive and viscose, and contains hundreds of compounds rich in oxygen. Besides, organic compounds with different oxygen-containing functional groups mixing together lead to the high chemical and thermal instability; hence, over time bio-oil forms separated phases due to phase stability and/or aging reactions. Bio-oil valorization requires proper characterization, kinetic studies, new separation systems, new reactors, and new catalytic systems, optimization of pyrolysis yield, process intensification, bio economic analysis, environmental assessment, and supply chain optimization. Bio-oil must be properly upgraded by physical and chemical refining routes. From the economic point of view, the step of extraction of high-value chemicals like phenols and aldehydes (furfural and butanedial) before hydrodeoxygenation is desirable. Lignin bio-oil can be the largest source of aromatic/phenolic compounds such as phenol, guaiacol, catechol, syringol, p-cresol, o-cresol, xylenol, and hence can reduce/remove the dependence on petro-based phenols in the chemical industry [6]. Catalytic cracking of bio-oil using a solid catalyst such as zeolite helps remove oxygen and yield a hydrocarbon-rich liquid fuel [10]. When sodium hydroxide is added to adjust the pH of aqueous bio-oil, organic-phase precipitation occurs at approximately pH=6. The neutralized organic bio-oil had approximately 37% less oxygen and increased heating value than the initial centrifuged bio-oil [11]. The ash content of biomass may affect the formation of separated phased during handling, storage, and use of bio-oils. Single phase is common when the ash content is small (0<2%wt db). The use of phase diagrams as a tool can predict bio-oil phase stability. This may have a significant impact on the development of new bio-oil production and separation processes, as well as on the production of bio-oil-derived chemicals and fuels [5]. Bio-oil fractions can be separated by the way of water extraction to obtain water-insoluble and water-soluble fractions. Oxygen free organics (hydrocarbons) generally are water insoluble while oxygenated components (phenols, aldehydes, ketones, alcohols, acids and so on) almost are water soluble. A solvent extraction method can separate the bio-oil into different chemical groups by their polarities to stabilize bio-oils and improve the quality. The solvent phase contains high concentrations (85%) of phenols

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Received: October 25, 2017 **Accepted:** October 28, 2017 **Published:** October 30, 2017

and guaiacols with no sugar and very low acid and alcohol contents [12,13]. Various solvents used for bio-oil extraction are pentane, n-hexane, cyclohexane, toluene, dichloromethane, and benzene for nonpolar to less polar compounds, ethyl acetate, acetone, methanol for polar compounds, NaOH for solubilization, $NaHCO_3$ for extraction of strong acids, HCL for hydrolysis, and water for precipitation of lignin oligomers. Separation of bio-oil components by adding water, organic solvents (hexadecane and octane), and sodium hydroxide may help extract acetic acid and phenolic compounds in aqueous and organic phases. Aromatic building blocks derived from lignin bio-oil are particularly attractive for use in polymerization, as substituent of fossil fuel-derived phenols, e.g. phenol formaldehyde resins or epoxy resins. Phenols are used in preparation of resins, dyes, explosives, lubricants, pesticides, and plastics. Phenols are also used as solvent to dissolve alcohols as well as for medical purposes [1]. However, the need for large amount of expensive solvents and recovery of them make the solvent extraction too costly for commercialization. High-value chemicals can also be separated from the water phase by distillation. Oil phase is divided into different fractions through atmospheric and vacuum distillation units, and then one can decide whether or not they need further hydro treating according to the properties of the fractions. Another approach may be combining atmospheric distillation of bio-oil with co-pyrolysis without waste. Around, 51.86 wt% of distillate containing dozens of separable organic components, such as acetic acid, propionic acid, and furfural could be recovered using this approach [13]. The atmospheric distillation may result new compounds within the distillate indicating that it is a reactive distillation process. Bio-oil starts boiling below 100°C at atmospheric pressure and distillation takes place up to 250-280°C with around 35-40% residue. Bio-oil has a high content of carboxylic acids, which can be esterified by acid or base catalyst leading to bio-oil with increased heating value. Molecular distillation is a vacuum distillation process below the pressure of 0.01 Torr where the time for exposure of components and distance between reboiler and condenser are very short. In Molecular distillation the fluids are in the free molecular flow regime. It is good for separation, purification, and concentration of natural products, complex and thermally sensitive chemical, such as vitamins and polyunsaturated fatty acids. Supercritical fluid extraction at low temperatures may prevent undesirable reactions of the thermally sensitive compounds. Supercritical CO_2 extraction can be used for separation of compounds with low polarity including aldehydes, ketones, and phenols, while acids and water remaining in the residue phase may undergo further separation by distillation. The maximal extraction efficiency of bio-oil on water-free basis could reach to 88.6% and increases with rising pressure. After supercritical CO_2 extraction, the calorific value and stability of the extract fraction may increase [14]. Single ring phenols and low carbon carboxylic acids are valuable compound groups for end products or intermediate commodity chemicals, which may be separated by supercritical extraction. Solubility data of compounds and thermodynamic modeling of complex bio-oil phase equilibria help achieve an efficient supercritical extraction [15]. Column chromatography using silica gel stationary phase with adsorption and desorption can help separate valuable compounds. Hexane or pentane is used as an eluent for separating aliphatic compounds. Switchable hydrophilicity solvent such as N,N-Dimethylcyclohexylamine can extract phenols as a mixture from bio-oil with recoveries up to 72% of guaiacol and 70% of 4-methylguaiacol, the most abundant phenols in the bio-oil with high rate of solvent recovery.

Lignocellulose biorefinery

A biorefinery designed for catalytic lignocellulose processing can valorize both polysaccharide and lignin components into various final or intermediate chemicals and fuels. A biomass may undergo simultaneously solvolysis and catalytic hydrogenolysis in the presence of a Ru on carbon catalyst (Ru/C) in methanol under a H_2 atmosphere at elevated temperature, resulting in a carbohydrate pulp and lignin. The lignin bio-oil yields above 50% of phenolic monomers (mainly 4-n-propylguaiacol and 4-n-propylsyringol) and about 20% of a set of phenolic dimers, relative to the original lignin content, next to phenolic oligomers. The structural features of the lignin monomers, dimers and oligomers can be identified by a combination of GC/MS techniques, showing interesting functionalities for various polymer applications. Several key operating conditions including temperature, reaction time, biomass particle size, reactor loading, and catalyst stability influence the phenolic product yield. The separated carbohydrate pulp contains up to 92% of the initial polysaccharides, with a nearly quantitative retention of cellulose [6]. Valorization of lignin is one of the foremost challenges of new biorefinery strategies. Processing lignocellulosic biomass in the proposed biorefinery results in valuable product groups including C5 and C6 polyols, methyl acetate, alkyl phenolic monomers and some larger phenolic oligomer products, which represent about 80% of the convertible fraction of the lignocellulosic feedstock. To further improve the biorefinery economy, cheaper catalysts (nickel-based), its regeneration, as well as a continuous flow design are essential [6].

Conclusion

There is a growing consensus that lignin valorization through pyrolysis-based bio-oil can have a positive impact on the sustainability and bio economics of a lignocellulosic-based biofuels and Bioproducts. Fractionating lignocellulose into its main components, namely carbohydrates and lignin is the first step. Pyrolysis of the lignin into bio-oil can be the second step toward valorization. Separation of acids, aldehydes, ketones, and phenols, as well as many other chemicals provide the industry with renewable chemicals and biofuels. This can reduce the dependence to petroleum oil and natural gas for producing fuels, basic commodities, as well as specialty chemicals.

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