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Lignin fractionation in ethanol/water: correlation between structure, functionality and molecular weight

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PURPOSE OF THE ABSTRACT

The conventional refinery process it is still the one producing the majority of the petroleum based chemicals, serving as a main feedstock for the synthesis of the conventional plastics. The main issue is intensively decreasing amounts of the crude oil that consequebtly encourages us to make a huge step forward and to transform into the biobased society, specifically, to develop new, alternative and sustainable proceses to replace petroleum-based products.

Biomass, especially lignocellulosic, represents this alternative renewable material with a high potential to be converted into the various chemicals as well as the precursors for the polymer synthesis. Moreover, economic operation of biorefinery requires valorisation of all three components of lignocellulosic (LC) biomass cellulose, hemicellulose and lignin into more valuable products.1-3 Lignin is a natural polymer composed of aromatic monomeric units. It represents a very promising renewable source for chemicals production considering its aromatic, highly-functionalised structure and abundancy. Lignin conversion into value-added chemicals usually involves three steps: isolation from other LC biomass components, depolymerisation and upgrading of obtained platform chemicals. Lignin isolation is crucial one as it defines the structure and reactivity of isolated lignin. Biorefineries use ethanol-based organosolv process for the biomass fractionation consequently producing organosolv lignin with more preserved structure wich reflects in the amount of the ether bonds in the structure. Additionally, organosolv lignin contains less impurities compared to the kraft lignin and lignosulfonate as sulphur or alkali/alkaline metals are not involved in the treatment.

In this study, lignocellulosic biomass was treated in acidified ethanol/water at three different tempeatures to produce the black liquor. A gradual change of the solubilty parameter attained with the addition of the anti-solvent induced the formation of the insoluble lignin. By varying the volume of the gradually added anti-solvent, the overall isolated lignin was distributed differently within the fractions as shown in Figure 1. All of those isolated lignin fractions were characterized using size-exlusion chromatography (SEC), to obtain molecular weight distributions (MWDs) of the acetylated fractions, while the NMR analysis provided information about the functional group distribution and the main stuctural features. Specifically, 31PNMR was used to quantify the different OH groups, while 2D NMR showed the distribution of the main lignin motifs within the fractions.

SEC data analysis disclosed the possibility of the Mw tailoring depending on the process temperature. Specifically, higher the temperature was used for the lignin isolation, fractions with the lower Mw were obtained. Quantitative 31P NMR disclosed a general trend that lignin with the lower Mw had a higher OH group content/reactivity. In addition, isolation of the lignin with comparable Mw at different temperatures enables the change of the aliphatic/phenolic OH ratio, by maintaining the initial OH group content. The content of the most important ?-O-4 linkages in lignin structure determined using 2D NMR was found to reduce together with the fraction molecular weight. However, with fractionation lignin Mw was reduced from 6000 to 1000 Da, while the ?-O-4 content was reduced only by approx. 40 %.

The development of the specific fractionation protocol employing the anti-solvent methodology in combination with the process conditions enables isolation of lignin with the specific properties. Such a material has a high potential to be use as a building block in polymer synthesis, (de)functionalization and conversion into monoaromatics.

FIGURES

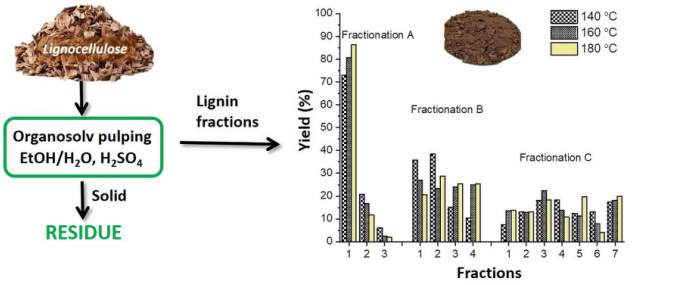

FIGURE 1

Organosolv lignin fractionation: temperature and solubility parameter effect on lignin distribution within the fractions.

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FIGURE 2

KEYWORDS

lignin | fractionation | size-exclusion chromatography | 31P NMR

BIBLIOGRAPHY