Fractionation and physicochemical characterization of lignin from waste jute bags: Effect of process parameters on yield and thermal degradation

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ABSTRACT

In this work lignin was extracted from waste jute bags using soda cooking method and effect of varying alkali concentration and pH on yield, purity, structure and thermal degradation of lignin were studied. The Lignin yield, chemical composition and purity were assessed using TAPPI method and UV–vis spectroscopy. Yield and purity of lignin ranged from 27 to 58% and 50–94%, respectively for all the samples and was maximum for 8% alkali concentration and at pH 2 giving higher thermal stability. Chemical structure, thermal stability and elementary analysis of lignin were studied using FTIR, [H]NMR, thermo gravimetric analysis (TGA) and Elemental analyzer. FTIR and [H]NMR results showed that core structure of lignin starts breaking beyond 10% alkali concentration. S/G ratio shows the dominance of Syringyl unit over guaiacyl unit.

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1. Introduction

Over the last decade, a strong interest worldwide is on the conversion of biomass into clean fuels and high value added chemicals to replace the petroleum based industry due to increasing energy costs and environment concern from nonrenewable fossil resources [1]. Among the diverse biomass lignocelluloses due to their low cost and high abundance are most attractive. Further its processing is or will shortly become more economical than petroleum without effecting food supplies and the chemicals obtained from it will have a lower environmental impact. The lignocellulosic biomass consists of intertwined cellulosic fibers bounded by lignin and hemicellulose. Among these, cellulose is most abundant biopolymer with a total annual biomass production of about 1.5×10^{12} tons. Cellulose due to its renewable nature, wide availability, non-food agricultural based economy, low density, high specific strength and modulus, high aspect ratio, and reactive surface is being used in various application such as paper, textile and clothing industry [2].

Lignin, the second most abundant biopolymer after cellulose is an amorphous, highly branched polyphenolic macromolecule with complex structure. It consists primarily of three phenyl propane units, namely syringyl propane (3,5-dimethoxy-4-hydroxyphenylpropane) (S), guaiacyl propane (4-hydroxy-3-methoxyphenylpropane) (G), and 4-hydroxyphenylpropane (H) groups resulting from the enzymatic polymerization of sinapyl, coniferyl, and p-coumaryl alcohols, respectively linked with dominance of ether bonds as well as carbon bonds [3,4]. A great variability of functional groups occurs including aliphatic hydroxyl groups, phenolic groups, and carboxylic groups, which makes it widely applicable in various areas such as emulsifiers, dyes, synthetic floorings, sequestering, binding, thermosets, dispersal agents, paints and fuels [5]. Further high purity or sulphur free lignin is widely being used as sustainable alternatives to nonrenewable products, such as phenolic and epoxy resins, and isocyanates apart from its industrial application as a principal component of thermoplastic material [6]. Also high grade lignin can be used in the production of carbon fibers, Vanillin and phenol derivatives which are widely being used for advanced applications like automobile industry, sports industry, polyurethane formation etc [7]. Lignin is insoluble in common solvents but soluble in special solvents.

Among the variety of processes aimed at the fractionation of biomass, soda cooking is considered to be an efficient pretreat-

ment for component separation of lignocellulose due to the less environment impact, lower investment cost and energy consumption [8]. Soda cooking process results in physical breakage of cell wall i.e. cleavage of β-aryl ether bonds, hemolytic cleavage and hydrolysis of glycosidic bonds in the hemicelluloses, increasing the water solubility of hemicelluloses and the solubility of lignin in alkaline medium, leaving the cellulose as the solid residue [4,9]. The mother liquor obtained after soda cooking process is subjected to acid precipitation at low pH value yielding high purity lignin.

Three main methods, organic solvent extraction, membrane technology and acid precipitation method have been proposed for lignin extraction. But the extraction using organic solvents increase the cost of the lignin production. Moreover extraction using membrane technology results in higher equipment cost that affects the industrialization of the technology [8]. Hence the last method of acid precipitation, which involves extraction of lignin from solution by decreasing the pH, is a convenient and commonly used method for lignin recovery from black liquor [10]. However, major disadvantage with it is, lignin with different molecular weights is co-precipitated when the pH is abruptly decreased. The pH value during precipitation has a significant effect on the structural and chemical properties of lignin [11]. Thus, it is possible to separate lignin by sequential precipitation at gradually declining pH. Moreover, it is critical to separate lignin from the mixture as it contains the co-precipitated products of non lignin materials which can further be separated by evaporation with ethanol favoring the degradation of polysaccharides.

Published literature have reported the lignin extraction using soda cooking followed by acid precipitation technique however the effect of important process parameters i.e. alkali concentration and pH on yield, purity, structure and thermal stability has not been adequately studied. Therefore, the main objective of this study is to optimize the process parameters i.e. alkali concentration and pH to obtain high yield, purity and thermal stability of the lignin from waste jute bags using soda cooking process followed by acid precipitation. The purity of lignin was assessed using TAPPI method and UV–vis spectroscopy. Chemical structure, thermal stability and elementary analysis (C, H, O, and S &N) of lignin were studied using FTIR, NMR thermo gravimetric analysis (TGA) and Elemental analyzer respectively.

2. Materials and methods

2.1. Materials

Jute fibers were obtained from the waste jute bags supplied by Grain Market, Chandigarh. Sodium hydroxide (AR) and Sulfuric acid (AR) were procured from Qualigens India and Ethanol (AR) from Changshu Yangyuan Chemical, China.

2.1.1. Pretreatment of the jute bags

Jute bags were chopped into small pieces and washed with hot distilled water several times and dried in direct sunlight. Dried fibers were dewaxed and dewatered in a soxhlet apparatus. Dewaxed jute fibers were characterized for moisture, ash, acid insoluble lignin and hollocellulose content.

2.2. Extraction of lignin using soda cooking method followed by acid precipitation

Lignin was extracted from jute fibers by soda cooking method followed by acid precipitation. Dewaxed jute fibers were first subjected to soda cooking at different alkali concentrations i.e. 6, 8, 10 and 12% with fiber to alkali ratio of 1:20 in an IKA laboratory LR 1000 basic reactor at 120 °C for 4 h. Thereafter the insoluble cellulose and the black liquor containing lignin were separated using

vacuum filtration. The pH of black liquor so obtained was lowered by slow addition of dilute sulphuric acid (20% v/v) with stirring [12]. At pH nears 6 an apparent change occurred in the appearance of the solution from black to murky brown which may be due to the initial stages of lignin precipitation so the acidification was stopped and mixture was stirred for 15–20 min for the growth of the lignin particles. Thereafter dilute sulphuric acid (20% v/v) was again added to further lower the pH within 2–5 and the mixture was mechanically stirred for 40–45 min at 65 °C. The lignin was then separated by evaporation with drop wise addition of aqueous ethanol solution (50% v/v) with stirring at 65° ± 5 C for 1 h which resulted in the dissolution of hemicellulose and other extractive materials in the solution thus giving the pure lignin. Thereafter the precipitated lignin was then vacuum filtered and centrifuged at 4000 RCF for 10 min with diluted acid (0.01 M) to remove the co precipitated ash and silicon The soda lignin so obtained was then dried in a vacuum oven at 55 °C for 24 h prior to further analysis. All extractions were conducted in triplicate.

2.3. Characterization of lignin

2.3.1. Yield and purity

Yield of the lignin was calculated using Equation (1) [13]

$$\%Lignin Yield = \frac{Mp}{Mr} \times 100 \tag{1}$$

Where Mp is the Mass of soda lignin and Mr is mass of lignin in Raw Material

Purity was determined by content of acid-insoluble lignin in accordance with TAPPI method T222 om-83 (1999) [14] and is referred to as "Klason–lignin".

2.3.2. Fourier transform infrared spectroscopy

The chemical structure of Lignin obtained at various pH values and alkali concentrations were characterized by Fourier transform infrared spectroscopy (FT-IR) in Perkin Elmer RZX spectrometer using KBr technology i.e. by making pellets of lignin powder with KBr. FTIR spectra were recorded in a spectral range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1} with two scans for each sample.

The relative level of cross linked lignin can be calculated by absorbance ratios of peaks at 1500 and 1600 cm^{-1} [15]. The higher is the ratio more condensed and cross linked is the lignin.

S/G ratio was calculated by the estimating the intensities of the bands around 1327 cm^{-1} (S units) and 1271 cm^{-1} (G units), after resolution enhancement (subtraction of ×1000s derivative), moving-average smoothing (×100) and baseline correction between valleys ca. 1401 and 1172 cm^{-1} [16].

2.3.3. ^{H}NMR

The chemical structure was studied using nuclear magnetic resonance (NMR) spectrometry. ^{H}NMR spectra were recorded on a Bruker AV II 400 MHz spectrometer. The 1H NMR spectrum was obtained at 400 MHz using 10 mg acid-insoluble lignin in 0.5 ml of dimethylsulfoxide-d6 (DMSO-d6). The chemical shifts of 1H NMR spectrum were calibrated with reference to DMSO, used as an internal standard, at 2.49 ppm. The acquisition time was 2.7 s, and relaxation time was 1.0 s.

2.3.4. UV–vis spectrophotometer

For the UV spectra, a Shimadzu spectrophotometer model UV-1200 was used. Prior to the analysis, 5 mg of sample was dissolved into 10 ml 90% (v/v) dioxane-water aliquot. 1 ml of aliquot was further diluted into 25 ml by using 50% (v/v) dioxane-water. The absorbance was measured for the range of 200 nm–400 nm [12].