Journal of Nanomaterials & Molecular Nanotechnology

Research Article A SCITECHNOL JOURNAL

Lignin Extraction and Characterization from Rice Straw by Organosolv Pulping Method

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Received: 03 April, 2020, Manuscript No. JNMN-20-8905;

Editor assigned: 08 April, 2020, Manuscript No. JNMN-20-8905;

Reviewed:22 April, 2020, QC No. JNMN-20-8905;

Revised:25 August, 2022, QI No. JNMN-20-8905; Manuscript No. JNMN-20-8905;

Published: 22 September, 2022, DOI: 10.4172/2324-8777.1000350

Abstract

Rice straw has been acknowledged as one of the most abundant and cheap lignocellulosic biomass resources for potential use to produce chemical and biomaterials. In this study, lignin extraction from rice straw was done with formic acid and acetic acid by the Organosolv pulping system. The crude lignin was purified by 1, 4 dioxane and diethyl ether. The percent yield of purified lignin was 12.06%. The purified lignin fractions were characterized by non-destructive techniques such as Infrared spectroscopy (IR), Gas Chromatography-Mass Spectrophotometer (GC-MS), Scanning Electron Microscope (SEM), Simultaneous Thermal Analysis (STA), etc. IR spectra confirmed the existence of lignin by showing the presence of alkyne stretch and aldehyde functional groups. The extracted lignin's thermal properties were observed from Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). The melting point of extracted lignin was supposed to between 250 and 275 °C; however, TGA found its melting point slightly above the range. GC-MS spectrum of purified lignin from rice straw showed the presence of vanillin and O-Guaiacol. Rice straw illustrated great potential to produce vanillin from purified lignin. SEM analyses indicate the presence of nanoparticles ranges 597 nm-200 nm from purified and crude lignin which is better for nanotechnology. Some particles under 200 nm also observed.

Keywords: Rice straw; Lignin; Infrared spectroscopy (IR); Gas Chromatography-Mass Spectrophotometer (GC-MS); Scanning Electron Microscope (SEM); Differential Scanning Calorimetry (DSC); Thermo Gravimetric Analysis (TGA)

Introduction

As the world's most abundance and cheap resource, rice straw has been acknowledged for potential use to produce chemicals and biomaterial. As an organic polymer lignin can be derived from reusable resources that have inevitable potential as a reinforcement material in composites. It is non-toxic, cheap and available in large amounts. Lignin is particularly that much important in the wall formation of cells, most importantly in wood and bark, due to the fact that they lend rigidity and do not gangrene easily.

Agriculture based residue is one of the most valuable and reusable lingo cellulosic biomass and a promising alternative for cellulosic materials. Among all other different sources of agriculture based residues, rice straw has been enormously investigated because of its huge consumption which is about 650-975 million tons per year all over the world [1,2]. Composition of Rice straws includes 35% cellulose, 18% hemicellulose and 15% lignin approximately [3]. The lignin, together with cellulose and hemicellulose, is one of the most abundant polymers on Earth, it is estimated that its annual production is around 10 to 50 billion tons [4]. We can use lignin as raw material for conversion to high value-added products through chemical, biochemical and physical processes. Lignin is a phenyl-propanoid (C9) polyphenol, mainly linked by carbon-carbon bonds and arylglycerol ether bonds between the monomeric phenolic p-coumaryl (H), coniferyl (G) and sinapyl alcohol (S) units [5]. Isolation techniques of lignin from softwood and hardwood are available and its chemistry being much better known [6]. Lignin from hardwood, softwood and non-wood has been studied by numerous researchers [7-9].Lignin could be extracted from natural resources like rice straw and many others but rice straw was chosen in this study because of its low cost and availability in Bangladesh.

Lignin can be used in a wide range of applications, ranging from fuels to advanced chemicals and materials including fire retardants, thermal stabilizer, hydrophobicity agent, aerogels and antioxidants. As a natural source, lignin has huge opportunity in generation of adhesives, resins and carbon fibers in future.

Few feasible lignin extraction methodologies are there which do not affect the original structure. Therefore, new extraction processes development and study are becoming increasingly important. Extraction process largely controls the chemical structure of the extracted lignin, the original source of the raw materials is also matte [10]. One of the most recent processes of delignification, called Organosolv pulping system with low cost formic acid and acetic acid was used to extract lignin from rice straw. Then the crude lignin was purified by 1, 4 dioxane and diethyl ether. Percent yield of purified lignin was 12.06%. Extracted lignin's were characterized by FTIR, Scanning Electron Microscopy (SEM), Gas Chromatography Mass Spectrophotometer (GC-MS), Simultaneous Thermal Analysis (STA), Differential Scanning Calorimetry (DSC) and Thermos Gravimetric Analysis (TGA).

Materials and Methods

Natural resources were collected from local fields near Dhaka, Bangladesh. Various chemicals used for extraction of lignin like formic acid, acetic acid, hydrogen peroxide; sodium hydroxide and distilled water of high purity.

Experimental procedure

Formic acid/acetic acid treatment: In the first step of the extraction process of lignin, the original resource material cut into

very small size and collected in a clean conical flask. An 85% organic acid mixture (formic acid/acetic acid 70:30 by volume) was added to the conical flask where the fiber to liquor ratio of 1:8, allowed to boil on a hot plate for 2 h. After the completion of heating the flask and its content were removed from the hot plate and cooled to room temperature. Then the fibers were allowed to filter in a Buchner funnel and washed with 80% formic acid followed by hot distilled water.

Extraction of lignin: Lignin became extracted by following the procedure. After the pulping and de-lignification process, the spent liquor became heated at 105°C. The lignin which dissolved in formic acid was prompted by the way of adding distilled water (5 times more than the extent of concentrated liquor) and the precipitate turned into filtered in a Buchner funnel. Finally, the triggered lignin turned into washed with distilled water and vacuum dried over P_2O_5 (Figure 1).

Figure 1: Schematic diagram of the process of lignin extraction

Characterization

Structural and thermal characterization of lignin was carried out through Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA). FT-IR dimension of the extracted lignin samples was taken using Spectrophotometer (Shimadzu, IRPrestige-21). DSC measurement of extracted lignin from rice straw was performed using Shimadzu, DSC arrangement. Approximately 5.00 mg ± 0.25 mg of the sample was placed in a hermetic pan and sealed. DSC scans were carried out at a heating charge of 5°C/min from 30 to 400°C under the Nitrogen environment. Thermo-Gravimetric Analysis (TGA) was used to determine the thermal stability, decomposition temperature and char yield for each extracted lignin. Sample of each measurement was maintained at 14 mg ± 5 mg and scans were performed from 30°C to 800°C at 10°C/min to observe thermal degradation and stability of lignin. The morphological traits of the extracted lignin samples were observed by scanning electron microscopy.

Results

Acid fractionation of lignin from rice straw

Extraction of lignin from rice straw used in this study was carried out using a mixture of formic acid/acetic acid/distilled water for pulping with the main goals of degrading of lignin molecules by the way of dissolving them in the solution and consequently through retrieving them with the aid of washing. Organosolv (acetic acid/ formic acid) under acidic situation cleaves ether bonds between lignin and hemicellulose, thereby accelerating the delignification process [11]. This studied the effect of formic acid on de-lignification and concluded that the acquired pulp after formic acid treatment still incorporates a few lignin, hemicellulose and ash [12]. Percent yield of lignin after acidic treatment become determined gravimetrically and observed 12.0426% of lignin. The moisture content of the rice straw was 7.28% and ash content discovered on the sample become 11.54%.

DSC and TGA

The DSC curve showed the standard behavior of the purified lignin sample. The endothermic transformation is present only at the starting of heating and it attributed to water loss up to 100°C [13]. The samples presented Tg (Glass transition temperature) between 80 and 90°C as the data of other Organosolv lignin in literature [14,15].About the contaminants, it is possible to see in the DSC curves a low contamination by carbohydrates or poliosis, because the presence of these compounds would cause some endothermic peaks, which are characteristic of these poliosis between 200°C and 400°C (Figure 2) [16].

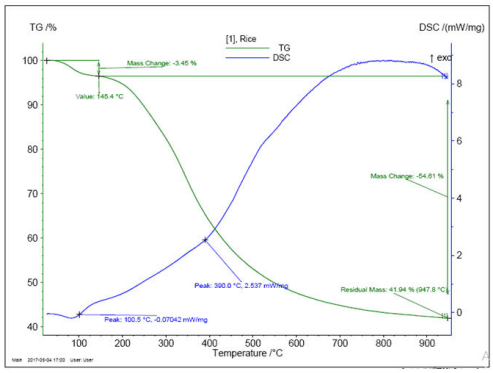

Figure 2: DSC and TGA curves of the analyzed lignin sample.

It is possible to observe through TGA curve that the sample, besides presenting almost the same decomposition curve showed good thermal stability. The great degradation temperature range obtained in all extractions is the result of the stability supplied by the aromatic rings, besides the absence of contaminants that would result in changes in the curves slope.

Fourier Transforms Infrared spectroscopy (FT-IR)

The chemical structure of extracted lignin samples was analyzed using FT-IR which showed alkenyl C≡C stretching at 3336 cm^{-1}, alkenyl C-H stretching at 2936 cm^{-1} (Figure 3).

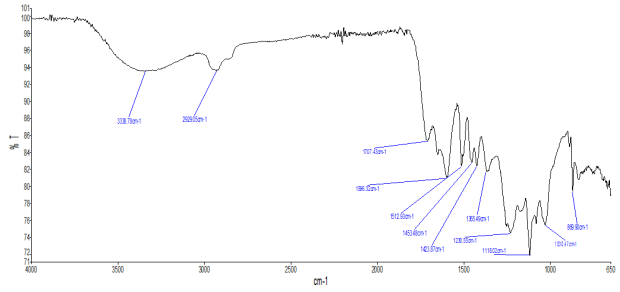

Figure 3: FT-IR spectrum of purified lignin sample, FT-IR in the region between 500 cm^{-1} and 4000 cm^{-1}

As the thermal analysis, FT-IR spectroscopy showed a great similarity between lignin samples with the standard value. The most

important region to observe the main structures in the obtained lignin samples are between 2000 cm^{-1} and 500 cm^{-1} (Figure 4). The region in which is situated the major number of functional groups, becoming more evident the similarity between the obtained value with the standard value. Therefore, functional groups are pointed for purified lignin in Table 1.

Wavelength(cm^{-1})	Types of vibration
3354	Alkyne C≡Cstretching
2929	Alkyne C-H stretching
1707	Aldehyde C=O stretching
1654	Amide
1597	Alkene
1512	Aromatic C=C bending
1453	Alkanes bend
1424	Alkanes bend
1365	Alkanes bend
1230	Amines
1118	Alkenes stretch
1031	Sulfoxide
869	Aromatic stretch

Table 1: Attribution of FT-IR spectrum wavelength (cm^{-1}).

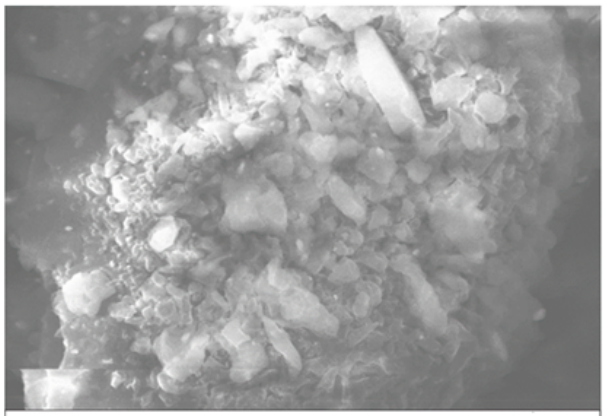

Figure 4: SEM image of lignin sample extracted from rice straw.

Discussion

It is possible to see in SEM (Scanning Electron Microscopy) images that the lignin particles accumulated in large conglomerates. In the scanning electron microscope, the Nano sized ball milled purified lignin is observed. In the scanning electron microscope, we see different sizes of particle. Some lignin fragments are small and some are massive. All the particles coagulate to each other very tightly and hold each other. Some shapeless particles are clearly observed in scanning electron microscope. The white color Nano sized particles are large size particles. In other study was suggested that the amount of ethanol present in the extraction liquor can have a fundamental role in the morphology of the lignin obtained.

Conclusion

Lignin was extracted from rice straw by Organosolv pulping process which characterized through GC-Ms, DSC, IR, SEM testing method. We have found percent yield of lignin 12.0584%, which is very near to standard lignin content in rice straw. IR spectra confirmed homogeneity inside the chemical structure of extracted lignin samples with treatments of organic solvents. From infrared spectroscopy, we found alkyne stretch, aldehyde and useful alkane functional group. The thermal traits of the processed lignin were observed using DSC and TGA. DSC was carried out to observe the heat of reaction of lignin samples. The TGA analysis carried out to evaluate the thermal behavior of lignin. Enthalpy measurements were higher than rice straw lignin melting point. Actually, rice straw lignin melting point in the region between 250°C-275°C, we have found in TGA in its upper vicinity where rice straw lignin melted. In the temperature 100°C-145°C the moisture removed and ended in 900°C where low molecular weight compounds, volatile compounds remain as residue. This is an ongoing procedure, our desired product vanillin have remarkable gain in production of vanilla. SEM indicated nanoparticle from purified and crude lignin, which size was on the range of 150 nm-597 nm.

References

1. Santos F, Machado G, Faria D, Lima J, Marçal N, et al. (2017) Productive potential and quality of rice husk and straw for biorefineries. Biomass Convers Biorefin 7: 117-126.
2. Sun JX, Xu F, Geng ZC, Sun XF, Sun RC (2005) Comparative study of cellulose isolated by totally chlorine-free method from wood and cereal straw. J Appl Polym Sci 97: 322-335.
3. Jiang M, Zhao M, Zhou Z, Huang T, Chen X, et al. (2011) Isolation of cellulose with ionic liquid from steam exploded rice straw. Ind Crops Prod 33: 734-738.
4. da Rosa MP, Beck PH, Müller DG, Moreira JB, da Silva JS, et al. (2017). Extraction of organosolv lignin from rice husk under reflux conditions. Biol Chem Res 87-98.
5. Jahan MS, Al-Maruf A, Ahsan MA, Mun SP (2019) Characterisation of lignin extracted from six mangrove species grown in Bangladesh. Cellul Chem Technol 53: 63-70.
6. Chakar FS, Ragauskas AJ (2004) Review of current and future softwood kraft lignin process chemistry. Ind Crop Prod 20: 131-141.
7. Pandey KK (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. J Appl Polym Sci 71: 1969-1975.
8. Kilpelaeinen I, Sipilae J, Brunow G, Lundquist K, Ede RM (1994) Application of two-dimensional NMR spectroscopy to wood lignin structure determination and identification of some minor structural units of hard-and softwood lignins. J Agric Food Chem 42: 2790-2794.
9. Nuruddin M, Chowdhury A, Haque SA, Rahman M, Farhad SF, et al. (2011) Extraction and characterization of cellulose microfibrils from agricultural wastes in an integrated biorefinery initiative. Biomaterials 3: 5-6.

10. Xu F, Sun JX, Sun R, Fowler P, Baird MS (2006) Comparative study of organosolv lignins from wheat straw. Ind Crops Prod 23: 180-193.
11. Dence CW (1992) The determination of lignin. InMethods in lignin chemistry 33-61. Springer, Berlin, Heidelberg.
12. Laurichesse S, Avérous L (2014) Chemical modification of lignins: Towards biobased polymers. Prog Polym Sci 39: 1266-1290.
13. Vázquez G, Antorrena G, González J, Freire S (1997) The influence of pulping conditions on the structure of acetosolv eucalyptus lignins. J Wood Chem Technol 17: 147-162.
14. Yang H, Yan R, Chen H, Lee DH, Zheng C (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86: 1781-1788.
15. Zhang H, Zhao X, Ding X, Lei H, Wang Z (2013) Preparing spherical lignin from rice husk. Bioprocess Biosyst Eng 36: 1149-1155.
16. Villas-Bôas SG, Højer-Pedersen J, Åkesson M, Smedsgaard J, Nielsen J (2005) Global metabolite analysis of yeast: Evaluation of sample preparation methods. Yeast 22: 1155-1169.