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Research Article

Isolation and Characterization of Lignin obtained from *Calliandra calothyrsus* shrub using FT-IR Spectroscopy

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Abstract

To explore and use of woody biomass, lignin was isolated from the stem of Calliandra calothyrsus by the acid hydrolysis procedure, in accordance with TAPPI T 222 om-06 which is standard literature method. This technique is employed frequently as it is relatively rapid and yields a lignin which is free of carbohydrate contamination and of relatively high purity. Lignin isolated by acid is characterized by Fourier transform infrared spectroscopy (FT- IR). The study showed that FT-IR analysis can be used reliably to predict Klason lignin in Calliandra calothyrsus.

Keywords: *Acid, Calliandra calothyrsus, Lignin, FT-IR*

1. Introduction

Plant biomass is abundant in nature and is important part of renewable resources for food, energy and useful chemicals. Woody biomass is made of many chemical components, primarily extractives, carbohydrates, and lignin, which are nonuniformly distributed. Lignin is a most important component in biomass after cellulose and hemicellulose, which is studied less and usually varies in the range of 20-30% (wt.%) in plants. Annually 50 million tons of lignin is generated during the industrial conversion of wood into paper (Ling-ping et al., 2011). Lignin is an amorphous polyphenolic lignocellulosic material, made by polymerization of three major phenylpropanoid monomers (coniferyl, sinapyl and pcoumaryl alcohol) forming 3dimensional network inside the cell wall. Lignin in material is covalently linked to polysaccharides, forming a lignin-carbohydrates compound made by of benzyl-ether (Yaku et al.,1981; Lawoko et al.,2003; Sun et al., 1998), benzyl-ester (Watanabe and Koshijima 1988; Lundquist et al., 1983; Sun et al.,1997) and phenyl-glycoside bonds (Yaku et al.1976; Kondo et al.1990). In all the solvents lignin is insoluble and by chemical or physical treatments it can be degraded. Isolation of lignin from lignocellulosic materials can be done in large quantity by using strong dilute acid, alkali, organosolve isolation or sulphite pulping process. Delignification involves the cleavage of non-phenolic β-O-4 bond, phenolic β-O-4 bond from the associated polysaccharide (Gellerstedt and Lindfors,1984 ; Groot et al.,1995).

Many useful products like lignin-based polyurethanes, carbon fibers, aromatic chemicals, adhesives, can be produced with pure lignin as a starting raw material.

Calliandra calothyrsus, is a thorn less, small, perennial, shrub grows to 4-6 m high, with diameter of trunk up to 30 cm with white-reddish brown bark. It belongs to *Leguminosae* family. Distributed widely in humid and sub-humid regions of Central America and Mexico. It was brought to Indonesia in 1936 to control soil erosion and from there to other parts of the tropicals, particularly in South-East Asia. Calliandra grows in Warm climates (20 - 28°C) and on all types of soil. Its leaves and twigs contain high quality protein so used as a feed for cattle and goats. Literature shows the wood has a calorific value of 4,500–4,750 kcal per kg (Lowry and Macklin (1988), *Calliandra calothyrsus* contains 30–75% fiber, 4–5% ash, 2–3% fat, and 1–3% tannin (Kaitho et al.,1993). However no information is available concerning structural characteristics and composition lignin from *Calliandra calothyrsus.*

The objective of this study was to acquire the information on composition and structure of lignin polymer of *Calliandra calothyrsus*.

2. Materials and Methods

2.1 Material

Calliandra calothyrsus was obtained from Sirsi, Karnataka. The leaves and twigs were removed, and stem were chipped into small pieces. It was dried under sunshine and ground into powder in a laboratory and particles passing through 40 mesh and retained on 60 mesh were collected and used as a raw material. The raw material shown in Figure 1was then oven dried at 60°C for 16 h, and dewaxed with 1:2 (v/v) ethanol-benzene in a Soxhlet apparatus for 6 h. The main component of C. *calothyrsus* is lignocellulose, which has compact structure

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of cellulose (46%) and hemicelluloses (14%) linked closely with Klason lignin (31%). Samples after dewaxing was dried at 60°C for 16 h, and stored before use. All calculations were made on oven dried basis.

Fig.1 Raw material

Fig.2 Klason lignin extracted

2.2 Fractional isolation of lignin

Lignin content in *C. calothyrsus* is determined by measurement of acid-insoluble (ie, Klason) lignin by Klason lignin method (TAPPI 222 om-06). Klason method is based on hydrolysis and solubilization of cellulose and hemicelluloses present in lignocellulosic material. Accordingly, 1 g of dewaxed sample was placed in a 100 ml beaker to which 15 ml of 72% sulfuric acid was added. The mixture was left at room temperature with constant stirring for 2 h. The solution was transferred to 1 L Erlenmeyer flask, and final hydrolysis was done with 3% sulfuric acid for 4 h by diluting the solution with 560 ml of deionized water, maintaining constant volume by using reflux condenser. Insoluble lignin was allowed to settle and separated using filtering crucible. Lignin extracted was washed with hot water, dried in an oven at 105°C for 12 h, and after cooling in desiccators, acid insoluble lignin was determined gravimetrically. Figure 2 shows the Klason lignin extracted from *C. calothyrsus.*

2.3 Characterization of lignin fractions

FT-IR spectrophotometer (Alpha T, Bruker, Germany) was used to analyze Fourier Transform Infrared spectroscopy (FT-IR) using a KBr pellets containing 1% fine powder of lignin sample. Scans were recorded from 500 to 4000cm^{-1} at a resolution of 2 cm^{-1}.

3. Results and Discussion

3.1 FT-IR analysis

FT-IR spectroscopy has been used in wood chemistry to characterize cellulose, hemicellulose and lignin by transmission technique in KBr pellets. Figure 3 showed a lower number of absorption bands for Klason lignin, isolated from *C. calothyrsus*. The corresponding assignments of FTIR spectra of acid-soluble lignin are given in Table 1. The spectra of the Klason lignin in the region from 1800 cm·1 to 4000 cm^{-1} did not show any useful information of isolated lignin other than broad hydroxyl and aliphatic CH absorptions. This observation was also noted by others (Buta *et al.,*1989; Roy *et al.,*1987) However, the a finger print region between 1800 and 600 cm^{-1}, was directly interpreted and ascribed to a particular chemical composition in the extracted lignin.

Table 1 Assignments of functional group in FTIR spectra of *Calliandra calothyrsus*

Band position (cm^{-1})	Assignments
1696	Unconjugated carbonyl stretching of lignin
1510	Aromatic skeletal vibrations(C=C) of lignin
1461	Asymmetric C-H bending in $-CH_2$ and $-CH_3$, Aromatic C-H deformation[15]
1263	Guaiacyl ring structure in lignin
1212	C-O in Guaiacyl ring of lignin
1094	C-O in cellulose
1020	C-H in Guaiacyl lignin, C-O deformation in prim. Alcohols [20]
636	Skeletal deformation of aromatic ring, substituted groups and side chains
593	Skeletal deformation of aromatic ring, substituted groups and side chains
540	Skeletal deformation of aromatic ring, substituted groups and side chains

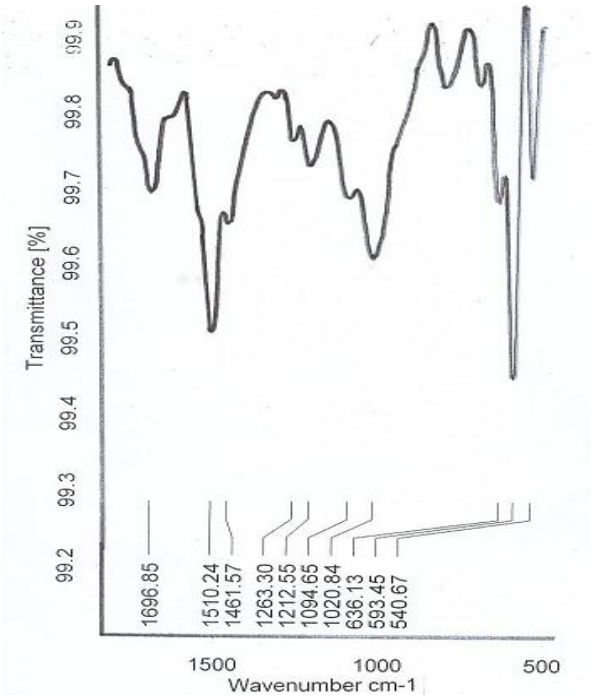

Fig.3 FT-IR spectra of Klason lignin

With reference to Figure 3 it is observed that absorption band at 1510 cm^{-1} is attributed to aromatic characteristic of lignin (Lad and Ibrahim 1992). The band at 1263 cm is typical for guaiacyl ring structure in lignin (Faix 1986; Kimura *et al.*,1992; Kajihara et al.,1993). The 1212 cm peak is assigned to lignin characterization by C-O bond of guaiacyl ring (Faix ,1986) This indicates that lignins in *Calliandra calothyrsus* contain a higher amount of guaiacyl group. In this study it was observed that disappearance of typical hemicellulose bands due to dissolution of hemicellulose in strong acid. Due to strong acid treatment there was disappearance of most of polysaccharides bands between 900-1200 cm-^{1}. Bands between 800-500 derive from skeletal deformation of

aromatic ring, substituted groups and side chains Bands between 800-500, 1212, 1263, 1510 and 1696 cm^{-1} suggests greater delignification from the sample. A small band at 1094 cm^{-1} indicates exposure of cellulose fibers after acid treatment.

Conclusions

The structure of Klason lignin fraction separated from *C. calothyrsus* has been characterized by FT-IR spectra. The spectra showed typical lignin characteristic. The results obtained suggest that extracted Klason lignin mainly composed of guaiacyl units. Work is being done in our laboratory. The results illustrated here represent the first comprehensive study on Klason lignin extracted from *C. calothyrsus.*

References

XIAO Ling-ping, SHI Zheng-jun, XU Feng, SUN Run-cang, Amar K Mohanty, (2011) Structural Characterization of lignins isolated from Caragana sinica Using FT-IR and NMR spectroscopy, *Spectroscopy and spectral Analysis* 31: 2369

Yaku F, Yamada Y, Koshijima T, (1981) *Holzforschung* 35: 177-181

Lawoko M, Henriksson G, Gellerstedt G, (2003) *Holzforschung* 57: 69-74

Sun R C, Xiao B Lawther J M, (1998) *J. Appl. Polym. Sci* 68: 1633-1641

Watanabe T, Koshijima T, (1988) *Agric. Biol. Chem* 52:2953-2955

Lundquist K, Simonson R, Tingsvik K, (1983) Svensk Papperstidn 86: 44-47

Sun RC, Lawther J M, Banks W B, (1997) *Ind. Crop. Prod* 6: 1-8

Yaku F, Yamada Y, Koshijima T, (1976) *Holzforschung* 30: 148-156

Kondo R, Sako T, Limori T, (1990) Mokuzai Gakkaishi 36: 332-338

Gellerstedt G, Lindfors EL, (1984) *Holzforchung* 38:151-158

Groot BD, Dam J E G V, Riet KV, (1995) *Holzforchung* 49:332-342

Lowry J B, Macklin W, (1988) *Calliandra calothyrsus* - an Indonesian favorite goes pan- tropic. NFT Highlights. NFTA, Hawaii, USA. 88-02.

Kaitho R J, Tamminga S, Bruchem J (1993) Rumen degradation and *in vivo* digestibility of dried *Calliandra calothyrsus* leaves. *Animal Feed Science and Technology* 43:19– 30.

Lad S, Ibrahim R, (1992) FT-IR Spectroscopic Studies on Lignin from Some Tropical Woods and Rattan. *Pertanika* 14: 75-81

Faix O, (1986) Investigation of lignin polymer models (DPH´s) by FTIR spectroscopy. *Holzforschung* 40: 273-280

Kimura F, Kimura T, Gray T G, (1992) FTIR study of UV-irradiated stone-ground wood pulp *Holzforschung* 46:529-532

Kajihara J, Hattoris T, Shirono H, Shimada M, (1993) Characterisation of antiviral water-soluble lignin from Biogases degraded by Lentinud edodes *Holzforschung* 47: 479-485.

Roy AK, Bag SC and Sen SK, (1987) Studies on the Chemical Nature of Milled Wood Lignin of Jute Stick, *Cellu. Chem. Technol.* 21: 343-348.

Buta J G, Zadrazil F and Galletti G C, (1989) FTIR Determination of Lignin Degradation in Wheat Straw by White Rot Fungus *Stropharia mgosoannulata* with Different Oxygen Concentrations. *J Agric. Food Chem*. 37: 1382-1384.