Assessing Lignin Extraction Techniques: A Study on Wet and Dry Coconut Husk

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ABSTRACT

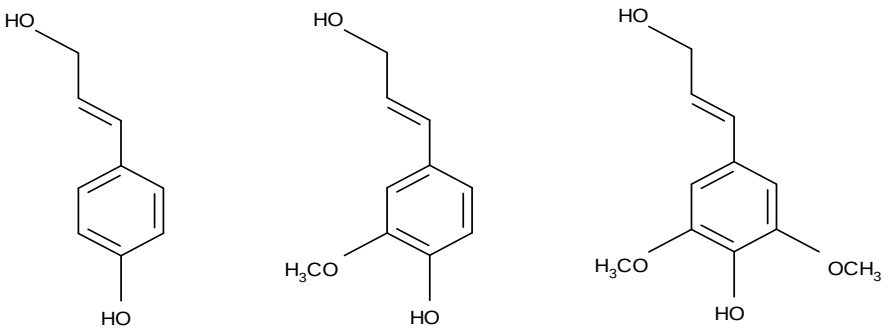
Recently lignin has been the object of a renewed interest because of the need to use raw materials from renewable resources. One such resource is coconut husk, a material usually discarded during the copra extraction process. Due to its high lignin content, coconut husk can be pursued as having a variety of applications. Therefore, it is important to know the approximate structure of coconut husk lignin and those variations introduced by different isolation methods. This work reports extraction and a general characterization of dry coconut husk and wet coconut husk lignin through FTIR. Results of percent yield of lignin obtained from different isolation processes are also discussed.

KEYWORDS: Lignin, Dry coconut husk, Wet coconut husk, Isolation.

I. INTRODUCTION

The world commands a renewable and sustainable material that can substitute the present synthetic products which are generally obtained from non renewable sources and lignin is one among such a materials. It is considered to be one of the most encouraging future organic compounds as it is not only renewable but also comprises nearly one third of the material found in any plant. Lignin being purely natural can be obtained from agricultural and agro based industrial products or by products at economical prices. Given the abundant supply, excellent physical and chemical properties & potential to substitute petrochemical sourced products, research work is being conducted for converting these into industrial applications.[1]

Lignin is the second most abundant natural polymer next to cellulose. Its complex structure helps it to function like adhesive that binds cellulose and hemicelluloses. It is formed by photosynthesis and makes up to 15-25% of substance of every wood/plant. Lignin is a complex phenolic polymer which is important for mechanical support, water transport, defence in vascular plants. Compressive strength and hydro-phobisity of xylem cell wall is due to lignin polymer. The complexity and insolubility of the lignin polymer makes it resistant to degradation by most microorganisms. Therefore lignin serves an important function in plant defense. Variation in structure, content and location is likely to affect these essential processes. It is a complex hydrophobic network of phenylpropanoid units, which contain p–hydroxy phenyl, guaicacylandsyringyllignin as shown in Fig. 1.[2]



p-coumaryl alcohol **coniferyl alcohol** **synapyl alcohol**

Fig. 1 Lignin - Phenyl propanoid units

These mono-lignol differ in the extent of methoxylation. This variety of subunit substitution pattern indicates the various possibilities of formation of intermolecular linkages that can emerge during polymerization. Thus lignin varies not only in its subunit composition but also in intermolecular linkages. Lignin can also vary within a given cell wall in composition and overall quantity depending on location in the wall. It is alsodifferent between cell types and between tissues within the same plant.

Lignin is obtained from almost every part of every plant. Coconuts have high lignin content and can be considered as potential source of lignin. Coconut palms are abundantly growing in coastal areas of all tropical countries like India. It is widely applied in food and non food products. The coarse coir fibers are traditionally extracted by various decortication methods from husk for the production of ropes & yarns, mats, brushes and padding of mattresses. Worldwide 40 to 50 million tons of coconut are grown annually producing 15 to 20 million tons of husk. The productivity for coir fibers and fiber products is estimated to around 7 lakh tons per year which is only a small part of otherwise wasted raw material. India lies in top 5 countries for production of coconut with 21665 million nuts and its coir based commodities contributes largely in economy of India. Thus lignin extraction from coconut proves to be a viable and economic sector for value added lignin based products.

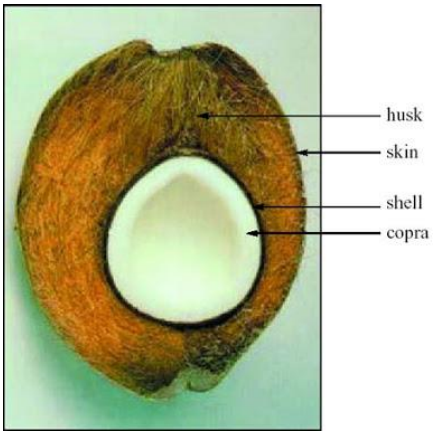


Fig. 2 Mature Coconut.

In a mature coconut, the white meat which is 28%wt, is surrounded by a hard protective shell which is 12%wt and thick husk which comes around 35%wt as shown in Fig 2. The coconut husk consists of fibrous matter containing selereids with numerous ramiform pits which is surrounded by thin waxy skin. The coir fibers are embedded in porous and elastic cork like parachymatous tissue called pith. Freshly opened husks are of light color (wet husk) but darken soon upon drying(dry husk) in air. Only a small part of the husk volume comprises the fiber while the pith material makes up the rest of the volume. The coir fibers consists 20-30% of husk weight and 70-80% of pith. Both fiber and pith are extremely high in lignin and phenolic content. The lignin from coconut is rich in syringyl with appreciable amounts of p-hydroxyphenyl content.

This paper focuses on extraction of lignin from coconut husk both wet and dry and its characterization. Different extraction processes are employed and the products obtained are characterized with FTIR (for both wet and dry husk). A comparative study based on interpretation of spectrogramis done and reported accordingly.

II. LITERATURE REVIEW

H. Vazquez-torres, G. Canche-escamilla, and C. A. Cruz-ramos' performed extraction of lignin from coconut husk. This study highlighted the contents ofhydroxyland non-condensed guaiacylunits, the extractability of the lignin in alkaline and "organo-solv" media along with thermal properties of the extracted lignins.The extraction system of NaOH-anthraquinone at 150ºC was used. When organo-solv systems were used, lower yields are obtained. The amount of lignin present in the samples was determined by analysis with 72% H_2S0_4 (TAPPI standard method T13m-54). Reducing sugars were detected in the filtrate of hydrolyzed (6*N* HC1) lignin samples using Fehling's reagent. The colorimetric method of Adler and Lundquist was followed for estimation of Non-condensed phenolic units. A differential scanning calorimeter (DSC) (Perkin-Elmer DSC 2C) was used to obtain the thermograms of the extracted lignins.[3]

H. Vazquez-torres, G. Canche-escamilla, and C. A. Cruz-ramos' even studied the evaluation of the reactivity of polyphenolic extracts of coconut husk with formaldehyde in both acidic and alkaline media. The objective of this evaluation was to determine if the extracts could be used in the preparation of phenol formaldehyde- type resins. Extracts were obtained using aqueous solutions of NaOH(with and without anthraquinone) and NH_4OH. Extractsobtained with NaOH, especially at 100 and 120°C, showed sufficient reactivity with formaldehyde in

basic conditions and may therefore be considered suitable for resin preparation in an alkaline medium. The resins were characterized using infrared spectroscopy (IR) ,differential scanning calorimetry (DSC) , and thermal gravimetric analysis (TGA).[4]

III. MATERIALS AND METHODS

Objective

The objective is to extract lignin from wet and dry coconut husk. It aims at extraction of lignin from different variety of raw material. The characterization is to be carried to validate the claim of extraction of lignin.

Methodology

The schematic representation of methodology followed in the present work in lignin extraction using soda pulping process has been shown in Fig. 3.

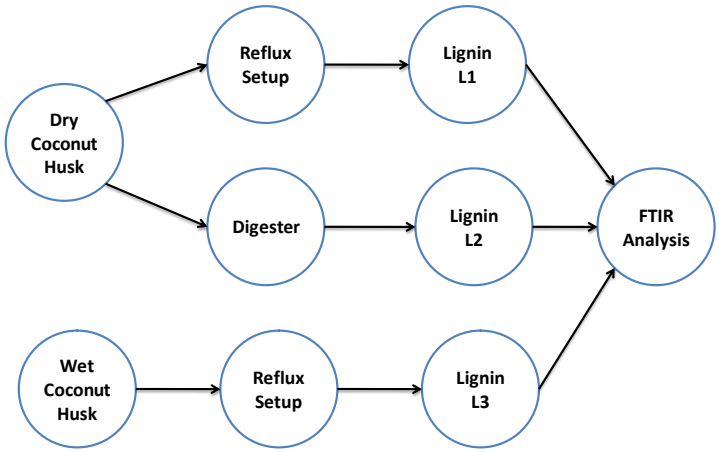


Fig. 3 schematic representation for lignin extraction

Materials

Coconut husk was obtained from local market. Laboratory grade sulphuric acid, sodium hydroxide, Whatman filter paper were used.

Experimental Procedure
Extraction of Lignin

Dry coconut husk was washed, dried, cut into pieces of approx. 0.5 cm and crushed.
Wetcoconut husk was similarly air dried for 12 hours and cut into small pieces.
An aqueous 2% by wt of NaOH solution was prepared.

- For Run L1- Reflux setup:
  The mixture of dry husk and NaOH in round bottom flask was attached to reflux setupto carry out extraction.
- For Run L2- Digester:
  The mixture of dry husk and NaOH was allowed to digest in a digesterto carry out extraction.
- For Run L3- Reflux setup:
  The mixture of wet husk and NaOH in round bottom flask was attached to reflux setup to carry out extraction.

The respective solutions obtained were filtered & the filtrates were acidified to pH 1 using Conc. H_2SO_4.
The respective acidified mixtures were heated to 100^{o}C followed by dilutionto a volume ratio of 1:5, and allowed to precipitate overnight.

The respective solutions were filtered using whatman filter paper, and the solid mass aggregates were oven dried at 105ºC.

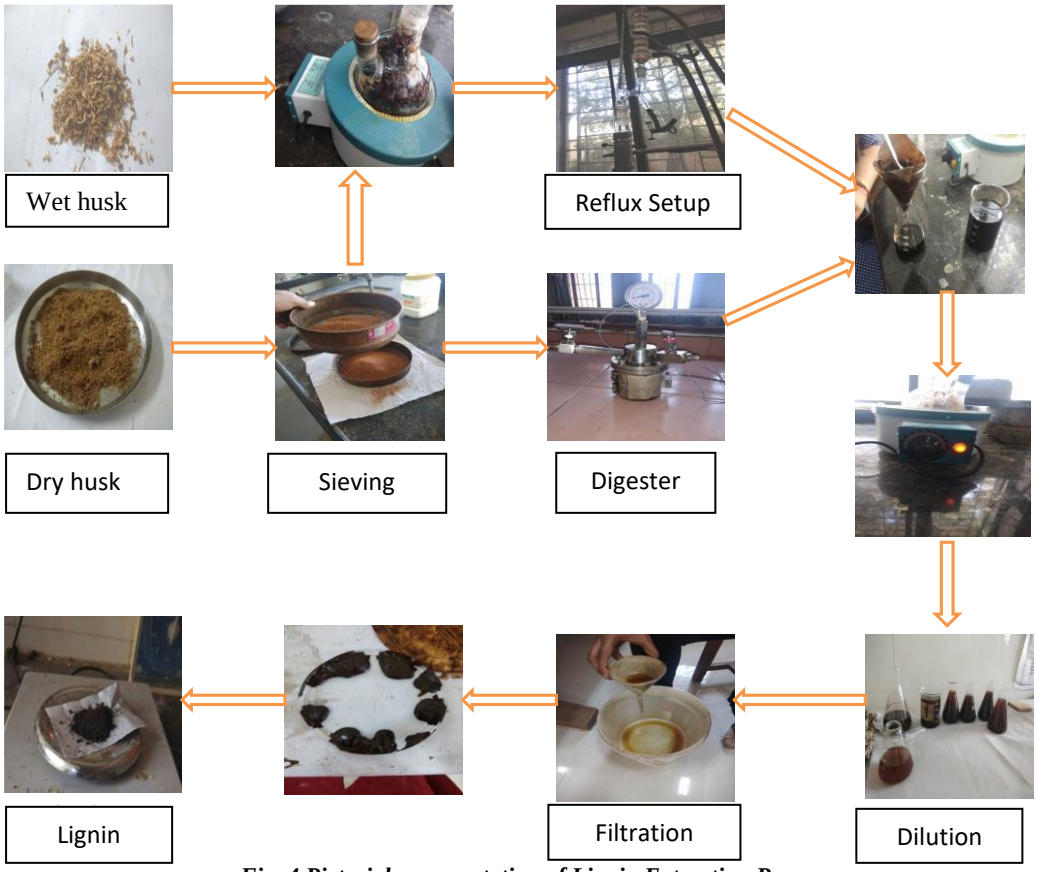


Fig. 4 Pictorial representation of Lignin Extraction Process

IV. OBSERVATIONS

The details of process parameters such as quantity of reagents, temperature, and time period are given in Table No. 1.

Sample	Weight of husk (g)*	Process followed	Volume of NaOH (ml)	Run time (hr)	Temperature (ºC)
L-1	10	Reflux	430	4	100
L-2	5	Digester	115	2	160
L-3	10	Reflux	230	4	100

Table No. 1 Details of Process parameters

****Air dried samples***

V. RESULTS AND DISCUSSION

The products obtained L1, L2 & L3 are analyzed for their lignin content using FTIR.The FTIR spectrogram for L1, L2, L3 and Pure Lignin are shown in Fig no. 5, 6, 7, 8.

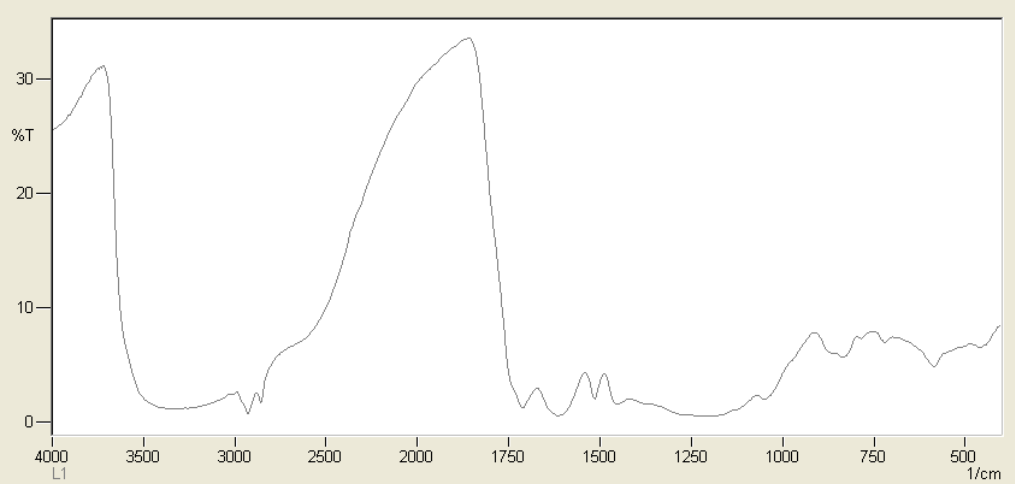


Fig. 5 FTIR spectrogram for L-1

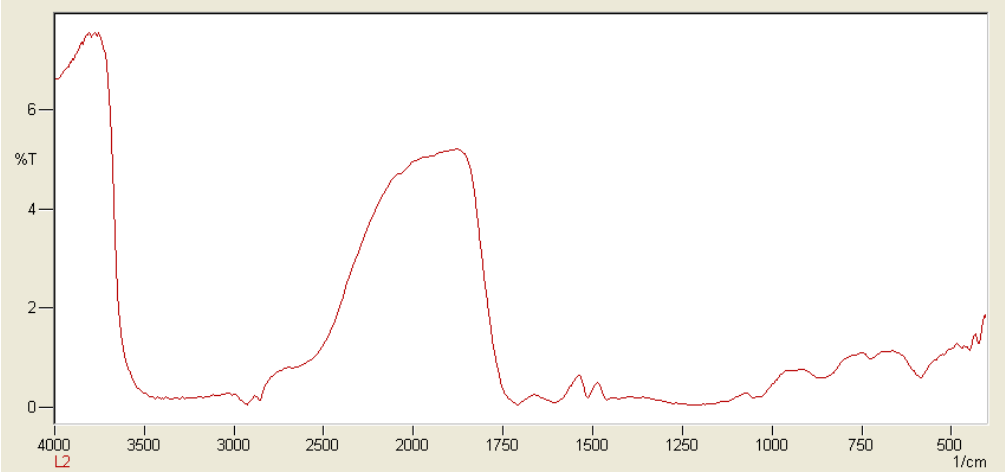


Fig. 6 FTIR spectrogram for L-2

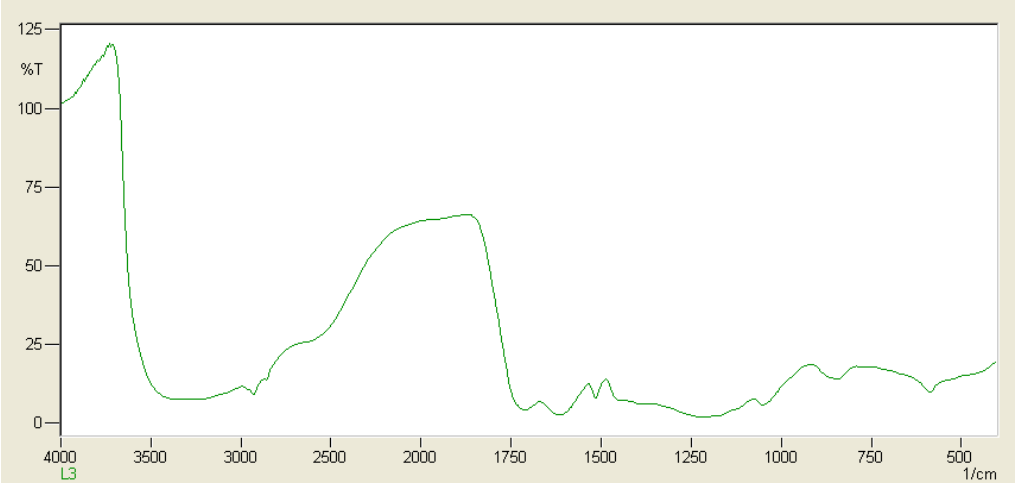


Fig. 7 FTIR spectrogram for L-3

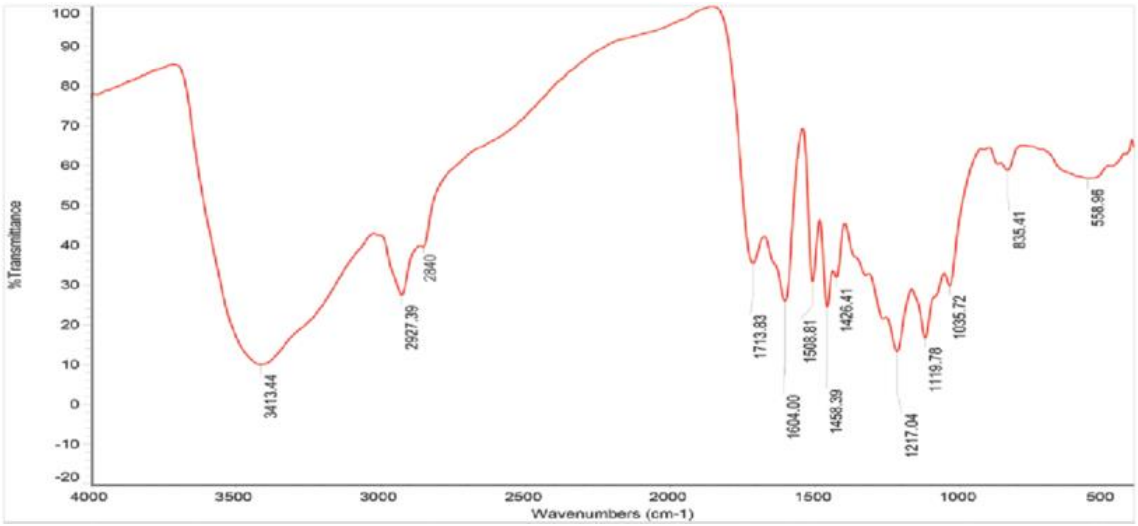


Fig. 8 FTIR spectrogram of Pure Lignin from literatur

Sr.no	Functional group	Wave number			Wave number from literature	General range of wave number from literature.
		L-1	L-2	L-3		
1	OH and NH stretching	3323	3408	3194	3413	3230-3460
2	CH3	2924	2922	2926	2927	2915-2940
3	CH2	2852	2856	2856	2840	2835-2895
4	C=O	1078	1720	1712	1713	1705-1730
5	C=C	1612	1598	1612	1604	1580-1660
6	C=C and C=O(beta-ketone)stretching	1514	1514	1514	1508	1500-1550
7	C-H deformation vibration stretching	1436	1438	1436	1426-1450	1426-1450
8	C-O-C	1219	1228	1215	1217	1210-1250
9	C-O stretching(for secondary, tertiary alcohols)	1117	1120	1220	1119	1085-1125
10	C-O stretching(alicyclic sec. alcohols)	1049	1051	1051	1035	1030-1080
11	CH3-methyl group	835	831	840	835	700-900
12	C-C	584	582	586	558	490-580

Table No. 2 Comparison of Spectrogram of L1, L2, L3 and Pure lignin.

The FTIR analysis of all the samples were carried out and compared with the reference [5][6] wave numbers of lignin reported in the literature. The details are given in the table no. 2. It can be observed that the wave numbers fairly agreed with the values reported in literature proving presence of lignin in the extract. The stretching patterns indicate the presence of compounds like phenols, hydroxides, methyl groups, which are present in lignin. Thus it can be inferred that the present work has successfully extracted lignin from dry & wet coconut husk.

The details of weight and yield of lignin extracted from different processes and raw materials are shown in Table No. 3.

Sample	Weight of lignin obtained (g)	Yield
L-1	2.38	23.8%
L-2	1.35	27%
L-3	0.28	2.8%

Table No. 3 Details of yield for various experimental runs.

Theoretically, there is almost 33%wt of lignin present in dry coconut husk while almost 28%wtin wet husk. However due to tenderness the % may decrease further in wet coconut husk. Thus the extraction methods followed in the present work have been successful in good amount of isolation of lignin present in these raw materials. The highest yield of 27% is obtained by using higher pressure and temperature condition in digester. Whereas low % yield of extraction is observed for wet coconut husk. This may be due to higher tenderness.

VI. CONCLUSION

The present work is aimed at exploring possible utilization of coconut husk as a source of lignin. Dry and wet coconut husk have been used as raw materials, so as to provide an alternative waste minimization& value added product generation. Two methods of lignin extraction have been tried, that include soda pulping process using reflux &high temperature and high pressure in digester. Characterizations of the samples were done using FTIR analysis.From comparative observations of spectrograms, it can be concluded that present work successfully extracted ligninin good percentage from wet & dry coconut husk. Percentage extraction of lignin varies from 2.8% to 27%. The %yield is relatively lower for wet coconut, this may be due to the higher % of initial moisture present.

The present work is demonstrative and it is felt necessary to conduct more experimental runs for varying process conditions, supported with appropriate characterization to substantiate the claim further.

VII. ACKNOWLEDGEMENTS

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VIII. REFERENCES

[1]. Jan E.G. van Dam, MartienJ.A.van den Oever, WouterTeunissen, Edwin R.P.Keijsers, Aurora G.Peralta process for production of density/high performance binders boards from whole coconut husk Part 1: Lignin as intrinsic thermosetting binder resin.

[2]. AneSequeiros, Darci Alberto Gatto, Jalelabidi, and Luis Serrano-Different Extraction Methods to Obtain Lignin from Almond Shell.

[3].H. VAZQUEZ-TORRES,* G. CANCHE-ESCAMILLA, and C. A. CRUZ-RAMOS',"Coconut Husk Lignin. I. Extraction and Characterization" .

[4].H. VAZQUEZ-TORRES,* G. CANCHE-ESCAMILLA, and C. A. CRUZ-RAMOS'," Coconut Husk Lignin.III. Reactivity of Alkaline Extracts with Formaldehyde".

[5]. www.science-and-fun.de > tools

[6] Nandanwar R.A, Chaudhari, Ekhe J.D, "Nitrobenzene Oxidation for Isolation of Value Added Products from Industrial Waste Lignin."