

Effect of Different Prehydrolysis Processes on Lignin Extractability of Coconut Husk Fibres

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ABSTRACT: *Lignin is a biopolymer usable in many ways once it has been separated and delignified from biomass. In this training report, delignification of coconut husk fibres is performed, with the aim of recovering isolated lignin. In order to do so, different processes are carried out (autohydrolysis, dilute acid, organosolv and soda pulping treatments). The obtained lignin is characterised afterwards through Fourier transform infrared (FTIR), 1H and 13C nuclear magnetic resonance (NMR) in order to check lignin presence and quality. Analyses show that lignin is indeed obtained in both experiments, though the yield is greater for the treatment with autohydrolysis. However, the global yield is quite low, adjustments of experimental parameters (time, temperature, ratio) shall be carried out.*

Keywords: Biomass, delignification, coconut husk, organosolv, autohydrolysis

1. INTRODUCTION

Coconut husk, a common and substantial part of biomass, is one of the main industrial and agricultural wastes in South Asia. Coconut husk fibres are a natural product that can be used to produce useful matter or energy.

The cell walls of coconut husks fibres are made of three biopolymers: lignin, cellulose and hemicellulose, and are naturally present on earth. They can be used to convert biomass into renewable energy or useful chemicals, which is part of a big challenge humanity has to overcome since fossil energies has become rarer.

The three biopolymers exhibit different properties. Cellulose is a crystalline polymer made up of only glucose. It hardly undergoes hydrolysis. Hemicelluloses, on the other hand, are amorphous polymers made of several saccharides (xylose, mannose, glucose, etc.) that can undergo hydrolysis. As it is made of different sugars, there is not one but several hemicellulose structures. Lignin is an amorphous polymer with an intricate structure made of three different motifs, bound to each other by specific linkages. Like hemicelluloses, a unique structure does not exist. Each of these motifs are labelled H, G and S as shown in Figure 1. As for biomass, cell walls of plant material are a mix of cellulose, hemicellulose and lignin. Lignin is the binder of cellulose and hemicellulose, as shown in Figure 2.

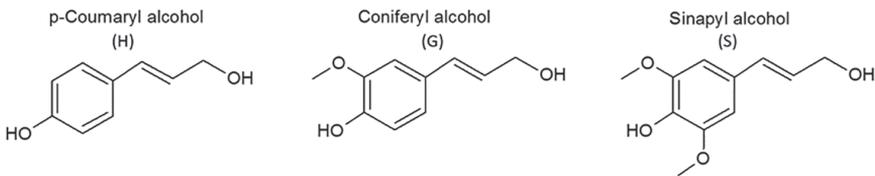


Figure 1: Lignin sub-units.

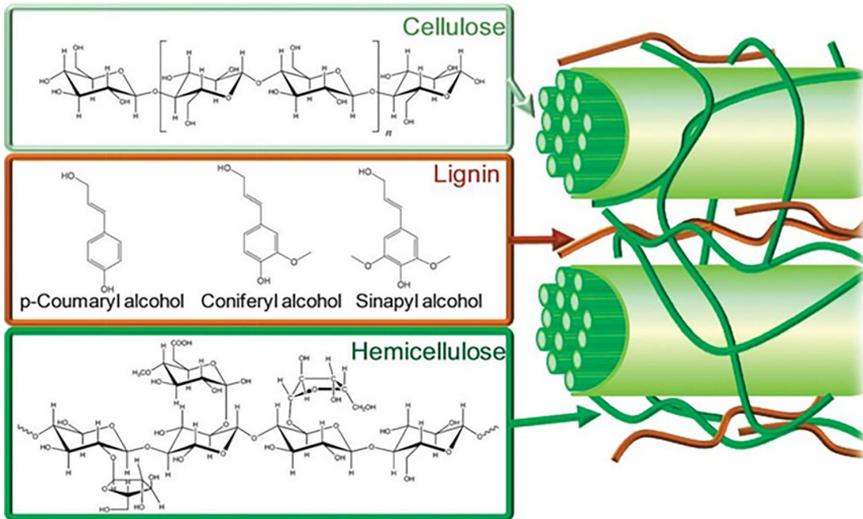


Figure 2: Biomass structure.¹

However, in the treatment of biomass, it is more convenient to use these three biomolecules when they are isolated as higher yield can be achieved if these three biomolecules are used separately. Therefore, several processes allowing separation of these three components have been found and studied.²

In this context, four different types of delignification processes will be performed to separate lignin from hemicellulose and cellulose. Eventually, obtained lignin will be characterised through nuclear magnetic resonance (NMR) (¹H and ¹³C) and Fourier transform infrared (FTIR) spectroscopy.

The global objective of this work as well as the numerous related studies, is to separate intricate natural polymer molecules, present in huge quantity on earth, in a renewable way, in order to turn them into useful products or energy, in the scope of developing sustainable chemistry. Coconut husk fibres is chosen for this work as it is known to be non-toxic, relatively easy to use chemically, rich in lignin, and stronger than other natural fibres found in biomass.

2. EXPERIMENTAL

2.1 Proximate Analysis

Coconut husks have been firstly characterised through simple proximate analysis. This analysis is useful to investigate the contents in coconut husks, such as biomass molecules content or ash and moisture contents.

In order to carry out these experiments, the traditional variety coconut husks (Malaysian Tall species) were collected in the state of Kedah, Malaysia. Coconut husks had to be ground using a blender (Waring commercial blender) and sifted with a 0.25 mm sieve. A powder was obtained and used in the experiments of this work. Each experiment is triplicated, and the average results are displayed.

2.2 Pre-treatment Processes

Common processes of delignification are sulfite, Kraft, soda and aqueous ethanol organosolv processes, steam explosion and enzyme.³ If lignin obtained through sulfite process can be used as dispersant, emulsifier, or ion-exchange resin and Kraft lignin as lignin for biofuel production, it would be interesting to develop organosolv process.⁴⁻⁶

However, considering a major drawback can happen on organosolv-treated (and soda-treated) lignins, namely degradation of hemicelluloses into undesired products such as furfural or hydroxymethylfurfural (HMF), a two-step pre-treatment process is usually considered to be a good option. In order to do so, autohydrolysis (also called water treatment), or dilute acid treatment, will be performed prior to organosolv and soda pulping processes.

2.2.1 Autohydrolysis

Autohydrolysis is known to be the most environment-friendly process as it uses only water. The principle is based on the cleavage of glycosidic bonds in hemicelluloses (ether linkage between two molecules of glucose). Furthermore, the splitting will generate hemicellulose by-products able to dissolve in the hydrolysis solution since the degree of polymerisation has been reduced. On the other hand, lignin will undergo some fragmentation but will remain insoluble in the hydrolysis solution.

The autohydrolysis occurs in a 500 ml reactor at pressure value 10–12 bars where a ratio of 1:15 (solid:liquid) is heated at 150°C for about 6 h at 600 rpm. Solid corresponds to blended and sieved coconut husks powder. Liquid is plain distilled water. The reactor used is a KeXing Instruments TGYF, a miniature desktop high-pressure reactor. The same reactor is used for each experiment.

2.2.2 Dilute acid treatment

Dilute acid treatment is another way of hydrolysing hemicellulose by breaking polymeric bonds. Usually, inorganic acids, H_2SO_4 or HCl, are used in low concentration. Indeed, high concentrations of acids are known to produce undesirable HMF and generate corrosion problems.

A solid:liquid ratio of 1:20 is stirred for 24 h using sulfuric acid as the solvent (0.9% H_2SO_4 wt.). The mixture is then heated to 170°C for 2 min. The obtained pulp is filtrated, and oven dried at 50°C.

After the pre-treatment operation, a phase mixture will be obtained. The liquid (the filtrate) does contain sugars that could be analysed, but these analyses will not be part of this work. The precipitate, will be recovered, washed with warm water (80°C, around 800 ml) and dried at 50°C. In order to see if lignin has been hydrolysed during the process, a Klason lignin experiment (such as done in proximate analysis) will be performed. The remaining pulp will represent the solid part in organosolv and Soda pulping processes.

2.3 Delignification Processes

2.3.1 Organosolv pre-treatment

Organosolv process entails the use of an aqueous alcohol solution that degrades lignin under high temperature. Classic solvents such as methanol, ethanol, butanol, ethylene glycol or acetic acid can be used in this process. Ethanol is the most convenient, because it removes lignin from the precipitate by making it soluble in the solvent and it can be recycled using flash distillation.

Therefore, in this experiment, solvent is ethanol (used in an aqueous mixture of 65% EtOH, 35% H₂O v/v). Solid:liquid ratio is 1:10, the mixture is put in the reactor, heated at 190°C for 1 h and stirred at 800 rpm. The liquid part (liquor) is recovered, while the solid part, where hemicellulose and lignin contents have been lowered will not be used in this work but can undergo other pre-treatment with the aim of biofuel production.

The liquor is then filtrated and washed with 150 ml of aqueous ethanol (80% EtOH v/v). The filtrate is mixed with three volumes of distilled water of the liquid volume obtained, so as to form a precipitate, and the mixture is then stored in a fridge for 3 days. The mixture precipitate is eventually recover through centrifuged (3500 rpm, 10 min) and dried at 50°C for overnight.

2.3.2 Soda pre-treatment

Soda pre-treatment is another way to extract lignin. It uses an alkaline solution of 30% (w/v) NaOH. Sodium hydroxide pellets are used and dissolved in distilled water. Solid to liquid ratio is 1:15, temperature is 170°C, and time is 3 h. The mixture is put in the same 500 ml reactor as before at pressure 10–12 bars.

After pre-treatment, black liquor obtained is filtrated and the liquid part is recovered. It is acidified with H₂SO₄ (20% wt) until pH 2 is reached. A precipitate is formed.

The formed precipitate is recovered through centrifugation same as organosolv treatment. The solid is then washed with 150 ml acidic distilled water (pH = 2 acidified with H₂SO₄ 20%), gravity filtered and eventually oven dried at 50°C for overnight.

2.3.3 Lignin recovery

The lignin from organosolv and Soda processes will then be calculated using this formula in order to obtain the percentage yield of lignin recovery:

$$\text{Yield \%} = \frac{\text{Mass of lignin recovered (g)}}{\text{Mass of coconut husk powder (g)}} \times 100 \quad (1)$$

An overview of every method done in this work is given in Figure 3.

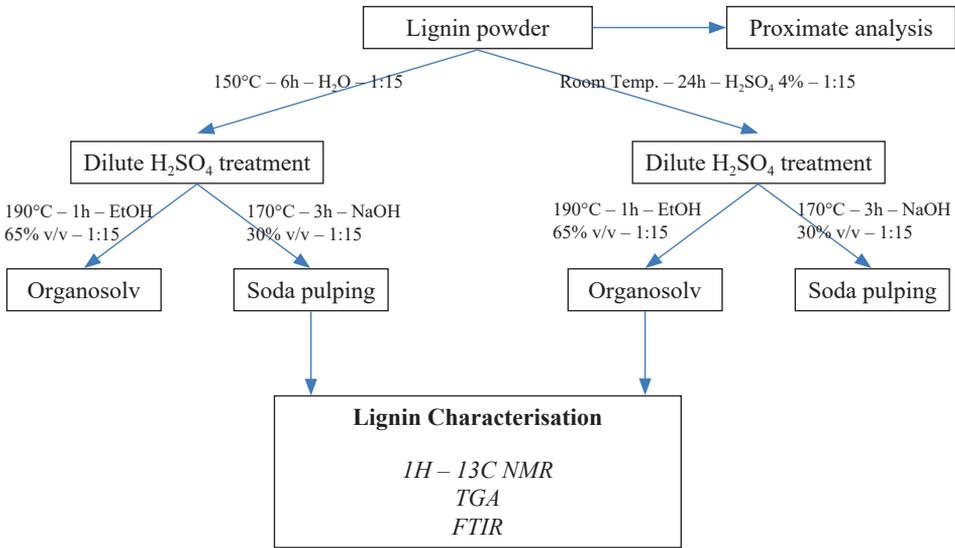


Figure 3: Overview of experimental procedure.

2.4 Characterisation of Lignin

2.4.1 Severity factor

Severity factor R_0 , obtained through the following formula leads to the severity of the process as shown below.⁷ It is used to describe the treatment conditions and it informs on the harshness of the process.

$$\log(R_0) = \log\left[t \times \left(e^{\frac{T - T_{ref}}{14.7}}\right)\right] \quad (2)$$

In the equation, t is time (min), T is temperature (°C) and the reference temperature T_{ref} is 100°C. The pH is obtained at the end of each experiment through the liquid obtained after filtration (liquor). Its measure is done through a pH-meter (Sigma-Aldrich pH 211).

2.4.2 FTIR spectroscopy

The obtained lignin is analysed with an FTIR spectrophotometer in a direct transmittance mode using Perkin Elmer model System 2000 instrument at the region between 4000 cm^{-1} and 600 cm^{-1} with a resolution of 4 cm^{-1} , and 100 scans are done.

2.4.3 NMR spectroscopy

Lignin will have to undergo an acetylation reaction before NMR analysis, in order to make it soluble in DMSO- δ_6 . The purpose is to transform -OH groups to acetyl groups. The procedure follows the method outlined by Sa'don et al.⁸

An amount of 500 mg lignin is mixed with 7.5 ml of a 1:1 pyridine/acetic anhydride mixture and stirred for 24 h at room temperature. Then, 75 ml HCl 1% (v/v) are added dropwise to the mixture. A precipitate is formed, filtered and neutralised with an excess of distilled water. The precipitate is then dried in a 50°C oven for overnight and is eventually ready for NMR analysis.

The spectra are obtained with a Bruker Avance 500 NMR spectrometer in liquid state (DMSO- δ_6) using a standard pulse program. Quantitative NMR spectra were attained using an inverse-gated decoupling (Waltz-16) pulse sequence to avoid Nuclear Overhauser Effect.

3. RESULTS AND DISCUSSION

3.1 Proximate Analysis Results

Proximate analysis results from this experiment are correlated with the previous studies as shown in Table 1. Since the biomass has a moisture content less than 30%, it is suitable for thermochemical conversion.⁹ Proximate analysis thus confirms that coconut husks can be used in the pre-treatment processes. Besides, it confirms that coconut husk has a rather low ash content and a high lignin content for non-woody biomass.

Table 1: Proximate analysis of coconut husk.

	This work	Aziz et al. ¹¹	Lertwattanak and Suntijitto ¹⁰
Moisture content (%)	11.67	13.3	NA
Ash content (%)	2.5	2.1	2.65
Extractives (%)	12.1	10.62	NA
Klason lignin (%)	34.4	32.1	29.8

3.2 Lignin Recovery

It has been found that post autohydrolysis lignin had a Klason lignin content of 45.5%. This is an expected result. Autohydrolysis process breaks bonds in lignin structure, yielding more lignin fragments, hence increasing the percentage of lignin content.

After soda treatment, more pure lignin was eventually obtained. Lignin coming from autohydrolysis-soda was obtained with a yield of 9.05%. Lignin from dilute acid-soda was obtained with a yield of 8.54%. These yields are rather low compared to Aziz et al. results, that were closer to 30% yields.¹¹ A higher severity for water treatment can explain why the Autohydrolysis process gave a slightly higher yield than the sulfuric acid process.

The small difference between the two yields indicates that both processes give almost the same amount of lignin, but it is not an indicator of lignin quality.

3.3 Lignin Characterisation

3.3.1 Severity factor

In Table 2, the pH decrease or increase for respectively dilute H₂SO₄ and soda treatments were expected, for their use directly an acid and a base. However, pH decreases also in organosolv and water treatment processes. It can be explained by the fact that H₃O⁺ ions are created in the medium through high temperature water autoionisation. These hydronium ions will act as acid catalysts that will hydrolyse hemicelluloses polysaccharides into monomers. From this reaction, acids will be produced (mainly acetic acid) and will be responsible for pH decrease. As for organosolv process, it also generates acetic acid through hemicellulose that helps acid hydrolysis and creation of phenolic hydroxyl groups, hence decreases the pH.¹²

Table 2: Severity factor of different pre-treatment processes.

Process	t (min)	T (°C)	pH	log (R ₀)
Autohydrolysis	360	150	4.2	4.03
Dilute H ₂ SO ₄	2	170	1.6	2.36
Organosolv	60	190	4.3	4.43
Soda pulping	180	170	13.3	4.32

About the different severity factors (in Table 2), the most severe process (autohydrolysis-soda) yielded a slightly higher yield. The same characteristic was observed in their organosolv treated biomass by Hussin et al.⁷

Besides, lignin treated with dilute acid underwent a less severe process than lignin treated with autohydrolysis, which could create differences between both lignin structures, as the reaction is different.

3.3.2 FTIR analysis

The obtained FTIR spectrum is displayed in Figure 4. This spectrum was interpreted on the IR tables and on the other hand thanks to previous studies relevant on oil palm fronds biomass treated with organosolv or soda process.^{8,13–15} The assignments for the IR bands are reported in Table 3.

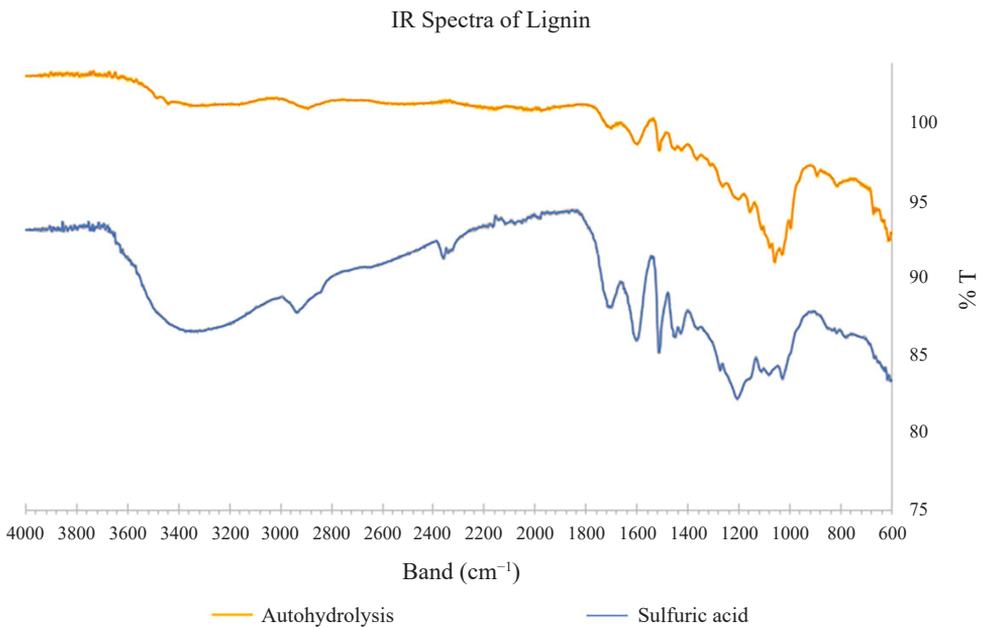


Figure 4: IR spectra of autohydrolysis and sulfuric acid treated lignins.

Table 3: Assignment of IR bands of soda treated lignin.

Band (cm ⁻¹)		Assignment
Autohydrolysis	Dilute acid	
3326	3330	O-H stretching
2892	2936	Aliphatic (CH ₂ and CH stretching)
1700	1705	C=O stretching
1600	1602	C=C stretching from aromatic ring
1365	1362	O-H bending in phenolic groups
1312	–	C-O stretching (syringyl unit)
1201	1206	C-O-H in guaiacyl and syringyl units
1157	1161	Typical H-G-S absorption
1111	1112	Ar-C-H deformation in syringyl unit
1030	1029	C-O-C in guaiacyl unit
813	816	C-H (syringyl unit)

In the band assignments, 3330 cm⁻¹ is the typical intense and broad band due to -OH stretching group. Other alcohol bands, 1200 cm⁻¹ and 1360 cm⁻¹ are typical phenolic groups (as expected 1200 cm⁻¹ and 1310–1410 cm⁻¹). It can be seen that 3330 cm⁻¹ and 1200 cm⁻¹ peaks are more intense for H₂SO₄ treatment, which can mean a more severe process generates less alcohol groups. It could be showed a greater presence of xylose (a sugar containing 4 -OH groups) is verified when the severity factor is lower.¹⁶

The peak at 1030 cm⁻¹ (1000–1050 cm⁻¹) and aliphatic peaks at around 2900 cm⁻¹ and 815 cm⁻¹ were expected since lignin structure does contain methoxy groups and carbon chains.

Aromatic rings presence is confirmed with 1600 cm⁻¹ and 1111 cm⁻¹ bands, while carbonyl group is verified at 1705 cm⁻¹ (as expected between 1705 cm⁻¹ and 1725 cm⁻¹).

At 1155 cm⁻¹ and 1312 cm⁻¹ bands are also typical bands present in lignin that confirm the presence of purified lignin in the sample. From the previous papers, it revealed that S units (1312 cm⁻¹, 1102 cm⁻¹, 813 cm⁻¹) and G units (1200 cm⁻¹, 1028 cm⁻¹) are present in the lignin structure.

3.3.3 NMR analysis

Main peaks in ¹³C spectrum are identified and illustrated in Figure 5. In addition, an aromatic equivalence has been calculated as summarised in Table 4. Indeed, previous studies have shown the region between 102 ppm and 162 ppm corresponds

to an aromatic ring. This aromatic ring is made of 6 aromatic carbons bound to 0.12 vinylic carbons (from the unsaturated side chain of coniferic and coumaric moieties).^{15,16} This aromatic ring can be set as the reference and is the equivalent of 6.12 carbons.

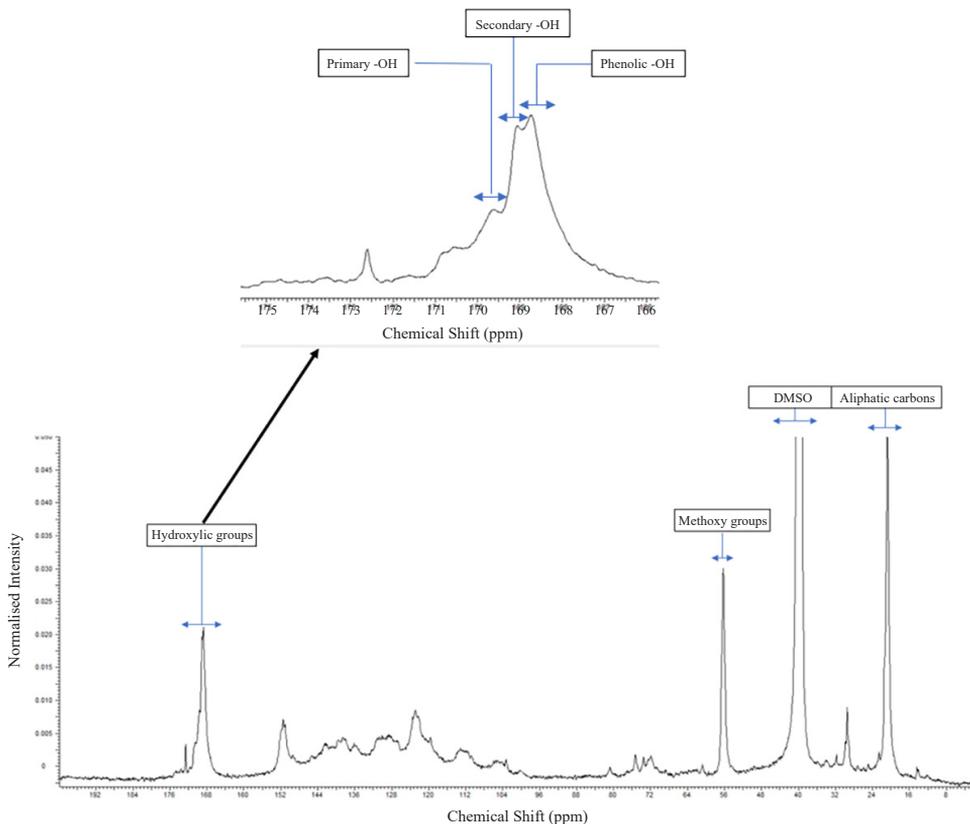


Figure 5: Assignment of ¹³C NMR spectrum of autohydrolysis + soda treated lignin.

Therefore, the integration value between 102 ppm and 162 ppm, divided by 6.12 is the integration value of one aromatic benzene ring. In our case, the integration value is 234. Thus, 38.2 as integration value corresponds to one Ar. The greater the value, the greater the presence of the group in the lignin structure.

Table 4 shows that phenolic groups are more common than aliphatic alcohols in soda lignin. This is in accordance in previous study showed that soda and Kraft lignins are rich in phenolic groups compared to organosolv lignin which is rather poor in phenolic groups as described by Hussin et al.¹⁴ This is probably due to soda lignin that favours aryl-ether cleavage during the reaction.

Table 4: Assignment of ^{13}C NMR Spectroscopy.

Group	Range (ppm)	Integral (mm)	Value/Ar
Primary -OH	171–172	5	0.13
Secondary -OH	169–170	11	0.28
Phenolic -OH	166–169	18	0.47
Methoxy -O-Me	56-59	43	1.12
DMSO	40	/	/
Aliphatic carbon	18-22	/	/

4. CONCLUSION

It is concluded that lignin can be isolated from coconut husks. Two-step pre-treatment (autohydrolysis-Soda treatments and dilute H_2SO_4 -Soda treatments) yielded a rather pure lignin, whose structure contains guaiacyl and syringyl units, and a great quantity of phenolic groups. The general output of lignin recovery is less than 10%, which is a problem if delignification of coconut husks had to be processed on an industrial scale. Considering previous studies, it would be interesting to adjust experimental conditions or changes of parameters in order to increase yield of lignin. Autohydrolysis and organosolv lignin are two environmental-friendly processes, the combination of those two for efficient lignin recovery is of interest.

5. ACKNOWLEDGEMENTS

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