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SYNTHETIC WOOD ELABORATION FROM DEPOLYMERIZE LIGNIN BY UV IRRADIATION, EXTRACTED FROM LOW RANK COAL

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ABSTRACT

This research purpose is to determine ideal conditions for lignin depolymerization so its reactivity may be increased and later to develop a process with this lignin to get an industrial synthetic wood with good mechanical properties. Process was made in three stages. First stage consisted in lignin extraction by Sosa Method and its subsequent characterization by IR, UV, elemental analysis and solubility. Second stage consisted in lignin depolymerization by UV irradiation and later a hydroxymethylation with formaldehyde was made. Third stage was the wood product elaboration with modified lignin and melamine-formaldehyde using rice husk as natural fiber. In second stage, optimum depolymerization time by UV irradiation was found, it was 12 h. With hydroxymethylation process, in depolymerized lignin oxygen level was increased to 32.1 % so more reactive sites that became methylene bridges between lignin and resin were generated. Polymerization reaction submitted to autoclave (121°C and 15 psi) developed a synthetic wood product with better mechanical properties.

KEYWORDS: Depolymerization, Lignin, Low Rank Coal, Synthetic Wood

INTRODUCTION

Due to indiscriminate use forests logging is necessary to propose alternatives so it can be reduced. Gaitán et al. (2006) posed the possibility to manufacture synthetic wood starting with reaction between phenol-formaldehyde resin and extracted lignin from coal peat using sawdust and paper as natural fiber. They found that Sosa extraction method yielded best efficiency for lignin production than Fukushina and sulfate methods.

Lignin reactivity in natural condition is too low. El Mansouri (2006) found that its hydroxymethylation with formaldehyde increased its reactivity. This procedure joined with lignin depolymerization with UV, potentiated its reactivity as posed by Gordilllo and Vega (2010). Besides, they found that the best resin to couple with lignin was melamine-formaldehyde.

This research aims to find the optimal exposure time with UV irradiation to generate a more reactive lignin, as well as improve the reaction conditions in the elaboration of the final product.

MATERIALS AND METHODS

First Stage

Coal characterization, lignin extraction and its characterization were made in first stage.

Three coal samples were analyzed. They came from Paipa – Boyacá and were found 50 m deep. They were crushed and grinded to 106 µm. After, they were characterized by next analysis according to ASTM D 3172

(% moisture-ASTM D 3173, % ash-ASTM D 3174, % volatile matter- ASTM D 3175), elemental analysis (% C, H, N, S, O) with the *FLASH 2000 Series CHNSO Automatic Elemental Analyzer of Thermo-scientific* and calorific power determination by *IKA C 2000 Basic calorimeter.*

Humic acids were extracted by Nagoya Method (Kuwatsuka, 1992) from 236.22 g of low rank coal. For lignin extraction, 202.54 g of low rank coal free of humic acids were used. It was made by Coal Sosa Standardized Method (Jiménez, J. et al., 2012). Obtained solution was purified adding H_2SO_4 98% drop by drop until gas production finished. It was necessary to let it rest by 12 hours. Lignin was separated by filtration with Whatman qualitative filter paper.

Lignin and standard sample (Kraft Lignin distributed by Sigma-Aldrich) were characterized by elemental analysis (%C, H, N, S, O) with the *FLASH 2000 Series CHNSO Automatic Elemental Analyzer of Thermo-scientific*, by UV spectroscopy with *UV-VISIBLE Perkín Elmer 35 Digital* with rank between 200-400nm equipment using a concentration of 0,016 mg/mL, by IR spectroscopy with IR spectrophotometer with *Shimadzu IR Affinity -1 Fourier Transformed* and finally by solubility (1 mg: 6 ml) using these solvents: NaOH 15%, H_2O, HCl 0.1 N, HCl 32%, Acetone, Isopropanol, Butanol, Allyl alcohol, Ethanol, Methanol, Ethyl acetate, Butyl acetate, THF and Glycerin.

Second Stage

Second stage was the lignin depolymerization by UV irradiation, and its hydroxymethylation with formaldehyde.

1 g of extracted lignin was deposited in each of 5 Petri Dish. Every dish was irradiated by UV for 10, 12, 14, 16 and 18 h respectively, using a 15 W TUV15 Germicidal Philips lamp with ozone filter. Depolymerized samples were immediately hydroximethylated with formaldehyde using El Mansouri Method (2006), changing agitation to 10 h. Product was then dried to 50 °C until a solid lignin was obtained. By elemental analysis (% C, H, N, S, O) was determined which sample coupled more oxygen amount. Later, depolymerization by 12h irradiation and hydroxymethylation was repeated with 5 g of extracted lignin. Results were demonstrated by IR spectroscopy.

Third Stage

Third stage was the elaboration of synthetic wood.

3 g of depolymerized and hydroximethylated lignin was mixed with 3g of sawdust and 6 g of melamine. Lately, mixture was heated to 120 °C and 7 ml of formaldehyde 37 % were added with constant stirring until a viscous paste was obtained. Paste was deposited inside of 2 mold and each one was compressed. The first one was dried for 24 h and 80 °C. The second was autoclaved to 15 psi and 121 °C for 3.5 h.

RESULTS AND ANALYSIS

First Stage

3 coal samples were characterized in order to know which one was a low rank coal. Table 1 shows results. Sample 3 was chosen because it had higher percentage of H, O, volatile matter and lower percentage of C and combustion heat.

Table 1: Characterization of the 3 coal samples

Analysis	Sample 1	Sample 2	Sample 3
%C	65.50	66.22	**62.38**
%H	4.59	4.40	**6.54**
%N	0.95	0.98	0.40
%S	0.80	0.73	0.83
%O	12.93	12.18	**17.15**
% Moisture	7.88	6.59	7.90
% Ashes	9.55	8.91	4.52
% Volatile matter	53.36	51.13	**74.38**
Combustion heat (J/g)	27,012	27,327	**26,665**

In order to get free impurity lignin extract, humic acids extraction must be done before. Since the lowest rank coal is sample 3, 236.22 g were taken to extract HA. HA extraction is made by their solubility in weak alkaline solution. Coal residue containing lignocellulosic extract is obtained on this way. A 14.26% of Humic Acids was obtained.

Lignin extraction is made by its solubility in strong basic medium. This process was made in high pressure (autoclave) in order to facilitate the dissolution. A lignocellulosic liqueur was obtained and purified by acid hydrolysis with H_2SO_4. An oxidation of oxygen bridges between lignin and carbohydrates happens.

$$H_2SO_{4(l)} + \text{Lig-O-Carbohydrate}_{(s)} \rightarrow SO_{2(g)} + \text{Lig-OH}_{(s)} + \text{HO-Carbohydrate}_{(ac)} \quad (1)$$

Carbohydrates joined to lignin are cellulose, hemicelluloses and starch. By acid hydrolysis they become sugars and they can be separated easily by solubility in water. Acid medium in solution helps lignin precipitation. The extracted lignin obtained was 28.02 % free of impurity.

Respect to characterization of extracted lignin and Standard Kraft lignin, in UV analysis peaks were found on 227 and 226 nm for standard. In IR analysis, results are shown on Table 2.

Table 2: Comparison between the IR Spectrums of Extracted Lignin and Standard Kraft Lignin

Assignment	Extracted Lignin (cm^{-1})	Standard Kraft Lignin (cm^{-1})
-OH intermolecularly associate stretch in polymers	3464	3448
CH_2 asymmetric stretching. O-CH_3 stretch (guaiacyl; syringyl)	2930	2940
CH_2 symmetric stretching O-CH_3 stretch (guaiacyl; syringyl)	2850	2845
C=O stretch	2380	2385
Aromatic fingerprint vibrations	2000-1750	2000-1750
C=O stretch - cyclohexanones. O=C-C=C stretch - arylketones	1700-1730	1690
O=C-C=C stretch - 1,2 and 1,4 quinones	1680	1660
Ar-C=C stretch	1625	1597
C=C aromatic ring. CH_2-Ar stretch	1500-1400	1500-1400
Ar-O-C asymmetric stretching. (guaiacyl; syringyl; 4-hydroxiphenyl).	1246	1265
C-O stretch - phenol (guaiacyl)	1200	1219
C-O asymmetric stretching – ether.	1120	1138

Ar-H in-plane rocking vibration		
Ar-O-C symmetric stretch (guaiacyl; syringyl; 4-hydroxiphenyl).	1045	1043
Ar-H out of plane rocking vibration	883-900	865-850

In a solubility analysis for the two different samples, similar results were found in different solvents. These results show how similar functional groups are in every sample. It was found that Standard Kraft lignin sample was more polar due to incorporation of SO_3 coming from Na_2S that was used as solvent in extraction process.

Finally, elemental analysis proved that both samples had similar composition. On Table 3, results show that % of S and O from standard lignin are greater than % of S and O from experimental sample proving former hypothesis.

Table 3: Elemental Characterization for Extracted Lignin and Standard Kraft Lignin

Analysis	*Extracted Lignin*	*Standard Kraft Lignin*
%C	57.34	46.47
%H	4.90	4.62
%N	1.13	0.06
%S	1.95	3.27
%O	29.27	32.70

Second Stage

For synthetic wood elaboration, extracted lignin must be coupled with synthetic resin and a natural fiber. Since extracted lignin is not very reactive, it is necessary to modified it structurally. In order to get it, its tridimensional structure must be fragmented so is possible to get more interaction points between lignin and synthetic resin. On this stage, process is made by UV irradiation.

Lignin depolymerization obtained by UV irradiation, generate on its structure free radicals due to homolytic rupture among their phenylpropanoids unions. Lignin irradiation time is proportional to produced fragments. The key is to find the exposition right time to produce lignin with enough depolymerization degree in order to increase its reactivity. Gordillo and Vega (2010) analyzed the reactivity increase with different exposition time to 15 watts UV beam (6, 12, 24, 36, 48 and 60 hours). Right time was found at 12 hours. 10, 12, 14, 16 and 18 hours were worked in this project.

Generation of high reactivity points due to lignin fragmentation let lignin to get more functional groups on its molecular structure so it becomes more reactive, then, when lignin reacts with synthetic resin more union points can be generated and a better coupling and compaction process can be made. One of lignin structural modifications that let to increase its reactivity is the hydroxymethylation with formaldehyde (El Mansouri, 2006). Marton et al. (1963) have found that for this modification the presumable reaction is the Lederer-Manasse's, where hydroxymethyl groups are introduced on active position of aromatic ring. These groups help polymerization reactions due to methylenic bridges formation between lignin and synthetic resin. By means of this reaction, oxygen is bonded with high reactivity points generated by depolymerization. It lets quantify the oxygen increment in lignin by elemental analysis. Mixture that shows more coupled oxygen will be the one with optimal UV irradiation time. Hydroxymethylation reaction must be performed immediately after depolymerization with UV since lignin fragments react spontaneously. It decreases the amount of generated reactive sites as the amount of hydroxymethyl groups that could be incorporated generating a less reactive lignin. Lignin sample that had more oxygen coupling was the exposed by 12 hours to UV beam (table 4). It was noted that oxygen increase relation with to unmodified lignin (table 3) was 32.1 %.

Table 4: Elemental Analysis of Lignin Samples with Different Exposure Times to UV Radiation

Analysis	*10h*	*12h*	*14h*	*16h*	*18h*
%C	20.89	23.60	34.02	16.89	23.87
%H	3.60	3.83	3.83	4.63	3.64
%N	0.30	0.35	0.37	0.26	0.36
%S	0.07	0.00	0.17	0.00	0.00
%O	54.06	**61.37**	45.31	54.26	41.21

Increase of characteristic bands of OH groups on depolymerized lignin by 12 hours with UV was proved by IR analysis.

Third Stage

Gordillo and Vega (2010) found that melamine-formaldehyde presented better mechanical properties. It due to melamine has three amine groups that are easily condensable. That is the reason because this project was worked with this resin so it was possible to coupled with modified lignin.

Modified lignin hydroxymethyl groups are condensed with melamine amine groups releasing water and creating methylenic bridges that give compaction to final product. On this reaction rice husk works as junction agent due to possess a great amount of siloxanes that improve interaction between lignin and resin improving mechanical properties of final product.

Final products are shown on figure 1. Obtained product by autoclave process (figure. 1b) shows a better mechanical resistance, better cohesion, great impermeability, less fragility and better organoleptic properties.

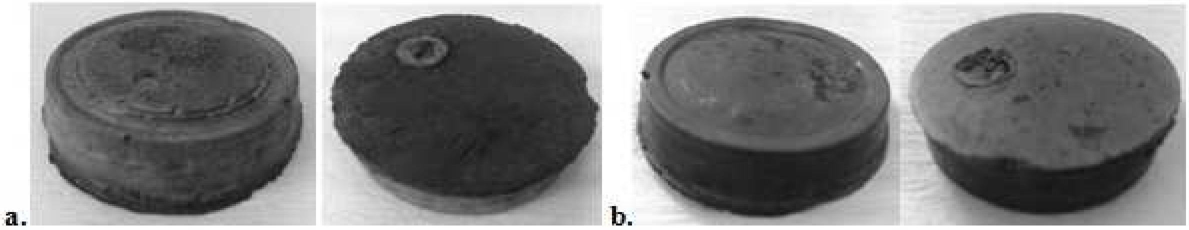

Figure 1: Final Products, Generated after Modified Lignin. a. Generated Product by Drying to 80 °C for 24 Hours. b. Generated Product by Autoclave for 3.5 Hours

CONCLUSIONS

Extracted and purified lignin shared structural features with Kraft Lignin standard sample except for SO_3 groups.

Optimal depolymerization time for lignin irradiation was 12 hours. With this sample, we obtained an increase of reactivity of 32.1% after hydroxymethylation.

Autoclaving process in the polymerization reaction generated an improvement in the mechanical properties of the wood product as well as reducing the reaction time.

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