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DEPOLYMERIZATION OF LIGNIN EXTRACTED FROM LOW-RANGE CARBON BY THE UV/TIO2 RADIATION METHOD AND ITS USE IN THE ELABORATION OF SYNTHETIC WOOD BOARDS

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ABSTRACT

On this research, lignin depolymerization by ultraviolet radiation and catalyzed by titanium dioxide was studied and later it was used as a copolymer in making boards with rice husks. Lignin was extracted from a low-rank coal sample coming from Paipa-Boyacá using Sosa Method. Depolymerizations on samples of 100 ml 50 mg/L lignin for 0, 2, 6, 10 hours and catalyst amounts in ratios 1:1; 1: 3.3; 1: 6.6; 1:10 lignin and TiO_2 respectively were standardized by irradiation with 45W UV light. Results allowed selecting optimal values of 6 hours of irradiation and the catalyst in the proportion of 1 lignin by 3.3 of TiO2 for depolymerization. It produced 22% degradation on lignin. Later, depolymerized lignin was activated by the hydroxymethylation reaction with formaldehyde. For boards, preparation components were mixed in proportions of 60% rice husk, 7.4% lignin, 14.9% melamine and 17.7% formaldehyde. The mixture was heated to 100 ° C for one hour in molds. Three boards were produced with the above-mentioned proportions and with following characteristics: board 1 was made with unmilled rice husk and Kraft lignin (Sigma-Aldrich); board 2 was made with milled rice husk and Kraft lignin and board 3 was made with milled rice husk and activated lignin. All boards were subjected to mechanical tests of bending, compression, and traction and water absorption. Board 2 showed the most suitable results according to ASTM D 143 norms.

KEYWORDS: *Aglomerated, Depolymerization, Lignin, Low-Rank Coal, Rice Husks*

INTRODUCTION

Currently, particle board's manufactures involve as raw materials wood waste and utilization of some kind of low durability small trees. Other types of raw materials that have been used are rice husks and sugar cane bagasse. Lignocellulosic characteristics of waste materials are used due to resin condensation produce a product with excellent properties for remanufacturing systems (1).

The most resin types used are phenol formaldehyde (PF), urea formaldehyde (UF) and melanin formaldehyde (MF). On pf resin has been investigated the partial substitution of phenol by lignin, so residual lignin of paper industry can be used and to diminish phenol amount due to its toxicity. Implementation of unmodified lignin instead of resin does not get good results. It is what El Monsuri found (2). So, different methods have been developed in order to modify the lignin

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structure. Usually, two stages have been developed. First, a depolymerization that can be made by acid hydrolysis, basic hydrolysis, heterogeneous catalysis, homogeneous catalysis, hydrogenation (3), enzymatic degradation (4), photocatalysis (4-9). After depolymerization, phenolation, demethylation or hydroxymethylation reactions could be performed so active sites on aromatic rings could be increased (10).

Lignin is an aromatic polymer, amorphous and highly concentrates. It is found in the wood between 20 to 30 % in weight. It gives to superior plants hardness, flexibility and protection against harmful agents (11). Lignin is found in high proportion in lowrank coal structure as lignite and peat. Lignin can be extracted directly by mechanical and chemical process from raw materials like wood, coal, and pulp coming from wood after paper manufacturing process (3,8). Is a risky possibility that lignin can be structurally modified during the extraction process.

The main purpose of this research is to study lignin depolymerization by UV radiation catalyzed with titanium dioxide so it can be used later as the copolymer in manufacturing synthetic wood boards. In order to get the main goal in this research, specific steps were planned as coal (from Paipa – Boyaca) characterization, chemical lignin extraction and evaluation of depolymerization yielding of black liqueur lignin and purified lignin. Lately, lignin hydroxymetylation and depolymerization process were performed so synthetic wood using lignin, melanin, formaldehyde and rice husks could be made. Finally, flexion, traction, compression and water absorption tests of the final product (synthetic wood)were performed so they can be compared with ASTM standards.

This research has been planned to be developed in three stages. On first stage, coal samples were analyzed to select the best one for the research and later lignin is extracted. On stage 2 lignin was quantified, depolymerization method was evaluated and lignin was depolymerized. On stage 3 board manufacturing was made. Obtained synthetic wood physical properties as flexion, compression, and torsion and water absorption were compared with ASTM standards. (ASTM D 143 standard)

METHODOLOGY

Four samples were analyzed. They came from a coal mine localized on Paipa-Boyacá. Sampling was made between 3 and 5 meters depth. Each sample was analyzed by proximate analysis. Moisture, ash, volatile matter and fixed carbon were determined as calorific power. In order to extract lignin, sample 1 was selected since it had optimum physical and chemical conditions.

Lignin Extraction

100 g of coal sample one was taken. Humic acids were extracted by shaking it during 12 hours and using NaOH 0.25 N. Lignin was extracted from coal without humic acids by Sosa Method were black liqueur was obtained (solubilized lignin in basic medium). For its extraction from solid H_2SO_4 30 % was used until pH 2 were reached. Finally, lignin was characterized by UV spectroscopy (solubilized in NaOH 0.5 N) and FTIR (KBr tablet).

Lignin Quantification by UV Spectrophotometer

Starting from purified lignin to pH 2 a calibration curve in 237 nm was made. The standard solution was prepared to dilute 25.3 mg of lignin in 5 ml of NaOH 15 % and to dilute to 500 ml. starting with this solution, 6 dilutions for 7 points on the curve. Calibration curve let quantified lignin amount in black liqueur and in that way to know the whole lignin without to precipitate it. To quantified extracted lignin from black liqueur on the direct way, a dilution by 5000

factor was prepared. Solutions were measured in UV-1800 UV-VIS spectrophotometer equipment.

Depolymerization and Hydroxymethylation

In order to evaluate and standardize Depolymerization method, 100 ml of 50 mg/l lignin samples were irradiated with 45 W UV beam during 2, 6 and 10 hours and catalyst amounts were added in proportions of 1:0, 1:1, 1:3.3, 1:6.6 and 1:10 g lignin and titanium dioxide respectively. In this way, an experimental design was made with 20 samples. Once radiation was finished, each sample was analyzed in UV spectrophotometer to 237 nm. Absorbance decrease is related to lignin depolymerization. Samples data were registered in Stat graphics Multifactorial Analysis software so optimal values in irradiation, time and catalyst amount could be selected. Selected values were applied to lignin (black liqueur) to depolymerize it. Depolymerized lignin was hydroxymethylated by addition of 0.5 of formaldehyde for each gr of lignin and pH 12 and reflux by 10 hours.

Boards Manufacturing

Inboard manufacturing process, components were mixed as follows: 60% of rice husk, 7.4 % lignin, 14.0 % melanin and 17.7% formaldehyde in a mold. The mixture was placed in the oven by 1 hour and 100 °C of temperature. 3 boards were manufactured with proportions already named and next characteristics: board 1 (CNMLK) was manufactured with no milled rice husk and lignin Kraft (Sigma-Aldrich). Board 2 (CMLK) was manufactured with milled rice husk and lignin Kraft. Board 3 (CMLP) was manufactured with milled rice husk and depolymerized and hydroxymethylated lignin. Boards were cut in accordance with ASTM D 143 standards and later submitted to mechanical tests as flexion, compression, traction and water absorption.

RESULTS AND DISCUSSIONS

Coal Classification

Proximate analysis (chart 1) and caloric power (chart 2) results for four coal samples let us classify them by rank in accordance with ASTM standards. Sample 1 and 2 were classified as lignite and samples 3 and 4 were classified as sub-bituminous. Sample 1 was selected as the best for this project since its values are: moisture 24.7 %, ashes 11.7 %, fixed carbon 7.3 %, Volatile matter 56.03 % calorific power is 15.580 J/g. These results show that this sample has lower carbonification index, so higher organic matter content without to degrade where lignin is.

Table 1: Proximate Analysis for Four Coal Samples

Sample	Humidity %	Ash %	Volatil Matter %	Fixed coal %
1	24,7026	11,7213	56,2643	7,3119
2	27,3151	9,1751	47,5993	15,9104
3	11,3707	14,7513	63,1027	10,7753
4	13,5326	8,0826	58,4545	19,9303

Table 2: Calorific Analysis for Four Coal Samples

Sample	Weight (g)	Combustion Heat (J/g)
Benzoic acid	0,50000	26091
1	0,67637	**15580**
2	0,35795	19905
3	0,49660	22719
4	0,50698	24887

Lignin Extraction

Extraction made in basic medium (NaOH) 0.25 N with 12 hours of agitation using coal sample 1 produces 17.8 % of humic acids and a 63 % of lignin indicating high lignin content and approving the good election of coal sample.
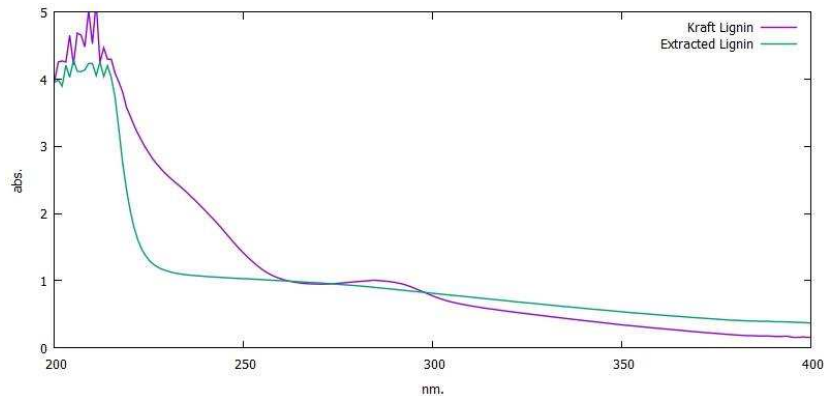

Figure 1: Extracted Lignin from Coal Sample 1 (Purple Line), Kraft Lignin (Sigma-Aldrich)(Green Line)

UV spectrums let to compare extracted lignin from coal with Kraft lignin standard. Shown peaks on Kraft lignin UV spectrum (figure 1) around 203 nm corresponds to unsaturated chains portions while absorbance around 280 nm correspond to hydroxyl phenol groups non-conjugates and aromatic rings (12). Shoulder between 240 and 290 nm correspond to aromatic or unsaturated compounds with quinone and/or ketone conjugation (13). On extracted lignin from coal UV spectrum (figure 1). Absorbance decrease is noted from 220 nm to 290 nm compared with a standard sample. It indicates a notable decrease of phenolic groups choosing that lignin has gone through humification process due to temperature conditions and high pressure that coal has been suffering during the carbonification process. As a result of the process, extracted lignin from coal is structurally different to any extracted lignin from the fresh vegetable material. These structural changes decrease lignin reactivity toward melanin and formaldehyde so it is justified to make hydroxymethylation reaction. With FTIR spectrophotometry (figure 2) similar peaks were identified in both samples, so is possible to say that extracted substance from coal has functional groups as Kraft sample lignin. Outstanding peaks are compared in table 3.
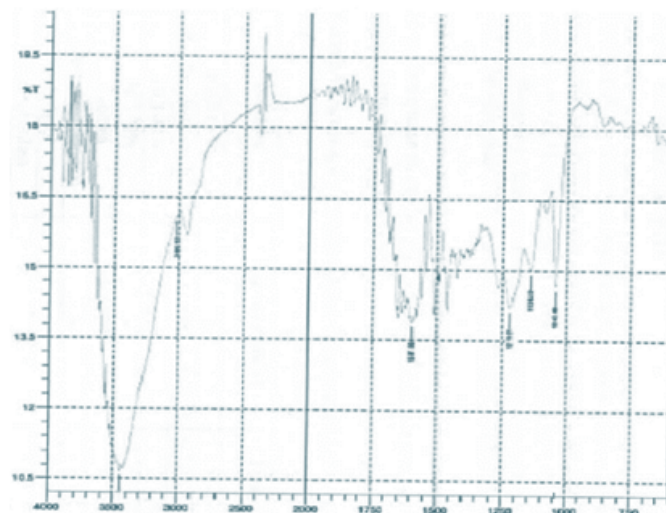

Figure 2: Lignin FTIR Spectra. (Left-Green) Lignin Extracted from Coal. (Right-blue) Kraft Lignin

Table 3: Kraft Lignin Outstanding Peaks and Coal (Sample 1) Extracted Lignin

Functional Groups	Streching	Peaks (cm^{-1}) Kraft Lignin	Peaks (cm^{-1}) Extracted Lignin
Alcohol	-OH	3411	3400
Carboxílic acid	-C(=O)-OH	3411	3400
Aromátic	-C=C-C=C-	3056	3001
Alkanes	-CH	2917	2900
Carboxilic acid derivates	-C(=O)-OH	2380	2380
Benzene tracks	-C=C-C=C-	2000-1750	2000-1750
Éthers	C-O-C	1503	1500
Carboxílic acid	-C(=O)-OH	1278	1226
Carboxilic acid derivates	C=O	1715	1720
Aromátic	-C=C-C=C-		867
halide	C-X	620	

Lignin Quantification by UV Spectrophotometry

Calibration curve made shows a good linear correlation as it is possible to see on figure 3. It indicates that quantification by this method is possible. Predicted yield by this method was 55.7 %, minor valued compared with experimental valued of 63.7 %. A difference could be due to interference in absorption in 237 nm by oligosaccharides and soluble lignin (14).
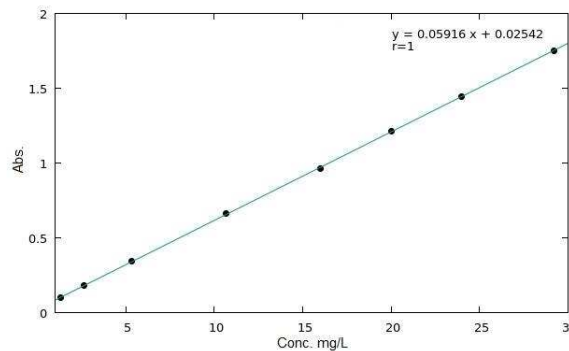

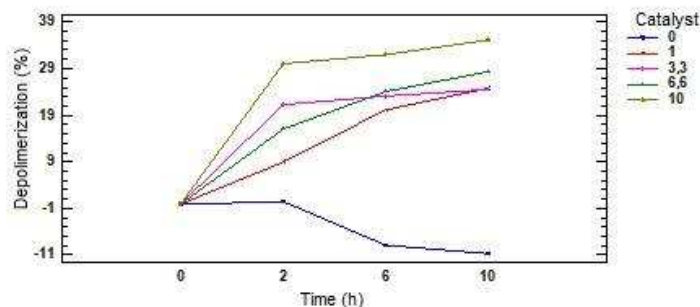
Figure 3: Lignin Calibration Curve in 237 nm

Figure 4: Interaction Chart of the Multivariate Analysis ANOVA

Method Standardization by Depolymerization UV/TiO$_2$

Depolymerization by photocatalysis was made by spectrophotometry UV. Positive variable exit for depolymerization is the decrease in absorbance since it is associated with chromospheres degradation contents in lignin (14). ANOVA statistic analysis yield $p<0.05$ values for time variables, catalyst amount and its respective interaction. Interaction chart (figure 4) let to see absorbance decreasing when different levels of variables are applied. Optimal values

as 6 hours of irradiation and a proportion between TiO$_2$ and lignin of 3:3 to 1 respectively for depolymerization. It produced 22 % of degradation over lignin black liqueur.

In ANOVA statistical analysis made, we see results for five depolymerization process, and the more evident are four times (0, 2, 6, 10 hours) used with a proportion of (0, 1, 3.3, 6.6, 10) g of catalyst for each g of lignin. Similar lignin depolymerizations were evident, were stand out catalyst concentrations (3.3 and 10) who in times of 2, 6 and 10 hours has depolymerization efficient percentages. 6 radiation hours Uv/TiO2 get close percentages (23.1 % and 31.9 %) respectively. Those percentages are taking in mind to establish optimum radiation time on the black liqueur.

Mechanical Tests

Three boards were made in accordance with described methodology (photography 1) where results in table 3 appear. For such tests, graduate cylinders named on ASTM D-143 standard were used. A machine type C with 5000 tons of resistance was used following strictly the standard.

Photography 1: CNMLK Board. No Milled Rice Husk Board with Kraft Lignin (a). CMLP Board. Milled Rice husk Board with Resin of Depolymerized and Hydroxymethylated Lignin (b). CMLK Board. Milled Husk Board with Kraft Lignin(c)

Mechanical tests for three boards produced results shown on table 4, where it is possible to see that board 2 has optimum mechanical properties required by ASTM D 143 standard with results shown on table 3. For mechanical tests developed on those three boards previously described and seen in figure 1, 2 and 3, minimal request established on ASTM D-143 is observed where two boards high density are identified. The common characteristic is the elaboration with milled husk so no milled husk board has characteristics with a low density. Better resistant properties in the material are detected when a board is made with Kraft lignin but board produced with activated lignin is very resistant to deformation presented by compression evaluation.

Table 4: Mechanical Tests Results for Three Elaborated Boards

	Density (g/cm3)	Tracción P (kg/cm2)	Compression P (kg/cm2)	Flexión E (kg/cm2)	Water Absorption24h (DIN %)
Standard ASTM D 143	0,600-0,800	3,2	486	1,8	60%
Wood 1 CNMLK	0,617	3,8	582	1,1	31,84%
Wood 2 CMLK	0,848	5,0	972	1,8	32,90%
Wood 3 CMLP	0,868	9,1	632	---	48,97%

CONCLUSIONS

UV spectrophotometry indicates that extracted lignin from any type of coal has a modified and oxidated structure if it is compared with lignin extracted from wood. These structural modifications make than lignin has similar properties than humic acids.

With low concentrations standardization it was determined than depolymerization using just UV radiation is not very effective in any time of treatment so catalyst use in the process is indispensable. Besides, catalyst amount was selected in proportion 3.3:1 g and 6 hours time since it gave optimum results in standardization with catalytic degradation values of 22 %.

Three boards were made, two with high density (CMLK and CMPL) and one with low density (CNMLK). CMLK board overcome mínimum requests by ASTM D-143 standard for mechanical tests as flexion, traction, compression and water absorption. It is possible to replace partially melanin used in resin by commercial lignin or extracted lignin from coal.

In relation with properties as flexion, compression and water absorption was not seen a significant difference between CMLK board and CMLP board. In traction properties CMLP board showed better characteristics what indicate that in order to elaborate more efficient boards in relation with this properties is necessary to modify lignin structure.

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