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# A COMPARATIVE ANALYSIS OF AGROWASTES MODIFIED FIBER AND LIGNIN AND THEIR HYDROTHERMALLY CARBONIZED PRODUCTS

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## ABSTRACT

This study investigated the use of gravimetric method of analysis to determine the Acid Detergent Fiber (ADF) and Acid Detergent Lignin (ADL) of some Agro wastes and their hydrothermally carbonized products with a view of evaluating the energy production potential. The results showed that most of the carbonized products had more ADF values as compared to their uncarbonized precursors except for cassava peels and plantain peduncle, which have values of 39.20% as against 21.65% and 41.19% and 28.22% respectively. The ADL values were all lower than those of ADF. The percentage difference for the pairs of the crop wastes and their hydrothermally carbonized products gave the highest of ADF of 54.91% for maize comb and -44.77% for cassava peels. For the ADL, the range of percentage difference is between 60.20% for rice husk and -62.23% for beans husk. With the high ADF values for the agro - wastes and their hydrothermally carbonized products, these materials could be exploited for various energy generation.

**Keywords**: agro wastes; hydrothermal carbonization, Acid Detergent Fiber; Acid Detergent Lignin

## INTRODUCTION

Crop wastes are usually not considered as materials that are of economic value, they are usually discarded indiscriminately, thereby causing environmental problems. Modernization and divergence in material usage have made so many materials that are considered wastes to find usefulness to man, animals, plant and the environment. With the world battling with waste disposal issues, some waste materials especially crop wastes may be investigated for their use in different areas. Crop wastes are usually rich in cellulose and lignin, which if investigated could be used to produce materials that can be used to generate energy (Adila *et. al.*,2019*)*. Confirming that these wastes contain cellulose and lignin only be ascertained by carrying out tests, of which Acid Detergent Fiber (ADF) and Acid Detergent Lignin (ADL) (Moller, 2009 and ISO 13906:2008*)*.

These methods have been used vastly in the determination of the energetic values of forages and animal feeds (Font *et al*., 2003; Kong *et al*., 2005; Moller, 2009) but studies using the procedure on agro wastes have not been investigated. This study investigates the use of gravimetric techniques of ADF and ADL on some crop wastes and their hydrothermal carbonized products to determine if they have the potential to be used as energetic materials. The wastes studied included Rice husk (RC), Beans husks (BN), Maize comb (MZ), Groundnut shell (GN), Cassava peels (CS) and Plantain peduncle (PT). These wastes were hydrothermally carbonized and their cellulosic, hemicellulosic and lignin contents were determined using ADF and ADL techniques.

## MATERIALS AND METHODS

### *Sample Collection*

Rice husks were collected from a rice milling plant in Mando, beans husks were collected from a beans farm in Afaka, maize combs were collected from a maize farm in Jaji, groundnut shells were collected from a groundnut farm in NDA old site and cassava peels were collected from Kakuri all in Kaduna state and the plantain peduncles were collected from plantain farms in Amasoma in Bayelsa state.

### *Sample Pre-treatment*

All the samples were washed air-dried at room temperature in a drying cabinet for one month. The weights were taken weekly to determine the loss in moisture content and by the fourth week, all the samples were oven-dried at 100 °C until a constant weight was obtained for the samples. The samples were pulverized using a *100 kg PH pulverizer machine* to a fine powder and sieved with a 1.00mm sieve, kept in plastic bags until they were analyzed.

### *Hydrothermal Carbonization*

The samples were carbonized at 200 °C using microwave (Haier Thermocool, HTMO-2070E, maximum power 700 W) assisted hydrothermal carbonization (Elaigwu and Greenway, 2017).

#### *Rice Husk*

The pulverized rice husks were carbonized by weighing 19.20 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 °C in 5 mins and then held at 200 °C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled RCC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

#### *Beans Husk*

The pulverized beans husks were carbonized by weighing 20.70 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 °C in 5 min, and then held at 200 °C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled BNC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

*Maize Comb*

The pulverized maize comb was carbonized by weighing 14.30 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 $^{o}$C in 5 min, and then held at 200 $^{o}$C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled MZC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

*Groundnut Shell*

The pulverized groundnut shell was carbonized by weighing 18.90 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 $^{o}$C in 5 min, and then held at 200 $^{o}$C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled GNC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

*Cassava Peels*

The pulverized cassava peels were carbonized by weighing 32.90 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 $^{o}$C in 5 min, and then held at 200 $^{o}$C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled CSC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

*Plantain Peduncle*

The pulverized plantain peduncle were carbonized by weighing 17.20 g of the husk into a 100 ml Teflon liner of the hydrothermal reactor autoclave, 50 ml distilled water was added. The Teflon liner was sealed and placed in the autoclave, which was placed in the microwave oven. The microwave was set to ramp to the temperature of 200 $^{o}$C in 5 min, and then held at 200 $^{o}$C for 60 min after which the autoclave and its content were allowed to air-cool to ambient temperature before the carbonized products were collected onto aluminum foil, labeled PTC, allowed to air-dry to constant weight and kept for ADF and ADL analysis.

***Acid Detergent Fiber Solution***

Acid Detergent Fiber (ADF) Solution was prepared as described by the Association of Official Analytical Chemist (AOAC), 1990. The ADF solution was prepared by weighing 360 g of Cetyltrimethylammonium bromide (technical grade) into a 20 L container containing 10 L of water, 500 mL concentrated tetraoxosulphate VI acid (Analytical grade) was added, water was added to 18L and allowed to stand for 24 hours before use.

***Acid Detergent Fiber***

The method used was as described by Holtzapple, 2003, AOAC, 2005, AOAC, 1990 and Van Soest et. al., 1991. The empty crucible was dried in an oven for 4 hours and the weight was recorded as tare weight ($W_1$), 1g ($W_3$) of the dried and pulverized sample was measured into a beaker, 100ml of Acid Detergent solution was added and placed on a heating magnetic stirrer. The mixture was allowed to slowly heat up until it started boiling, 5 ml ADS was used to rinse the sides of the beaker, 4 drops of n-octanol was added as an anti-foaming agent and the mixture was heated for 1hour. After the heating, the beaker was swirled and its content filtered into the crucible, hot water was used to soak the filtered solid in the crucible and dried using the vacuum pump. This was repeated three times, to wash the ADS and residual acid off the residue. 30 ml of acetone was added to the content of the crucible and allowed to stand for 5 minutes, the acetone was dried using the vacuum pump. This process was repeated until there was no colour coming from the treated sample. The crucible and its content were dried overnight in the oven at 105$^{o}$C and the weight of the crucible and its content was recorded as ($W_2$) after allowing to cool in a desiccator. This procedure was repeated three times for all the samples.

***Acid Detergent Lignin***

The method used was as described by Holtzapple, 2003, AOAC, 2005, AOAC, 1990, ISO 13906: 2008 and Van Soest et. al.,1991. The content of the crucible was placed on an enamel tray, 72% $H_2SO_4$ was poured to cover the content of the crucible and stirred with a glass rod until a smooth paste without lump is obtained. The acid was added to about halfway of the crucible and left for 3 hours, acid was added at intervals to maintain the halfway volume of the crucible. After the three hours, the acid was filtered using the vacuum pump after which hot water was used to wash the content of the crucible and tested with pH paper until the blue filter paper could not react to the acid. The stirring rod and sides of the crucible were rinsed with hot water and the crucible was dried in an oven at 105 $^{o}$C for about 3 hours and cooled in a desiccator, this was repeated until a constant weight ($W_4$) is obtained. The crucible and its content were placed in a furnace and ignited at 525$^{o}$C for 3 hours, after which it was transferred while still hot to the oven for 1 hour at 105$^{o}$C and was cooled in a desiccator and its weight ($W_5$) was recorded. This procedure was repeated three times for all the samples.

ADF was calculated as $((W_2 – W_1) X 100)/W_3$

ADL was calculated as $((W_4 – W_5) X100)/W_3$

## RESULTS AND DISCUSSION

**Table 1: ADF and ADL Determination for Carbonized and Uncarbonized Crop Wastes in %**

| | RC | RCC | BN | BNC | MZ | MZC | GN | GNC | CS | CSC | PT | PTC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ADF( %)** | 18.21 | 34.16 | 38.94 | 42.11 | 32.10 | 71.20 | 62.14 | 68.21 | 39.20 | 21.65 | 41.19 | 28.22 |
| **ADL( %)** | 3.26 | 8.19 | 24.20 | 9.14 | 5.16 | 8.12 | 19.28 | 14.16 | 15.54 | 16.11 | 9.63 | 7.42 |

*ADF*

Acid detergent fiber is a measure of the cellulose content and a potential for such material to be used as a source of energy. The results obtained from the ADF analysis show that almost all the hydrothermally carbonized products have a higher ADF percentage than the original crop waste, except for cassava peels and plantain peduncle. The higher values seen in the carbonized products could be as a result of the modification caused by the carbonization.

**Table 2: Percentage Difference in ADF Values for Carbonized against Uncarbonized Crop Wastes**

| Sample | RCC/RC | BNC/BN | MZC/MZ | GNC/GC | CSC/CS | PTC/PT |
|---|---|---|---|---|---|---|
| **ADF Difference (%)** | 46.69 | 7.52 | 54.91 | 8.90 | - 44.77 | - 31.49 |

The percentage difference in ADF values between the carbonized and raw crop wastes as shown in Table 2, is significant. For beans husk, 7.52% increment was observed for the carbonized sample over the husk of the untreated bean. Maize comb shows that hydrothermal carbonization has a modification on the carbonized product with 54.91 % increase in ADF value over the uncarbonized. However, the negative values obtained for cassava peels and plantain peduncle (-44.77 and -31.49 respectively) could suggest that the process of hydrothermal carbonization converted some of the cellulosic materials to materials that were digestible by the ADF process.

*ADL*

The ADL values obtained from this study show that Carbonized Rice husk, Maize comb and Cassava peels have higher values than that of the uncarbonized which could suggest that some of the constituents of the raw wastes were converted to materials that are lignin-like. While for beans husk, groundnut shell and plantain peduncle, the uncarbonized samples had higher ADL values which could suggest that the process of hydrothermal carbonization converted some of the lignin/lignin-like materials to other materials.

**Table 3: Percentage Difference of ADL Values for Carbonized and Uncarbonized Crop Wastes**

| Sample | RCC/RC | BNC/BN | MZC/MZ | GNC/GN | CSC/CS | PTC/PT |
|---|---|---|---|---|---|---|
| **ADL difference (%)** | 60.20 | -62.23 | 36.45 | -26.56 | 3.54 | -22.95 |

The percentage difference between the carbonized and uncarbonized crop waste is significant for all the samples with cassava peels having the least percentage difference of 3.54% while beans husk and rice husk having very high percentage difference of -62.23% and 60.20% respectively.

Generally, it was observed that the ADF values, which suggest the cellulosic/cellulose-like content, are higher than the ADL values, which suggest the lignin/lignin-like content for all the samples both carbonized and uncarbornized. This goes along with studies done by other researchers that have compared the ADF and ADL values of different materials. Adila et. al., 2019 got ADF values of 30%, 37% and 42% for the leaves, stem and root of pineapple biomass as against 20%, 20% and 19% ADL values for the respective plant parts. Similar results were obtained for Moller, 2009, who worked on sawdust, wheat, cattle feed, soy meal, clover silage, and grass silage, Dorez *et. al.,*2014, worked on cotton linter, flax, hemp, sugar cane, bamboo and coconut, and Wenwu *et. al.,* 2010, who worked on wild and cultivated rice.

## CONCLUSION

The conclusion can be made that from the present study, the cellulose and lignin content of the crop wastes and their hydrothermally carbonized products are high and they can be passed for potential materials that can be used as sources of energy generation. Their heating values and suitability as alternative energy should be investigated. The value of the lignin and cellulosic analysis is dependent on the samples collected from the various areas and might be slightly different from the previous studies and other research on crop wastes due to the species of the agro wastes, the season of collection of the samples, other factors during sample preparation and the process of analysis.

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