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# Thermal and Dimensional Stability of NBS-catalyzed Acetylated Rice Husks

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**ABSTRACT**
*Rice husks have been treated by acetylation for use as oil spill sorbents. The thermal and dimensional stabilities have been presented and discussed in this study. The thermal degradation studies were carried out within the temperature range of 26-600$^oC$. Weight loss as a result of degradation of cellulose, hemicellulose and lignin was used to investigate the stability of the acetylated products. The dimensional stability was tested at 26$^oC$ and was found to increase by 35.57%. The results indicated that acetylation leads to a decrease in thermal stability and consequently an increase in the dimensional stability of the rice husks.*

**Keywords**: Rice husks, Acetylation, dimensional stability, thermal degradation, swellability.

## INTRODUCTION

Any substance that contains both cellulose and lignin is lignocellulosic [1]. The use of lignocellulosics as sorbents in an oil spillage situation has been gaining acceptance in recent times [2, 3, 6, 4, 5]. In general, what is true for wood is also true for other lignocellulosics even though they may differ in chemical composition and matrix morphology [1]. Lignocellulosic materials are potentially very reactive due to the abundance of hydroxyl groups on the polymeric unit. The natural reactivity of lignocelluloses can be utilized to enhance their properties with the resulting material being superior in terms of performance and versatility [8]. The hydroxyl groups are available in such large numbers that hydrogen bonding within and between the polymeric species occurs throughout the material. It is this hydrogen bonding that allows hydrophilic substances like water from humid environments to enter the structure and interact with polymers and alter their properties [5, 8]. This is a great disadvantage in relation to industrial use of plant fibers [9] and could give rise to other problems such as microbiological decay [8].

Products and material based on plant fibers are not dimensionally stable under moisture conditions. Changes in dimension are a great problem in lignocellulosic composites as compared to solid wood [10]. One strategy to improve the water absorption and dimensional stability of the fiber is to chemically modify the cell wall polymers which will modify the physical properties of the lignocellulosic material [5]. The hydrophilic O-H groups will be converted into larger, more hydrophobic groups. Different technologies of wood (lignocellulose) modification have been known for a long time, but in the past there was no economic or environmental urgency to develop these technologies. Wood modification can change important properties of the wood including biological durability, dimensional stability, hardness and UV-stability [11]. Modification aims at altering the molecular structure of the cell wall components. One of the most practical of these is the reaction of a hydroxyl group with acetic anhydride, known as acetylation [12, 5]. Acetylation occurs when the hydroxyl groups of the lignocellulose reacts with acetic anhydride to form esters of lignin, cellulose and hemicellulose, in addition to the byproduct acetic acid. The generalized chemical reaction is shown below.

$$\underset{\text{Lignocellulose}}{\mathrm{LC-OH}} + \underset{\text{Acetic Anhydride}}{\mathrm{R_2(C=O)_2O}} \longrightarrow \underset{\text{Acetate}}{\mathrm{LC-O(C=O)R}} + \underset{\text{Acetic acid (by-product)}}{\mathrm{RCOOH}} \quad (1)$$

In Equation 1, LC represents Lignocellulose and the reaction explains the acetylation of accessible hydroxyl groups in the lignocellulose cell wall with the formation of by product acetic acid. As a consequence, the wood is in a swollen condition because of the acetyl groups within the cell walls [8]. Dimensionally stable materials are created because the cell wall itself will be in a permanently swollen state that will attract no or very little water [11]. Since the water molecule sorbed is smaller than the acetyl group, some swelling can occur in ‘completely acetylated wood’, but swelling does not exceed the elastic limit of the cell wall [10]. Chemical modification of the hydroxyl groups of wood with acetic anhydride esterifies the material making it more hydrophobic and dimensionally stable.

Rice husk (RRH) is a lignocellulosic material whose dimensional stability is dependent on its state and the prevalent surrounding environmental conditions. Extreme variations in those surrounding conditions like temperature relative humidity, moisture, amongst other will almost always affect untreated material [13]. Rice husk is principally composed of cellulose, hemicellulose and lignin (35, 25 and 20% by weight respectively). The former two components are hydrophilic [14]. As a lignocellulosic material, it is expected that RRH will absorb and or release moisture to the surrounding environment at the required condition. This study aims at improving and evaluating the thermal and dimensional stability of RRH through chemical modification of its lignocellulosic strands. The presence and availability of the hydroxyl groups in lignocellulosic materials increases their strength and versatility but it is also the reason for the problems arising with lignocellulosics. This is the first study as far as the authors are aware where NBS catalyzed acetylation is applied to improve the dimensional stability of rice husks. The methods and the results have been reported in details and conclusions and recommendation were made in line with the outcome of the study.

## MATERIALS AND METHODS

**Acetylation of rice husks**

Raw rice husks (RRH) were obtained from a local rice milling plant in Kura Local Government in Kano State, Nigeria. They were washed with water and dried at 60oC for 24hrs in an oven. The particle size distribution was controlled using the BS410/1986 laboratory test sieves of 1.4mm aperture size screens. The acetylation of the rice husk under mild conditions, in the presence of N-bromosuccinimide, using acetic anhydride was carried out using the sun *et al.* [15] method of acetylation in a solvent free system, with a few modifications. All reagents used were analytical grade from BDH and Riedel de Haĕn, with no further purifications carried out. A specific amount (15g) of rice husks was placed in a 500ml round bottom flask containing 300ml of acetic anhydride and 30g N-Bromosuccinimide (NBS). The flask was placed in a thermostated water bath set at 100$^{o}$C, under atmospheric pressure, with a reflux condenser fitted. The flask was removed from the bath and the hot reagent was decanted off. The rice husks were thoroughly washed with ethanol and acetone to remove unreacted acetic acid by-product. The procedure was repeated, varying time, temperature, catalysts concentration and acetic anhydride volume. The new products were dried in an oven at 60$^{o}$C for 16hours prior to reweighing. The dry materials were reweighed to determine the weight gains on the basis of initial oven dry measurements. Weight Percent Gain (WPG) of the rice husk due to acetylation was calculated thus:

$$WPG(\%) = \left[\frac{weightgain}{originalWeight}\right] \times 100 \qquad (2)$$

The oil sorption test was then carried out to determine the oil sorption capacity of the acetylated products using the methods described by Nwankwere *et al.* [9], using crude oil.

**Thermal analysis**

The effect of acetylation on the thermal properties of rice husks were analyzed using a carbolite Sheffield GLM3 furnace for the functional group analysis of the sorbents within the temperature range of 20-600$^{o}$C.

**Dimensional Stability**

Swellability (S) and anti-swelling efficiency (ASE) test: Sets of control, raw and acetylated sorbents were placed in separate beakers, for each test sample, filled with distilled water. There was replacement of water daily for 5days [10]. The time being adapted to suit the material's dimension. The samples were weighed and the water absorption (or swellability) values (S) and anti-swelling efficiency (ASE) were calculated according to the equations 3 and 4 below, after each water replacement in line with the procedures of Temiz *et al.* [16].

$$S\ (\%) = [(V_{wet}-V_{dry})/V_{dry}] \times 100 \qquad (3)$$

$$ASE = [(S_o-S)/S_o] \times 100 \qquad (4)$$

Where $W_2$ = wet weight of the sample after soaking in water; $W_1$ = oven dry weight; $S_o$ = volumetric swelling of untreated samples and S = volumetric swelling of treated samples. The ASE and water absorption data are summarized in Table 2.

## RESULTS AND DISCUSSION

### Acetylation Results

Rice husks were acetylated at different reaction conditions. The results obtained for some selected samples are presented in Table 1. The weight percent gain (WPG) of the samples due to acetylation increased as the acetylation parameters increased. The RRH had the lowest OSC of 1.9g/g sorbent. While ARH14 with the highest WPG value of 19.44% produced the highest OSC value of 9.44g/g sorbent. The increase in OSC was a consequence of the increasing WPG. This is because the hydroxyl groups in the cell wall of the RRH have been replaced with heavier, more hydrophobic acetyl groups. The WPG is an indication of the extent of acetylation. Therefore the higher the extent of acetylation, the heavier the products would be. The results also showed that the parameters; time, temperature and catalyst concentration, influenced the extent of acetylation and consequently the values of the OSC.

**Table 1: Results of selected samples**

| Sample | Acetylation conditions | | | | |
|---|---|---|---|---|---|
| | Time(hr) | T($^{o}$C) | %NBS | WPG | OSC (g/g sorbent) |
| RRH | - | - | - | - | 1.90 |
| ARH9 | 1.0 | 100 | 1.0 | 10.8 | 6.62 |
| ARH14 | 3.5 | 100 | 1.0 | 19.6 | 9.44 |
| ARH17 | 1.0 | 100 | 2.0 | 16.00 | 8.88 |

OSC stands for oil sorption capacity (g oil absorbed/ g acetylated Rice husks). WPG represents the weight percent gain of Rice husks due to acetylation, %NBS represents the concentration of NBS catalyst used (in %) and T represents temperature.

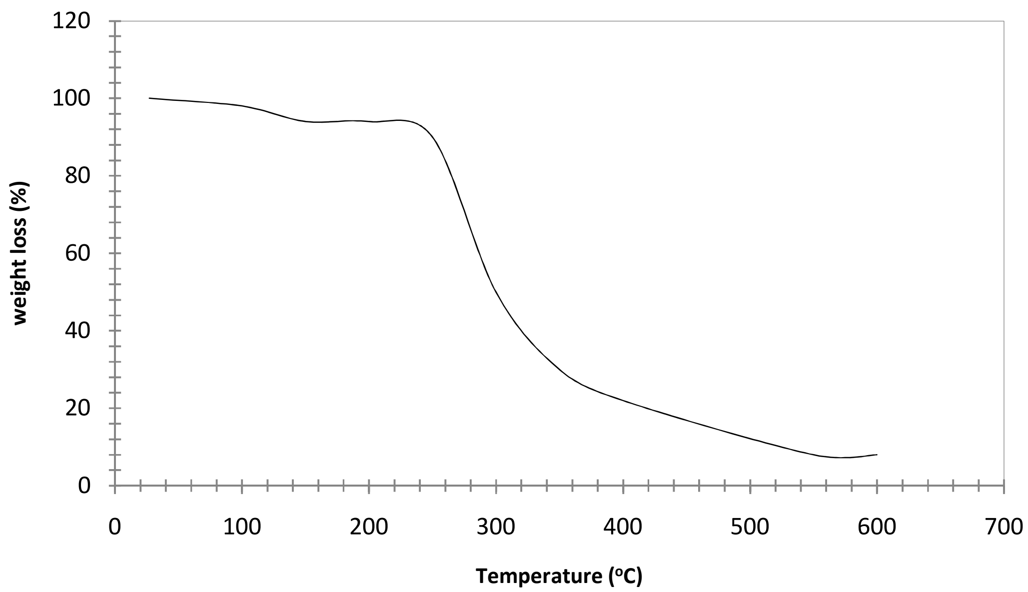


**Figure 1: Thermogram of Raw Rice Husks**

**Thermal Degradation of Samples**

The thermal degradation analysis was carried out to provide information on the bulk composition of compounds [17]. The effect of acetylation on the thermal properties of the raw and acetylated rice husks were examined by thermal studies in the temperature range of 27-600$^{o}$C. The results obtained from the thermal properties of the raw and acetylated rice husks are explained in Figures 1 and 2 respectively.

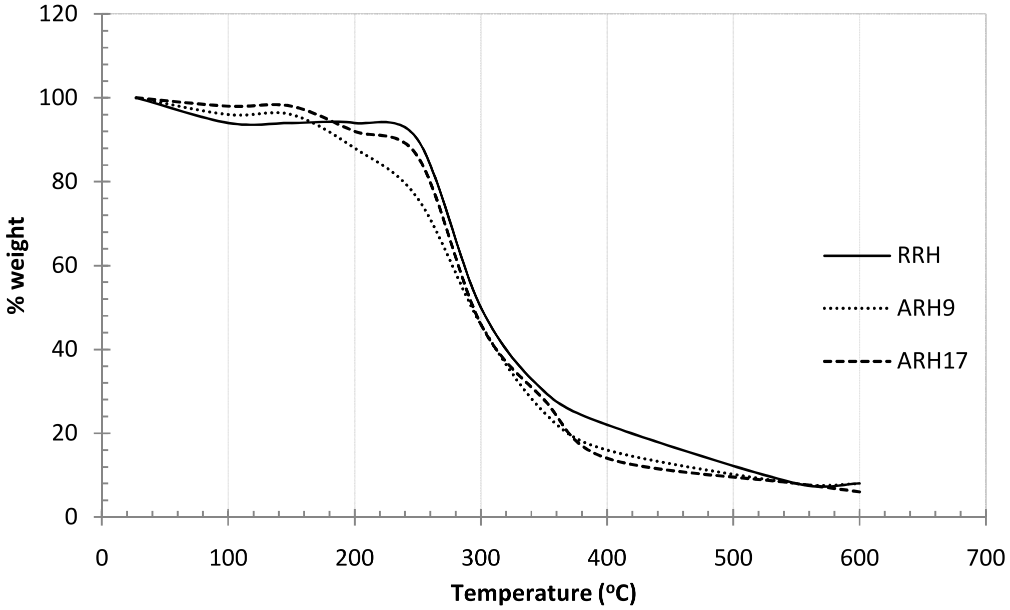


**Figure 2: Thermogram of acetylated rice husks**

The fiber mass of the samples decreased from 100-50% at 290$^{o}$C. The optimal thermal degradation temperatures were considered to start at 240$^{o}$C for the raw rice husks (Figure 1), 200$^{o}$C for sample 9 (Figure 2) and 240$^{o}$C for sample 17 (Figure 2). Different regions can be associated with weight loss, retained water at 100$^{o}$C, hemicellulose degradation at 200-260$^{o}$C, cellulose degradation at 240-350$^{o}$C and lignin degradation at 280-500$^{o}$C [17]. Initially the acetylated samples seemed more stable than the RRH till they reach 170$^{o}$C, with the thermogram of RRH showing less weight loss than those of the acetylated samples. This phenomenon occurred because of changes in hemicellulose and lignin structure which were replaced with less recalcitrant acetyl group. Decomposition stops at 550$^{o}$C. The Thermogram of raw rice husks showed minor weight loss at 140$^{o}$C which is attributed to water desorption [6], this minor loss is not obvious in the ARH samples. This was because the acetylated samples were more hydrophobic than the raw samples. This indicates that the raw sample is more stable than the ARH samples. This effect was undoubtedly due to the disintegration of intramolecular interactions such as hydrogen bonds between molecules [15]. Hence, the thermal stability of acetylated rice husks increases slightly with a higher WPG values, though the acetylated materials have essentially the same thermal properties as the unmodified materials [10]. The results may not be in conformity with those of other researchers [6, 10, 16]; it proves the success of the acetylation procedure on the RRH substrate.

## Swellability of Sorbents Used

The essence of water absorption experiment is to verify the hydrophobic properties of a sorbent. The lower the water absorbed by a sorbent, the better the potential with regards to collection of oil products from a water surface [18]. The swellability of the commercial, raw and acetylated sorbents were tested in triplicates and the means were recorded. The trends in moisture absorption are represented in Figure 3.

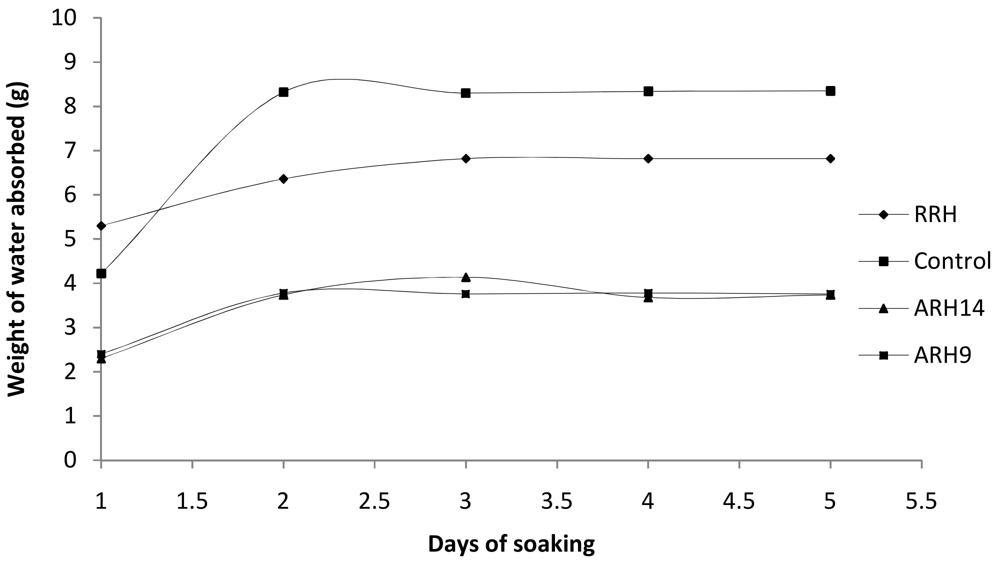


**Figure 3: Swellability pattern of Raw and Acetylated rice husks samples.**

ARH represents acetylated rice husks; $W_{moist}$ is the new weight with moisture gain, $W_{oven\ dried}$ is the weight of sorbent after oven drying and ASE represents the anti-swelling efficiency (dynamic stability).

Figure 3 shows the swellability behavior of the sorbents during the five day experiment. The acetylated samples had the same pattern of swellability, they tend to stop absorption on the second day. The control had the highest water absorption value. It reaches its maximum on day 3 and remains constant. The raw sample also stops absorption on day 3. The swellability of each sample was calculated using the formula for swellability in equation 2 and the values used to calculate the dimensional stability of the acetylated rice husks.

## Dimensional Stability

The dimensional stability expressed as the anti shrink efficiency (ASE) of the acetylated rice husks, as obtained for some of the acetylated samples are given in Table 2.

**Table 2. Swellability after soaking of test samples in water for 5days**

| Sample condition | WPG | Mean $W_{moist}$ (g) | Mean $W_{oven\ dried}$ (g) | S(%) | ASE |
|---|---|---|---|---|---|
| Control | -- | 8.35 | 1.00 | 835 | -26.29 |
| RRH | -- | 6.82 | 1.00 | 582 | -- |
| ARH9 | 6.62 | 3.76 | 1.00 | 376 | 35.40 |
| ARH14 | 9.44 | 3.74 | 1.00 | 374 | 35.74 |

The bulk of the research into chemical modification has been focused on improving dimensional stability [18]. Dimensional stability is very crucial in structural products made from lignocellulosic materials, because the safety and comfort in a structure made from such lignocellulosic materials for instance depends on it [13]. When wood is acetylated, it is far less susceptible to shrinking and swelling in the presence of varying atmospheric conditions. Any increase in the WPG affects the moisture sorption and the water repellence in the fibers [19]. The reason for this is simply explained. The mechanism of this performance enhancing modification is the reaction of a small chemical to a hydroxyl group on one of the cell wall polymers. The cell wall is now filled with chemically bonded acetyl groups which take up space within the cell wall. As a consequence, the husk is already in a swollen condition, the extent of which depends upon the level of modification. However since all reacted chemicals used so far are larger than water molecule, some swelling always take place.

The results on Table 2 show that the dimensional stability of the rice husks was over 35% after the 5days experiment. This is evidence that the hydrophobicity of the rice husks reduced by over 35%. The rate and the extent of swelling in RRH reduced as a result of acetylation. After the 5day experiment, the control sample swelled by 835% , while the ARH9 and ARH14 swelled by 376% and 374% respectively (both less than 500%), giving an ASE of 35.40 and 35.75% respectively. The mean ASE for the acetylated samples is 35.57%. After drying, the RRH showed a greater degree of the irreversible swelling compared to the ARH samples.

The mechanism of dimensional stability of ARH resulting from acetylation is a result of building of the bonded acetyl group in the cell wall polymer hydroxyl groups in the cell wall. The Dimensional Stability of the ARH was greatly improved by acetylation with acetic anhydride. Our results are in agreement with those made by other workers [1, 7, 8, 10, 19, 20] regarding the acetylation of wood and particle boards.

## CONCLUSION

This study aimed at evaluating the moisture absorption, thermal and dimensional stability of RRH by acetylation in the presence of NBS. Physical and mechanical standards were not compromised and husks exhibiting superior dimensional stability were produced by the methods used. The results show that the thermal strength of the rice husks slightly changed as a result of the replacement of OH groups in its matrix though the thermal properties still remain the same. This change is an evidence of successful acetylation. The dimensional stability of the ARH was 35.69. This is evidence that the hydrophobicity of the rice husks increased by over 35%. Acetylation using NBS is therefore feasible and useful to improve the dimensional stability of Lignocellulosic compounds.

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