



## Hydrophobic treatment of corn cob by acetylation: Kinetics and thermodynamics studies



Joseph O. Nwadiogbu<sup>a,\*</sup>, Patrice A.C. Okoye<sup>b</sup>, Vincent I. Ajiwe<sup>b</sup>, Nnaemeka J.N. Nnaji<sup>a</sup>

<sup>a</sup> Department of Industrial Chemistry, Caritas University, Amorji-Nike, Enugu State, Nigeria

<sup>b</sup> Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

### ARTICLE INFO

#### Article history:

Received 12 February 2014

Accepted 5 June 2014

Available online 13 June 2014

#### Keywords:

Acetylation

Corn cob

Fourier transformed infrared spectroscopy

Surface reaction

Intra-particle diffusion

### ABSTRACT

Fourier transform infrared spectroscopy (FTIR) has been used to investigate the acetylation of corn cobs such that the effects of time were not significant, but the effects of temperature and catalyst were significant. Kinetic analyses suggest surface reaction and intra-particle diffusion mechanisms for corn cob acetylation at 30 °C and 100 °C. Thermodynamic models used enabled the evaluations of heat of acetylation ( $0.0291 \text{ Jmol}^{-1}$ ), critical temperature ( $0.814 \text{ }^\circ\text{C}$ ), heat capacity ( $4.157 \times 10^{-4} \text{ Jmol}^{-1} \text{ K}^{-1}$ ), entropy change ( $5.005 \times 10^{-4} \text{ Jmol}^{-1}$ ) and values of Gibb's free energy changes at studied temperatures for corn cob acetylation respectively. The water absorption capacity studies showed that the raw corn cobs had its water absorption capacity reduced after treatment indicating a considerable increase in hydrophobicity, thereby enhancing its potentials for use in: non-aqueous absorption processes like oil sorptions and oil spill remediations.

© 2014 Elsevier Ltd. All rights reserved.

### Introduction

Huge amounts of agricultural wastes like corn cobs are produced in many countries of the world, particularly in Nigeria. In Nigeria however, only a fraction of these materials are 'usefully' reused because they are thereafter used majorly as domestic sources of fuel (cooking). One of the features of these agro-wastes is that it can absorb by capillary forces an amount of fluid/liquid like: oil; and water, greater than its own weight [1]. In addition, this natural material can be completely degraded in nature by biological, physical, chemical and photochemical processes [2].

In the past two decades, the reuse of agricultural byproducts as oil sorbents has received growing attention due to their low cost and biodegradability [3]. Most agricultural byproducts derived from plants such as bagasse, coir, kenaf, rice straw, sisal and saw dust have been investigated for oil spill cleanup applications [4]. The main drawbacks of these plant-derived sorbents are: not easily available; cost; relatively low oil sorption capacities; low hydrophobicities; and poor buoyancy compared to synthetic sorbents such as polypropylene [5,6].

Once plant-derived sorbents are applied to saturated environments, preferential water sorption is favoured over the sorption of

oil because the sorbents are generally hydrophilic in nature. A better understanding of the chemical composition of these natural fibres is necessary for developing natural fibre sorbents. As such, agricultural byproducts can be considered polymeric composites made up primarily of cellulose, hemicellulose and lignin [7–9]. These polymers make up the cell walls and are responsible for most of the physical and chemical properties exhibited by these materials [1]. Agricultural byproducts have well-documented problems of water sorptions and lack of dimensional stabilities, due to associated hydroxyl functionalities. These groups are abundantly available in all the three major chemical components of plant based materials and are responsible for their hydrophilicity [1].

Hydrophobicity (oleophilicity) is one of the major determinants of sorbents properties influencing the effectiveness of oil sorption in the presence of water. The effectiveness of the sorbents in saturated environments would be enhanced if the density of the hydroxyl functionality is decreased [1]. The hydroxyl functionality of these fibres can be reduced by chemical modification such as acetylation, methylation, cyanoethylation, benzoylation, acrylation, acylation etc. [10–13].

The acetylation reaction is one of the most common techniques used for hydrophobic treatment of lignocellulosic materials (e.g. wood) by a substitution reaction of a hydroxyl group (hydrophilic) with an acetyl group (hydrophobic). This reaction is usually carried out by heating lignocellulosic material in the presence of acetic anhydride with or without catalyst [10]. Various catalysts have

\* Corresponding author. Tel.: +234 8187824871.

E-mail address: [Onyebuchinwadiogbu@yahoo.com](mailto:Onyebuchinwadiogbu@yahoo.com) (J.O. Nwadiogbu).

been used for enhancing the efficiency of acetylation reactions. Pyridine and 4-dimethyl amino pyridine (DMAP) have been commonly applied for acetylation for many years [11]. However, they are too toxic and/or expensive for commercial use(s). Sun et al. [12] recently reported that acetylation of sugarcane bagasse with N-bromosuccinimide (NBS) as catalyst in a solvent-free system was a convenient and effective method. In addition, they claimed modified bagasse applied in oil–water system presented an enhanced oil sorption capacity exceeding that of commercial synthetic sorbents.

This present effort investigated the effects of catalyst, time and temperature on the acetylation of corn cob. Respectively, kinetic and thermodynamic investigations were done to understand the nature and mechanism of the modification process.

## Materials and methods

### Material preparation

Corn Cobs used were collected from a local market in Enugu metropolis, Nigeria. They were thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed cobs were dried properly in sunlight for 12 h (4 h for three days) and then left to dry at 65 °C in the oven. They were size reduced and sieved through 20 and 25 British Standard Sieve (BSS Sieves). Reagents and Chemicals used were from British Drug House (BDH) and include Acetic Anhydride, N-bromosuccinimide (NBS), acetone, ethanol and n-hexane, and were used without further purification.

### Soxhlet extraction

To reduce the influence of the fibre extractible on acetylation, 10 g of the sieved materials was extracted with a mixture of acetone and n-hexane (4:1 v/v) for 5 h. The extracted samples were dried in a laboratory oven for 16 h. The extractible content was calculated on a percentage of the oven-dried test samples.

### Acetylation of corn cob

The acetylation of the corn cob under mild conditions, in the presence of NBS, using acetic anhydride was carried out using the method of Sun et al. [12] for acetylation in a solvent free system. The amount of substrate and reactant were combined in a ratio of 1:20 (g dried corn cob/mL acetic anhydride). The reaction temperature, time and amount of catalyst were varied respectively from 30 °C to 130 °C, 1 to 3 h and 0 to 4%. The mixture of raw corn cob, acetic anhydride and catalyst was placed in a round bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device, thereafter, the flask was removed from the bath and the hot reagent was decanted off. The corn cob was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid as by-products. The new products were dried in an oven at 60 °C for 16 h prior to analysis. The extent of acetylation (EA) was estimated from the infrared spectra by calculating the ratio of the absorption intensities (I) for the vibration signals of C=O (around 1740–1745 cm<sup>-1</sup>) and C–O (1020–1040 cm<sup>-1</sup>), as shown below [14]:

$$\text{Extent of acetylation (EA)} = \frac{I_{1740}}{I_{1020}} \quad (1)$$

### Fourier transform infrared spectroscopic analysis

The properties of raw and acetylated samples were characterised using FT-IR Shimadzu 8400s spectrophotometer in the

range of 4000–400 cm<sup>-1</sup>. Samples were run using the KBr pellet method at the National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna-Nigeria.

### Statistical analyses

Statistical package for the social sciences (SPSS) version 16 was used for the statistical analyses of obtained data.

### Water absorption capacity

The raw and acetylated samples were subjected to water absorption test. The materials immersed in water and allowed to absorb water for specific soaking times (10, 20, 40, 60 and 80 min). After the specific soaking times, the wet sorbents were drained on the filter paper for 10 min under vacuum filtration. The water absorption capacity in g/g was calculated as follows;

$$\text{Water absorption capacity (WAC)} = \frac{AW - AD}{AD} \quad (2)$$

where AW stands for amount of wet sorbent and AD stands for amount of dry sorbent.

## Results and discussions

### Infrared spectroscopic studies

Figs. 1 and 2 represent infra-red spectra for untreated and treated corn cobs respectively. The proposed assignments of the observed signals, as suggested elsewhere [1,14,15], are presented in Table 1. The major changes before and after treatment are increased carbonyl absorption peak at 1735 cm<sup>-1</sup> (C=O ester), C–H absorption peak at 1371 cm<sup>-1</sup> (–C–CH<sub>3</sub>) and –C–O stretching band at 1239 cm<sup>-1</sup> which confirmed the formation of ester bands [1]. The lowering of intensities of –OH stretching band at 3400–3600 cm<sup>-1</sup> and –OH out of plane at 1430, 1336, 1159, 857, 766, 581 and 522 cm<sup>-1</sup> indicated that some hydroxyl group content of were reduced after the reaction [14]. These changes in the FT-IR spectra are consistent with those of acetylated cellulosic materials reported by other researchers [1,3,12,14]. The results indicate that some acetyl functional group has been attached to the corn cob at the expense of the hydroxyl group. The absence of peaks at around 1700 cm<sup>-1</sup> and 1840–1760 cm<sup>-1</sup> in the treated samples indicate that the acetylated products were free of acetic acid byproduct and unreacted acetic anhydride [14,15].

### Corn cob-extent of acetylation

The effects of time, catalyst and temperature are shown in Figs. 3–5. The trends observed in Figs. 3–5 are not steady (neither decreasing nor increasing) in the variations of the extent of acetylation with reaction time, catalyst and temperature and may be due to the complex nature of corn cob. Evidence, as reported by Sun and Cheng [22], reveals that cellulose is the major component of corn cob (about 45%), while other constituents in corn cob include lignin (6.7–13.9%), and hemicelluloses (39%). Furthermore, phenolic, benzylic or alcoholic (primary and secondary) hydroxyl groups are present in the lignin region while only the alcoholic hydroxyl groups are found in the carbohydrate. Phenolic hydroxyl groups are attached to aromatic rings containing various substituents [16].

The different types of hydroxyl groups will react differently with acetic anhydride. For example, in the study of the acetyl distribution in acetylated (whole) wood and reactivity of isolated wood cell wall components to acetic anhydride, Rowell et al. [17]

Download English Version:

<https://daneshyari.com/en/article/222004>

Download Persian Version:

<https://daneshyari.com/article/222004>

[Daneshyari.com](https://daneshyari.com)