

Acetylation of Corn Cobs Using Iodine Catalyst, For Oil Spills Remediation

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ABSTRACT

This study investigated the process of cleaning oil spills using both raw corn cobs (RCC) and acetylated corn cobs (ACC). The corn cobs were acetylated in a solvent free system using acetic anhydride, in the presence of Iodine, under mild reaction conditions. The acetylation was carried out at 100°C for 2 hours using 1% iodine. The system conditions played significant roles on the extent of acetylation expressed as Weight Percent Gain (WPG). The weight percent gain (WPG) due to acetylation was found to be 17.6%. Sorption studies were also carried out on both RCC and ACC. The result of the analysis showed higher values of oil sorption capacities (g/g) for ACC than RCC. This goes to prove that acetylation increased the oil sorption capacity of the corn cobs. It was found that particle size, sorption time, sorbent dosage and temperature has very significant effects on the oil sorption capacities of the modified corn cobs. To investigate the acetylation reaction, functional analysis of the RCC and ACC were carried out using Fourier transform infrared spectroscopy (FT-IR). The FT-IR data showed a clear evidence of successful acetylation. ACC are therefore recommended for oil spillage clean up, as well as for further development.

Keywords: Acetylation, Corn cobs, Oil spills, Sorbents, and Sorption capacity.

Date of Submission: 17 May 2016



Date of Accepted: 22 August 2016

I. INTRODUCTION

An oil spill is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters. The oil may be a variety of materials, including crude oil, refined petroleum products (such as gasoline or diesel fuel) or by-products, oily refuse or oil mixed in waste. Spills take months or even years to clean up [1]. There are countless reasons for oil to go out of control. Many are due to mechanical failure of the equipment or due to human carelessness or mistakes. According to the [2] Report, spills occur accidentally and also through the deliberate actions of the local people, who sabotage pipelines in protest against the action of the Federal Government and oil companies. There are also risks implicated in the materials involved and the means of transporting the oil. The risks involve terminals, loading docks, refineries, tankers, freighters and pipelines, tanks, trucks, filling stations, just to name a few [3].

In addition, the changing pattern of refining location has significantly increased the proportion of crude products moved over greater distances. This change has resulted in an increased chance of sea pollution. The increasing movement and storage of products has also increased the risk of instant water contamination [4].

The environmental effects of oil pollution are well known. They include the degradation of forest and depletion of aquatic fauna. Long term impacts are also possible, as in cases where mangrove swamps and ground water resources are harmed. In aquatic habitat, oil can be toxic to the frogs, reptiles, fish, water fowl and the animals that live in or other wise use the water [5]. Oiling may affect not only wide life but also plants that are rooted in or float in water, harming both the plants and the animals that depend on them for food and shelter. The implications of these findings are frightening, given that human health is tied to the food web [2].

The adverse impact to ecosystems and the long term effect of environmental pollution call for an urgent need to develop a wide range of materials for cleaning-up oil from oil impacted areas especially as the effectiveness of oil treatment varies with time, the type of oil and spill, the location and weather conditions [6]. Thus various processes have been developed to remove oil from contaminated areas by use of booms, dispersants and skimmers, oil water separators or by use of different kinds of sorbents [7].

Sorbents are used in different arrangements to collect spilled oil and oil products [8]. Absorbents materials are attractive for some applications because of possibility of collection and complete removal of the oil from their oil spill site. The addition of absorbents to oil spill areas facilitate a change from liquid to semi-solid phase and

once this change is achieved, the removal of the oil by the removal of the absorbent structure then becomes much easier. Furthermore these materials can in some cases be recycled [6].

Oil sorbents can be categorized into three major classes: Inorganic mineral product, organic synthetic products and organic vegetable products [9]. According to [10], sorbents with large surface areas and affinity to organic compound could be developed from cost effective and readily available agricultural by-products.

II. MATERIALS AND METHODS

2.1 Materials

Corn cobs (CC) was obtained from Inyi Achi in Oji River Local Government area, Enugu state. The crude oil sample was collected from Port Harcourt Refinery Rivers State. Other samples like premium motor spirit (PMS), diesel and house hold kerosene (HHK) were obtained from NNPC mega filling station, Emene, Enugu.

2.2 Methods

2.2.1 Sample preparation

Corn cobs sample preparation: The corn cobs were thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed cobs were dried properly in sunlight for twelve hours and then left to dry at 65°C in the oven.

Soxhlet extraction: Soxhlet extraction was carried out using hexane as solvent. The extraction of corn cobs was carried out for four hours to wash and to remove extractible components from the corn cobs. The extracted samples were dried in a laboratory oven for 16hours at a temperature of 60°C.

Sieving: After drying, the cobs were sieved with laboratory sieves to obtain homogenous particle sizes. The corn cobs (CC) were sieved using the BS410/1986 laboratory test sieves of aperture sizes, 0.43, 0.85, 1.18, 1.4mm. A mechanical shaker was used to separate the corn cobs into the desired particle sizes.

2.2.2 Acetylation of corn cobs

The acetylation of the corn cobs under mild conditions, in the presence of iodine, using acetic anhydride was carried out using the [11] method of acetylation in a solvent free system. Weight Percent Gain (WPG) of the corn cobs due to acetylation was calculated thus:

$$WPG(\%) = \left[\frac{\text{weightgain}}{\text{originalWeight}} \right] \times 100 \quad (1)$$

2.2.3 Oil sorption studies

The sorption studies was carried out using a scaled down modification of the method presented by [12].

The mass of oil sorbed was calculated thus:

$$M_{oil} = M_{final} - M_{wglass} - M_{sorbent} \quad (2)$$

Where M_{oil} is the mass of oil sorbed, M_{final} is the mass of sorbent + mass of oil + mass of watch-glass after oven drying, M_{wglass} is the mass of the watch-glass and $M_{sorbent}$ is the mass of the sorbent

The oil sorption capacity (OSC) was then obtained thus:

$$OSC = \frac{\text{Weight of oil sorbed}}{\text{weight of sorbent}} \times 100 = \frac{M_o}{M_{sorbent}} \times 100 \quad (3)$$

The oil sorption capacity (OSC) was recorded as gram per gram of sorbent. The procedure was carried out in duplicates and the mean of the results reported.

2.2.4 Fourier Transform Infrared Spectral Analysis

The properties of the reaction products were characterized by Fourier Transform Infrared (FTIR) using KBr to determine whether a chemical reaction took place between corn cobs and acetic anhydride. The FT-IR spectra were recorded on a SHIMADZU (FTIR-8400S) Fourier Transform Infrared Spectrometer at the National Research Institute for Chemical Technology (NARICT) Zaria. 20 scans were collected for each measurement over the spectral range of 4000-400cm⁻¹ with a resolution of 4cm⁻¹. All spectra were presented without baseline correction or normalization.

III. RESULTS AND DISCUSSION

3.1 Sorption Studies on Corn Cobs

3.1.1 Effects of particle size on the oil sorption capacity of ACC

The curves of Fig 1 below explained the effect of particle size on the sorption capacity of ACC. The sorbent showed an increase in sorption capacity as the particle size decreases for all the oil samples. This phenomenon is as a result of the effect of the surface area subjected to the oil. The increase in oil sorption capacity with decreasing particle size is due to the accumulation of small particles on each other which is a result of plugging pores and capillaries existing between fibers [9]. Adsorption is a surface phenomenon that is directly related to surface area; therefore increasing the surface area increases the specific adsorption. Also surface area affects the absorption of the material to a good extent. As the surface area increases, it increases the capillaries that are being formed and hence increases the absorption [13].

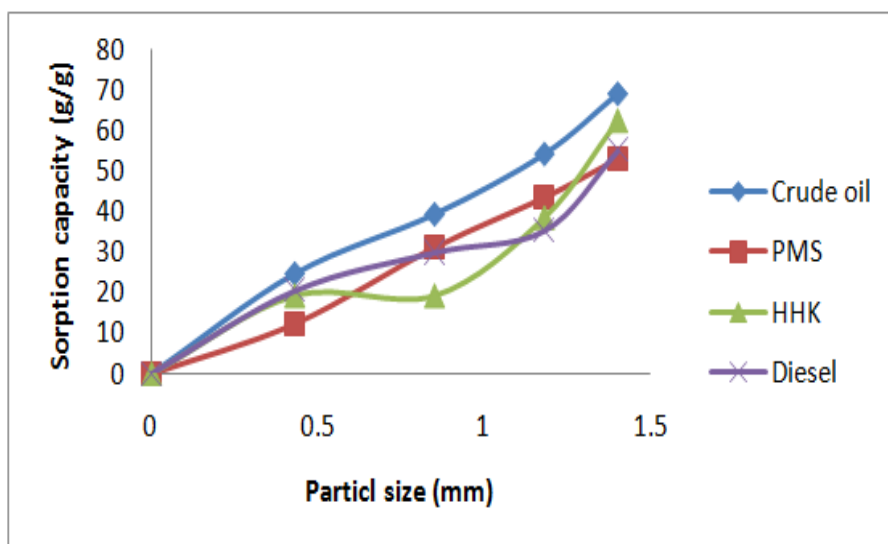


Figure 1: Effect of particle size on the oil sorption capacity of ACC for the oil samples at 20⁰C. Where PMS is premium motor spirit and HHK is house hold kerosene.

3.1.2 Effects of sorption time on the oil sorption capacity of ACC.

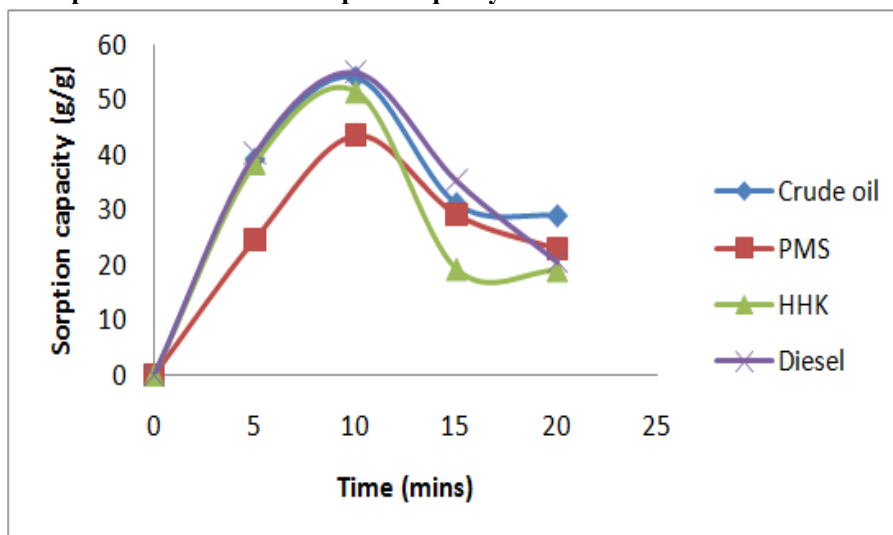


Figure 2: Effect of sorption time on the oil sorption capacity of the ACC for the oil samples at 20⁰C. Where PMS is premium motor spirit and HHK is house hold kerosene

The effect of sorption time on the sorption capacity of the ACC is represented in fig 2 above. The figure shows an increase in sorption capacity as time increased from 5mins to 10mins for the oil samples, and then a gradual decrease from 15mins. This may be due to the fact that the more time oil spends in an open environment, the less viscous it likely becomes, thus leading to the release of oil from the fibers.

3.1.3 Effects of temperature on the oil sorption capacity of ACC

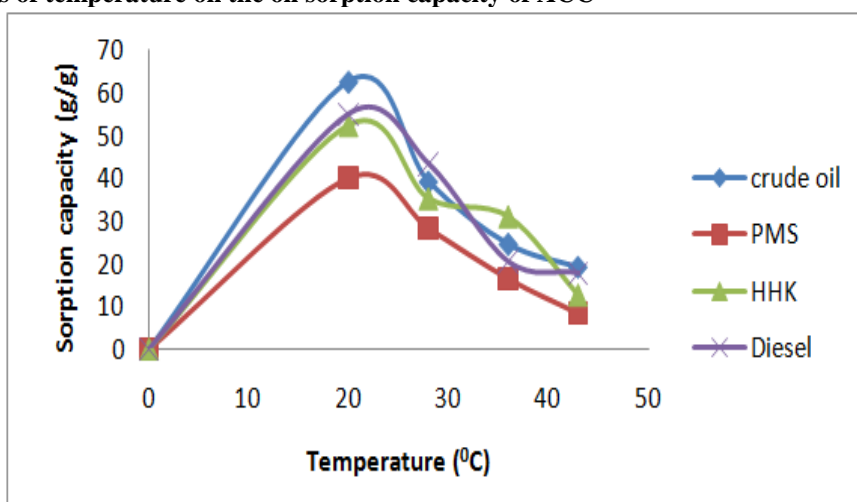


Figure 3: Effect of temperature on the oil sorption capacity of ACC for the oil samples at 10mins.

The result shown in fig 3 indicates that there was a gradual decrease in sorption capacity as the temperature increases from 20°C to 43°C for all the oil samples studied. This means that temperature affects the oil sorption. Meanwhile, at lower temperatures, the high oil viscosity may plug pores and prevent oil to penetrate and increasing temperature more than at room temperature (i.e less or greater than 25 °C, depending on the location), starts to decrease the sorption capacity because oil starts to be very light which leads to the release of oil from fibers again. [14] and [15] agree with these results.

3.1.4 Effects of Sorbent dosage on the oil sorption capacity of ACC

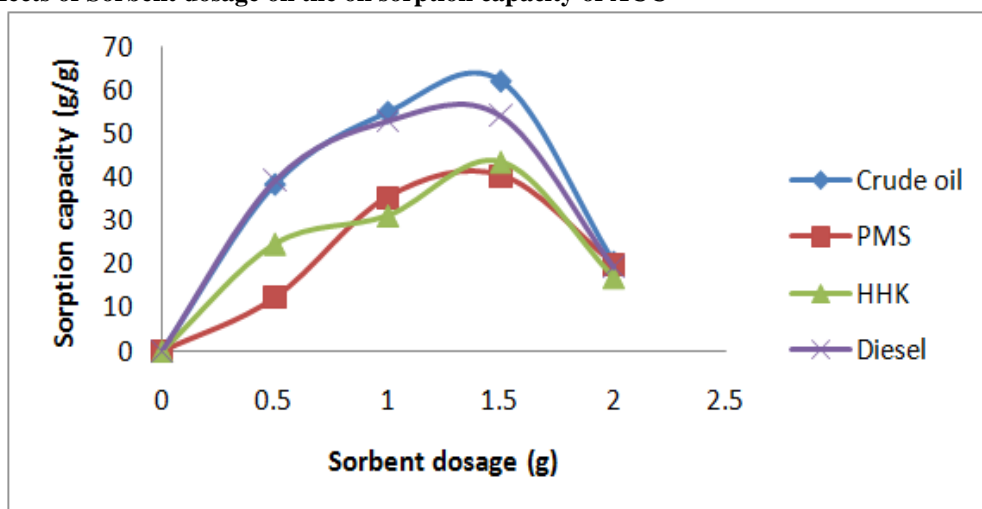


Figure 4: Effect of sorbent dosage on the oil sorption capacity of ACC for the oil samples at 20°C and 10mins.

The curve of fig 4 shows the effect of sorbent dosage on sorption capacity at constant temperatures. To study the effect of increasing sorbent weight on sorption capacity, different weights (from 0.5 to 2.0g) were investigated at constant temperature of 20°C and sorption time of 10mins. The curve showed the increase in sorption capacity of sorbents with increase in sorbent weight from sorbent dosage 0.5 to 1.5g after which they tend to decrease. This decrease may be due to compacting of the fibers as weight increases which may decrease the ability of oil to penetrate the fibers evenly.

3.2 Fourier Transform Infrared Spectral Analysis

3.2.1 FT-IR Spectra

The spectograph for corn cobs, in Fig 5, has a similar structure for most lignocellulosic materials. C-H stretching in methyl and methylene groups (2923cm^{-1}), a distinct O-H stretch at 3430cm^{-1} and a strong broad superposition with sharp and discrete absorptions in the region from 1076 to 1729cm^{-1} are characteristics of these materials.

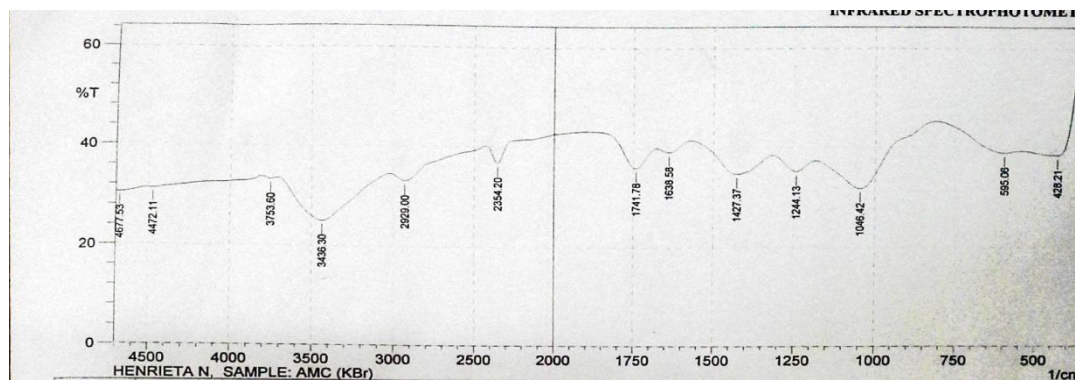


Figure 5: Spectrograph for RCC

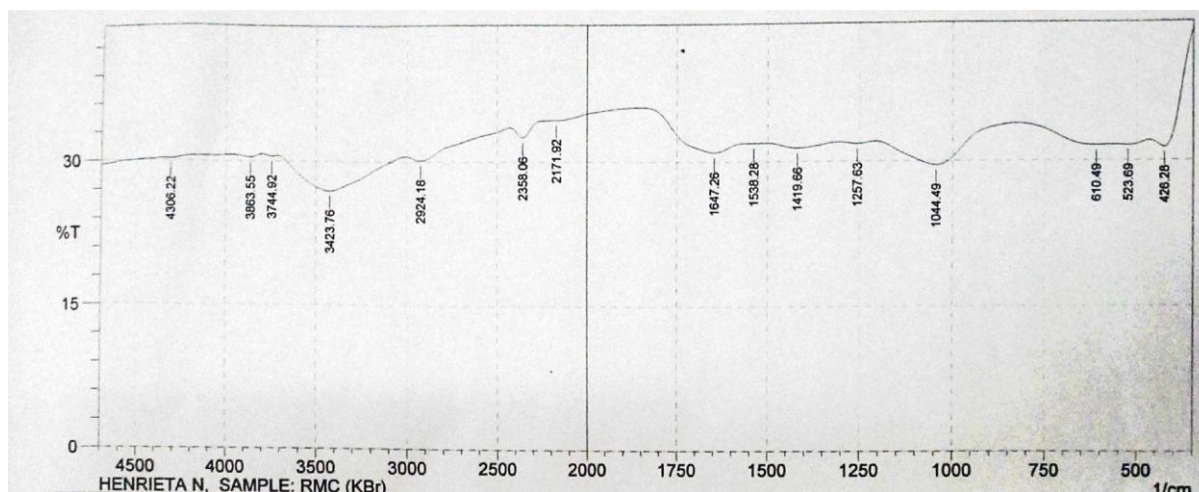


Figure 6: Spectrograph for ACC

Table 1: Assignment of IR bands of functional groups in RCC

Peak (cm ⁻¹)	Intensity	Functional group	
523.69	31.55	Halides	-(CH) ₃ =C-X
610.49	31.56	Bromides /Chlorides	
1044.49	29.57	Alcohols/Phenols O-H & C-O	Aromatic Skeletal vibration of lignin.
		Esters unconjugated	C=O & C-O stretch
1419.66	31.4	Ammonium ion	CH ₃ -N=(R ₁ R ₂)
1647.26	30.94	Alkenyl	C-H & C-C
			Carbon-carbon links of hemicellulose.
2171.93	34.38	Alkynyl	C-H C≡C Stretch
2924.18	30.12	Alkyl	C-H Stretch
		Carboxylic acid	C=O & OH Stretch
3423.76	26.91	Alcohol/Phenol	O-H & C-O Stretch

Table 2: Assignment of IR bands of functional groups in ACC

Peak (cm ⁻¹)	Intensity	Functional group	
595	38.90	Iodides	-(CH) ₃ =C-I
1046.42	31.78	Esters unconj	C=O & C-O
			Aromatic Skeletal vibration of lignin.
1244.13	35.22	Acetate	C=O-O-
		Esters unconj	C=O & C-O
			Strong and broad. Evidence of introduction of an acetyl group.

1427.37	34.74	Ammonium ion $\text{CH}_3\text{-N}=(\text{R}_1\text{R}_2)$		Indicating the presence of an aromatic ring stretch. Shift in band location indicating a structure as a result of acetylation.
1638.58	39.09	Alkenyl Amide	C-H & C-C N-H & C-O stretch	From hemicellulose.
1741.78	35.88	Esters unconj	C=O & C-O stretch	C=O stretch of esters (ascribed to hemicellulose). Confirmation of the introduction of an acetyl group.
2354.2	36.77	Esters unconj	C=O & C-O Stretch	Confirmation bands
2929	33.11	Alkyl group From Methylene	CH stretch from (-CH ₂ -) CH	From cellulose in cobs.
3436	25.07	Alcohol	OH & CO	From cellulose and hemicellulose components of the cobs. A decrease in intensity and a shift away from 3423 to 3436 is indication of a decrease in OH groups present in the sorbent material.

The hydroxyl stretching region (3700-3200cm⁻¹)

The hydroxyl group mainly dominates this region, giving rise to very characteristic band profiles. The strong band at 3423cm⁻¹ in Fig 5 is attributed to OH stretching vibrations from the lignin and cellulose structures. Reduction in the hydroxyl (OH) stretching band at 3450-3100cm⁻¹ for the acetylated sample spectra indicates partial acetylation. This decrease was accompanied by a significant increase in the absorption at around 1638cm⁻¹ characteristic of the C=C stretching bands of alkene. The band 2924cm⁻¹ in RCC spectra indicates a C-H stretch associated with cellulose.

The region 1900-1100cm⁻¹

This region comprises of bands assigned to the main components (cellulose, lignin, hemicellulose). In the FTIR spectra of the ACC, a prove of acetylation is clearly shown by the enhancement of 1741cm⁻¹, which are carbonyl C=O stretching of esters, and the appearance of 1240-1230cm⁻¹ which is a C=O stretching of acetyl group. It was also observed that there was no absorption in the region 1840-1760cm⁻¹ in the spectra of the acetylated sample which indicate that the acetylated product is free of unreacted acetic anhydrides [16; 11]. Also, the absence of peak 1700cm⁻¹ for carboxylic group in the spectra also indicates that these products are free of the acetic acid by-product [16].

IV. CONCLUSION

In this research, the possibility of using raw and acetylated corn cobs as sorbents for eliminating spilled oils from water bodies and mangroves was investigated. The oil capacity of the materials was characterized in this case by oil sorption in simulated conditions. The oil sorption capacity was found to be dependent on the reaction conditions such as particle size, sorption time, temperature, sorbent dosage and the acetylation process. Acetylation of corn cobs with acetic anhydride using iodine as a catalyst in a solvent free system has proved to be a successful method to obtain fibers with high sorption properties under mild conditions. Oil sorption capacity of the modified sorbent were twice as high as the unmodified sorbent. A high WPG of 17.6% is also an evidence of successful acetylation. The results obtained showed the maximum values of oil sorption capacity of the corn cobs to be 28.2g/g CC, while that for acetylated corn cobs was 68.8g/gACC. Successful acetylation was also proven by the FT-IR spectra of the acetylated corn cobs. It is therefore feasible for highly substituted lignocellulosic esters to be obtained under mild conditions. The enhanced carbonyl peak of C=O ester, C-H absorption and -C-O- stretching confirmed the formation of ester bonds. These peaks were observed to be absent in the spectra of unmodified corn cobs sample.

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