EFFECTS OF DILUTE ACID PRE-TREATMENT ON WASTE PEELS OF *MANIHOT ESCULENTA CRANTZ* IN BIOETHANOL PRODUCTION

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ABSTRACT

This work examined the suitability of dilute acid pre-treatment for treating waste peels of *Manihot esculenta crantz* (tropical specie of cassava) for bioethanol production. Waste cassava peels constitute an abundant agricultural waste mostly prevalent in Nigeria. Cassava peels were collected, washed, the brownish parts removed and the white parenchymatous layer dried and ground into powdery form. Dilute acid pre-treatment was carried out using an autoclave. 100ml of 0.5% sulphuric acid was added to 30g of the sample to remove the lignin, to reduce cellulose crystallinity and increase porosity of the material. The mixture was heated to 120 ℃ under a pressure of 25 psi for 1 hour. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy were carried out on the untreated and pre-treated samples. Significant disruption of the outer layer of the cassava peels and removal of lignin due to dilute acid pre-treatment were observed as evidenced in the SEM and FTIR analysis. It was inferred that dilute acid pre-treatment of waste cassava peels using 0.5% sulphuric acid is a suitable method for pre-treating waste cassava peels for bioethanol production.

Keywords: Agricultural waste, bioethanol, cassava peels, parenchymatous, pre-treatment

INTRODUCTION

Bioethanol is the most widely used biofuel worldwide, partially able to replace fossil fuels, reducing the environmental impact of greenhouse gas emissions [1, 2]**.** Bioethanol due to its high energy density, reduced CO_2 emission, greater air-fuel ratio, and more heat of vaporization is one of the promising renewable energy which has a high potential for the replacement of fossil fuels [3, 4].

There has been growing research on viable feedstocks for use in bioethanol production. First generation bioethanol is produced mainly from C6 sugars such as sugar beets, cereals, and sugarcane while second-generation bioethanol is produced from renewable lignocellulosic biomass and industrial by-products or residues [5, 6]. The second generation production of ethanol derived from lignocellulosic materials is being tested in pilot plants [7-9].

Bioethanol can be produced from agricultural crops and biomass example of which is cassava *(Manihot esculenta)* a plant with high starch content. It is often grown in Asia and Africa most especially tropical regions such as Nigeria, India. In Africa, Nigeria is the largest producer of cassava recording about 50 million tonnes per annum, because it is one of the common staple foods [10]. Cassava is a tuberous cash crop with about 94% carbohydrate content and small content of protein and vitamins. Cassava can be processed into different forms for consumption such as garri, fufu, garri flour. There is a renewed interest for the production of cassava and invariably more cassava peels (agricultural waste).In the process of peeling, the two outer coverings, that is, a thin brown outer covering and a thicker leathery parenchymatous inner covering are removed from the roots. The cassava peel is the solid waste removed from the cassava tuber during processing. Study shows that for every 100kg of cassava processed about 10 kg of cassava peel is generated [10]. The peels constitute wastes and serious environmental pollutions especially in the processing center. Study has shown that the agricultural waste biomass can be used as feed stock for ethanol production, hence eliminating the menace it causes to the environment and also provide means by which farmers generate income. In the context of biological processing of cellulosic biomass to sugars for fermentation to ethanol and other products, pre-treatment generally refers to the disruption of the naturally resistant carbohydrate-lignin shield that limits the accessibility of enzymes to cellulose and hemicellulose [11-14]. Pre-treatment plays a significant role in ethanol production from lignocellulosic materials. The objectives are to increase the surface area and porosity of the substrate, reduce the crystallinity of cellulose and disrupt the heterogeneous structure of cellulosic materials. Thus far, no single pre-treatment method has been found to meet all these requirements, instead, a combination of different methods might be applied [15]. Hydrolysis without preceding pre-treatment yields typically 20% bioethanol, whereas yields after pre-treatment often exceed 90%, hence, the need for pre-treatment of any lignocellulosic feedstock for bioethanol production cannot be overemphasized. Since lignocellulosic materials have complex structures, their pre-treatment is not simple. An ideal pre-treatment should fulfill the following conditions [16]:

- Simple and economical operation
- Limited requirements of energy, process water and chemicals
- Limited corrosion
- Ability to alter the structure of lignocellulosic materials
- Selectivity towards polysaccharide losses
- High recovery of valuable hemicelluloses derived products
- Limited production of undesired degradation products (for example, phenolic acids, furfural, or 5-hydroxymethylfurfural)
- Production of substrates with high cellulose

There has not been much research on the use of cassava peels for bioethanol production and the pre-treatment stage is key in determining the overall feasibility of the production of bioethanol from any particular lignocellulosic feed stock, hence the importance of this paper.

Dilute acid pre-treatment is considered a popular and somewhat preferred chemical pre-treatment method due to an abundance of research information on the use of the method for pre-treating a wide range of lignocellulosic feedstock. This paper seeks to investigate the suitability of the use of the dilute acid pre-treatment method for pre-treating *manihot esculenta crantz* peels, an abundant agricultural waste mostly prevalent in Nigeria being the largest producer of cassava in the world [10], for bioethanol production.

EXPERIMENTAL

The materials used in this work include cassava peels which were collected from a local famer in Ekosodin, Benin City, Nigeria. Chemicals used are sulphuric acid and distilled water.

Chemicals

Table 1: Materials and reagents used

Reagents	Uses
Distilled water	Used in the preparation of solutions with specific molarity.

	It is used as an analytical medium It is used for qualitative and quantitative analysis
Dilute sulphuric acid	Used in the pre-treatment of the grinded cassava peels.

Equipment / Apparatus

The equipment and apparatus used in carrying out the experiments include the following: autoclave, round bottom flask, heating mantle, beakers, measuring cylinder, weighing balance, thermometer, conical flask, molecular sieves, oven, grinding machine, scanning electron microscope, fourier transform infrared spectrophotometer, Model FTIR- 8400S at the National Research Institute for Chemical Technology, Zaria.

Feedstock Preparation

Waste Sample of cassava peel was collected, the brownish was part removed and whitish layer with starch content was carefully washed to remove all sand and dirt present. The cassava peel was next dried for approximately three days using sun as a source of heat to remove extract moisture. After drying, the sample was ground using a grinding machine to powder form of about 0.5-1 mm to reduce the surface area. It was sieved to get a homogenous powder.

Pre-treatment of Grinded Cassava Peels

Cassava peels pre-treatment was carried out using an autoclave. 100 ml of 0.5% sulphuric acid was added to 30g of the sample to remove the lignin, reduce cellulose crystallinity and increase porosity of the material. The mixture was heated to 120 under a pressure of 25 psi for 1 hour [17].

Examining Surface Features of the Cassava Peels

Microstructures and the surface property of the treated and untreated sample were observed using Scanning Electron Microscopy at an accelerated voltage of 5.00 kv - 10.00 kv. Digital images for pre-treated and untreated samples were obtained at a magnification of 200,400 micrometres and 1mm respectively.

Fourier transforms infrared spectroscopy was performed to determine the presence of functional group in cassava peels for the treated and untreated sample from which comparison were made.

RESULTS AND DISCUSSION

Effect of Cassava Peel before and After Pre-treatment

The different characterization techniques were used to examine the effects of the cassava peel used for production of bioethanol before and after acid pre-treatment process. The techniques used include Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy. These equipment were used to analyze for the morphology, i.e. the structure and form, and the functional groups present before and after pre-treatment process and as such ascertain if any observable changes were noticed before and after pre-treatment process [18].

Scanning Electron Microscopy

SEM micrographs were taken for native and acid pre-treated cassava peel. The images were captured at 500x magnification in Figures 1 and 2.

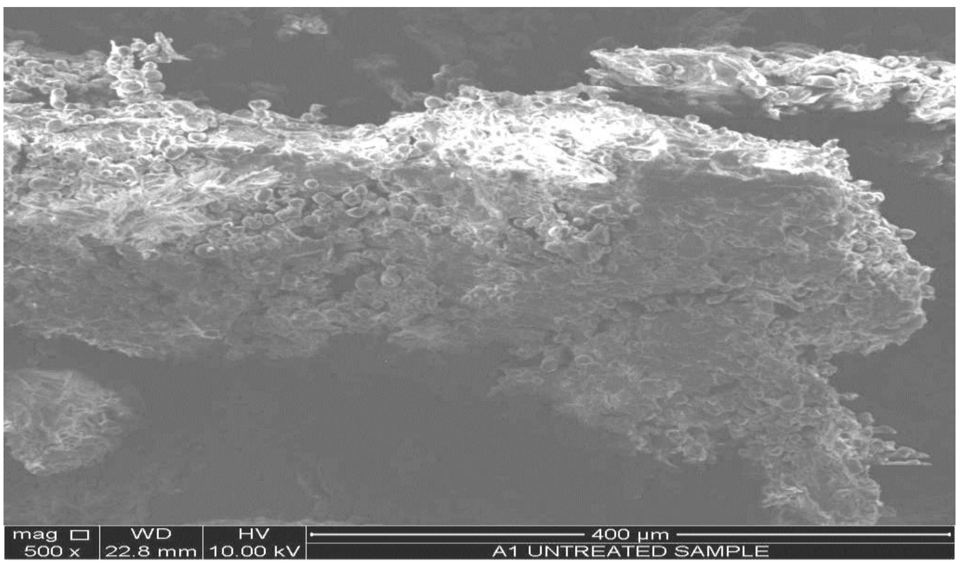

Figure 1: SEM Image under Magnification of 500x of Untreated Sample

From the SEM image in Figure 3.1 it is seen that the un-treated cassava peel shows a tight crosslink structure which looks very compact and rigid in surface structure. This implies an abundant presence of hemicellulose and lignin. It also implies that the cell walls are rigid and very intact.

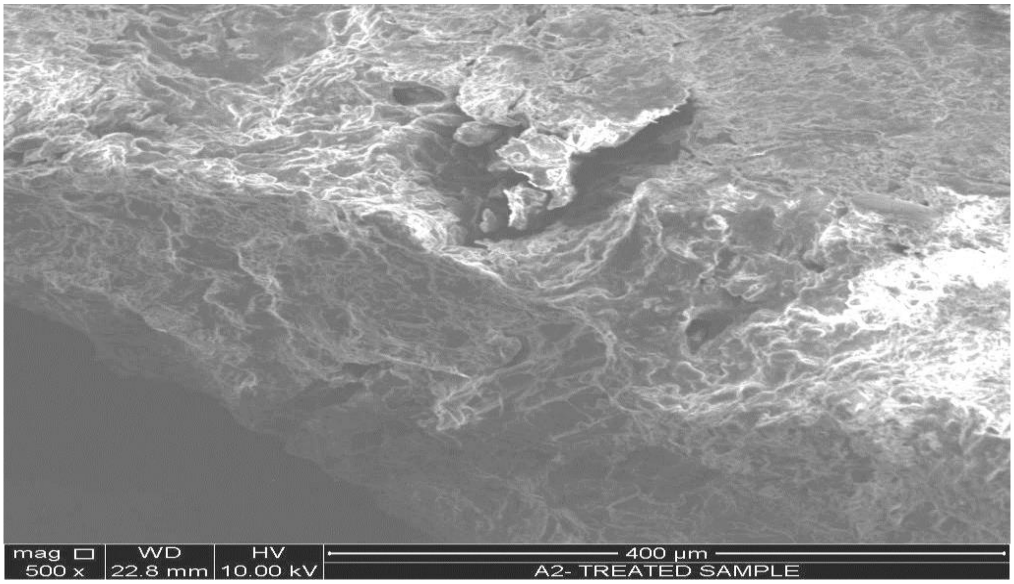

Figure 2: SEM Image under Magnification of 500x of Acid Pre-Treated Sample

An observation of Figure 2 shows that the outer layer of the cassava peels has been significantly disrupted. This disruption is likely due to a partial removal of hemicellulose and lignin. The cell wall was distorted during acid pre-treatment resulting in more surface exposure of the cassava peels. These will in turn give rise to a much more porous structure which will enhance the use of the cassava peels for bioethanol production [18]. The morphological features of the lignocelluloses biomass from cassava peel observed in this study are comparable to the studies of cellulose fibres obtained by [19] and rice straw by [20].

Fourier Transform Infrared Spectroscopy

FTIR was used as a tool to evaluate the changes in chemical composition due to the acid pre-treatment, by analysing the bands that referred to the main components of cassava peels in terms of cellulose, hemicellulose, and lignin. The FTIR spectra of untreated and pre-treated cassava peels are illustrated in Figures 3 and 4.

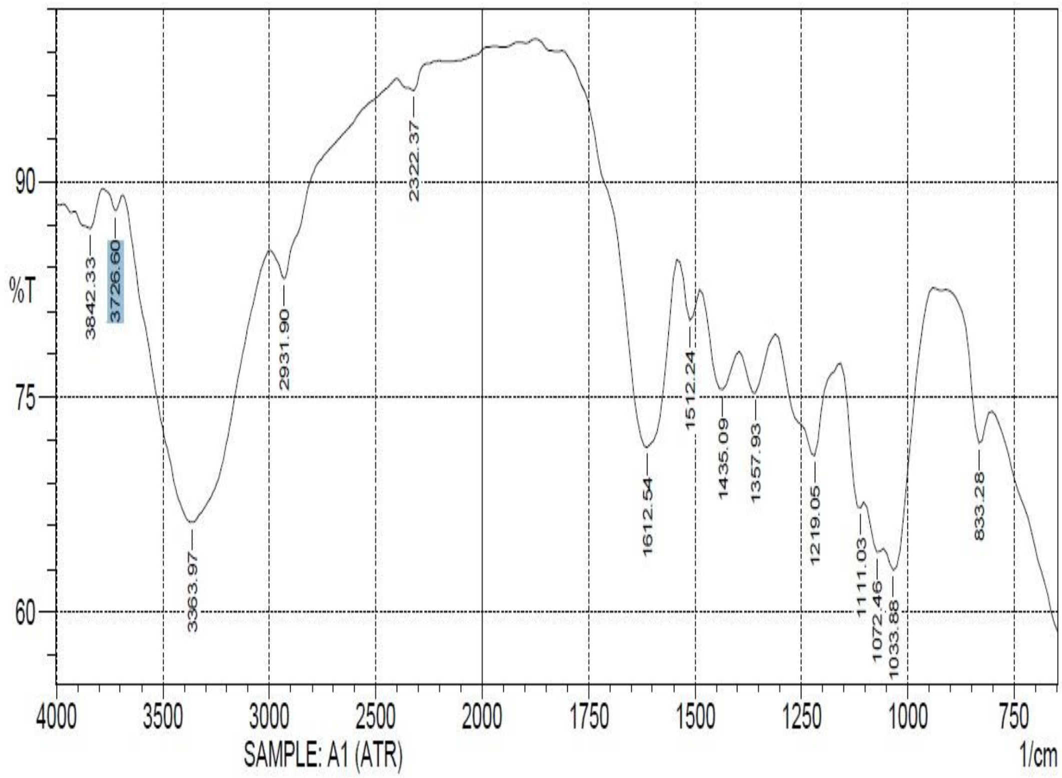

Figure 3: FTIR Spectra of Untreated Sample (Cassava Peels)

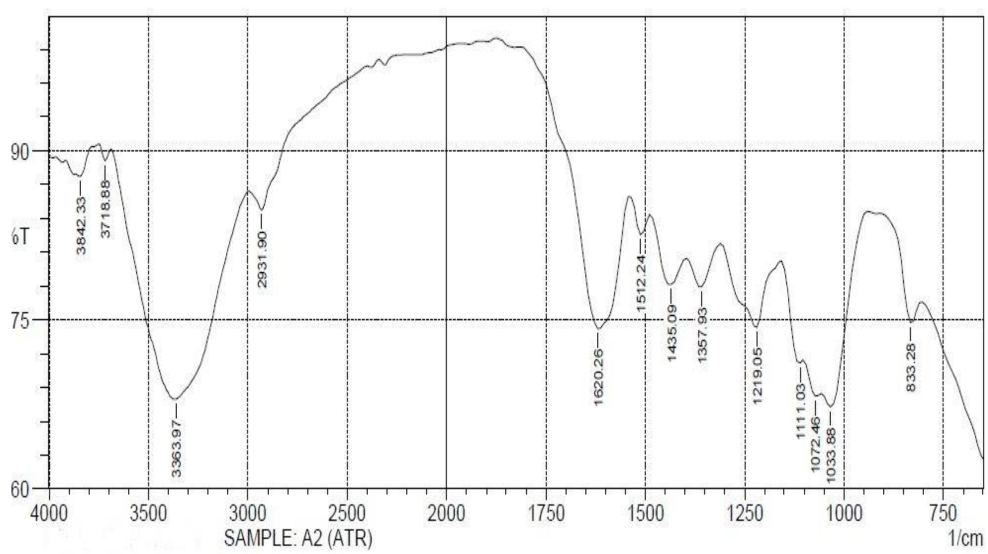

Figure 4: FTIR Spectra of Pre-treated Sample (Cassava Peels)

It can be observed that the FTIR spectrum of the pre-treated sample is similar to those of the untreated samples (native), suggesting that the acid pre-treatment did not cause any serious changes to the biomass. Same result was also obtained by Pereira *et al*. [19]. However, there are some differences in the spectral bands of the different residue fractions, as can be seen in Figures 3 and 4. From the IR chart it is observed that the broad band in the region of 3,600 – 3,200 cm^{-1} is attributable to the OH (e.g., water, alcohol, and phenol) and N-H (amines) stretching vibrations. The broad band at 3,363.97 cm^{-1} is attributable to the phenolic and aliphatic OH group presence in cassava peels. This strong band can be connected to the lignin structure that has linked carbon-carbon and ether bonds, including three major phenylpronanoid monomers consist of sinapyl alcohol, coniferyl alcohol and p-coumaryl alcohol similar to results obtained by Ngadi and Rusli [21]. The strong band at 2,931.90 cm^{-1} relates to C–H vibration of methyl group. The small signal showed the conjugate C–H content in lignin of cassava peel is relatively low. Removal of outer layer of biomass such as lignin and other depositions during delignification is in agreement with weaker FTIR bands at 1512.24 cm^{-1} after acid pre-treatment.

CONCLUSION

SEM and FTIR analysis carried out showed that after the pre-treatment, the removal of outer layer of biomass such as lignin and other deposits during the delignification changed the micro structure and form of the cassava peels. Furthermore, considering the significant disruption of the outer layer of the cassava peels due to dilute acid pre-treatment and the removal of lignin as evidenced in the SEM and FTIR analysis, it can be inferred that dilute acid pre-treatment of waste cassava peels using 0.5% sulphuric acid is a suitable method for pre-treating waste cassava peels for bioethanol production.

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