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Thermo-gravimetry(TGA) and DSC of thermal analysis techniques in production of active carbon from lignocellulosic materials

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ABSTRACT

In this study, the thermal behaviours of two lignocellulosic biomass, (Epicarp Fruit shells of Detarium microcarpum and Balanite eaegyptiaca) were investigated using TGA. The activated carbon produced from the precursors were investigated using BET and DSC. On TGA Profile, Balanite aegyptiaca shell decomposed initially with a weight loss of 12.84% at temperature range within 27.4^{o}C to 245.9^{o}C. The decomposition profile shows weight losses of 41.6% for hemicellulose, 43.2% for both cellulose and lignin, which occur at temperature range of 250^{0}C to 350^{0}C, slightly > 350^{0}C and up to 890^{0}C respectively. Detarium microcarpum decomposed initially with weight loss of 15.9% at temperature range of 42.4^{0}C to 386.7^{0}C due to moisture and volatile matter. The volatilization associated with weight loss of 75.5% within temperature range of 397^{0}C to 536^{0}C is due to the release of hemicellulose and cellulose. Finally, a weight loss of 2.58% occurred within a temperature range of 540^{0}C to 890^{0}C, due to the released of lignin. From the DSC analysis, the level of heat energy flow through the carbon decreases as BET surface area increases. The BET surface area were in the order; ACDMPA > ACDMZC > CAC > ACBAPA > ACBAZC, while that of heat energy transfer through the carbon produced were in this order; ACBAZC > ACBAPA > CAC > ACDMZC > ACDMPA. The thermal behaviour exhibited by the precursors and activated carbon from TGA and DSC results respectively, verified that the precursors are good biomass that produce a good characteristic carbon.

Key words: TGA, DSC, BET, Cellulose and Lignin.

INTRODUCTION

In recent years, studies have been carried to utilize biomass in various systems at their utmost efficiency. For this, biomass can be characterize to study their behaviour during thermal conversion. Valuable information such as reaction mechanism, kinetic parameters, thermal stability, heat transfer, melting point, boiling point and phase transformation [1].

Regarding characteristics of Lignocellulosic materials can be obtained from thermos-gravimetry analysis (TGA) and differential scanning calorimeter (DSC). Besides, these analyses also give useful data on specific temperatures where various heterogeneous reactions occur throughout the pyrolysis of biomass inside the TGA [2].

The behaviour of cellulose, hemicellulose and lignin, which constitutes the three major components of biomass must be well understood in order for researcher to understand their pyrolysis [3].

Hemicellulose is the easiest to be pyrolyzed among the three major fractions of a lignocellulosic biomass due to its linear polymer structure with short side chains [1,4]. In contrast, cellulose is constructed of semicrystalline arrays of chains associated with one another, while lignin is a complicated structure of phenolic polymer that envelop the polysaccharides of the cell walls which produces hard and durable composite materials [5, 6]. According to [1] and [7], the most reactive compound, hemicellulose decomposes at temperature between 200 to 350^{0}C, whereas

cellulose decomposes from 305 to 375^{0}C, lignin steadily decompose over 250 to 500^{0}C. However, some reported that pyrolysis of heavier volatiles such as lignin occurs from temperature as low as 150 up to 900^{0}C since it is more thermally stable in contrast to cellulose and hemicellulose [8].

Thermal analysis Instruments and its applications are very important for characterization of activated carbon precursors, as well as intermediate and final products.

Activation studies have been done in the TGA to determine appropriate conditions for activation of carbon samples in larger scale test facilities [1].

The aim of this study is to perform a thermogravimetry Study and DSC measurement to observe the pyrolytic behaviour of two lignocellulosic biomass (*Detarium microcarpum* and *Balanite eagyptiaca*) widely available in Northern - Nigeria at wide temperature range, and to observe decomposition or transformation profiles throughout the process.

MATERIALS AND METHODS

2.1. Collection of precursors and pre-treatment.

Balanite aegyptiaca fruits and *Detarium macrocarpum* fruits were purchased from Dutsin-ma market in Dutsin-ma Local Government area of Katsina State. The edible parts of *Balanite aegyptiaca* and *Detarium macrocarpum* fruits were removed leaving behind the epicarp shell , which were washed throughly with distilled water to remove impurities. The samples were sundried for a week, washed again with distilled water and then dried in a thermostatic Oven at 105^{0}C for 48 hours which facilitated easy crushing and grinding. The dried samples were pulverised using mortar and pestle and sieved with a mechanical shaker into particle size of 850µm.The fine sieved particles were stored in a clean air tight plastic containers ready for further treatment.

2.2. Thermogravimetric analysis (TGA) of the Precursors.

The Thermogravimetric analysis (TGA) profile of the raw material clearly gives an approximation about the weight loss with respect to temperature due to the release of moisture and volatile matter. TGA of the raw precursor (epicarp of *Balanite aegyptiaca* and *Detarium macrocarpum* seedshell) were carried out by a Shimadzu, DTG – 60H thermogravimetric analyzer. About 30 mg of the sample was taken in silica crucible, and was subjected to pyrolysis under N_2 flow (35 cm^3/min) at 500 ^{o}C with heating rate of 10 ^{o}C/minutes [9].

2.3. Production of activated carbon.

The activating agents used were H_3PO_4 and $ZnCl_2$**.** Standard methods were followed in the production of carbon as described when Neem husk was used [10].

The dried product (Carbon) obtained was stored in a clean air tight containers for BET surface area characterization and DSC analysis.

2.4. Surface area characterization

Nitrogen (N_2) gas adsorption-desorption isotherms on prepared Activated carbon at liquid nitrogen temperature (–195.6 ^{o}C) were carried out using an automatic adsorption unit, Autosorb – 1 (Quantachrome). The samples were degassed at 200 ^{o}C for 5 hrs prior to analysis so as to remove any adsorbed moisture or other impurities bounded to the surface of the sample, and then standard method were followed to determine the BET surface area as described in the analysis of carbon produced from Bael Fruit shell [9].

2.5. Differential Scanning Calorimetric measurement.

The heat flow pattern of the porous carbon obtained from ACBAPA, ACBAZC, ACDMPA, ACDMZC and the commercial activated carbon (CAC) which served as standard were displayed on the monitor attached to the TA-60 unit of the Calorimeter as described in the analysis of carbon produced from Brachystegia eurycoma and prosopis Africana seed hulls [11].

RESULTS AND DISCUSSION

3.1. TGA of the precursors

The Thermo-gravimetric analysis (TGA) profile of the raw materials (precursors) clearly gives an approximation about the weight loss with respect to temperature due to the release of surface bounded water, volatile matter, hemicellulose, cellulose and lignin present in the precursors. It also gives an insight of the carbonization temperature range required for production of activated carbon.

The TGA profiles for *Balanite aegyptiaca* and *Detarium microcarpum* raw samples are shown below in Figures 1 and 2 respectively.

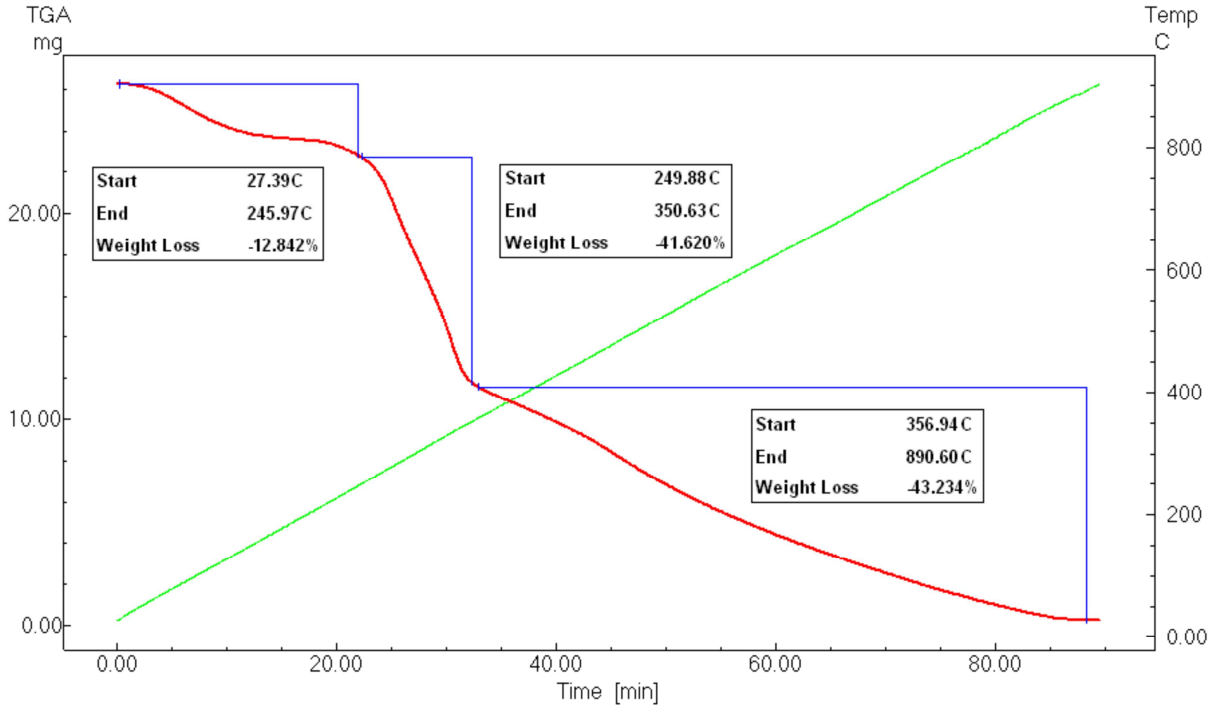

Figure 1: TGA of *Balanite aegyptiaca* shell

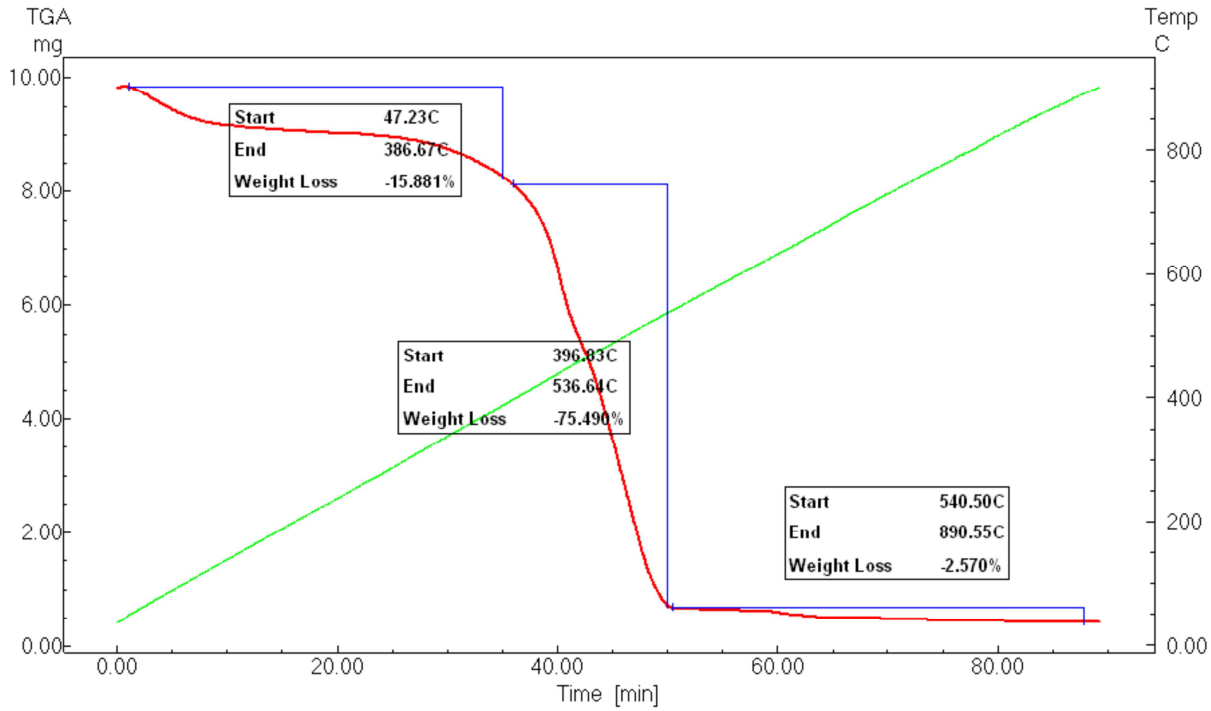

Figure 2: TGA of *Detarium microcarpum* shell

Figure 1 shows the thermo-gravimetric analysis (TGA) of the raw sample of *Balanite aegyptiaca* shell. On the TGA profile, the initial step shows weight loss of 12.84% in the temperature range of 27.4^{o}C to 245.9^{o}C, which might have resulted from the release of moisture and volatile matter. The second step shows steep weight loss of 41.6 % at the temperature range from 250^{o}C to 350^{o}C.

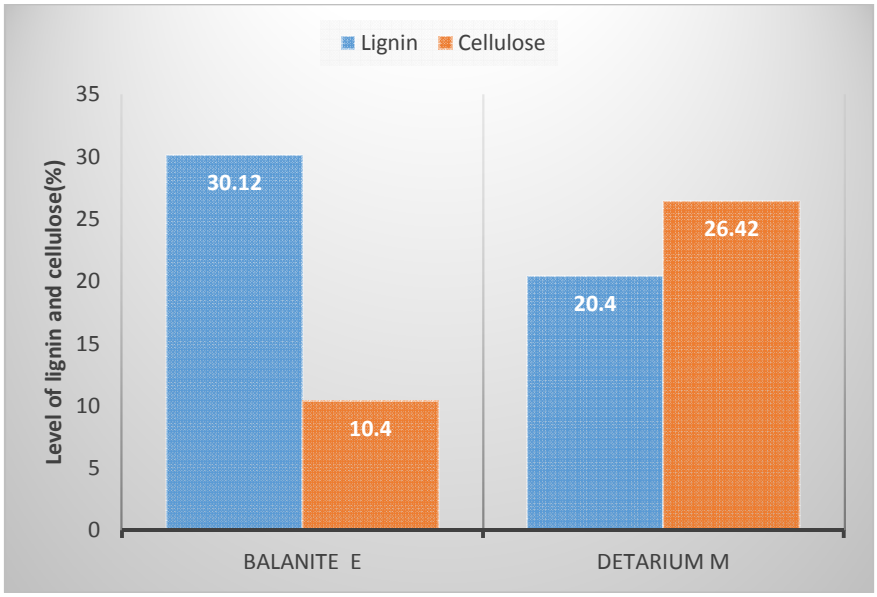

Figure 3. Level of lignin and cellulose in the precursors

The weight loss may be associated mainly to the decomposition of hemicellulose and other low molecular weight polymer of furan derivatives. The third step involved a gradual loss in weight at temperature above 350^{o}C, which may be attributed to decomposition of cellulose and continued up to 891^{o}C due to the decomposition of lignin with weight loss of 43.2%. On the other hand, Figure 2 illustrate the TGA profile of *Detarium microcarpum* raw precursor. At first, there was a weight loss of 15.9 %, which was attributed to the released of moisture content and volatile matter at a temperature range of 42.4^{o}C to 386.7^{o}C. The second decomposition stage of the profile shows a weight loss of 75.5 % at a temperature range of 396.8^{o}C to 536.6^{o}C,due to the decomposition of hemicellulose and cellulose. The final stage of the profile exhibited weight loss of 2.58% at a temperature range of 540^{o}C to 890^{o}C resulted from the decomposition of lignin. The TGA profiles of both precursors in this study resemble the one obtained, when Bael fruit-shell was used [9]. At this point, the carbonisation temperature range of 400^{o}C to 890^{o}C was consider for this research.

Figure 3 illustrate the amount of Lignin and cellulose in *Balanite aegyptiaca* shell to be 30.12% and 10.40% respectively, while its content in *Detarium microcarpum* shell was 20.40% and 26.42% respectively. Materials with high lignin content develops AC with high yield whereas, materials with high cellulose yields AC with high surface area and porosity. The results obtained is in agreement, when Bael fruits was used to produce carbon [9].

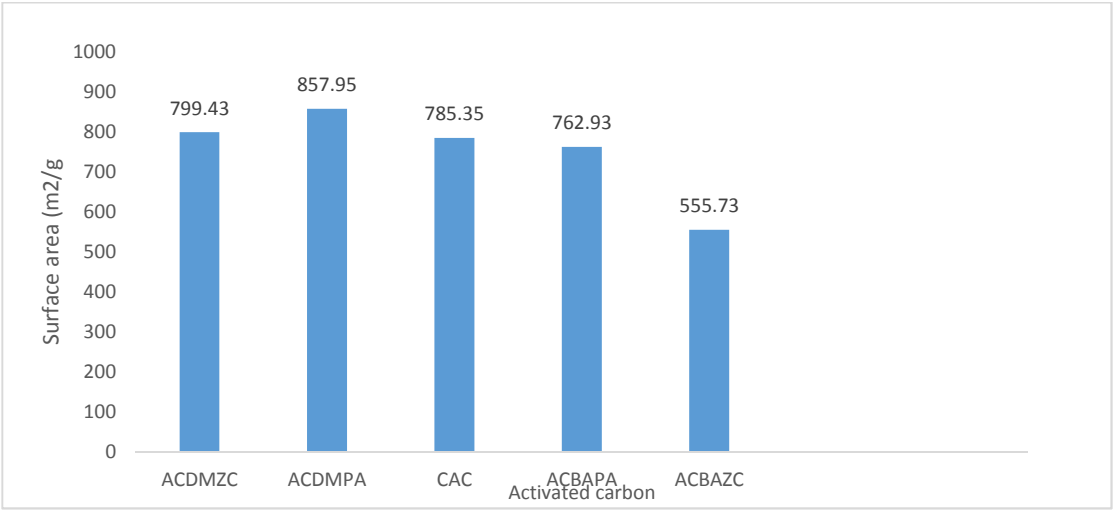

Figure 4: BET surface area of the carbon produced and commercial activated carbon
ACDMPA = Activated carbon from Detarium microcarpum activated with H3PO4
ACDMZC = Activated carbon from Detarium microcarpum activated with ZnCl2
ACBAPA = Activated carbon from Balanite aegyptiaca activated with H3PO4
ACBAZC = Activated carbon from Balanite aegyptiaca activated with H3PO4
CAC = Commercial activated carbon.

3.2. BET surface area

Figure 4 illustrate the BET Surface area of ACDMPA, ACDMZC, CAC, ACBAPA and ACBAZC were 857.99m^2/g, 799.43m^2/g, 785.35m^2/g, 774.76m^2/g and 555.73m^2/g respectively. Most widely used commercial activated carbons have specific surface areas ranging from 750- 1500 m^2/g [11], hence the chemically carbonized precursors produced activated carbons for this study possessed surface area that falls within the standard range of commercial carbon. However, the surface area of the carbon from *Detarium microcarpum* is greater than the ones produced from *Balanite aegyptiaca*. The nature of the precursors, in which the level of lignin and cellulose are not the same may be the reason for the differences.

3.3. DSC

Figures 5 to 9 illustrates the heat flow pattern based on the results obtained from the carbon produced and that of commercial activated carbon.

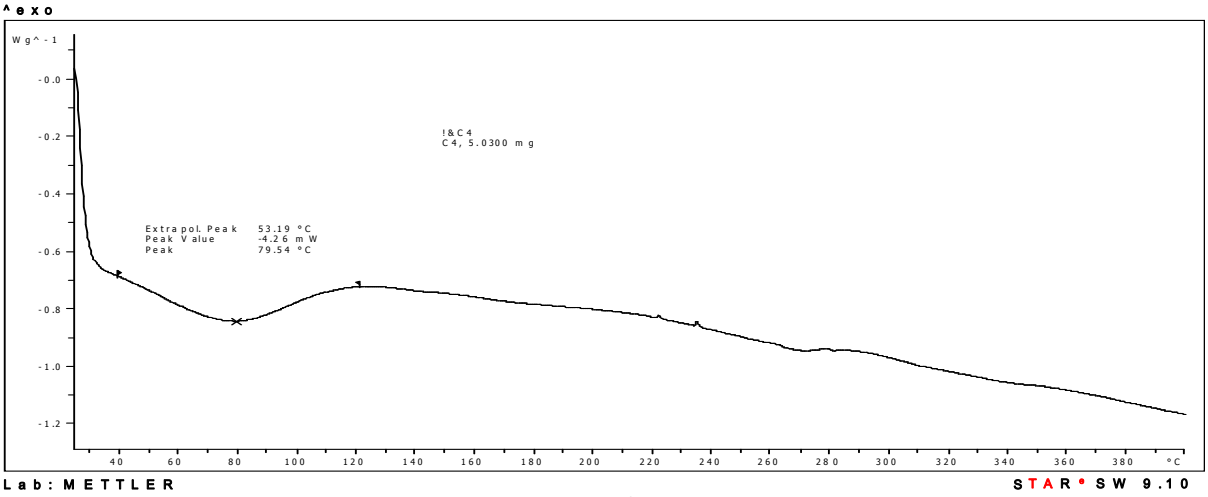

Figure 5: DSC of ACDMPA

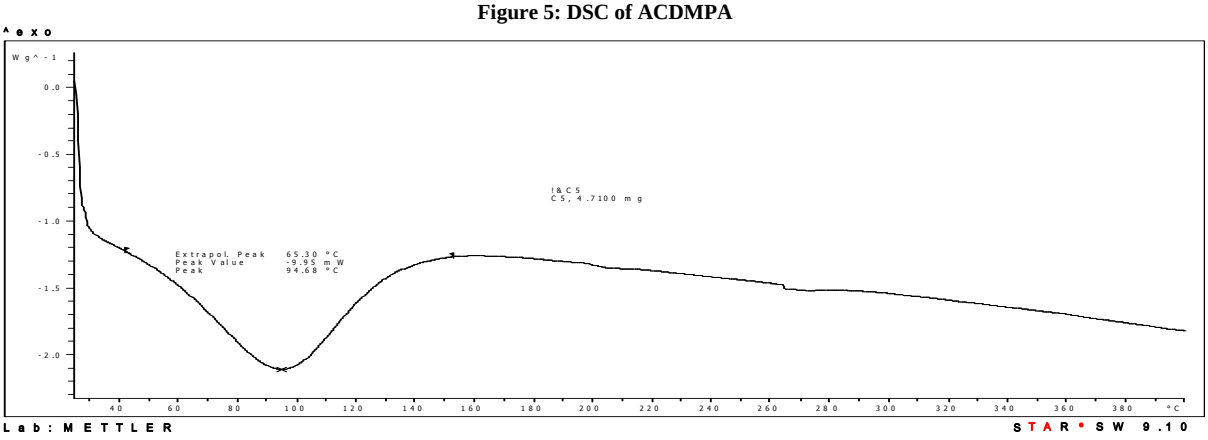

Figure 6: DSC of ACDMZC

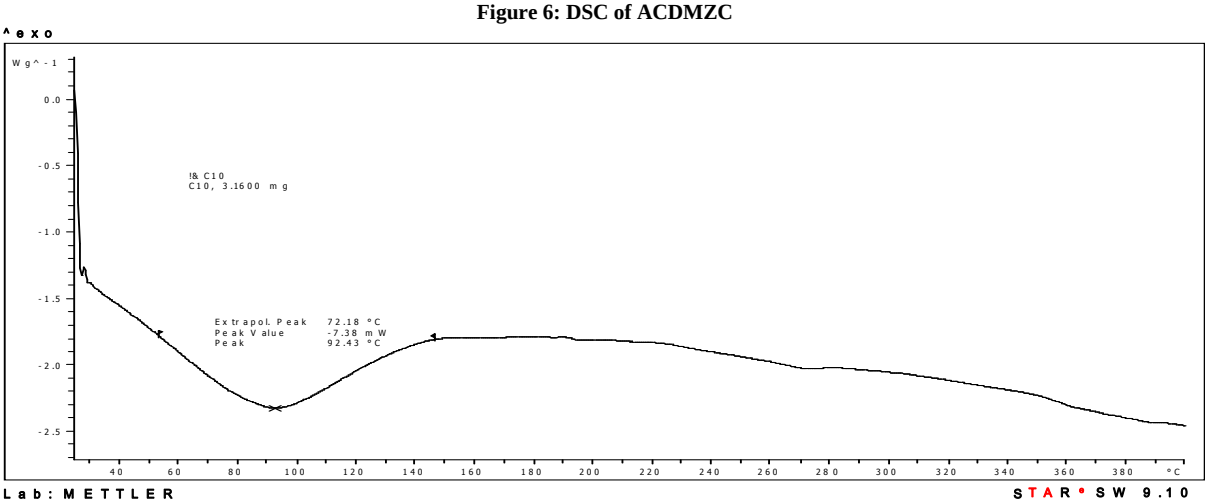

Figure 7: DSC of CAC

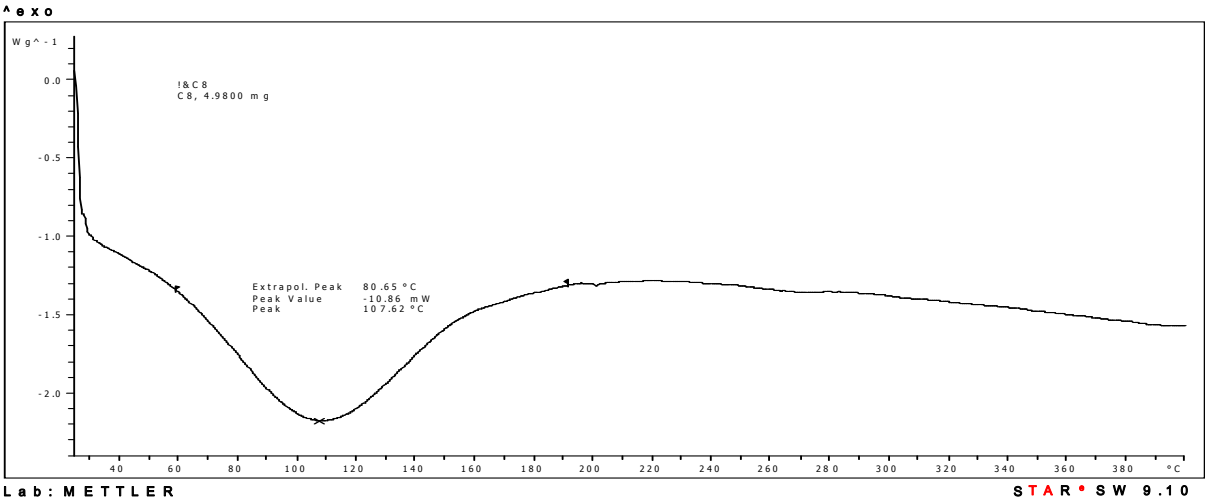

Figure 8: DSC of ACBAPA

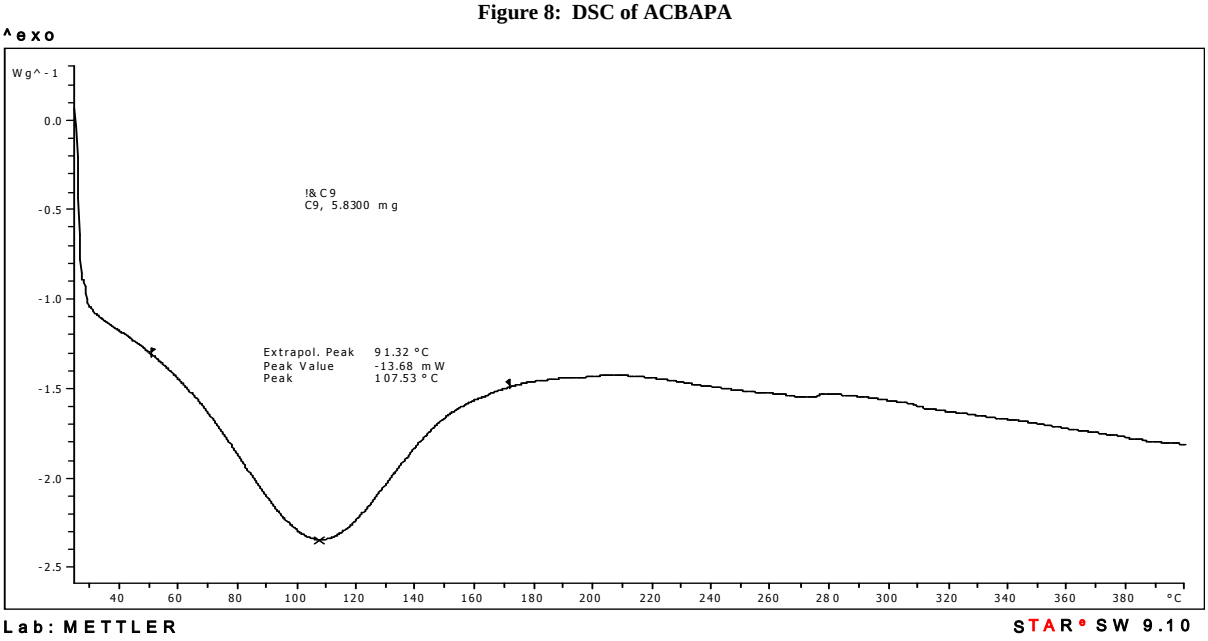

Figure 9: DSC of ACBAZC

Presented in Figures 5 – 9 were the DSC plots which illustrates the heat flow or heat transfer of the carbon produced from the precursors and that of commercial activated carbon, which indicate poor heat transfer, which may be attributed to the porosity nature of the carbon produced. From the results obtained, ACDMPA has the lowest value of heat transfer of 0.2555Jmin^{-1} due to its high porosity and surface area, while ACBAZC has the highest value of heat flow of 0.8206Jmin^{-1} when compared to other form of carbon because of its low porosity and surface area. The results obtained is similar to research carried out by [11] using *Brachystegia eurycoma* and *Prosopis africana* seed hulls. The heat transfer pattern or heat flow through the activated carbons produced for this research was very low generally due to high porosity, large surface area and discontinuity of the carbon structural frame work or lattice, which is in line with the research done earlier [11,12].

CONCLUSION

From the TGA analysis, it shows the decomposition profile of the epicarp of *Detarium microcarpum* and *Balanite aegyptiaca*, which indicated the percentage weight loss associated with Hemicellulose, Cellulose and Lignin at different temperature. Among the three components, volatilization of hemicellulose occur first, followed by cellulose and finally lignin as temperature increases. The carbonisation temperature range of 400^{o}C to 890^{o}C was consider for this study based on the decomposition profile from TGA. The BET surface area of the carbon were very high enough, when compared with standard from literature, which proved that the adsorbent has many sites ready to interact with adsorbate. The DSC analysis gives us useful information about the heat energy transfer through the carbon produced. The magnitude of heat transfer within the carbon generally decreases with increase in surface area

of the carbon due to discontinuity of the carbon structural framework, provided there is no intense surface modifications of the carbon.

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