

Thermal Activation of *Canarium Schweinfurthii* Nutshell

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Abstract: Activated carbon was thermally produced from *Canarium schweinfurthii* nutshell having particle size distribution of 2.0-2.8mm. In doing this, the effects of production conditions on the characteristics of the produced activated carbon were studied. Temperature and duration of carbonisation and activation were the conditions investigated. Carbonisation was carried out between 400 and 650°C for a period ranging between 20 and 60 minutes. The results obtained indicated that pyrolysis followed shrinking core model as expected. The best result within this range was obtained at 650°C and 60 minutes. The sample activated at 850°C for 20 minutes had the largest surface area and highest adsorptive capacity. The surface areas recorded were BET 41 1.99m²/g and Langmuir 1383.72m²/g with corresponding adsorptive capacity of 3mg/g, using methylene blue. The yield of the activated sample was found to be 21.4%. The quality of the best sample compares favourably with some of the available commercial activated carbon.

Key words: *Canarium schweinfurthii*, Thermal activation, Surface area, Adsorptive capacity, Mass and heat transfer, Yield

INTRODUCTION

Activated carbon is usually produced from carbonaceous materials by thermal or chemical activation methods. It is an amorphous solid with large internal surface area and pore volume. Typical range for surface area is given as 400-2000m²/g, though values as high as 5000m²/g have been reported (Dannenberg *et al.*, 1992; Dunicz, 1961). The pore and size distribution and surface area made available by activated carbon dictate its adsorptive capacity. These important characteristics of activated carbon are influenced by the raw material, activation method and processing conditions. The uses of the product are wide and varied, ranging from purification to catalytic supports (Dannenberg *et al.*, 1992; Hassler, 1963). Wood was the first raw material used in producing activated carbon in 1909 in Europe followed by peats in 1911 and coconut shell in USA in 1913 (Dannenberg *et al.*, 1992). Since then, this very versatile material has been produced from cellulosic materials (nutshells and other plant wastes, sawdust, etc), fossils (peats, asphaltene, coke, coal, etc) and industrial wastes such as pulp wastes and used tyres (Dannenberg *et al.*, 1992; Yehasker, 1978).

Nigeria is blessed with different types of materials from which activated carbon, which is ever in high demand, can be produced. There is abundance of nutshells (coconut shell, palm kernel shell, etc), sawdust and agricultural plant wastes (corn-cob, stalks, etc). Research works carried out on some of these materials indicated their usefulness (Akinyemi and Taiwo, 2004; Odebunmi and Okeola, 2001; Mkyula and Matumba, 1994; Ogbonnaya, 1992; Odozi and Akaranta, 1986). However, because of the need to find new raw materials and optimize the use of those already identified, research and development works on this versatile product must continue to be an on-going process. The nutshell of *Canarium schweinfurthii* (elemi) is presently an abundant waste after the fruit is processed for its oil or eaten. The plant produces the fruits all year round throughout Nigeria (Datti, 2000) and so its utilization principally to produce oil from the pumice and the kernel would leave the nutshell an environmental nuisance.

A preliminary report by Iretiola (2001) and Olawale *et al* (2005) indicated the potential of the nutshell of *Canarium schweinfurthii* for activated carbon production. It is thus necessary to carry out further study to obtain the optimal production conditions for activated carbon from *Canarium schweinfurthii* nutshell. The effect of production conditions on the quality of activated carbon produced from elemi nutshell is reported in this article.

Experimental Section:

Pretreatment of Sample:

The *Canarium schweinfurthii* nutshell was procured from Jos environ in Nigeria and was positively

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identified at the Herbarium, Ahmadu Bello University, and Zaria. It was conditioned, crushed and sieved to obtain particle sizes ranging between 2.0 and 2.8mm following the work reported by Guo and Lua (2003). The furnace and tubular furnace required for both carbonisation and activation processes respectively, were calibrated to facilitate accurate temperature readings. The moisture, ash, crude fibre contents and other properties of the starting raw material (*Canarium schweinfurthii* nutshell) were determined as described by Sheffler (1969). The result is given in Table 1.

Table 1: Proximate analysis of *Canarium schweinfurthii* nutshell

Characteristics	Value, %
Moisture content	10.3
Ash content	1.16
Protein	2.6
Fiber	40
Lipid	3.27
Carbohydrates	37.23

Carbonisation:

About 30g of the prepared nutshell was placed in a clean pre-weighed crucible, which was later transferred to the furnace. The furnace was hermetically sealed to provide an almost air-tight environment. The sample was heated for 20 minutes at 500°C, after which the crucible and its content were allowed to cool in a dessicator. The weight of the cooled sample was noted. This carbonisation procedure carried out at 500°C for 20 minutes was repeated for four other samples respectively at 30, 40, 50 and 60 minutes. Thereafter other batches of nutshell were heated at 550, 600 and 650°C for 20, 30, 40, 50 and 60 minutes. The yield, moisture, ash and carbon contents of the carbonised materials were determined as described by Sheffler (1969).

Activation:

About 10g of the carbonised material produced at 650°C and 60 minutes was activated in a steel tube placed in a tubular furnace. Activation was done at 750°C with steam for a period of 20 minutes, after which the flow of steam was replaced by nitrogen to facilitate cooling in inert environment. The activation at 750°C was further carried out for 30, 40, 50 and 60 minutes. The whole procedure described above was repeated at activation temperatures of 800°C, 850°C, and 900°C. The moisture, ash and carbon contents as well as adsorptive capacity and pH of the activated carbon were determined as described by Sheffler (1969), while the pH were measured with Kent digital pH meter (Model 7055), methylene blue was used to determine the adsorptive capacity. The surface area of some selected samples was determined using water adsorption method described by Adefila *et al* (2003).

RESULTS AND DISCUSSION

From the result shown in Table 1, it can be seen that the precursor is very low in ash content (1.16%) and very high in carbon containing constituents (88.64%). This is an indication of suitability of *Canarium schweinfurthii* nutshell as a precursor for activated carbon production. Other results are discussed in Sections 3.1 and 3.2.

Carbonisation:

Figure 1 shows carbonisation yield as a function of time at different temperatures. As observed, the carbonisation yield decreases with increased temperature and time.

It can be seen from Figure 1 that the percentage loss in weight between 400 and 650°C within a heating period spanning 20 to 60 minutes was between 2-4wt %. This seems to suggest that within this temperature range and after heating for 20 minutes, substantial volatilization and reactions had already taken place. This is in accord with the work reported by Cao *et al* (2004). Even with this, the rate of loss can be seen to increase with temperature. This agrees with the shrinking core model (Levenspiel, 2001) which inferred that non-flaking ash formed around the carbon was burning off and reducing the weight and diameter of the carbonised sample in the course of carbonisation. Using the essence of this model, it could be deduced that the mass and heat transfer associated with the process were enhanced as temperature and time increased (Beek *et al.*, 1983). This position is further buttressed by result shown in Figure 2.

From Figure 2, it is seen that heating between 500 and 650°C at both 20 and 60 minutes, led to constant weight loss rate, whereas for 30,40 and 50 minutes, the rate appeared to be stepwise. The constant rate at 20 and 60 minutes seems to suggest that between 500 and 650°C thermal and mass diffusion were the rate

limiting steps, respectively (Levenspiel, 2001; Beek *et al.*, 1983). At the other heating periods -30 to 50 minutes - , the change in the weight loss rate is an indication of existence of enhanced heat transfer (and reaction). Here it can be inferred that outward diffusion of the formed products is controlling. Heating between 400 and 500°C, for the period between 20 and 60 minutes seems to be associated more with reaction than transfer of mass and/or heat.

Figure 3 indicated increase in carbon content with time and temperature of carbonisation. This is another phenomenon which is supported by shrinking core model. It is expected at high temperature (in our case 650°C) more volatiles and impurities would be consumed as non-flaking ash, thereby leaving the relatively pure carbon as the unreacted core. Carbonisation time seems to favour increase in carbon content. Samples treated at different temperature for the same carbonisation time yielded higher carbon at higher temperature. This is so because supply of heat for prolong time provided the needed conditions for greater pyrolysis of the sample.

As seen from Figure 3, the sample with the highest carbon content was obtained when carbonization was carried out at 650°C for 60 minutes. This sample was chosen for subsequent activation studies, which results are discussed in Section 3.2

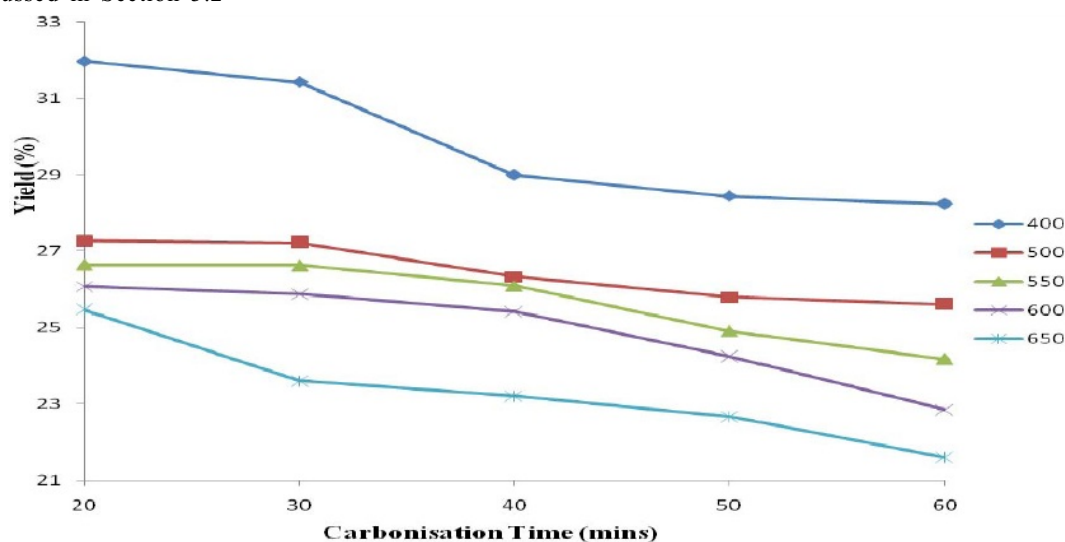


Fig. 1: Effect of Carbonisation Time and Temperature on Yield.

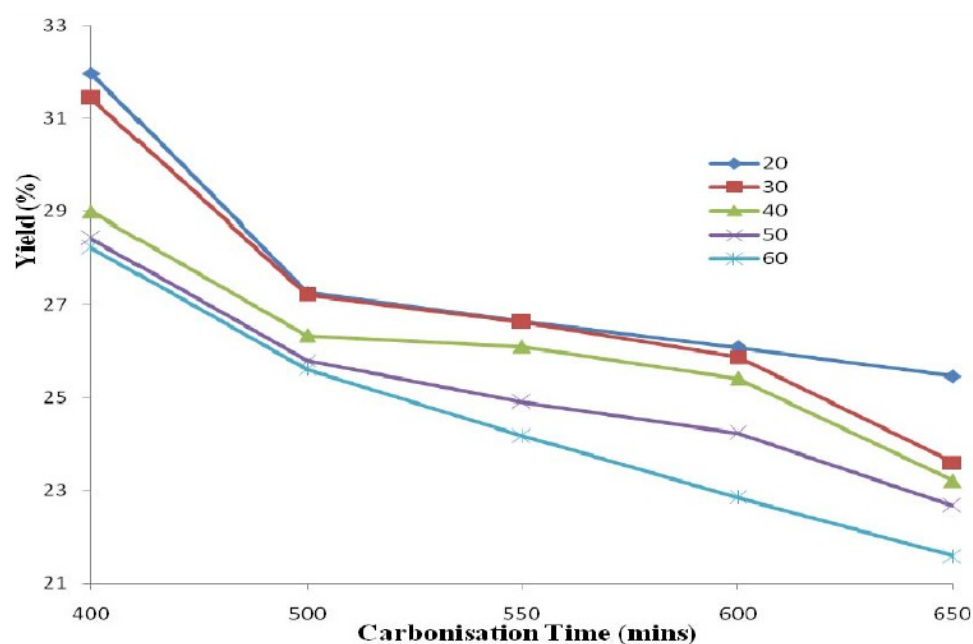


Fig. 2: Effect of Change in Temperature on Carbonisation Yield

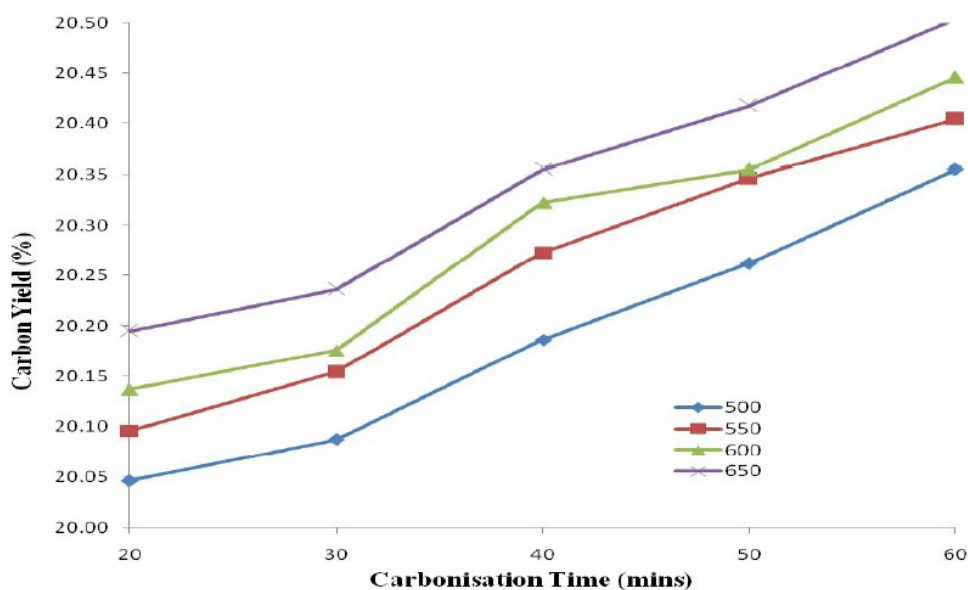


Fig. 3: Effect of Change in Carbonisation Time on Carbon Content

Activation:

Figures 4 and 5 show the effect of time and temperature of activation on the yield of activated carbon. It was observed that the yield of activated carbon decreased as time and temperature of activation increased.

This is expected since during activation, the activating agent (here steam) passes through the carbon skeleton burning out blockages within the body of carbon while expanding and extending the pore network. Therefore it is expected that the yield continues to decrease as temperature and time of activation increases. In specific terms, the reasons for this would include:

The oxidation reactions which involves burning off of some carbons and carbon related impurities such as tars;

The capability of the activating agent (water vapour in this case) for freeing, of the pores hitherto blocked by impurities, free carbons and tars. This phenomenon results from high inherent pressure force of water vapour under saturated to superheated condition at which the activation took place.

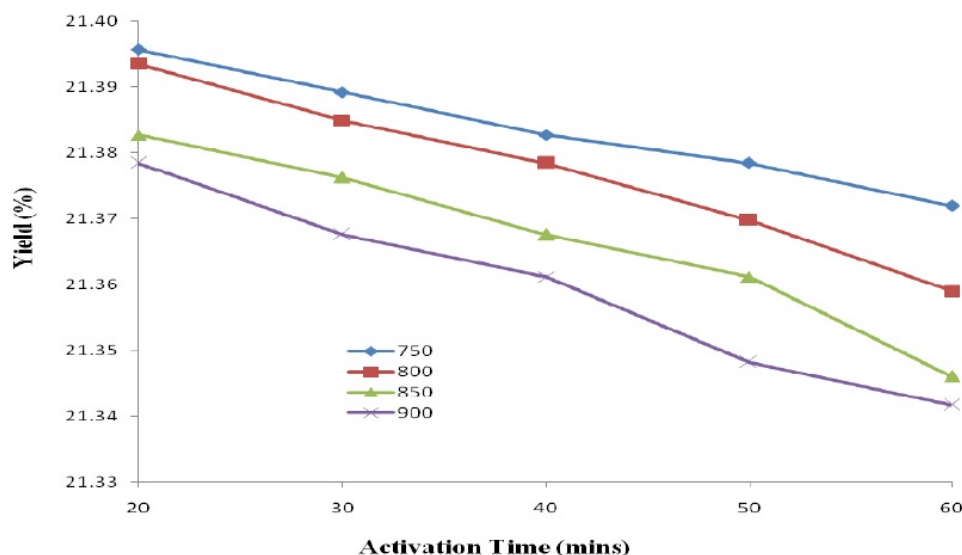


Fig. 4: Effect of Activation Time on Yield

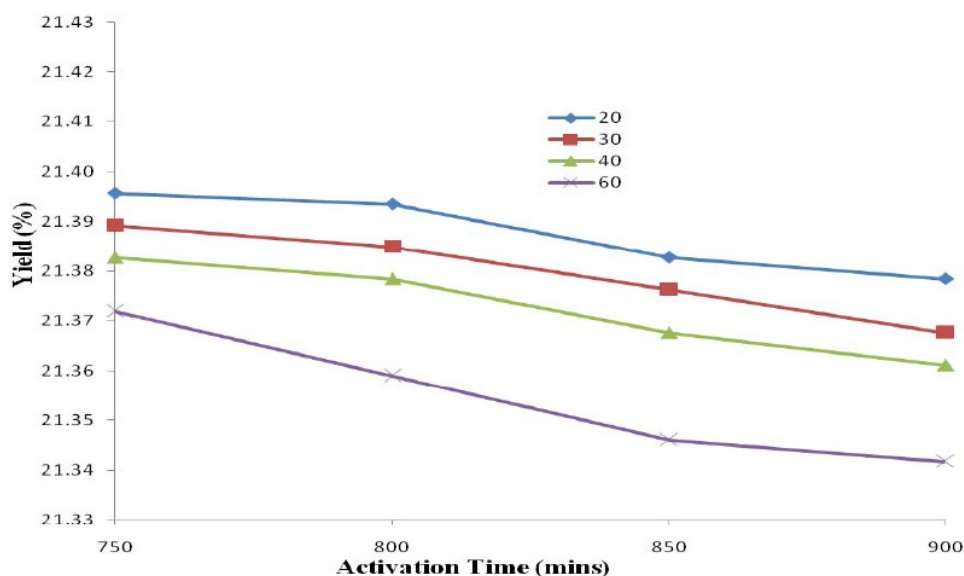


Fig. 5: Effect of Activation Temperature on Yield.

The result of adsorptive capacity of the developed activated carbon samples are presented in Figure 6. Expectedly, sample AS752 (treated at 750°C for 20minutes) has lower adsorptive capacity compared to AS753 (treated at 750°C for 30minutes). This shows the effect of heating temperature and time on pores formation. Ironically, sample AS852 (treated at 850°C for 20minutes) and AS853 recorded about the same adsorptive capacity values which are higher than that of sample AC854 (treated at 850°C for 40minutes). The same observations occurred at a longer heating times (50 and 60 minutes) at 850°C and 900°C. The reason for this is not immediately obvious. However, this may be partly due to the prolong activation time resulting in structural deformation, hence less surface area for adsorption.

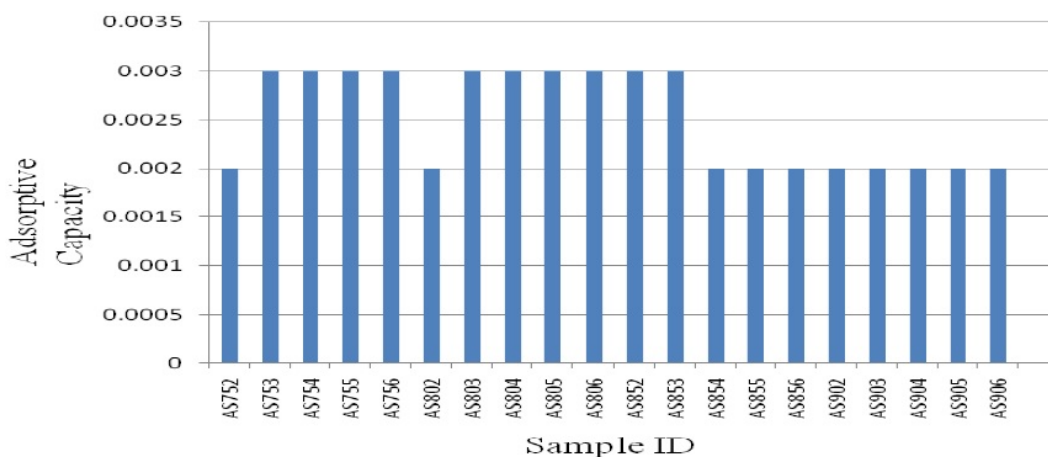


Fig. 6: Adsorptive Capacities of Some Activated Carbon Samples Produced

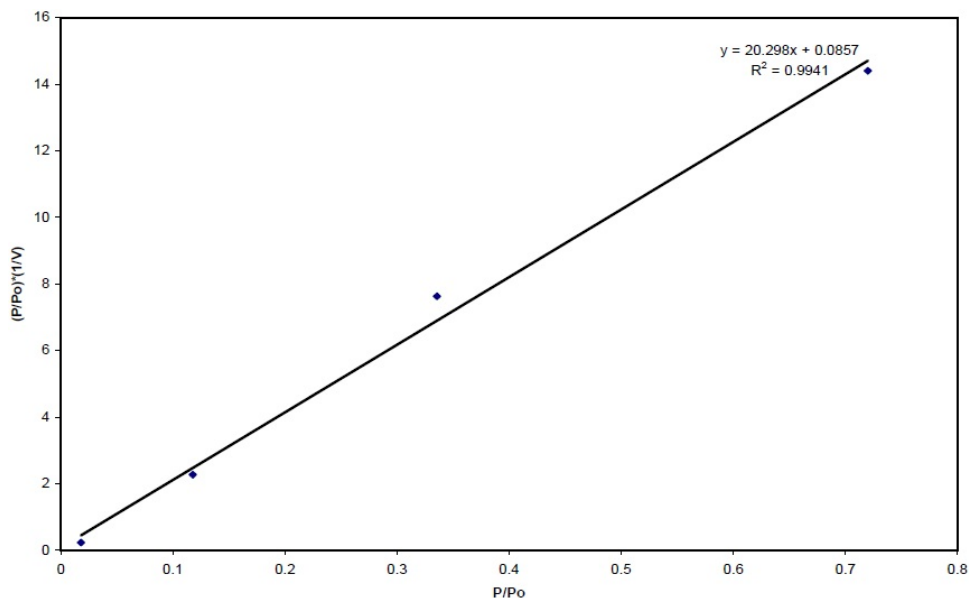
This reason is supported by the results obtained for the specific surface area of samples AC802, AC852 and AC854 shown in Table2.

The Langmuir adsorption isotherm for one of the selected samples AC852 is shown in figure 7.

The specific surface area reported here for our selected samples are in the same range with those reported by McKay and Matumbo (1994) and Dibinin *et al* (1983) for activated carbon prepared from similar starting raw materials. Additionally, it compares favourably with specific surface area of activated charcoal distributed by Fisher Scientific Company (Dunicz, 1961) and the American Norit Commercial (Dibinin *et al.*, 1964).

Table 2: Surface area of some selected activated carbon samples produced

S/No	Sample ID	Surface Area (m ² /g) Using BET Isotherm	Surface Area (m ² /g) Using Langmuir Isotherm
1	AS802	205.43	677.25
2	AS852	411.99	1382.72
3	AS854	250.00	843.74

**Fig. 7:** Langmuir Adsorption Isotherm for sample AS852**Conclusion:**

- The nutshell of *Canarium schweinfurthii* was successfully converted into active and effective adsorbent (with relatively large Langmuir surface area) by thermal activation.
- The activity and surface area of the activated carbon developed compare favourably with the commercially available ones.
- The adsorptive properties appear to depend on conditions of carbonisation and activation. $\frac{3}{4}$ The surface area decreased at higher temperature and prolong period of exposure to thermal treatment.

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