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ACTIVATED CARBONS FROM MATERIALS OF VARYING MORPHOLOGICAL STRUCTURE

Q. MORTLEY, W.A. MELLOWES and S. THOMAS

Department of Chemical Engineering, The University of the West Indies, St. Augustine, Trinidad (West Indies)

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ABSTRACT

This paper describes the production of activated carbon from West Indian biomass. Properties capable of numerical evaluation, both in the raw materials and the solid product of activation have been studied for Caribbean pine, bagasse, coconut husks, and coconut shells. The adsorptive properties of the activated carbons were evaluated and compared with two commercial carbons.

A new technique, using thermogravimetric analysis, for characterizing the development of surface in carbonaceous materials during activated carbon production is presented. It was found that materials displaying higher activation energies produced carbons with higher surface areas.

INTRODUCTION

The thermal behaviour of cellulosic materials to produce gas, liquid and char is well documented [1]. The effects of crystallinity, orientation and crosslinking on the pyrolytic behaviour of cellulosic fibres have been reported [5–7].

There is substantial literature relating to the pyrolysis and combustion of wood [1,8–12]. Little has been reported on the interrelationship between structural morphology and chemical composition of wood and its behaviour when subjected to thermal treatment. Zicherman and Williamson [13] examined the microstructure of wood subjected to fire conditions and related the microstructural responses to both the chemical make up of wood and the physical arrangement of wood structural elements. They noted the retention of high levels of morphological detail in char which were also seen in whole wood.

The thermal degradation of carbonaceous materials to produce activated carbon has received considerable attention [14,15]. The effect of activating media and conditions on the development of adsorptive properties in activated carbon production has been studied by several investigators

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[16–18]. However, apart from chemical analysis little attention has been given to the effect of raw material properties (chemical and microstructural) on the development of adsorptive properties.

This experimental work was carried out to investigate the production of activated carbon from West Indian biomass by carbonization and air activation.

EXPERIMENTAL

Materials

Coconut shells (CS) and husks (CH) were obtained as by-products of the copra industry. Shells consisted of 1 cm cracked fractions; husks being quartered portions of the lignocellulose fibre from the mesocarp of the coconut. Wood residue consisted of shavings from a wood working establishment. Bagasse (B) consisted of fractions exiting the final mill during the milling process in the cane sugar industry. The raw materials were untreated.

Thermal analysis

The thermal characteristics of the materials were investigated using a Paulik derivatograph Model Q-1500 D. Powdered samples (50 mg, 89 μm) were heated at 2.5 °C min^{-1} under flowing argon (50 ml min^{-1}) to 1000 °C. From the thermogravimetric data the topochemical equation of the decomposition reaction, and the kinetic parameters of the process were determined using the Coats and Redfern method [19] for initial parameter estimates, and a non-linear regression model.

Carbonization and activation

Carbonization was carried out in a fixed bed reactor [20] using nitrogen to carry away expelled gases. The temperature was increased linearly to the final temperature at a rate of 3 °C min^{-1}, and maintained at the final temperature for 1 h.

After carbonization the product was dried, ground and screened to 0.2–1.0 mm diameter, and air activated at 500 °C for 30 min using a 5–10 mol % mixture of air and nitrogen. The total pressure was kept atmospheric.

Evaluation of activated carbons

The activated carbons were characterized by BET surface area [21,22], methylene blue (MB) adsorption [23] and iodine adsorption [24]. These are all standard methods.

RESULTS

Raw material characteristics

The proximate, ultimate and chemical analyses of the raw materials are shown in Figs. 1–3. The average elemental composition of dry wood varies very little from 49% C, 6.3% H and 43.5% O. Coconut shells and husks exhibited high carbon contents of 52.8 and 51.5% respectively. Bagasse showed a lower carbon content of 45.5%. Caribbean pine (CP) displayed higher hydrogen content at 6.4%. Coconut husk and shells displayed high fixed carbon (FC) contents of 29.6 and 26.2% respectively, bagasse had a low value of 18.2%. Ash content for bagasse and coconut husk were high at 6 and 3.7%, respectively. Caribbean pine displayed high cellulose content at 51.4%. Bagasse, coconut husks and shells were lower at 42.8, 38.0 33.6%, respectively. The lignin contents in coconut shells and coconut husks were 38.4 and 32.8%, respectively, and significantly lower in bagasse at 15.8%. Volatile matter (VM) contents were 74.4, 72.3, 69.1 and 62.9% for Caribbean pine, bagasse, coconut shells and coconut husks, respectively. H/C ratios were 1.58, 1.46, 1.24 and 1.20 for Caribbean pine, bagasse, coconut shells, and coconut husks, respectively.

Chemical kinetics

The activation energies for the decomposition of the samples were determined using non-linear regression analysis.

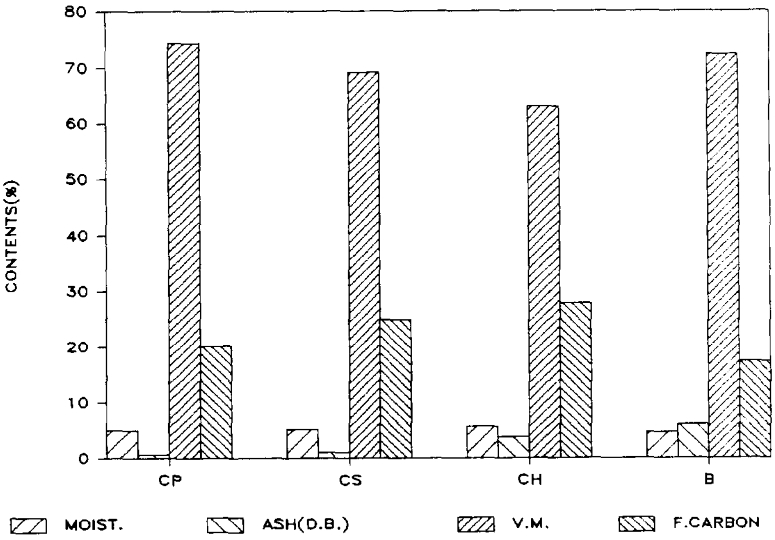

Fig. 1. Proximate analysis, starting materials (D.B. = dry basis).

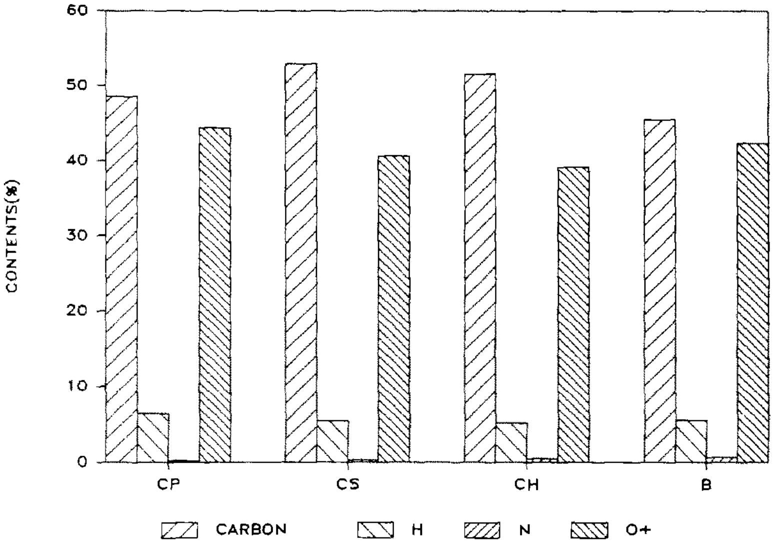

Fig. 2. Ultimate analysis, starting materials.

Pyrolysis of a solid is a typical irreversible chemical reaction. The stoichiometric equation for such a reaction is given by

$$aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)} \qquad (1)$$

where A, B, and C are the original solid, final solid residue, and volatile matter, and a, b, and c are the coefficients of the stoichiometric equation, respectively.

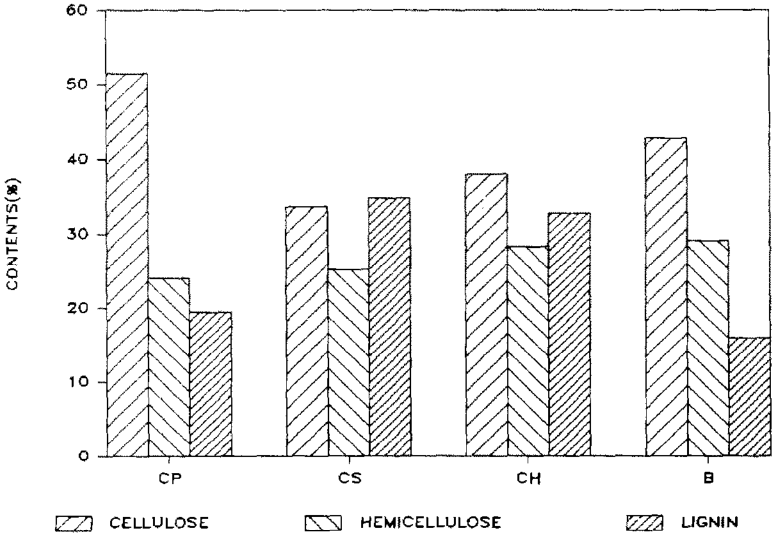

Fig. 3. Chemical composition, starting materials.

The decomposition rate of a solid can be represented by the general rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\mathrm{f}(\alpha) \tag{2}$$

where α is the fraction of the solid decomposed at time t, $\mathrm{f}(\alpha)$ is a function of α depending on the reaction mechanism, and k is the rate constant given by the Arrhenius equation as

$$k = A_0 \exp(-E/RT) \tag{3}$$

where A = frequency factor, E = activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature.

For a linear heating rate, say β K min^{-1}, the following relationship holds

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

Combining eqns. (2), (3) and (4) and integrating between the initial temperature T_0 and any final temperature T, and conversion between α_0 and α respectively, the result is

$$\int_{\alpha_0}^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A_0}{\beta} \int_{T_0}^{T} \exp(-E/RT)\, \mathrm{d}T \tag{5}$$

The right hand side of eqn. (5) is not analytically integrable. Use is made of the Coats-Redfern approximation [19], where

$$\int \exp(-E/RT)\, \mathrm{d}T \simeq \frac{RT^2}{E}\left(1 - \frac{2RT}{E}\right) \exp(-E/RT) \tag{6}$$

This is used for $\mathrm{f}(\alpha) = (1-\alpha)^n$, where n is the reaction order, to obtain initial estimates for the Arrhenius constants. Final values were obtained by regression analysis in a computer procedure. The results are shown in Table 1.

Ash content and pH

The level of impurities in the activated carbons are given by the ash contents shown in Figs. 4 and 5. Some of the impurities in the primary

TABLE 1

Activation energy from non-isothermal TGA

Substrate	Abbreviation	E (kJ mol^{-1})
Carribean Pine	CP	97.91
Bagasse	B	77.36
Coconut Shells	CS	55.97
Coconut Husk	CH	51.02

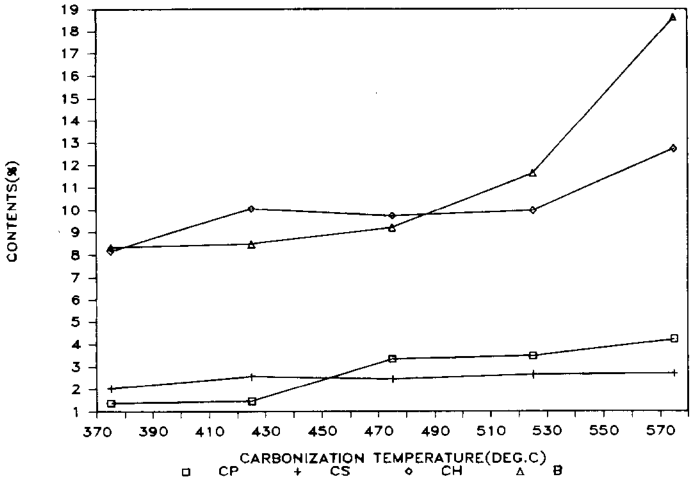

Fig. 4. Ash content, primary charcoal.

charcoal may act as a catalyst during the activation process [25,26]. For primary charcoal there is a temperature dependence for ash content, which showed an increase with final carbonization temperature. The ash contents for the activated carbons do not seem to depend directly on temperature due to oxidation reactions.

The carbons obtained were alkaline as shown in Fig. 6, indicative of the presence of soluble inorganic materials which may have to be removed to allow specific uses.

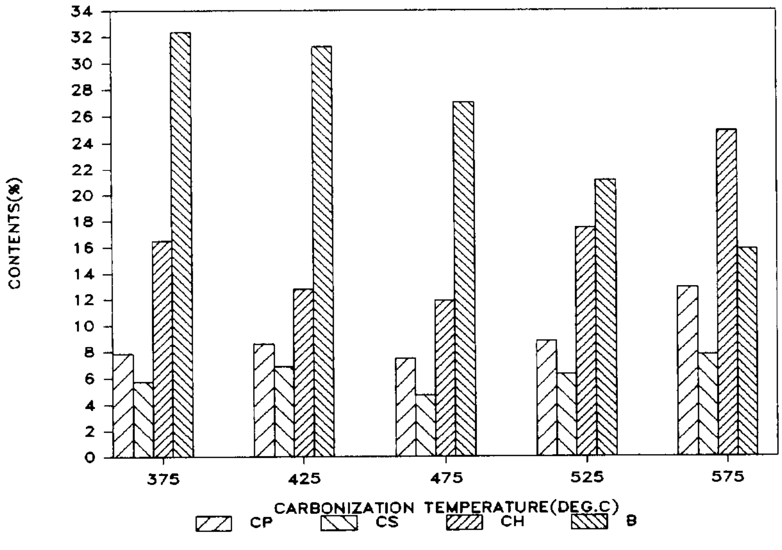

Fig. 5. Ash content, activated carbon.

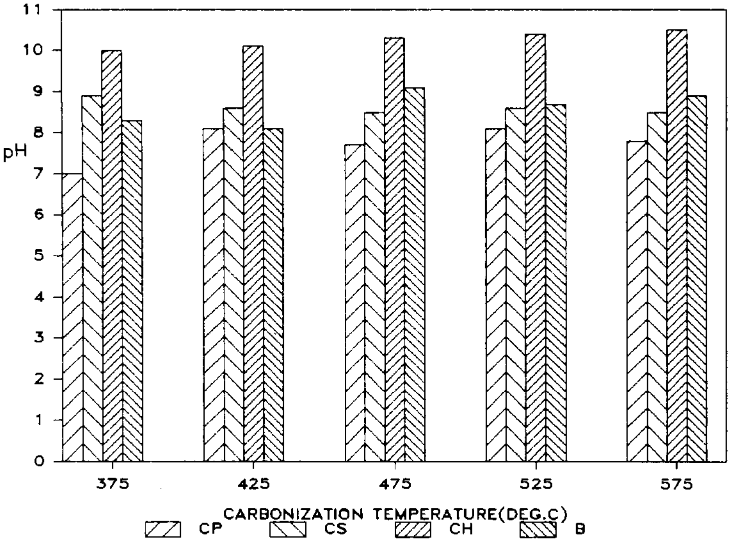

Fig. 6. pH of activated carbons. The pH of water is 7, of Darco is 4.3 and of bone char is 8.6.

Surface area

The specific surface area (BET) of the activated carbons are shown in Fig. 7. The surface area per gram of carbon increases with increasing carbonization temperature and drops at higher temperatures. The carbons did not develop high surface area when compared with the Darco commercial carbon which had a specific surface area of 769 m^2 g^{-1}. Caribbean pine carbons developed the highest surface areas.

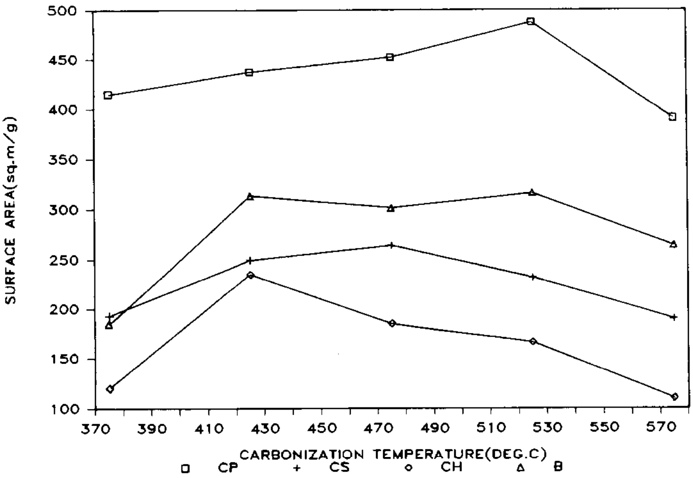

Fig. 7. Specific surface area, activated carbons.

It was observed that surface area showed the following trend CP > B > CS > CH.

Methylene blue adsorption

The effectiveness of the carbons as colour adsorbents was investigated using methylene blue solution. The monolayer adsorptive capacities of the carbons were determined using modified Langmuir plots [9]. The results are shown in Fig. 8. All the carbons showed favourable adsorptive capacity. It can be seen from Fig. 8 that there is an optimum carbonization temperature for the development of good adsorptive properties. The optimum for Caribbean pine is ~ 520 °C. For coconut husks, bagasse and coconut shells the optimum temperatures are 475, 450 and 525 °C. At all carbonization temperatures, Caribbean pine carbons proved to have superior adsorptive capacity to that of the carbons prepared from the other materials examined. CP, 475 and CP, 525 were comparable with the Darco commercial carbon (adsorptive capacity 499 mg per g carbon) which displayed a higher specific surface area of 769 m^2 g^{-1}. These two carbons were also superior to the bone char examined (adsorptive capacity 455 mg/g).

Iodine adsorption

The results for iodine adsorption are shown in Fig. 9. The carbons produced from Caribbean pine were superior to the ones made from the other materials. High adsorptive properties for iodine develop early (with respect to final carbonization temperature) in Caribbean pine and coconut

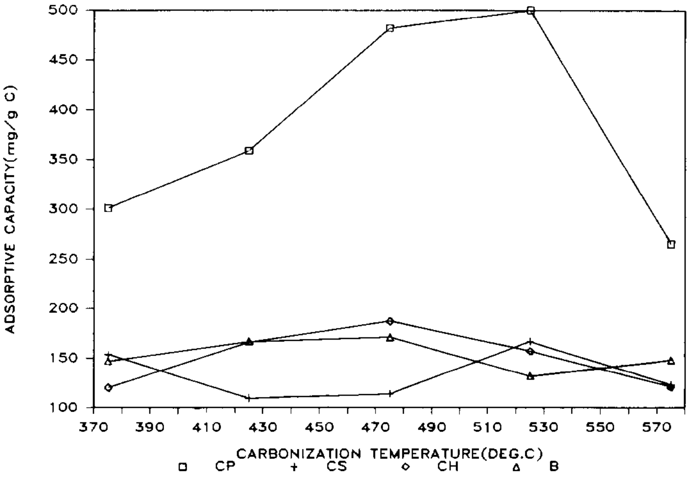

Fig. 8. Adsorptive capacity, methylene blue adsorption.

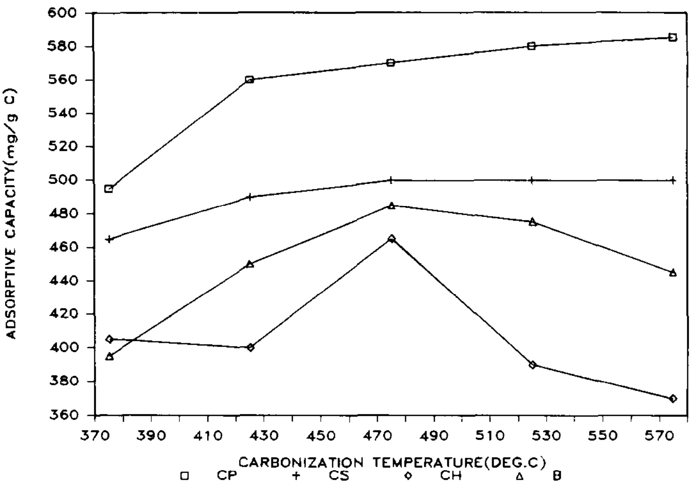

Fig. 9. Adsorptive capacity, iodine adsorption.

shells. Coconut husk and bagasse both display an optimum production temperature.

DISCUSSION

The results detailed above and displayed in the table and figures indicate a relationship between raw material properties and the development of adsorptive properties when these raw materials are subjected to appropriate thermal and oxidative conditioning. A striking feature is the dependence of adsorptive properties developed on raw material properties that are amenable to numerical evaluation.

Surface area

One significant change in the solid product of activation is the increase in surface area. The magnitude of the surface area is determined by the extent of the micro-capillary system existing in the residue tested. Raw material properties capable of numerical evaluation have been examined to determine their effect on the development of internal surface.

Cellulose

Cellulose is a linear polymer composed of anhydro-D-glucopyranose units linked by β-1-4 glycosidic bonds. The covalent bonding within and between glucose units results in a straight and stiff molecule with very high tensile strength. Lateral bonding of the cellulose molecules into linear bundles is primarily due to hydrogen bonding [27]. The large number of hydrogen bonds results in a relatively strong lateral association, which gives rise to crystalline regions. These crystalline regions occupy 67–90% of the cell wall [28].

The content of cellulose in Caribbean pine was 51.4%, with the contents of bagasse, coconut husks and coconut shells significantly lower at 42.8, 38.0 and 33.6%, respectively. All the materials examined showed an increase in surface area with final carbonization temperature followed by a decline at higher temperatures as can be seen in Fig. 7. Caribbean pine carbons developed the highest surface areas, from 415 m^2 per g carbon at 375 ° C to a maximum of 487 m^2 per g carbon at about 525 ° C, followed by a decline at higher temperatures. The carbons produced from bagasse, coconut shells and coconut husks displayed significantly lower surface area values with heirarchy being CP > B > CS > CH, in keeping with the cellulose hierarchy.

Hemicellulose

Hemicellulose, like cellulose, is a polymer composed of sugar units. It differs from cellulose in that it is a smaller polymer, is branched, does not form crystalline regions and usually contains more than one sugar type.

The hemicellulose contents for the raw materials were 24.0, 28.2 and 29.0% for Caribbean pine, coconut husks and bagasse, respectively. The correlation of hemicellulose content with surface area is opposite to that of cellulose, with Caribbean pine (exhibiting low hemicellulose content) producing carbons with higher surface areas.

Lignin

The major non-carbohydrate portion of the cell wall is lignin. The lignin molecule is a very complex, crosslinked, three-dimensional polymer formed from phenolic units [29]. The aromatic nature of the phenolic units makes lignin hydrophobic and the three-dimensional network provides rigidity to the cell wall. Lignin penetrates all wall layers [30].

Carbons prepared from coconut husks and coconut shells (lignin contents, 32.8 and 34.8%, respectively) developed lower surface areas than those prepared from Caribbean pine and bagasse (lignin contents, 19.5 and 15.8%, respectively). It is difficult to detect any significant difference for lignin content versus surface area developed.

Volatile matter

Volatile matter (VM) determination is a thermal technique. Under appropriate conditions volatiles constitute portions of hemicellulose, cellulose, lignin, extractives, which are a number of different chemical types such as terpenes and related compounds, fatty acids, aromatic compounds and volatile oils, that are driven off thermally.

The VM content of the raw materials were 74.4, 72.3, 69.1 and 62.9% for Caribbean pine, bagasse, coconut shells and coconut husks, respectively. There is a strong relationship between VM content and the development of surface area. High values of surface area were obtained in the materials with high VM content, i.e. CP > B > CS > CH. Most theories on the development of adsorptive properties in activated carbons stress the importance of VM removal.

Oxygen

The materials richer in oxygen showed markedly higher surface area development. Caribbean pine, bagasse, coconut shells and coconut husk had oxygen contents of 44.3, 42.3, 40.6 and 39.2%, respectively. It has been previously suggested [31] that the evolution of oxygen in combination with carbon (mainly as carbon monoxide) may be responsible for microporosity during carbonization. The mechanism suggested was a condensation reaction such as $R_1 \cdot OH + R_2H \rightarrow R_1R_2 + H_2O$, followed by the attack on the carbon by the steam generated. It was also suggested that such an action by oxygen would affect atomic configurations.

H / C ratio

The hydrogen/carbon (H/C) ratio for Caribbean pine, bagasse, coconut shells and coconut husk were 1.58, 1.46, 1.24 and 1.2 respectively. This is also supportive of the established hierarchy for surface area (i.e. CP > B > CS > CH). It is not clear how hydrogen will support the development of surface area, but work carried out by Dent et al. [32] has shown that in hydrogenation under 50 atm, nuclear carbon may be gasified readily as methane by hydrogen, in which special case a microcapillary system could be formed.

Pyrolysis of biomass

The major components of biomass (cellulose, hemicellulose and lignin) as well as the extractives and inorganic materials in cell walls and their lumens (cell cavities) have different thermal properties [33]. The pyrolytic decomposition of hemicellulose, cellulose and lignin have distinct temperatures of decomposition [34]. Thermal studies have indicated that the thermal breakdown of cellulosic is a composite of that of the individual components [2,35]. The responses of biomass to thermal treatment are the result of both the chemical makeup and the physical arrangement of the structural elements [13,36,37].

The raw material (biomass) properties can be characterized using thermogravimetry and small samples [38,39] which removes the complexities associated with heat and mass transfer effects. The activation energy values for Caribbean pine, bagasse, coconut shells and coconut husk were 97.91, 77.36, 55.97 and 51.20 kJ mol^{-1}, respectively. The differences in activation energies are attributed to chemical heterogeneity, species difference and cellular morphology. The materials showing greater activation energy are also the ones showing greater cellulose, VM and oxygen contents, as well as higher H/C ratio. Thus materials with higher activation energy produced carbons with higher surface areas.

Activation of the primary charcoal is viewed as lattice expansion. Here an attempt is being made to reverse the negative effects of the carbonization process which cause carbon to associate/bond as the encrustants and water are removed. During the process of activation the spaces between the elementary crystallites become cleared of various carbonaceous compounds and non-organized carbon, and carbon is also removed partially from the graphitic layers of the elementary crystallites. A suitable activation process causes an enormous number of pores to be formed so that the total surface area of their walls, i.e. the internal surface, is increased.

Application of activated carbons

The adsorptive properties of the activated carbons showed varying capacity for methylene blue (MB) and iodine adsorption. Caribbean pine carbons displayed high capacities for both iodine and MB. For MB, adsorptive capacities of 300 mg per g carbon at 375 ° C, peaking at 500 mg per g carbon (520 ° C), and declining after 520 ° C were obtained. In the case of iodine adsorption the capacities for Caribbean pine ranged from 490 mg per g carbon at 375 ° C to 580 mg per g carbon at 575 ° C.

The carbons from bagasse, coconut shells and coconut husks displayed comparable adsorptive capacities for MB. These were significantly lower than those for Caribbean pine carbons. Peak adsorptive capacities were noted at 475 ° C (187 mg per g carbon), 450 ° C (175 mg per g carbon), and at 525 ° C (167 mg per g carbon) for coconut husk, bagasse, and coconut shells, respectively.

For iodine adsorption, adsorptive capacity was in the order CP > CS > B > CH. Optimum temperatures were observed for coconut husk (475 ° C). For Caribbean pine and coconut shells there was no optimum temperature in the range investigated. Caribbean pine carbons produced at carbonization temperatures of 475 and 525 ° C were comparable to the Darco commercial carbon (capacity 499 mg g^{-1} carbon) which had a high specific surface of 769 m^2 per g carbon and superior to bone char (capacity 455 mg per g carbon) for MB adsorption. For iodine adsorption Caribbean pine carbons were comparable to the Darco commercial carbon (adsorptive capacity 616 mg per g carbon). All the carbons were superior to bone char (adsorptive capacity 216 mg per g carbon).

There was poor correlation between the adsorptive capacity and the activation energy of the raw materials in contrast to the observed correlation between activation energy and surface area. One explanation is the nature of the carbon surface. The adsorptive properties of activated carbons are determined not only by their porous structure, but also by their chemical composition. Activated carbons contain two types of admixtures [40]. One of them is represented by chemically bonded elements; in the first instance oxygen and hydrogen. These are derived from the raw materials and remain in the structure of the activated carbon as a result of the imperfect carbonization, or become chemically bonded to the surface during activation. The other type of admixture consists of ash, which is not an organic part of the product. The ash content of the carbons (and its composition) varies widely and is dependent on the raw material. Variation in these admixtures will make adsorptive properties subject to empirical variations and difficult to correlate.

CONCLUSIONS

The production of activated carbon from West Indian biomass has been demonstrated. The materials investigated were wood wastes and the agricultural residues, bagasse, coconut shells and coconut husks.

(i) The microcapillarity of the activated carbons as indicated by surface area (BET) was most fully developed in the carbons prepared from materials rich in cellulose, oxygen, hydrogen and volatile matter.

(ii) It was induced that under exactly determined conditions, the activation energy of the raw materials as determined by dynamic thermogravimetry, can be used to characterize the development of the microcapillary system in activated carbons.

(iii) There appears to be a relationship between activation energies of the raw materials and the development of adsorptive properties in activated carbons, the difficulty in correlation being attributed to the nature of the carbon surface.

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