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THE PRODUCTION OF ACTIVE CARBON FROM CORN COBS BY CHEMICAL ACTIVATION

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Abstract

Corn cobs obtained as waste from the corn industry, were analyzed by a TG-DTA unit in an atmosphere of flowing nitrogen. The carbonaceous products so formed were then produced on a preparative scale and activated chemically using potassium hydroxide. This resulted in the formation of a carbon with a very high surface area. The active carbon produced was then examined using thermal analysis in the temperature jump mode on a thermogravimetry unit. From this data the kinetics of degradation of the active carbon was determined using zero order rate kinetics. The pore structure of the active material was also examined using SEM. The E_a for activated corn cobs was found to be 106 kJ mol^{-1}.

Keywords: activation, carbon, corn cobs, SEM, TG

Introduction

In the separation of grains from the cob, there is a large amount of waste generated. This poses a problem not only in storage but also for disposal, and hence there is a need to efficiently utilize this waste. Though there are several end uses of this material a large portion of this still remains a waste. Active carbon is an extensively used adsorbent and, from its introduction, there have been continuing developments in its manufacture and applications. The raw materials used in preparing adsorptive carbons are polymeric in nature [1, 2]. A lot of work has been carried out on carbons derived from synthetic polymers. The term carbonization implies pyrolysing the original material in the absence of air to remove most of the elements other than carbon as volatile compounds, by a process of chain stripping [3]. For different materials the potential pore structure of the residual carbon depends on the conditions used for the process of carbonization.

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Kinetic studies of the carbonization have been carried out by following the process at different temperatures and measuring the surface area at each stage [4]. The weight loss during carbonization can be studied using thermal analysis.

In this study, corn cobs obtained as waste from the corn industry were used to form active carbon. The internal structure of the carbons so formed can be further developed by two methods. One is known as physical activation, in which the porous carbon is treated to gasification by heating it under an atmosphere of oxygen [5], carbon dioxide or steam at 700–800°C. Chemical activation involves treating the carbon to chemicals at an elevated temperature [6, 7]. In this study the porosity of the carbons produced from corncobs of varying granular size was enhanced using potassium hydroxide as the chemical activator. The surface area characteristics were determined by nitrogen adsorption using a specially designed unit. The rate of degradation of the activated carbon was studied by thermogravimetry [8, 9] (TG) in an atmosphere of dry air and the activation energy was calculated from this data. The pore structure of the active material was further examined using scanning electron microscopy (SEM). The thermal analysis was carried out using a temperature jump method for following the process of oxidation as described by Azizi *et al.* [10]. This method employs a combination of rising temperature and isothermal heating programs. In this process, the sample is placed in the TG crucible and the TG furnace is heated to a particular starting temperature. Then the temperature is held constant for 10 min and raised again by 10°C until complete oxidation of carbon is achieved. The kinetics of the reaction are then determined using the equation

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)$$

$$\text{and } \alpha = k(T)t$$

where α is the fraction decomposed at time t. $\mathrm{d}\alpha/\mathrm{d}t$ is the observed rate and $k(T)$ is the specific reaction rate, at temperature T. The carbon samples obtained from activation were subjected to SEM and compared with the original carbonaceous material.

Materials and equipment

Corn cobs processed to give granules called Grit-O-Cobs were obtained from Andersons and potassium hydroxide was procured from Aldrich. The simultaneous TG-DTA unit used for the thermal analysis study was from TA instruments model #2960. The SEM studies were performed on the JEOL JSM-6100 microscope wherein, the surface of the sample was coated with a thin, electric conductive gold film and the excitation voltage used was 25 kV.

Experimental

In order to proceed with the proposed research on the formation of carbonaceous material and activation of that carbonaceous material, corn cobs of different granular sizes were subjected to thermal analysis and heated under a controlled atmosphere of nitrogen to about 600°C (Fig. 1). The region where the maximum mass loss occurred was chosen as the temperature at which large scale conversion of corn cobs to carbonaceous residue was brought about in an atmosphere of flowing nitrogen using a tube furnace. The carbonaceous residue was further activated chemically using potassium hydroxide by mixing it with two times the weight of potassium hydroxide and liquid nitrogen poured in the crucible. The crucible was then covered with another crucible in a labyrinth arrangement and heated in a muffle furnace at 800°C for 30 min. After cooling, the activated carbon so formed was washed with distilled water until free of potassium and dried. The products formed at each stage were checked for their surface area using a single point volumetric apparatus [11]. The activated carbon produced was analyzed on the TG unit using a temperature jump method, to examine the oxidation products and also to calculate the activation energy of the material produced.

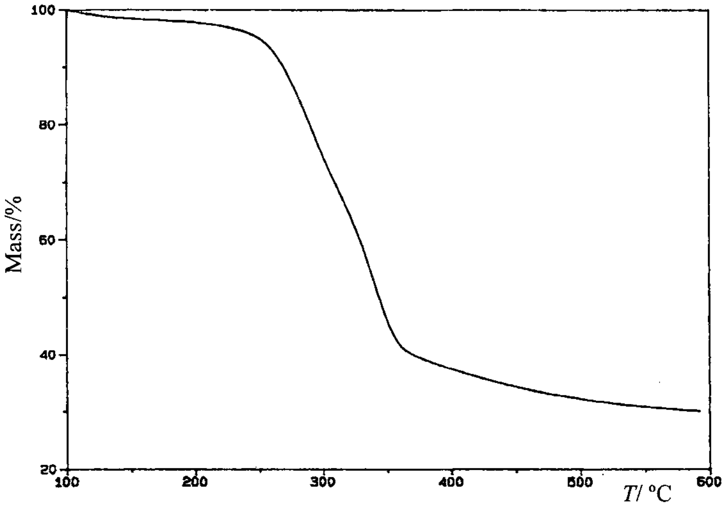

Fig. 1 Thermogravimetry plot of corn cobs #2040 under an atmosphere of flowing nitrogen showing degradation to carbon

Results and discussion

The physical changes that the carbon formed from corn cobs undergoes can be clearly seen from the SEM photographs. From Fig. 2 it can be seen that the original material, corn cobs does not have a well defined pore structure but that on carbonization pores are present (Fig. 3). These pores can be further enhanced by chemical activation, which results in formation of large cavities, as can be seen from Figs 4 and 5. As observed from Table 1, there is a significant increase in surface area after chemical activation.

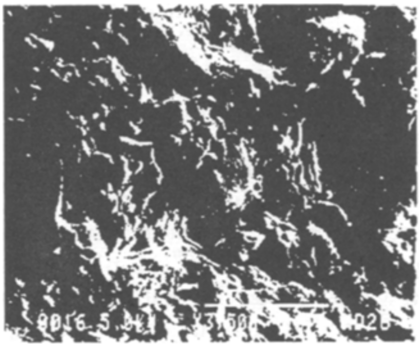

Fig. 2 SEM picture of a corn cob #2040 at 500×magnification

Fig. 3 Corn cobs carbonized under nitrogen viewed under SEM at 500×

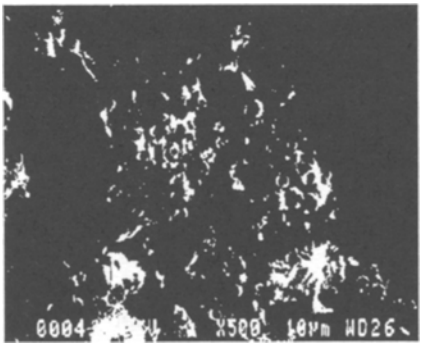

Fig. 4 Activated corn cobs showing the large pores formed due to chemical activation

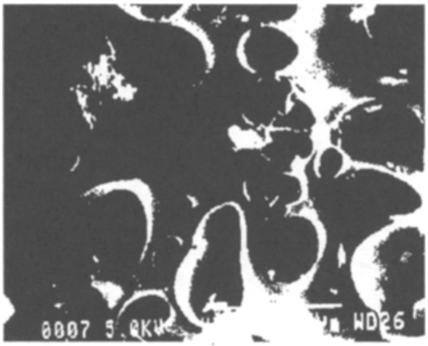

Fig. 5 Activated corn cobs, same as in Fig. 4, closer view

This activated carbon, formed by chemical activation was then treated to thermal analysis in air using the TG plot in the temperature jump mode. The temperature was raised to 300°C, then held at this temperature for 10 min, and raised again to 310°C. In this way the temperature was jumped each time by 10°C and then held at that temperature for a further 10 min. This procedure was continued up to a temperature of 400°C. The procedure and typical plots for carbon sub-

Table 1 Surface area obtained by single point volumetric method, before and after activation of corn cobs. Carbon used for calibration had a surface area of 106 $m^2\ g^{-1}$

Sample	Surface area/$m^2\ g^{-1}$
corn cob #2040 carbonized	1.96
corn cob #1014 carbonized	2.30
corn cob #2040 carbonized	1500
corn cob #1014 carbonized	1550

Table 2 A typical set of results obtained from the TG experiment on corn cobs #2040 for computation of the Arrhenius parameters

T/°C	$1/T \times 10^3$K	% mass	% loss	k=% loss/600	ln$k$
330	1.66	95.6	4.4	0.01	–4.92
340	1.63	93.5	6.5	0.01	–4.53
350	1.60	90.8	9.2	0.02	–4.18
360	1.58	87.3	12.7	0.02	–3.86
370	1.55	82.8	17.2	0.03	–3.55
380	1.53	77.1	22.9	0.04	–3.27
390	1.51	70.1	29.9	0.05	–3.00
400	1.49	62.1	37.9	0.06	–2.76

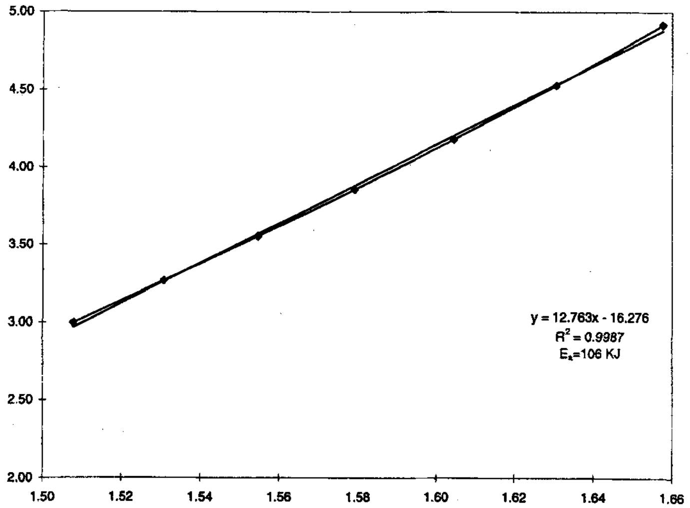

Fig. 6 Arrhenius plot of activated corn cobs for the calculation of activation energy

jected to these temperature jump treatments are explained by Azizi *et al.* The results are presented in Table 2. In each temperature period a linear response of mass change against time was recorded justifying the application of zero order kinetics. From the data so obtained, the activation energy was calculated, on the basis of observed zero order rate kinetics (Table 2). The data gave a good Arrhenius plot, with the activation energy calculated from the slope of a plot of $-\ln k$ *vs.* $1/T$, as seen from Fig. 6 for corn cobs #2040. The activation energy for activated corn cobs calculated in this way was found to be 106 kJ mol^{-1}.

Conclusions

The importance of this work lies in the urgent need to utilize cereal waste products which is a common problem in the farm scene. It is also important scientifically in that the carbon that can be produced by the process has an unusually high surface area. The reactivity of such carbon provides new avenues of use for these materials beyond their current usage. The most obvious is the use of the material in medicine as an antidote for poisons [12], and on a much larger scale as a storage medium for methane at high pressures [13]. The use of thermal analysis as a pivotal instrumental technique will also allow new methods of analysis and control to be developed using this kind of investigation.

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