THERMAL STUDIES OF SOME DYE ADSORBENT MATERIALS

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ABSTRACT

Thermal behaviour of untreated and treated sawdust, maize cob and bagasse materials with basic dye was investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The results showed that the thermal decomposition pattern can be divided into three peaks. The first peak is endothermic while the second and the third peaks are exothermic. The peak intensities and corresponding temperatures were different for untreated and treated materials. The effect of adsorption of basic dye treatment was more pronounced on sawdust and maize cob rather than bagasse. The calorific values of treated sawdust and maize cob are higher than those of untreated ones. These materials are considered new potential sources for energy conversion.

Key words:

Bagasse, maize cob, sawdust, thermal analysis, energy conversion.

1. INTRODUCTION

Treatments of effluent streams containing dyes are usually carried out using adsorbent materials. Recent studies have indicated that biomass products, obtained from non-woody plants such as bagasse pith can treat effluents effectively [1]. Most of non-woody plants are characterized by a porous structure which is essential for the adsorption process. The performance of bagasse, maize cob and sawdust as adsorbent materials is discussed else where [1,2]. Although the application of these materials in adsorption processes shows promising results, their presence as an additional solid waste materials represents a new burden on the local environments. Several studies show that biomass products could be utilized as a renewable source of energy [3,6].

Thermal analysis studies show the capability of biomass products such as rice hulls and bagasse to be used as new potential sources of energy. In general, the non-woody and woody materials are used as fuel materials either directly through combustion process or indirectly through production of char or gaseous and liquid products. The major advantage of these materials as fuel is the lower sulphur content obtained in comparison with other fossil fuels, therefore, clean environments are obtained. Although several studies are discussed in literature concerning the thermal behaviour of woody and non- woody materials, the thermal behaviour of treated materials is not studied.

The present study aims at investigating the effect of the adsorption of a certain process of basic dye on the thermal behaviour of maize cob, bagasse and sawdust. This will provide basic data and information to develop and implement methods for the combustion of these materials .

2. EXPERIMENTAL

The adsorbent materials used were saw dust from hard wood, crushed maize cob, and bagasse pith which are the fine fractions obtained from the residues remained after crushing the sugar cane during the extraction of sugar juice. All materials were sieved and the particles size of 250–355 μm were used as adsorbents. The dye stuff used as adsorbate was Basic Blue 69 (Methine dye) which is a commercial salt supplied by Bayer company.

The decolorization process was carried out by agitating a fixed mass of adsorbent with the adsorbate (dye solution of concentration of 1000mg/l) for a sufficient time period to ensure that equilibrium has been achieved. The adsorption capacity of the saw dust was 118 mg dye/g, for maize cob was 160 mg dye/g for bagasse pith was 167 mg dye/g [1,2].

Thermal analysis measurements were carried out using Shimadzu DT-30 apparatus, with the following conditions:

Sample weight 10mg, heating rate 20 °C/min. and air flow rate of 70 ml/min. Calorific values were determined using Cussons bomb calorimeter.

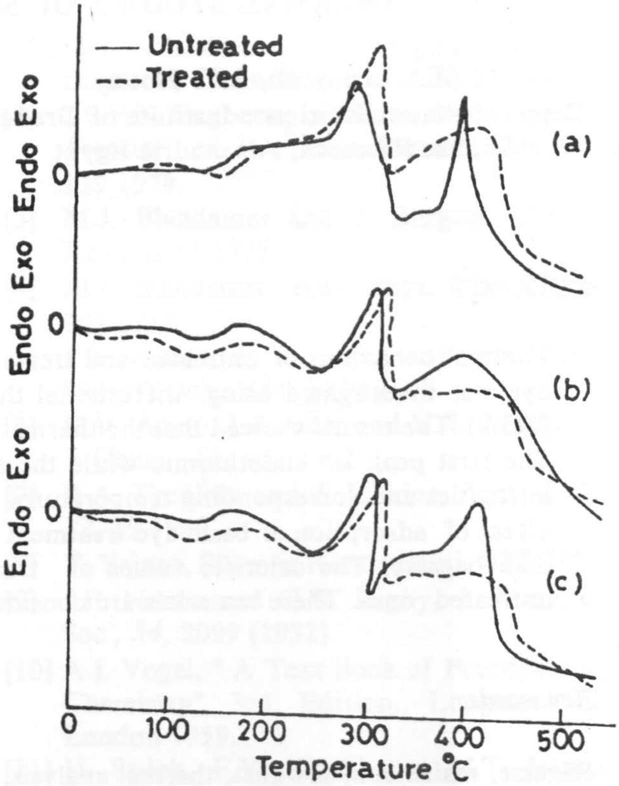

Figure 1. DTA curves for systems containing the absorbed materials in the absence and presence of the basic dye: (a) maize cob (b) bagasse (c) sawdust.

3. RESULTS AND DISCUSSIONS

Figure (1) shows DTA curves for untreated and treated materials (maize cob, bagasse and sawdust), and Tables (I–III) represent the characteristics features of the various stages. The results indicate that the three untreated materials have, in general, a similar decomposition trend. However their peak intensities and corresponding temperatures are different. The general trend for the thermograph is characterized by three peaks. The first peak is endothermic at temperature 25–125 °C while the second and the third peaks are exothermic. The first exothermic peak occurs at temperature range of 250–370 °C and the third peak at a temperature higher than 400 °C. The evaporation of adsorbed moisture occurs in the first peak, the oxidation of both the less stable components of the char and the volatile components formed during the combustion occurs in the second stage and finally the oxidation of the more stable char components occurs in the third stage and this is known as carbon burn off stage [7–9].

Table I. Differential Thermal analysis results of both untreated and treated maize cob.

DTA stages	Untreated	Treated
<u>Fisrt stage</u>		
Type of Peak	Endo.	Endo.
T_{max}	110°C	115°C
T range °C	25–125°C	25–125°C
<u>Second stage</u>		
Type of Peak	Exo.	Exo.
T_{max}	285°C	315°C
T range °C	250–340°C	270–350°C
<u>Third stage</u>		
Type of Peak	Exo.	Exo.
T_{max}	425°C	445°C
T range °C	340–500°C	350–500°C

Table II. Differential Thermal analysis results of both untreated and treated baggasse.

DTA stages	Untreated	Treated
Fisrt stage		
Type of Peak	Endo.	Endo.
T_{max}	120°C	120°C
T range °C	25-125°C	25-125°C
Second stage		
Type of Peak	Exo.	Exo.
T_{max}	315°C	325°C
T range °C	280-360°C	280-370°C
Third stage		
Type of Peak	Exo.	Exo.
T_{max}	430°C	480°C
T range °C	360-500°C	370-500°C

Table III. Differential Thermal analysis results of both untreated and treated sawdust.

DTA stages	Untreated	Treated
Fisrt stage		
Type of Peak	Endo.	Endo.
T_{max}	110°C	125°C
T range °C	25-125°C	25-125°C
Second stage		
Type of Peak	Exo.	Exo.
T_{max}	320°C	325°C
T range °C	270-350°C	270-355°C
Third stage		
Type of Peak	Exo.	Exo.
T_{max}	425°C	480°C
T range °C	350-500°C	355-500°C

The comparison of peak temperatures in case of treated and untreated materials indicates that there is a significant increase in the temperature at which the combustion of the volatile occurs (first exotherm peak) for treated materials than untreated ones as shown in Figure (1) and Tables (I-III). Moreover, the second exothermic peaks for treated materials were found to occur at relatively higher temperatures and less intense than untreated materials. For example, the combustion of volatile products of maize cob occurs at 30°C higher than untreated material and the increase in temperature of the carbon burn off stage (second isotherm peak) is 20°C. The results also indicate that adsorption of the dye affects maize cob thermal behaviour more significantly than bagasse or sawdust. For example, the increases in the first exothermic peak temperature are 30, 10 and 5°C for maize cob, bagasse and sawdust, respectively.

For more interpretation of DTA results, it is desirable to include TGA data. Figures (2)-(4) show TGA and DTG curves for treated and untreated materials, the results are also presented in Tables (IV-VI). The TG curves of untreated materials show similar thermal behaviour. The three thermograms have three stages of weight loss: first stage (25-125°C) exhibits small weight loss which corresponds to the first endotherm in the DTA thermogram; the second stage (250-435°C) includes the main decomposition stage and has a weight loss which ranges from 45 to 48.9% depending upon the type of material; the third stage (370-630 °C) has weight loss ranges show 17.4 to 23%. The extent of weight loss by DTG reaches a maximum in the second stage, where the combustion of volatile takes place exothermically as indicated by DTA.

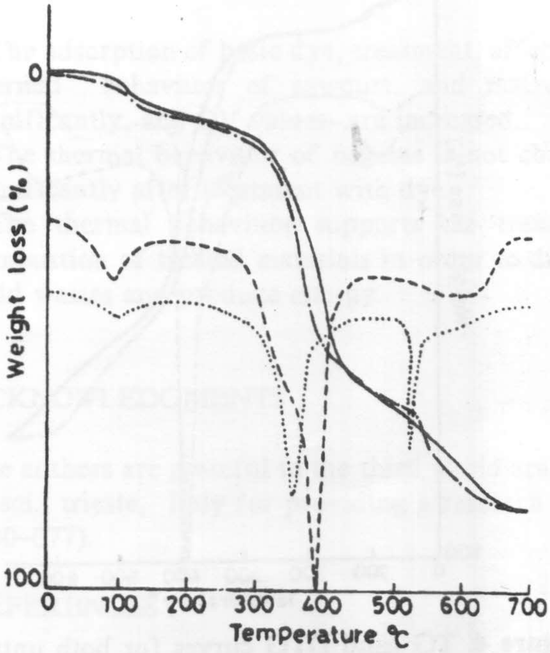

Figure 2. TG cand DTG curves for both untreated and treated maize cob.
--- TG treated ---- TG untreated
--- DTG treated ---- DTG untreated

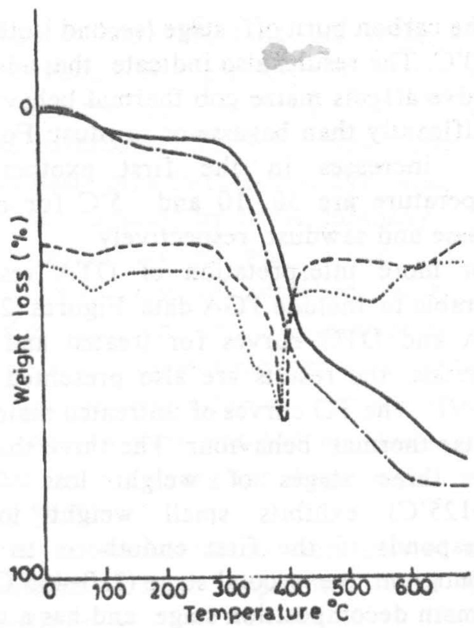

Figure 3. TG cand DTG curves for both intreated and treated maize cob.
--- TG treated ---- TG intreated
--- DTG treated ---- DTG untreated

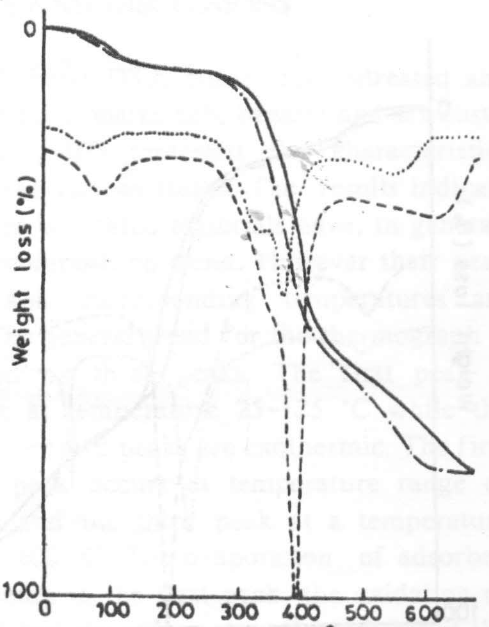

Figure 4. TG cand DTG curves for both untreated and treated sawdust.
--- TG treated ---- TG untreated
--- DTG treated ---- DTG untreated

Table IV. Thermogravimetric results of both untreated and treasted maize cob.

Stages of Weigh loss	Untreated	Treated
Fisrt loss:		
Weight loss %	7.3	8.3%
$T(DTG)_{Max}$ °C	45 °C	45°C
T range °C	25-125°C	25-125°C
Second loss:		
Weight loss %	47.2%	50.9
$T(DTG)_{max}$	375 °C	390°C
T range °C	275-370°C	256-425°C
Third loss:		
Weight loss	17.4%	23.8 %
$T(DTG)_{max}$ °C	525°C	600 °C
T range °C	370 °C-535°C	425°C-680°C

The results of the thermogravimetric analysis for all treated samples show an enhancement in the extent of weight loss of the main decomposition stage. However, the results shown in Table (V) indicate that the change in the temperature of the main decomposition stage for bagasse is relatively less significant comparatively to maize cob and sawdust.

Table VI. Thermogravimetric results of both untreated and treasted sawdust.

Stages of Weigh loss	Untreated	Treated
Fisrt loss:		
Weight loss %	6.7	6.8%
$T(DTG)_{Max}$ °C	45 °C	50°C
T range °C	25-125°C	25-125°C
Second loss:		
Weight loss %	48.8%	50.5
$T(DTG)_{max}$	390 °C	405°C
T range °C	285-435°C	270-430°C
Third loss:		
Weight loss	12%	22%
$T(DTG)_{max}$ °C	562°C	635 °C
T range °C	435 °C-630°C	430°C-690°C

Table V. Thermogravimetric results of both untreated and treated baggasse.

Stages of Weigh loss	Untreated	Treated
Fisrt loss:		
Weight loss %	8.5	6.5%
$T(DTG)_{Max}$ °C	45 °C	45°C
T range °C	25–125°C	25–125°C
Second loss:		
Weight loss %	44%	50.9
$T(DTG)_{max}$	375 °C	375°C
T range °C	275–400°C	265–415°C
Third loss:		
Weight loss	23%	23.2 %
$T(DTG)_{max}$ °C	525°C	595 °C
T range °C	400 °C–605°C	415°C–680°C

Table VII. The calorific values measured.

Material	Q (cal/gm)	
	Untreated	Treated
Saw dust	3700.0	4364.8
Maize Cob	3223.91	3684.58
Bagasse	4235.28	4302.39

The calorific values, QV, for treated and untreated absorbent materials are presented in Table (VII). The results indicate that values increases calorific by the treatment process in case of sawdust and maize cob materials only, e.g., QV are increased by 461 cal/gm for treated sawdust and maize cob, respectively. However, there is no appreciable increase in the calorific values for treated bagasse.

The effect of dye on the thermal behaviour of treated materials can be explained according to the reactions that occur in the combustion process. It is known that the combustion of cellulosic materilas is characterized by at least two major competitive reactions which are temperature dependent [10-11]. The first reaction produces mainly water, oxides of carbon and char. The second reaction supplies the levoglucosan, which is one of the major flammable components produced from the decomposition of the cellulosic materials. The first reaction occurs at relatively lower temperature <280 °C and requires less activation energy than the second reaction. The adsorption of the dye may interfere with the mode of the decomposition reaction, where the treated materials decompose at higher temperatures and produce less char than untreated materials. This is clear from Figure (1) where the reduction is significant in the amount of exotherm obtained from carbon burn off stage. In other words, the addition of basic dye to cellulosic materials may catalyze the decomposition reaction towards the formation of flammable gases rather than production of carbonesous residue.

The increase in calorific values also confirms the suggested mechanism which relates the addition of dye to the production of flammable gases. Although the mechanism does not fit well with bagasse, this is probably due to the occurence of some chemical and physical interaction between material and the adsorbed dye.

4. CONCLUSION

1.The adsorption of basic dye, treatment, affects the thermal behaviuor of sawdust, and maize cob significantly, and QV values are increased.
2.The thermal behaviuor of bagasse is not changed significantly after treatment with dye.
3.The thermal behaviuor supports the trend for combustion of treated materials in order to dispose solid wastes and produce energy.

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