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THERMAL DEGRADATION OF SUGAR CANE BAGASSE

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ABSTRACT

The thermal degradation of sugar cane bagasse and its components (cellulose and lignin) has been investigated between room temperature and 700 ° C in various atmospheres (nitrogen, dry air, oxygen) using dynamic thermogravimetric analysis. The component compounds of bagasse appear to pyrolyze independently, lignin being the more thermally stable and hemicellulose the less stable.

TG curves of thermal degradation for sugar cane bagasse and wood are compared and discussed.

INTRODUCTION

Bagasse, the fibrous residue left when sugar cane is milled, is used as primary fuel for energy supply in sugar factories. The bagasse surplus (10–30% of the total amount produced) is not usually utilized. In Guadeloupe (F.W.I.), this excess of bagasse which represents an energetic potential of 15000 TOE [1], 5% of the total energy demand in Guadeloupe, could be increased by a factor of two or three if better conditions of combustion in the mills' furnaces were realised. From amongst the different thermal processes of energetic conversion and valorization of this biomass one can choose gasification and/or rapid pyrolysis. These thermochemical techniques have already been studied for wood or forest residues. Before undertaking such a study on bagasse, it is necessary to have a good knowledge of the thermal degradation of this material. In the last decade there has been considerable research on the basic combustion process for cellulosic fuels, principally wood, but as far as we know nothing has been published on the thermal behavior of bagasse. Because the composition of

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bagasse is notably different from that of wood (high pentosane content, important yield of ash which can have catalytic properties, etc.) it was necessary to study the thermal degradation of sugar cane bagasse. This is the aim of the present study. We present the first results obtained for low temperature pyrolysis and combustion of bagasse by thermogravimetric analysis. These results are compared with those obtained for wood under similar experimental conditions (thickness, atmosphere, heating rate, etc.).

EXPERIMENTAL

Composition of bagasse and preparation of the samples

Bagasse is composed mainly of cellulose, hemicellulose and lignin. Also included in its composition are cane wax, organic acids, and other materials associated with plant life. The composition of bagasse is largely dependant on the variety of cane. For the bagasse that we studied, analysis of "pure fiber" gave the following composition: hydrogen, 6.30 ± 0.15% w/w; carbon, 48.6 ± 1.5% w/w; and oxygen, 45.1 ± 1.5% w/w. Thus, the empirical formula can be written (for 1 mole of carbon) $CH_{1.56}O_{0.70}$. Ash composition varies with cane variety, age, nature of the soil and the type and amount of fertiliser. Table 1 shows the analysis of bagasse ash. The amount of ash from bagasse depends to a large extent on the amount of dirt collected with the cane on harvesting. The average value we find lies between 3.5 and 4.0 wt.% of total bagasse.

The bagasse was pulverised in a crushing machine and finally sieved. All the analyses of the fiber were performed on particles of diameter 0.16–0.40 mm.

The cellulose was extracted by the Kurschner–Hoffer method: approximately 2 g of the sample is treated with 100 ml of a 1 : 4 (v/v) nitric acid–ethanol mixture and then raised to boiling for 1 h. After filtration the insoluble residue is treated twice again using the same process. Finally the solid is washed and dried at 105 °C to constant weight. Avicel cellulose supplied by Merck in the form of fine microcrystalline powder was also used in some experiments. Klason lignin prepared by digesting bagasse with 67% sulfuric acid at 20 °C for 6 h was then diluted to 2N acid, hydrolysis was continued for 5 h, and lignin was determined gravimetrically. Elemental analysis of the Klason lignin so prepared leads to the empirical formula $CH_{1.06}\ O_{0.38}$. The ash was obtained by incineration to constant weight of approximately 20 g of fiber in an oven at 450 °C.

Analysis of the bagasse gave the following composition in wt% (dry basis) of the component compounds: extractive, 4.0; cellulose, 41.7; pentosane, 28.0; lignin, 21.8; and ashes, 3.5.

TABLE 1

Chemical composition of sugar cane bagasse ash

Oxides	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	MnO	TiO_2	SiO_2
Percentage ash	12	8.5	7.3	4.5	3	0.4	3.1	0.3	0.8	58

For the comparison between the char yields of bagasse and wood, we have taken into account the influence of the inorganic salts initially present in the bagasse (Table 1). For all experiments, TG analyses were made on samples of about 100 mg.

Technique of thermogravimetric analysis

The reactions were carried out in a Ugine Eyraud B 60 thermobalance which permits one to follow the evolution of weight of the sample [2]. A Chevenard oven with automatic regulation had the ability to hold the temperature at the required values (within about 2 °C). A special device permitted the temperature to rise at a linear rate. Dynamic thermogravimetric analysis was used. The sample was weighed in a platinum crucible and the weight recorded continuously and automatically as a function of the temperature attained by the sample while it was being heated at a linear rate of 4.68 °C min^{-1}. The volatile and gaseous products were removed by the flow of gas (N_2, O_2 or dry air) which passed continually through the sample at a constant rate of 25 l h^{-1}. The graphs obtained by this dynamic thermogravimetric analysis disclosed the threshold temperature within which most of the reaction occurred and the yield of char when the reaction is practically completed.

RESULTS AND DISCUSSION

Thermogravimetric results

Figure 1 records the portion of the TG curves between 25 and 700 °C obtained for bagasse, lignin and cellulose under nitrogen atmosphere. The loss in weight of 1% for cellulose, bagasse and lignin recorded at 200 °C represents moisture initially present in the sample. Further loss in weight attributable to pyrolysis began near 210 °C for both lignin and bagasse, but not until 255 °C for cellulose. At 310 °C the extent of vaporisation is the same for lignin and cellulose (7%) while it reaches 25% for bagasse. Between 235 and 325 °C, the extent of vaporisation of bagasse is generally greater than that of pure cellulose. This is probably due to the thermal degradation of the major part of hemicellulose (mostly pentosan) contained in the bagasse. Ramiah [3] using dilatometric measurements and TGA on potassium xylan demonstrated that hemicellulose is less thermally stable than lignin and cellulose. This observation was confirmed elsewhere by the results of Tang [4] and Kosik et al. [5]. Above 235 °C the pyrolysis of cellulose proceeds very rapidly whereas that of lignin occurs very slowly. At 500 °C, the yield of char from cellulose pyrolysis is only 25% while 65% of lignin is still unvaporised at the same temperature. According to Brown and Tang [6],

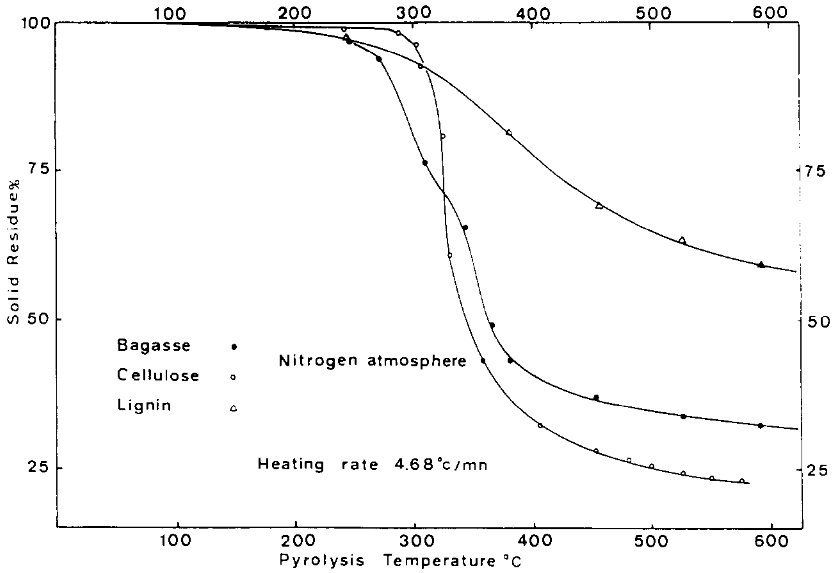

Fig. 1. Thermogravimetric curves for thermal degradation of bagasse, lignin and cellulose under nitrogen carrier gas at atmospheric pressure.

the rapid thermal degradation of cellulose within a narrow range of temperature, and the slower disintegration of lignin over a large broad band of temperature are explicable by the fact that cellulose is a repeating polymer of a single monomer [β-D-glucopyranose units which are linked together by (1-->4), glycosidic bonds] of moderate size while lignin is a more intricate macromolecule made up of phenolic hydroxyl, benzylic hydroxyl, and carbonyl groups, connected by straight links [7].

If we assert that the weight loss of the bagasse during pyrolysis can be expressed as a sum of the corresponding weight loss of each of its constituents, then at temperatures higher than 325°C, decomposition of lignin and cellulose occur together in the bagasse; and under 325°C, lignin and hemicellulose decomposition dominate the bagasse pyrolysis.

Effect of atmosphere on thermal degradation

It is well known that thermal degradation can be accelerated or inhibited according to the nature of the atmosphere. As can be seen by a comparison of Figs. 1, 2 and 3, an oxygen environment perceptibly lowers the temperature of thermal degradation and greatly increases the rate of weight loss. Thus, the temperatures at which 5% of the bagasse is vaporised are 262°C in N_2, 240°C in dry air and 228°C in oxygen. For cellulose, the corresponding temperatures for the same percentage vaporisation are 305°C in N_2, 293°C in dry air and 275°C in oxygen. Concerning the weight loss rate, the DTG

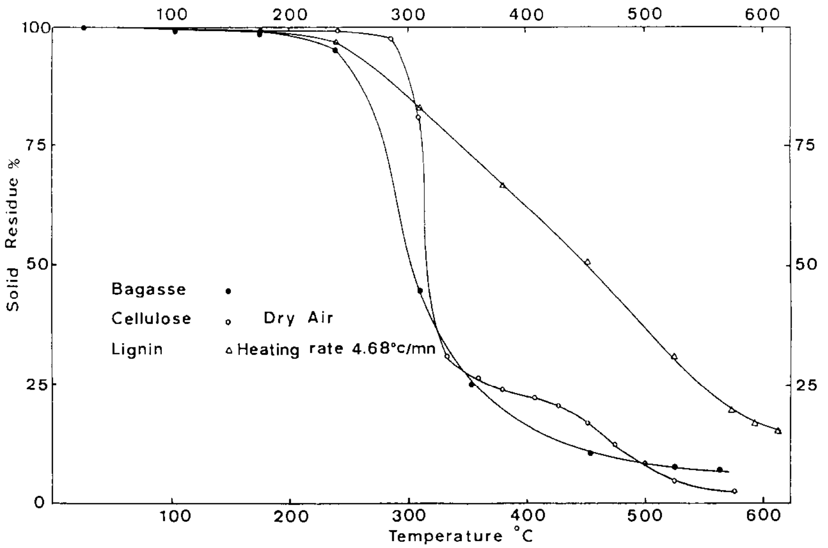

Fig. 2. Thermogravimetric curves for thermal degradation of bagasse, lignin and cellulose under dry air at atmospheric pressure.

curves in Fig. 4 show the increase of weight loss rate of cellulose and bagasse in oxygen, dry air and nitrogen, and clearly indicate the decrease of $T_{\max}$ (temperature at which maximum loss occurs) with increase of the oxygen content in the atmosphere.

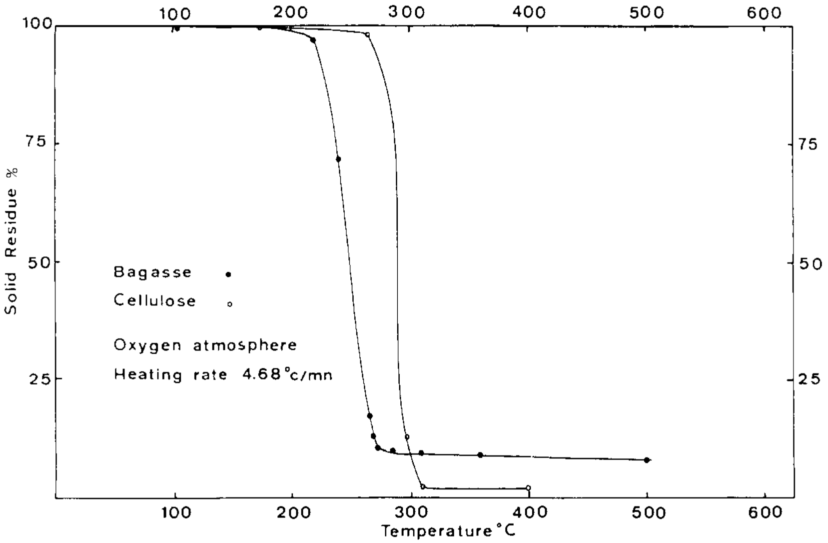

Fig. 3. Thermogravimetric curve for thermal degradation of bagasse and cellulose under oxygen carrier gas at atmospheric pressure.

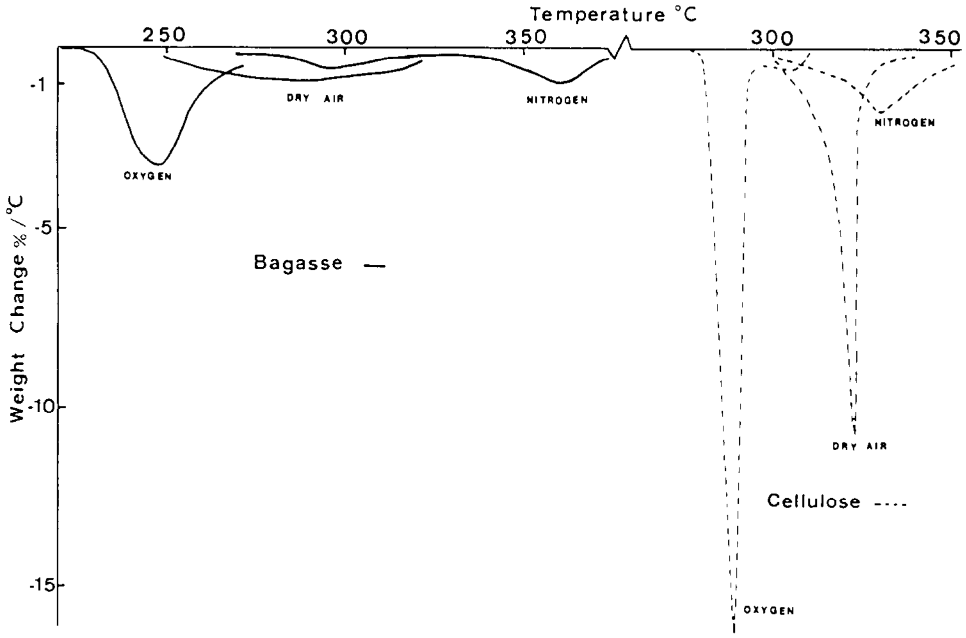

Fig. 4. Differential thermogravimetric curves for bagasse and cellulose in nitrogen, dry air and oxygen.

Other experiments on the thermal degradation of bagasse were performed at a heating rate of 3.55 °C min^{-1}. No substantial differences from the results reported above (heating rate 4.68 °C min^{-1}) were observed. It should be noted that Duvvuri et al. [8], by pyrolysis of cellulose samples in nitrogen atmosphere and with heating rates ranging from 10 to 160 °C min^{-1}, found that the increase in the heating rate led to an increase in weight loss rate and in T_{max}. These observations are in agreement with those given by Brunner [9] which showed that for the pyrolysis of cellulose the yield of char is dependant on the heating rate: high heating rates substantially lower char yields compared with low heating rates. The fact that no substantial differences were observed between the experiments at 3.55 and 4.68 °C min^{-1} is probably due to the very narrow temperature range of our pyrolysis study.

The products of the reaction (tar, water and gas) are swept away without reacting with the char, so we think that secondary reactions take place to a very limited extent. In particular there is a minimal secondary cracking of tar and thus a very big tar fraction generally located on the cold parts of the apparatus.

Comparison of thermal degradation curves of wood and bagasse in nitrogen

The results for thermal degradation of bagasse are compared with those obtained by Brown and Tang [6] for wood (*Ponderosa pina* sapwood venner

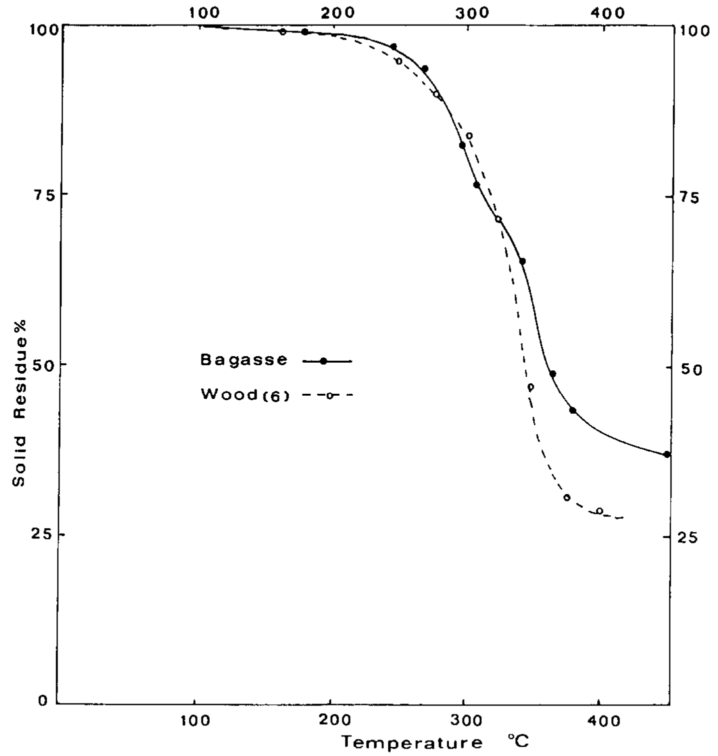

Fig. 5. Comparison of thermal degradation curves for bagasse and wood [6] in nitrogen carrier gas at atmospheric pressure.

0.16 mm thick) under similar experimental conditions: nitrogen at atmospheric pressure, heating rate 6 °C min^{-1} (see Fig. 5). It appears that below 325 °C, the weight loss for wood and bagasse are effectively the same: although slightly superior for wood below 290 °C, the thermal degradation of bagasse has the upper hand from 290 °C to 325 °C; these are temperatures for which the weight losses are effectively the same for the two materials. It should be noted that the TG curve for thermal degradation of bagasse presents an inflexion point for the temperature of 325 °C which indicates a modification in the reaction pathways of bagasse degradation. Beyond 325 °C, the gap between the two curves extends considerably, degradation for wood being the most important. These differences in the TG curves of the two compounds for temperatures above 325 °C, can be explained partly by the difference in composition of the two compounds, the difference in structure of the two compounds, and the high ash content in bagasse compared with that of wood.

On the first point, it is difficult to draw any conclusions because Brown and Tang [6] did not give the composition of the wood they studied. Concerning the second point, it has been indicated by Shijun [10] that the S_1

layer of bagasse fiber is thicker than that of wood fiber, so it is not impossible that the higher char fraction for bagasse than for wood could be due to the lower heating rates at the interior of the bagasse cell, the middle layer S_2 which forms the main portion of the cell wall being heated later in bagasse than in wood.

On the third point, the high mineral content in bagasse [4% ash compared with 1% (average) in wood] would have a measurable effect on the thermal degradation rate. The potassium and sodium content, shown in typical analyses in Table 1, may be particularly important. Recently, Zaror et al. [11], by using two experimental systems (McBain thermogravimetric balance and Gray–King retort), have demonstrated that salt impregnation of wood (Na_2CO_3, K_2CO_3) modifies weight loss rates and increases the charcoal yield in the presence of an inert carrier gas.

CONCLUSIONS

We present original experimental results of the thermal degradation of bagasse. It appears that the main constituents of sugar cane bagasse, hemicellulose, cellulose and lignin, pyrolyse independently. The important charcoal yield (compared to wood) when low heating rate pyrolysis is performed in the presence of nitrogen carrier gas may be explained by the high mineral content of bagasse compared with wood, and by the difference in their ultrastructures.

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