

Thermal Characteristics of Bagasse

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SYNOPSIS

Bagasse is a solid waste that remains after crushing sugarcane. Since bagasse is used as a fuel in sugar mills, characterization of its thermal degradation is rather important in order to use it efficiently. Thermal analysis of bagasse was carried out using differential thermal analysis (DTA) and thermogravimetry (TG) under oxidizing and inert atmospheres. Kinetic studies were based on weight loss obtained from TG analysis. Thermal degradation of bagasse takes place in two stages: volatilization and carbonization. The reaction rate, activation energy, entropy change, enthalpy change, and Gibbs free energy for the two thermal stages were calculated. The results indicated that activation energy for the volatilization stage is higher than that of decarbonization stage, and that both the rate constant and activation energy for combustion are higher than those of pyrolysis. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Bagasse is the spent fiber left from crushing sugarcane. It has been burned in boilers for many years to generate process steam. Sugarcane is not a homogeneous material but can be crudely regarded as consisting of peripheral fibers enclosing a soft central pith. After crushing sugarcane to facilitate extraction of sugar juice, bagasse remains, the larger fraction about 60% is fibrous and apparently cylindrical, while the smaller fraction, about 40%, is more spherical in shape.¹ Bagasse is a cellulosic material and its potential as an energy source is high.²

The aim of the present work is to describe the combustion behavior, the devolatilization, and the combustion of volatiles of bagasse. This can be accomplished by studying the combustion and pyrolysis of bagasse by DTA and TGA techniques to achieve efficient use of bagasse as a fuel for sugar mills.

EXPERIMENTAL

Air-dried Egyptian bagasse was chopped and screened to fraction 18/20 mesh number for the

thermal studies. The proximate and ultimate analysis of bagasse was done by ASTM techniques for coal analysis³ and chemical analysis was done using the method described in reference [1]. The data are given in Table I.

The thermal analysis was carried out by using a CST Stona Premco Model 202 DTA and Model 1050 TGA with temperature programmed at 5°C/min heating rate, from room temperature to 800°C. An 18-mg sample of bagasse was used; the reference material was aluminum oxide. The combustion study was carried out using air, while the pyrolysis study used pure nitrogen gas. Calorific values were determined by using Cussons bomb calorimeter.

RESULTS AND DISCUSSION

The calorific value of wet bagasse (50% moisture) is 2220 kcal/kg and for dry bagasse (7.3% moisture) is 4041 kcal/kg. Bagasse is normally used as a fuel in sugar mills, mainly for economical reasons. Bagasse price is therefore estimated by comparing its calorific value to that of fuel oil.⁴ In general, bagasse is a solid waste, renewable energy and it does not contain sulphur, making it a favorable fuel for sugar mill.

Figure 1 shows the thermal curves of DTA during combustion (air atmosphere) and pyrolysis (N₂-at-

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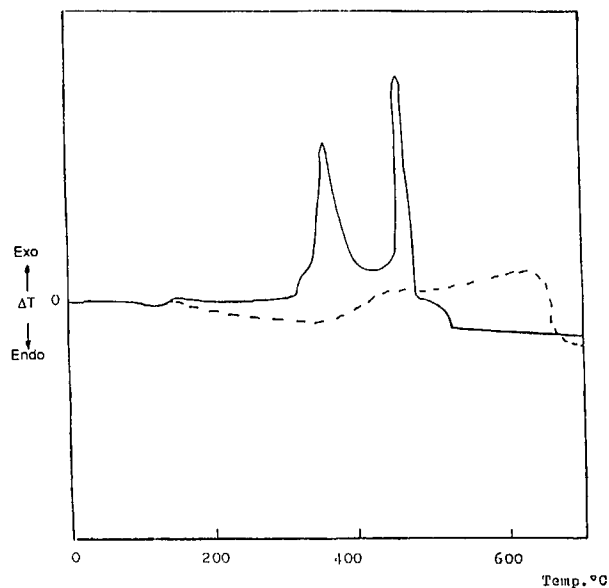
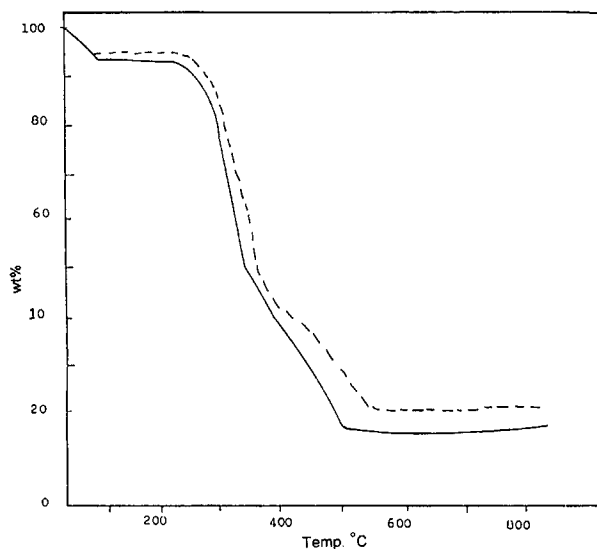
Table I Proximate, Ultimate, and Chemical Analysis of Bagasse

Proximate Analysis (wt %)	
Moisture	7.6
Ash (db)	3.4
Volatile matter (db)	84.3
Fixed carbon (db)	12.3
Ultimate Analysis (wt %)	
Carbon	51.7
Hydrogen	6.3
Oxygen (dif)	42.0
Nitrogen	
Sulphur	
Chemical Analysis (wt %)	
Cellulose	33.6
Pentosan	29.0
Lignin	18.5

db = dry basis; dif = by difference.

mosphere) conditions. The thermal curves reveal the general differences during thermal degradation patterns.

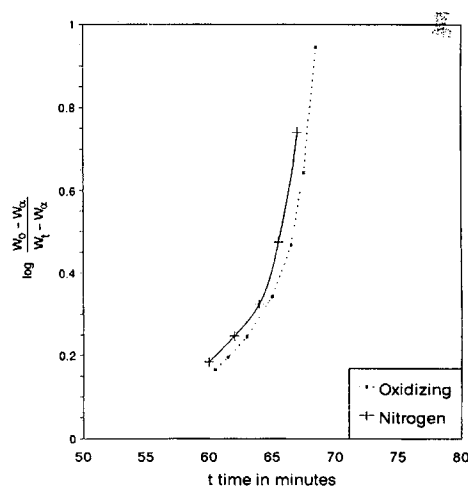
Endothermic reaction occurred between room temperature and about 200°C; a minimum at about 125°C was noticed for both combustion and pyrolysis reactions, which is attributed to moisture evaporation.⁵ Above 200°C active thermal reactions oc-

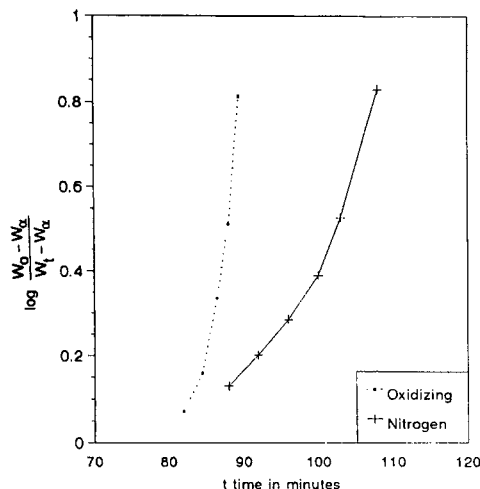
**Figure 1****Figure 2**

curred. During pyrolysis an exothermic reaction starts at about 450°C and ends at 700°C. During combustion, strong exothermic reaction begins at about 300°C and ends at about 500°C. This exotherm is interrupted by an endotherm, centered at about 450°C.

The main constituent of bagasse is cellulose. Endothermic nadir during combustion of cellulosic materials was attributed to the formation and evaporation of volatile products.⁶

During combustion, the first exothermic peak is due to oxidation of the volatile products and the second exothermic peak represents the oxidation of charred residue, while during pyrolysis the two exothermic peaks combined in a large shallow one.

**Figure 3**


Figure 4

Kinetic studies on combustion and pyrolysis of bagasse was carried out using TGA. Initial weight loss (about 6%) may be simply evaporation of the adsorbed water from surrounding, this is observed for both combustion and pyrolysis as shown in Figure 2. During combustion exothermic heat flow occurred between 280 and 520°C while during pyrolysis, an exothermic reaction occurred between 300 and 600°C, as shown in the DTA thermograms (Fig. 1). The major weight loss was observed within this temperature range; it reaches its maximum (about 50% weight loss) at ~ 350°C. This point can be considered as the end of volatilization combustion.⁵ Near 400°C, the pyrolytic endotherm and the weight loss indicated that active pyrolysis with the evolution of flammable products was almost completed.

The second stage of combustion, which appeared as the second exothermic peak in the DTA curve, is

due to glowing of char. The TGA combustion curve showed about 14 wt % residue.

Thermogravimetric analysis was carried out based on previous work by Nishizaki et al.⁷ Kinetic parameters such as: rate constant K , activation energy E , entropy change ΔS , enthalpy change ΔH , and Gibbs free energy change ΔG^0 for the initiation and carbonization stages in presence of air and nitrogen were calculated.

A first-order reaction was assumed and it is usually expressed by

$$-\frac{dC}{dt} = KC \quad (1)$$

where C is concentration of reactant in moles, t is time of reaction in minutes, and K is rate constant in minutes⁻¹.

If the concentration is replaced by the observed weight w_t , then

$$\frac{d(w_0 - w_t)}{dt} = K(w_0 - (w_0 - w_t)) = Kw_t \quad (2)$$

where, w_0 is the original weight of the preheated sample in milligrams, and w_t is the weight of sample after time t .

Integration of the above equation gives

$$\begin{aligned} \log e^{(w_0 - (w_0 - w_t))} &= \log e^{w_t} \\ &= Kt + c \end{aligned} \quad (3)$$

but at time

Table II Volatilization Stage for Bagasse in an Oxidizing Atmosphere

Time t (min)	Temp. (°C)	Residual Weight (wt %)	$\frac{w_0 - w_\alpha}{t_t - w_\alpha}$	$\log \frac{w_0 - w_\alpha}{w_t - w_\alpha}$	Δw (wt %)	Δt (min)	K (min ⁻¹ × 10 ³)	$\log K$
45.0	225	94 (w_0)	1.00	0.000	2.0	5.0	4.25	0.630
50.0	250	92	1.04	0.020	2.0	2.0	10.80	1.036
53.0	265	90	1.10	0.041	5.0	4.0	13.80	1.143
57.0	285	85	1.25	0.063	5.0	3.5	16.80	1.225
60.5	302.3	80	1.46	0.166	2.0	1.0	25.00	1.397
61.5	307.5	78	1.57	0.196	3.0	1.5	25.64	1.408
63.0	315	75	1.76	0.245	5.0	2.0	33.30	1.523
65.0	325	70	2.20	0.342	5.0	1.5	47.60	1.678
66.5	332.5	65	2.93	0.467	5.0	1.0	76.92	1.886
67.5	337.5	60	4.40	0.643	5.0	1.0	83.30	1.921
68.5	342.5	55	8.80	0.944	5.0	1.0	90.90	1.958
69.5	347.5	50 (w_α)	∞					

Table III Volatilization Stage for Bagasse in a Nitrogen Atmosphere

Time t (min)	Temp. (°C)	Residual Weight (wt %)	$\frac{w_0 - w_\alpha}{w_t - w_\alpha}$	$\log \frac{w_0 - w_\alpha}{w_t - w_\alpha}$	Δw (wt %)	Δt (min)	K ($\text{min}^{-1} \times 10^3$)	$\log K$
45	225	95 (w_0)	1	0	0.6	5.0	1.263	0.102
50	250	94.4	1.0180	7.93	0.65	2.0	3.440	0.54
52	260	93.7	1.0390	0.016	1.55	3.0	5.510	0.74
55	275	92.2	1.0927	0.038	1.20	2.0	6.510	0.818
57	285	91.0	1.1369	0.056	4.00	3.0	15.380	1.187
60	300	85.0	1.4400	0.156	3.00	2.0	24.760	1.394
62	310	82.0	1.6500	0.217	4.00	2.0	27.270	1.436
64	320	78.0	2.0620	0.314	5.00	2.0	32.050	1.506
66	330	73.0	2.9900	0.477	5.00	2.0	34.260	1.535
68	340	68.0	5.4900	0.740	6.00	2.0	44.117	1.645
70	350	62 (w_α)	∞					

$$t = 0, w_0 - w_t = 0$$

Hence,

$$c = -\log e^{w_0}$$

Therefore,

$$\log e^{w_0/w_t} = Kt$$

If the amount of residue at the end of heating w_α is considered, then

$$\log(w_0 - w_\alpha/w_t - w_\alpha) = Kt \quad (4)$$

Plotting $\log(w_0 - w_\alpha/w_t - w_\alpha)$ against time t for a first-order reaction should give a straight line, the slope of which equals the value of the rate constant K at the considered temperatures. Figures 3 and 4 show the plot of $\log(w_0 - w_\alpha/w_t - w_\alpha)$ against time t , as calculated for the volatilization and carbonization stages in inert and oxidizing atmospheres.

Straight lines are obtained except near the beginning in which a slight curvature occurs due to the initiations of the reactions. Therefore, the reactions can be considered as first-order reactions.

The rate constant K , for a first-order reaction, is calculated using equation (1):

$$K = -\frac{dC}{dt} \frac{1}{C} \quad \text{at temperature } T \quad (5)$$

Using the finite differences instead of differentials,

$$K = -\frac{\Delta C}{\Delta t} \frac{1}{C_{av}} \quad (6)$$

Equation (6) was used to calculate the rate constants K . The steps of calculations for the volatilization and decarbonization stages are shown in Tables II through V. The results revealed that the rate constant K is higher during combustion than during

Table IV Decarbonization Stage for Bagasse in an Oxidizing Atmosphere

Time t (min)	Temp. (°C)	Residual Weight (wt %)	$\frac{w_0 - w_\alpha}{w_t - w_\alpha}$	$\log \frac{w_0 - w_\alpha}{w_t - w_\alpha}$	Δw (wt %)	Δt (min)	K ($\text{min}^{-1} \times 10^3$)	$\log K$
80.0	400.0	39 (w_0)	1.00	0.000	2.0	5.0	25.40	1.409
82.0	410.0	37.0	1.18	0.725	2.5	2.5	27.02	1.431
84.5	422.5	34.5	1.44	0.159	2.5	2.0	36.23	1.559
86.5	432.5	32.0	2.16	0.357	2.0	1.5	41.60	1.619
88.0	440.0	30.0	3.25	0.511	2.0	1.5	44.40	1.647
89.5	447.5	38.0	6.50	0.812	2.0	1.5	47.60	1.677
91.0	455.0	26 (w_α)	∞					

pyrolysis and during the volatilization than during the carbonization stage.

Using the integrated form of Arrhenius equation, which shows the temperature dependence of the rate constant K of a reaction on the absolute temperature T :

$$\ln K = \frac{-E}{RT} + \ln c \quad (7)$$

where R is the gas constant, E is the activation energy (kJ/mole), and c is the integration constant.

Figure 5 shows the relationship of $\log K$ versus $1/T \cdot 10^5$. The activation energies of the reactions in air and nitrogen for the volatilization and decarbonization stages were calculated and are given in Table VI. As shown in the table the activation energies of thermal degradation of bagasse in air are larger than those of degradation in inert gas, which indicates that bagasse is thermally more stable in an oxidizing atmosphere than in an inert one.

According to the rate theory,⁸ the rate of reaction K can be expressed as follows:

$$K = \frac{kt}{h} e^{-\Delta G^0/RT} \quad (8)$$

where h is Plank's constant (6.6256×10^{-34} J s).

Expressing the change in free energy ΔG^0 in terms of entropy change ΔS and enthalpy change ΔH , one can write equation (8) in the form

$$K = \frac{kt}{h} e^{\Delta S/R} e^{-\Delta H/RT} \quad (9)$$

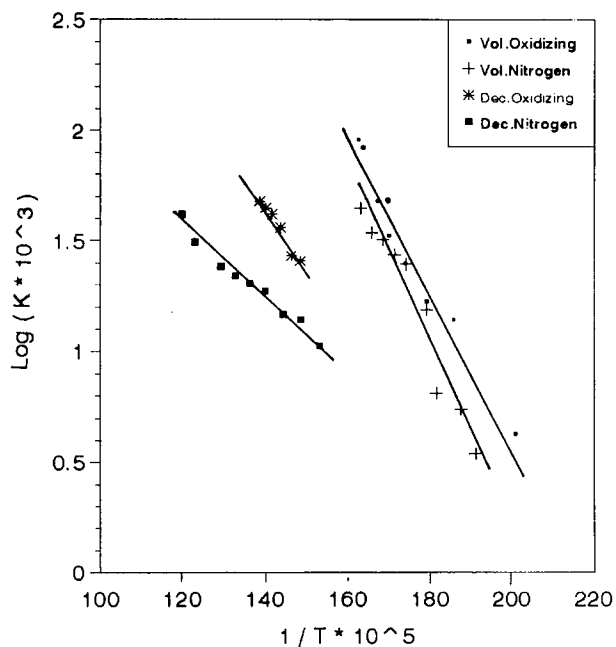


Figure 5

For the first-order reaction, the activation energy is related to the change in enthalpy⁹ by the following equation:

$$E = H + RT \quad (10)$$

Thus the rate of reaction may be written as

$$K = \frac{kT}{h} e^{\Delta S/R} e^{-(E-RT)/RT} \quad (11)$$

Table V Decarbonization Stage for Bagasse in a Nitrogen Atmosphere

Time t (min)	Temp. (°C)	Residual Weight (wt %)	$\frac{w_0 - w_\alpha}{w_t - w_\alpha}$	$\log \frac{w_0 - w_\alpha}{w_t - w_\alpha}$	Δw (wt %)	Δt (min)	K ($\text{min}^{-1} \times 10^3$)	$\log K$
76	380	47 (w_0)	1.00	0.00	2.0	4.0	10.360	1.026
80	400	45.0	1.08	0.033	2.5	4.0	13.880	1.143
84	420	42.5	1.19	0.079	2.5	4.0	14.700	1.167
88	440	40.0	1.35	0.130	3.0	4.0	18.750	1.273
92	460	37.0	1.58	0.200	3.0	4.0	20.270	1.306
96	480	34.0	1.92	0.289	3.0	4.0	22.050	1.340
100	500	31.0	2.45	0.389	3.0	4.0	24.190	1.384
104	520	28.0	3.37	0.528	4.0	4.0	35.714	1.553
108	540	24.0	6.75	0.892	4.0	4.0	41.600	1.619
112	560	20 (w_α)	∞					

Table VI Thermodynamical Parameter of Bagasse Decomposition

Stage	K (min^{-1})	Temperature ($^{\circ}\text{C}$)	E (KJ/mole)	ΔH (KJ/mole)	ΔS (KJ/mole K°)	ΔG° (KJ/mole)
Volatilization air	0.048	320	127.49	122.50	-0.105	185.06
Volatilization nitrogen	0.037	315	87.90	83.011	-0.170	183.46
Decarbonization air	0.032	450	68.22	62.160	-0.230	227.69
Decarbonization nitrogen	0.019	470	46.68	40.050	-0.270	237.40

Thermodynamic functions ΔS , ΔH , ΔG° were calculated from equations (8)–(11) and are given in Table VI. The rate constant values in Table VI represent the average value of the rate constant for the chosen temperature range, the positive values of the Gibbs free energy change indicate the non-spontaneous nature of the reactions as the free energy of the products are higher than those of the reactants.

CONCLUSION

Reaction rates in air were found to be higher than in an inert atmosphere. On the other hand, the decarbonization stage was considerably slower than the volatilization stage for both types of atmosphere. Activation energies for reactions in air are higher than those for reactions in inert atmosphere. Whereas activation energies for the decarbonization stages are remarkably smaller than those of the volatilization reactions.

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