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THERMAL DECOMPOSITION OF CELLULOSE AND TYPHA SAP — EVALUATION OF THE CATALYTIC ACTIVITY OF POTASSIUM CARBONATE

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ABSTRACT

The thermal decomposition of cellulose is studied at three different heating rates. The activation energy and the mechanism are affected by the heating rate. When heating is carried out in the presence of potassium carbonate the decomposition of cellulose is catalysed and the char percentage increases exponentially with the amount of salt.

The thermal decomposition of typha sap at different heating rates and under different atmospheres is also studied. Evidence could be found from kinetic plots that the decomposition of typha sap occurs in two steps.

INTRODUCTION

The exploration of alternative energy resources is a challenge for basic scientists, as well as engineers and economists. Among the progressing fields in this respect is biomass energy development. Hitherto several technologies have been described and evaluated for the extraction of energy from biomass materials. The thermochemical methods involve thermal destruction of the biomass structures in the presence of inert or reactive gases to give low molecular weight substances of valuable energy content. Cellulose is the main component in the composition of biomass feedstocks and hence a study of the thermal behaviour will help in the mechanism and design of such conversion technologies.

For the sake of evaluating local cellulosic substances, this piece of research describes the thermal behaviour of cellulose and the catalytic activity of alkali carbonate on it. The study also includes the degradation of typha sap, a naturally growing feedstock in the south of the country, under various working conditions.

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EXPERIMENTAL

Apparatus

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded on a Stanton-Redcroft thermobalance (model TG 760) equipped with a three-pen strip-chart recorder for the simultaneous recording of TG, DTG and temperature (T) signals.

The measurements were carried out on samples weighing 3–5 mg under flowing (30 ml min^{-1}) N_2 or CO_2 or static (air) atmospheric conditions. Other procedural details are given later.

Materials

Cellulose, avicel microcrystalline from Merck; potassium carbonate, laboratory reagent from Dakin Bros.; typha sap, the ground material has a particle size between 150 and 300 μm.

Procedure

Samples of cellulose (~ 1 g) were accurately weighed in small beakers and treated with increasing volumes of 1% K_2CO_3 solution to attain catalyst concentrations of 0.6, 1.0, 2.0, 4.0 and 10%. Distilled water was added to the samples to balance the differences in volume of the carbonate solution. Another sample was treated with an equal volume of distilled water to compensate for the soaking effect. The beakers were agitated on a steam bath to aid evaporation.

RESULTS AND DISCUSSION

TG of cellulose

TG signals of cellulose were obtained at 5, 10 and 20°C min^{-1} and displayed in the form of the degree of conversion, α, as a function of temperature (Fig. 1). The decomposition profiles are dependent on the rates of heating, but no significant change could be noticed in the initial and final decomposition temperatures. Above 270°C, cellulose undergoes degradation and the rate becomes appreciable at 310°C, when the weight loss exceeds 4%. The maximum rate of decomposition occurs at 323, 334 and 350°C for samples heated at rates of 5, 10 and 20°C min^{-1}, respectively. However, higher temperatures (360 and 375°C) were reported for cellulose of different origins studied under comparable operating conditions [1,2]. The weight loss corresponds to depolymerization by the transglycosylation reaction [3]. This

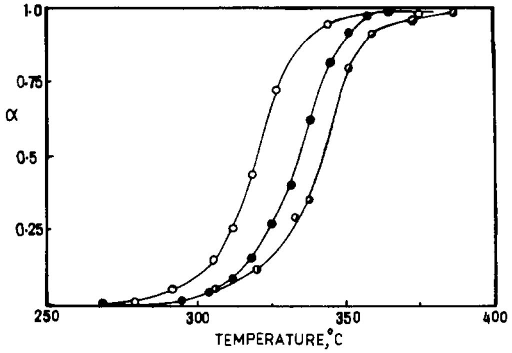

Fig. 1. Thermograms of cellulose at different heating rates: (○) 5, (●) 10 and (◒) 20°C min^{-1}.

initiated a kinetic study for the decomposition reaction of cellulose using the data extracted from the TG curves. A computer program was employed for this purpose based on the integral procedure of Coats and Redfern [4,5]. The results are listed in Table 1. The computed activation energy, E, values were significantly different for the different heating rates. Meanwhile, a slight difference is noticeable in the reaction order. The E values fall within the wide range of results given by others [6,7]; even though, a reason must be given for this discrepancy.

Plots were prepared of log β_j, the heating rate, vs. $1/T$ for selected values of α (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.75) to show the constancy of E with increasing degree of conversion [8,9] (Fig. 2). Two features may be seen from Fig. 2: the linearity of the plots is improved as α increases, and the overall slope of the plots becomes smaller. The first feature corresponds to the change in the mechanism of decomposition [8] while the second refers to the change in the activation energy with the extent of reaction

$$\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)} = 0.457\frac{E}{R} \tag{1}$$

At $\alpha = 0.75$, E attains a value of 181.5 kJ mol^{-1}, which is close to that obtained above.

TABLE 1

Kinetic parameters of cellulose decomposition

Parameter	Heating rate (°C min^{-1})	
	10	20
n	1.22	1.36
E (kJ mol^{-1})	274.09	171.58
log Z	28.66	18.48
Corr. coeff.	0.9991	0.9799

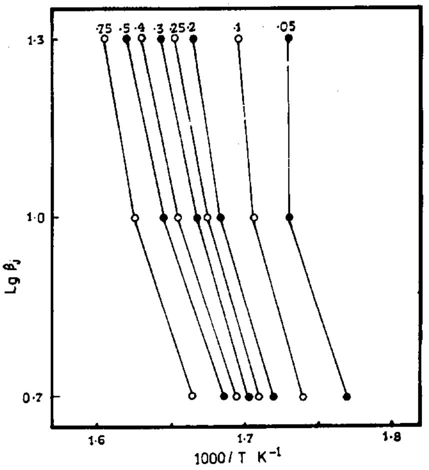

Fig. 2. Plots of log β_j vs. reciprocal temperature for cellulose.

Effect of potassium carbonate

The normalized TG plots of cellulose in the presence of increasing concentrations of K_2CO_3 are shown in Fig. 3. The DTG signals, however, indicated that increasing content of the salt causes the clear segmentation of the thermal decomposition of the cellulose into a low temperature reaction and a high temperature one (Fig. 4). The evolution of CO_2 could be the low temperature reaction. This may refer to the action of K_2CO_3 on the chemical nature of the reaction mechanism and products, rather than simple physical interaction with the decomposing material to facilitate degradation. Kinetic study showed that the overall reaction order remained constant in the presence of K_2CO_3 even at the highest concentration, while the activation energy changed significantly, which confirms the chemical effect on the

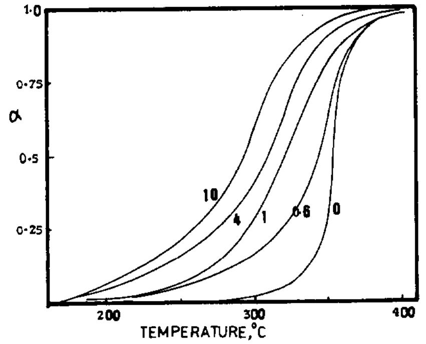

Fig. 3. Thermograms of cellulose decomposition in the presence of K_2CO_3. Heating rate 20°C $\min^{-1}$.

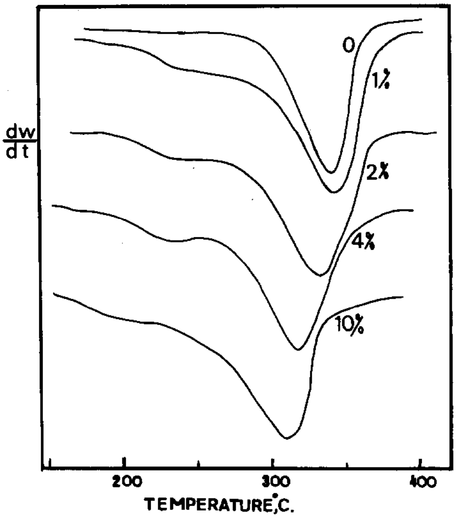

Fig. 4. DTG signals of cellulose in the presence of K_2CO_3. Heating rate 20°C min^{-1}.

reaction (Table 2). The catalytic activity of potassium may often be thought of in relation to its action in developing the surface area of a pyrolysed material due to its effect on microporosity through intercalation [10]. The estimated values of weight loss of cellulose are significantly lowered as the content of potassium carbonate increases in the samples (Fig. 5). The percentage weight loss decreases exponentially with the percentage of K_2CO_3 (x):

$$\text{Weight loss } (\%) = 82 \exp(0.0456x) \qquad (2)$$

Potassium carbonate, therefore, catalyses the carbonization reaction of cellulose which results in a significant decrease in the degradation reaction and, hence, less volatile-product formation. This is in agreement with previous reports on the action of alkali carbonate on increasing the yield of char at the expense of condensable volatiles [11]. The increased char yield accounts

TABLE 2

Kinetic parameters of the catalytic decomposition of cellulose

Percentage of catalyst	n	E (kJ mol^{-1})	log Z	Corr. coeff.
0.6	0.7	55.95	7.56	0.9923
1.0	1.15	62.83	9.01	0.9848
2.0	1.2	58.15	8.76	0.9955
4.0	1.12	50.98	8.02	0.9884
10	1.15	50.11	8.26	0.9894

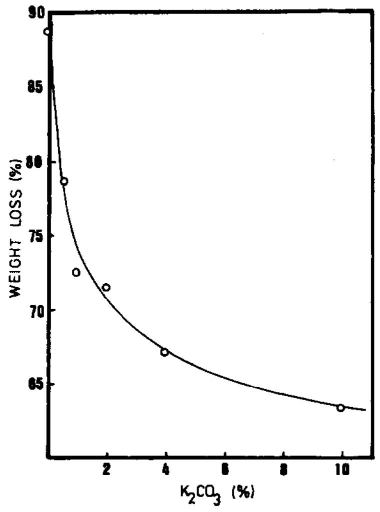

Fig. 5. Dependence of the extent of weight loss of cellulose on the percentage of K_2CO_3.

for the fact that alkali carbonate could increase the amounts of hydrogen and carbon dioxide without a proportionate reduction in the final yield of carbon monoxide and char [12].

TG of typha sap

The TG curves of typha sap recorded at 5, 10, 20 and 40°C min^{-1} are shown in Fig. 6. The moisture content of typha sap is 5.83% regardless of the heating rate used. The main pyrolysis reaction is influenced by the heating rate and shifted to higher temperature ranges as the rate increases (Fig. 6). The DTG curve of typha sap comprised two overlapping decomposition reactions (Fig. 7). The second resembles that found for the decomposition of

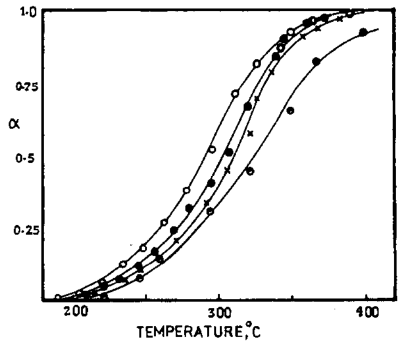

Fig. 6. Thermograms of typha sap at different heating rates: (○) 5, (●) 10, (×) 20 and (◒) 40°C min^{-1}.

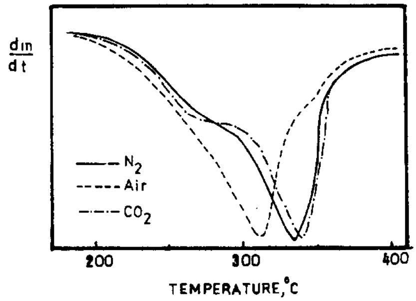

Fig. 7. DTG curves of typha sap under different atmospheres. Heating rate 20 °C min^{-1}.

cellulose, being slightly shifted to a lower temperature due to impurities of alkali metals. The first does not involve more than 30% of the weight loss and could be due to the hemicellulose and lignin contents. The data extracted from TG curves recorded at 10 and 20 °C min^{-1} were used to estimate the kinetic parameters of the decomposition. The reaction appeared to be of first order ($n = 1.09$ and 1.34) and proceeded with an activation energy of 57.82 and 67.09 kJ mol^{-1} when heated at rates of 10 and 20 °C min^{-1}, respectively. Barbooti [13] recently reported that the computed E values, could be the overall reaction activation energy and not necessarily the only predictable value, especially for multi-step reactions. The conversion functions were reconsidered using the most acceptable value of the reaction order, the first order. A plot of the Coats–Redfern function was

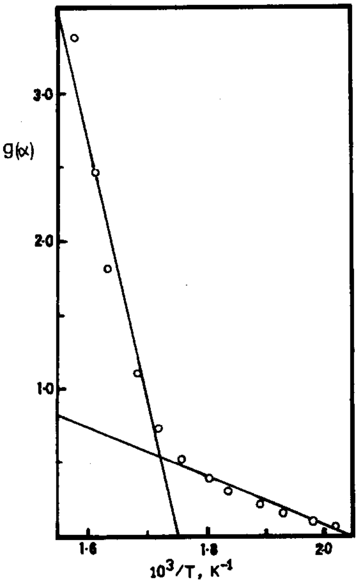

Fig. 8. Arrhenius plot of the thermal decomposition of typha sap for a reaction order of 1.

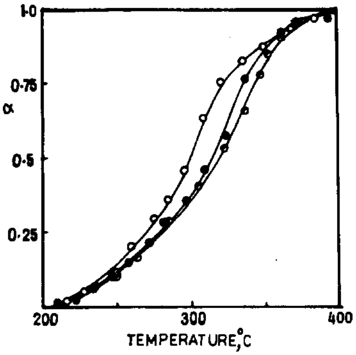

Fig. 9. Thermograms of typha sap under different atmospheres. (●) N_2, (○) air and (◒) CO_2. Heating rate 20°C min^{-1}.

prepared for the data of the decomposition of typha sap which was thought to be a two-step reaction, vide supra (Fig. 8). Accordingly, the plot indicated that the decomposition reaction of typha sap comprises two principal steps with different activation energy values; 13.72 and 148.18 kJ mol^{-1}.

When carrying out the procedure [13], the second decomposition started at 306°C, which corresponds to a degree of conversion of 0.5 (Fig. 6). Such a temperature is identical to that observed above at which an appreciable rate of decomposition of cellulose occurs. Furthermore, the composition of typha sap [14] agrees with such a value of α because the cellulose content approaches 50%. Another confirmation of this finding may be derived from the kinetic parameters, since the activation energy of the second stage is close to that obtained for pure cellulose.

The decomposition of typha sap is dependent on the atmosphere. The TG curves recorded under inert, N_2, oxidizing, air and carbon dioxide atmospheres are shown in Fig. 9. The corresponding DTG curves are given in Fig. 7. Under nitrogen the material decomposes in its ideal condition whilst a fast rate of weight loss was noticed under air, due to the oxidative action of oxygen which may be chemisorbed within the material [2] and reaction with the gaseous products [6]. Carbon dioxide has a retarding effect because it is one of the major products of the decomposition of cellulosic materials and hence it encourages the reversal of the reaction.

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