# THE APPLICATION OF THERMAL ANALYSIS TO THE COMBUSTION OF CELLULOSE

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## ABSTRACT

It is shown that the use of differential thermal analysis (DTA) to follow the pyrolysis of cellulose in air produces two and sometimes three exothermic peaks. The first peak is associated with the combustion of volatile material, released in the degradation process, the second is caused by the glowing combustion of the carbonaceous residue, and the final exotherm is probably due to the combustion of product gases.

The thermogravimetric analysis (TG) data in air show a preliminary loss of water followed by a mass loss of about 85% due to the production of the combustible volatiles. This second step appears identical to the degradation process in nitrogen, but in air the degradation products ignite to produce the first exothermic peak on the DTA. The glowing combustion DTA peak is associated with a further mass loss of about 15% on the TG plot. The use of a thermomechanical analyser shows that a small shrinkage of 3% occurs between 45 and 110°C, with the major collapse taking place between 300 and 370°C. There is, however, an expansion of 10% between 370 and 405°C, believed to be due to a crosslinking reaction.

## INTRODUCTION

Although the combustion of cellulose consists of a highly complex set of reactions, most workers agree on the general scheme [1] set out below. In
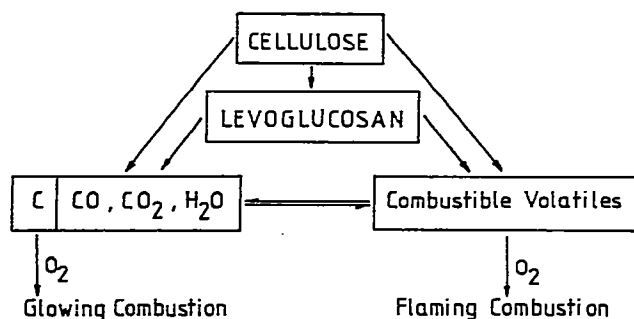


this scheme oxygen is shown as having an effect on the final products but not on the overall pattern of behaviour; varying the atmosphere may cause a different route to be favoured, but the general scheme remains the same. Other factors which can affect the reaction path are temperature, period of

heating (including the heating rate), and the physical and chemical properties of the cellulose.

Analysis of the products of the thermal degradation of cellulose in inert and oxidising atmospheres led Wodley [2] to conclude that the degradation processes were identical, whether or not oxygen was present. More recently it has been proposed [3] that, at the decomposition temperature of cellulose, the breakdown proceeds so rapidly that the accompanying slow oxidation of the cellulose is completely overshadowed. Thus at temperatures below 200°C the slow oxidative reaction predominates but at higher temperatures the principal reaction is depolymerisation of the cellulose to form levoglucosan (1,6 anhydro-$\beta$-D-glucopyranose).

Madorsky et al. [4] analysed the volatile products of the pyrolytic decomposition of cellulose and found the proportion of tar to be 65%. Tars produced in this way have been found to contain 80% levoglucosan and small amounts of 1,6 anhydro-$\beta$-D-glucofuranose, 5-(hydroxymethyl)-2-furaldehyde, 2-furyl hydroxymethyl ketone and 1,4 : 3,6-dianhydro-$\alpha$-D-glucopyranose. The highest levoglucosan yields can be achieved under vacuum conditions, when the oxidation reactions are suppressed and further decomposition of the levoglucosan is arrested by its rapid removal from the hot zone.

There is much discussion as to the mechanism of levoglucosan formation; transglycosylation [5] and free radical [6] mechanisms are two of many suggested alternatives. There is evidence [3] that the slow oxidation reaction is a free-radical process.

If the primary reaction products are not removed from the heated environment they will decompose to form a series of secondary reaction products of low molecular weight. If the findings of several workers [2,7—10] are combined, it can be shown that over 60 secondary products have been identified. Many of the primary and secondary products are inflammable and, when air is present, they will react with oxygen in the gas phase, giving rise to flaming ignition.

The majority of investigations using thermal analysis to follow the decomposition of cellulose have been performed in inert atmospheres; Dollimore and co-workers [11,12] used TG equipment operating under nitrogen to study the formation of the carbonaceous residue. In the study reported here, methods of thermal analysis and in particular DTA, were used to investigate the thermal degradation of cellulose in air.

EXPERIMENTAL

*Materials*

The cellulose used in this study was Whatman CC31, a white microgranular powder, supplied by W. and R. Balston Ltd. This cellulose powder is manufactured from high purity cotton and contains 98% $\alpha$-cellulose.

*Equipment*

All the DTA results presented in this study were obtained on the Dupont 900 DTA using the 1200°C cell. In this design the sample holders do not stand in a heated block but are isolated from each other on separate alumina insulating tubes. This gives greater sensitivity but a greater temperature inhomogeneity; however, this danger may be limited by using thick-walled crucibles. This combination of separate sample containers with the thermocouples placed outside the sample makes this head less suitable for quantitative work, since it increases the likelihood of distortion of the peak from its vertical shape [13]. However, using the "macro" cups supplied with the equipment, the sample weights are still relatively small (20—25 mg), thus minimising temperature gradients in the sample.

The supporting TG data were obtained using a Stanton Redcroft TG750 thermobalance, operated under the following conditions: heating rate, 10°C min$^{-1}$; gas flow, 50 ml min$^{-1}$ at atmospheric pressure; sample mass, 7—10 mg; platinum crucible.

The conditions employed for the TMA of cellulose, using the Stanton Redcroft TMA 691 Unit were as follows: heating rate, 10°C min$^{-1}$; static atmosphere of air; sample mass 30 mg; aluminium foil crucible.

RESULTS AND DISCUSSION

*DTA results*

In a real fire situation cellulose is unlikely to be found mixed with alumina. For this reason alone DTA on undiluted samples would seem preferable, moreover dilution of a sample which is to undergo oxidative decomposition is regarded as a dubious practice [14]. A comparison was nevertheless made between the results for cellulose diluted to 10% with cal-
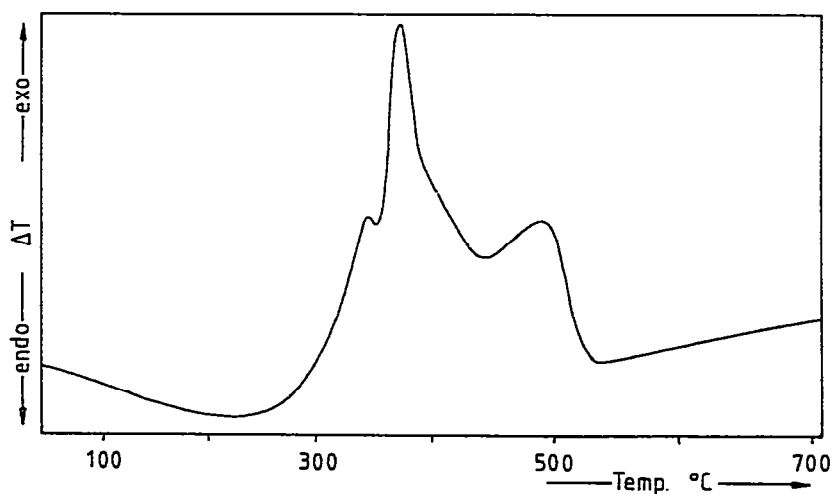


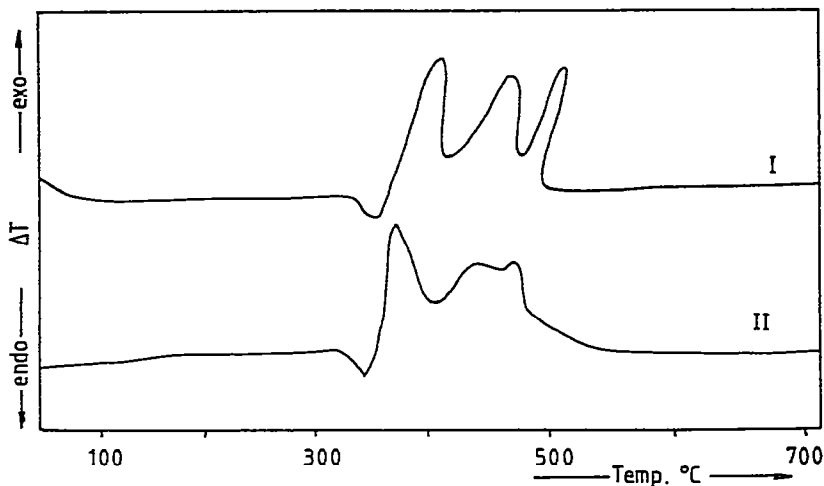Fig. 1. DTA of cellulose mixed 10% with calcined alumina.

Fig. 2. DTA of cellulose, measuring sample (I) and reference (II) temperatures.

cined alumina (Fig. 1) and for 100% cellulose (with an empty sample cup as reference) having the $\Delta T$ sensitivity reduced to 1/10 of that for the 10% cellulose sample [Fig. 2 (I)]. The latter curve shows an endothermic peak at 349°C followed by three exotherms with peak maxima at 404, 465 and 507°C, whereas the curve for the 10% sample is more difficult to interpret. However, Fig. 2 (I) has "sloping" peaks probably because of the large sample weight relative to that of the sample cup and liner. The heat evolved during the reaction causes the heating rate to increase up to the peak of the exotherm. After the exothermic peak the sample cools until it reaches the programmed temperature of the furnace. If the temperature of the reference is measured instead of that of the sample [see Fig. 2(II)] then the differential temperature ($\Delta T$) is recorded against a linearly increasing temperature and
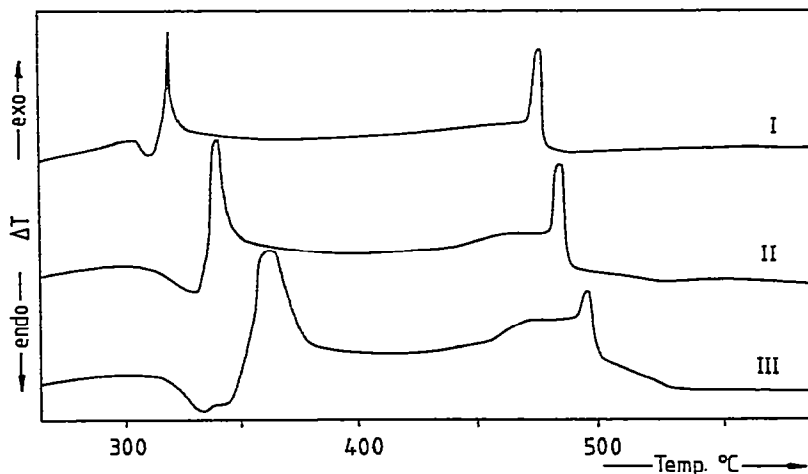


Fig. 3. DTA of cellulose — effect of heating rate. I, 5°C min$^{-1}$; II, 10°C min$^{-1}$; III, 20°C min$^{-1}$. N.B. Expanded temperature scale compared to Figs. 1 and 2.
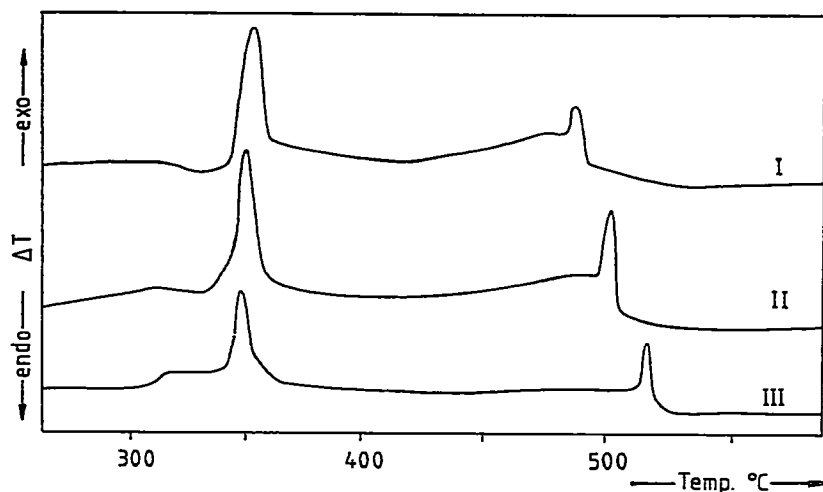
Fig. 4. DTA of cellulose — effect of sample weight variation. I, Sample cup completely filled; II, sample cup half-filled; III, sample cup quarter-filled.

the distortions no longer appear. The recorded peak temperature is not now the temperature of the sample which (for an exothermic change) exceeds the recorded temperature by the value of the peak height expressed in °C. It was decided to adopt the practice of measuring the reference temperature for all subsequent work on the Dupont 900 DTA.

All the above DTA results were obtained at a heating rate of $20°C$ min$^{-1}$. The effect of varying heating rates is shown in Fig. 3. Increasing the heating rate, (i) increases peak widths; (ii) increases peak temperatures; (iii) gives more detail — note the emergence of a "new" peak at about $470°C$; and (iv) gives a poor return to baseline between the major peaks. On balance the heating rate of $10°C$ min$^{-1}$ appeared most suitable and was adopted in subsequent work.

Using the above standardised conditions the effect of sample weight was investigated and this is indicated in Fig. 4. It can be seen that increasing the sample weight increases the width and/or the height of each peak, increases slightly the peak temperature of the first exotherm, and decreases markedly the peak temperature of the second exotherm. These effects can be explained by considering the case of a high sample weight, which will cause a proportionately large amount of heat to be evolved during the first exotherm. This will increase the sample temperature relative to the recorded temperature so that when the sample temperature is sufficiently high for the cellulose to undergo its second exothermic change the recorded temperature will still be several degrees lower than the sample temperature. Hence the position of the second exothermic curve is displaced towards lower temperatures by an increased sample weight. Three methods to minimise this effect were considered; namely (i) to use flowing air; (ii) to fill the sample cup by a standardised amount (up to the brim) for each determination, and (iii) to replace the platinum cup liners with alumina liners to provide a larger heat sink.
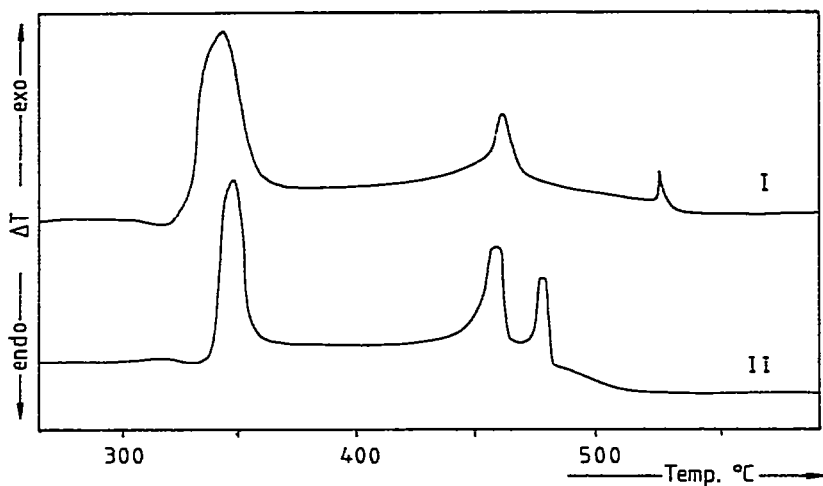
Fig. 5. DTA of cellulose — comparison between $Al_2O_3$ (I) and Pt (II) cup liners.

The effect of using flowing air to dissipate more quickly the heat produced at the sample resulted in a standard being adopted where air was passed over the sample at 350 ml min$^{-1}$. The effect of replacing platinum cup liners with alumina liners is demonstrated in Fig. 5. In flowing air (350 ml min$^{-1}$) and using platinum sample cups an additional exothermic peak is observed at around 455°C apparently positioned between the two exotherms observed in the previously recorded runs [Fig. 5(II)]. It should be noted that a third peak has already been seen to emerge under static air conditions at high heating rates [Fig. 3 (III)] and when a large sample weight is used [Fig. 4 (I)]. Three peaks are still observed if flowing air is employed with alumina cup liners instead of the platinum [Fig. 5(I)]. The greater heat capacity of the alumina liners reduces the temperature increase of the sample due to the first exotherm. A comparison of the two liner materials shows that the use of alumina has the following effects: (i) less flat baseline; (ii) increased peak width; (iii) decreased peak height; and (iv) increased peak temperatures.

The first three of these effects are disadvantageous. However, there are two advantages which compensate; firstly, the dependence of the curve on the sample weight is reduced, and secondly, the second and third exotherms appear on the DTA curve nearer to their "correct" temperatures. It was decided that the superior reproducibility conferred by the alumina cup liners (due to their diminished dependence on sample weight and packing) made them the better choice. Table 1 summarises the peak temperatures and experimental conditions of a series of DTA runs exhibiting two exothermic peaks, and Table 2 is a similar summary of DTA experiments in which three peaks were recorded.

The recommended "standard" conditions employed for the DTA of cellulose in air and the reasons for their implementation are summarised in Table 3, and results corresponding to these conditions are listed in Table 2, runs 19—29 inclusive. Figure 5 (I) may be regarded as a typical "standard" curve.

TABLE 1

Summary of DTA data for pure cellulose in air which showed two exothermic peaks

| Fig. | Run no. | Peak maxima (°C) | | Experimental conditions | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Peak 1 | Peak 2 | Dilution (%) | Atmosphere | Heating rate ($°C\ min^{-1}$) | Sample cup | Liner material | Temp. measured |
| 1 | 1 | 373 | 491 | 10 | Static air | 20 | | Pt | Sample |
| | 2 | 371 | 510 | 10 | Static air | 20 | | Pt | Sample |
| 3 (II) | 3 | 343 | 489 | 100 | Static air | 10 | Half full | Pt | Ref. |
| | 4 | 345 | | 100 | Static air | 10 | Half full | Pt | Ref. |
| 4 (II) | 5 | 349 | 503 | 100 | Static air | 10 | Half full | Pt | Ref. |
| 3 (I) | 6 | 319 | 477 | 100 | Static air | 5 | Half full | Pt | Ref. |
| 4 (I) | 7 | 354 | 454 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 8 | 353 | 488 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 9 | 350 | 457 | 100 | Static air | 10 | Full | Pt | Ref. |
| 4 (III) | 10 | 346 | 516 | 100 | Static air | 10 | Quarter full | Pt | Ref. |
| | 11 | 364 | 476 | 100 | Flowing air | 10 | | Pt | Sample |

TABLE 2

Summary of DTA data for pure cellulose in air which showed three exothermic peaks

| Fig. | Run no. | Peak maxima (°C) | | | Experimental conditions | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Peak 1 | Peak 2 | Peak 3 | Dilution (%) | Atmosphere | Heating rate ($°C\,min^{-1}$) | Sample cup | Liner materials | Temp. measured |
| 2 (I) | 12 | 404 | 465 | 508 | 100 | Static air | 20 | | Pt | Sample |
| 2 (II) | 13 | 369 | 439 | 472 | 100 | Static air | 20 | | Pt | Ref. |
| 3 (III) | 14 | 368 | 484 | 500 | 100 | Static air | 20 | Half full | Pt | Ref. |
| | 15 | 356 | 453 | 482 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 16 | 358 | 462 | 487 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 17 | 350 | 458 | 486 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 18 | 355 | 459 | 487 | 100 | Static air | 10 | Full | Pt | Ref. |
| | 19 | 349 | 453 | 475 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| 5 (II) | 20 | 347 | 458 | 478 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| | 21 | 353 | 420 | 459 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| | 22 | 344 | 420 | 459 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| | 23 | 341 | 432 | 462 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| | 24 | 353 | 476 | 536 | 100 | Flowing air | 10 | Full | Pt | Ref. |
| 5 (I) | 25 | 341 | 461 | 526 | 100 | Flowing air | 10 | Full | $Al_2O_3$ | Ref. |
| | 26 | 346 | 455 | 531 | 100 | Flowing air | 10 | Full | $Al_2O_3$ | Ref. |
| | 27 | 341 | 447 | 525 | 100 | Flowing air | 10 | Full | $Al_2O_3$ | Ref. |
| | 28 | 343 | 458 | 532 | 100 | Flowing air | 10 | Full | $Al_2O_3$ | Ref. |
| | 29 | 346 | 451 | 530 | 100 | Flowing air | 10 | Full | $Al_2O_3$ | Ref. |
| | 30 | 358 | 472 | 533 | 100 | Static air | 10 | Full | $Al_2O_3$ | Ref. |

# TABLE 3

Standard conditions for the DTA of cellulose in air using the Dupont 900 DTA

| Standard conditions | | Explanation |
|---|---|---|
| Measuring head: | 1200°C cell | Design of head ensures continuous flow of gas past sample |
| Atmosphere: | Flowing air 350 ml min$^{-1}$ | (i) Rapid removal of decomposition products; (ii) thermal equilibrium quickly restored after exotherm. |
| Dilution of sample: | Pure sample (no dilution) | (i) Closer model to real fire; (ii) dilution can impede access of gas to sample. |
| Sample weight: | 20—25 mg | Low weight: (i) minimises temperature gradient in sample; (ii) facilitates reaction with air by ensuring a high surface to volume ratio. |
| Cup liners: | Alumina | Large heat capacity: (i) increases reproducibility by decreasing weight effects; (ii) ensures system satisfies criteria for minimum peak distortion, also: catalysis unlikely. |
| Temperature measured: | Reference temp. | The reference temperature increases linearly (the sample temperature does not). |
| Heating rate: | 10°C min$^{-1}$ | (i) Most common heating rate for DTA work; (ii) gives best compromise between detail and sharpness of peaks for cellulose. |
| Instrument sensitivity settings $\begin{cases} T: \\ \Delta T: \end{cases}$ | 0.4 mV in.$^{-1}$ 0.02 mV in.$^{-1}$ | |

*Comparison of DTA results under standard conditions with literature values*

The "standard" results shown in Table 2 all exhibit three exothermic peaks. The first peak at about 345°C is preceded by a small endotherm; the second peak occurs around 460°C and the third peak typically is observed at 530°C immediately before a complete return to a flat baseline.

A visual check of exhaust gases coincident with the tracing of the small endotherm and the commencement of the first exotherm demonstrates that the endotherm corresponds to processes resulting in the evolution of volatile material and that the first exotherm is probably the result of flaming combustion of these volatiles. A DTA run in nitrogen (Fig. 6) showed the complete endotherm around 345°C uncomplicated by the presence of the first exotherm but accompanied by a rapid exothermic shift of the baseline.

Shafizadeh and Bradbury [3] have obtained DTA curves for cellulose heated at 15 deg min$^{-1}$ in air. These have been interpreted as representing an exotherm between 270 and ~400°C, interrupted by an endotherm centred at ~330°C. A second exotherm at ~480°C is also reported. Tang [15] used cellulose diluted to 8% with pyrex beads and a heating rate of 12 deg min$^{-1}$ in an atmosphere of oxygen. Two exothermic peaks were described; the first was ascribed to flaming of the volatiles (peak maximum at 335°C) and the second (ill-defined at about 400°C) to glowing combustion of the solid. Ramiah [16] reported DTA results on cellulose samples in nitrogen, air and oxygen. The baseline shift after the endotherm in nitrogen can be observed in his results. However, two definite exotherms were only revealed in the experiments in an oxygen atmosphere at 360 and 480°C. Akita and Kase [17] also failed to show more than one exotherm in air. In experiments reported by Broido [18] an absence of flowing air coupled with the use of a large sample produced DTA traces almost identical in both nitrogen and air.

Generally the results of all workers for the DTA of cellulose in an inert atmosphere are to show an endotherm in the region of 350°C followed by an
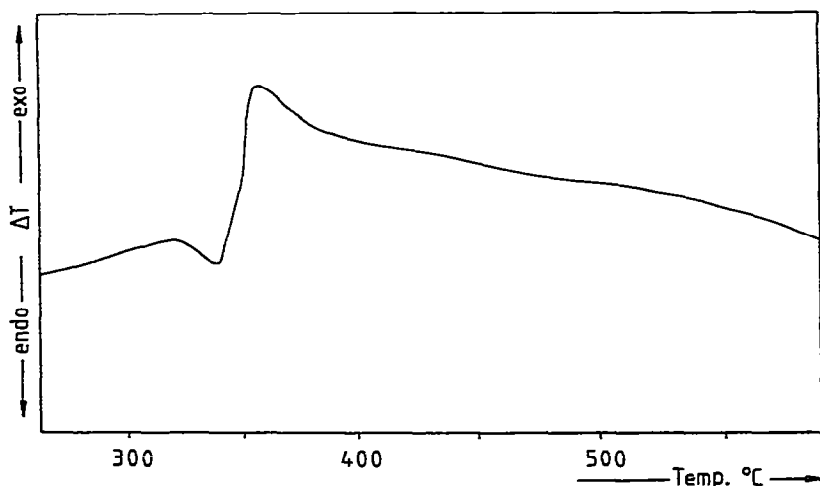


Fig. 6. DTA of cellulose in a nitrogen atmosphere.

exothermic shift of the baseline. By contrast there is a very poor correlation between the DTA results in an oxidising atmosphere. It is suggested here that the three strongly exothermic peaks obtained in this study result because the cellulose is surrounded by an oxidising atmosphere throughout the pyrolytic process.

*TG and thermomechanical analysis (TMA) results*

The instruments used to obtain TG and MTA data preclude an exact comparison with the DTA results; however they do allow certain points to be made. Figure 7 shows the TG data in air (I) and in nitrogen (II). Loss of sorbed water, about 2%, occurs between 50 and ~100°C. The major mass loss corresponding to the breakdown of the cellulose commences at the same temperature (~240°C) in both air and nitrogen. The maximum rate of mass loss occurs at a lower indicated temperature in air (~320°C compared with ~360°C in nitrogen) and the rapid mass loss is completed at a lower temperature in air (~330°C) than in nitrogen (~385°C). By 400°C the % mass losses are 89% in both air and nitrogen. The curves suggest a two-stage decomposition in air; after the first rapid mass loss, the second slower but acceleratory process starts. This second process does not happen in the inert atmosphere and can therefore be construed as being oxidation of the partially decomposed cellulose.

The TMA runs were performed on cellulose powder contained in a crucible and must, therefore, be regarded only as semi-quantitative. The data ob-
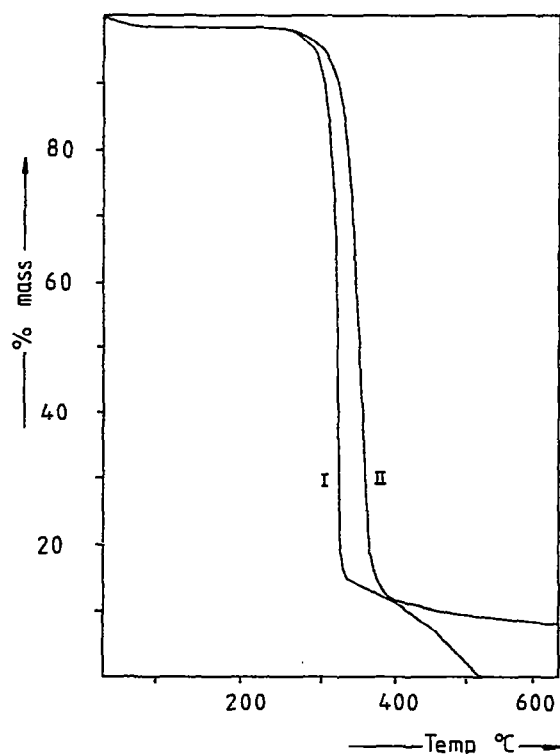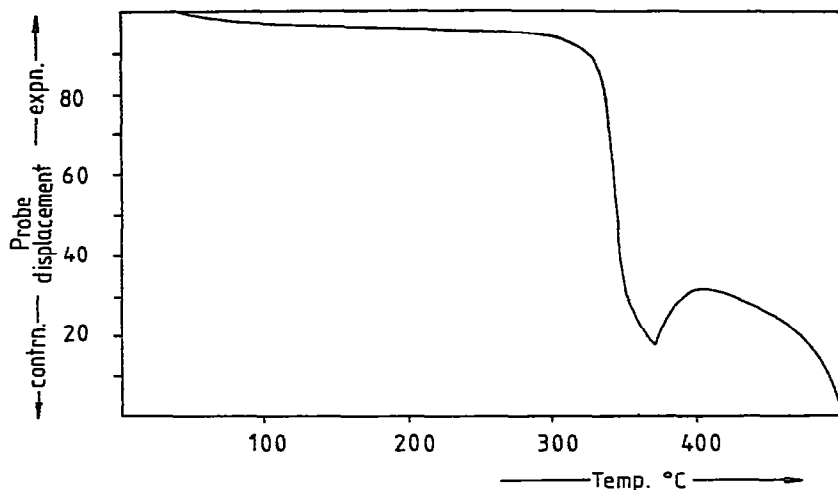


Fig. 7. TG of cellulose in air (I) and nitrogen (II).

Fig. 8 . TMA of cellulose in air.

tained are shown in Fig. 8. The probe displacement is plotted on an arbitrary scale where the original displacement equals 100% and the displacement at 500°C equals zero. A preliminary shrinkage of 3% occurs between 45 and 110°C but the sample only contracts by a further 2% between 110 and 300°C. The major collapse of the cellulose occurs between 300 and 370°C (with a maximum rate at 345°C). Both the preliminary and the major shrinkages can be linked to the TG mass losses in the same temperature ranges. However, between 370 and 405°C there is an expansion of approximately 10%. The phenomenon was shown to be reproducible throughout a series of experiments. Possible explanations for the observation include physical expansion, cross linking, opening of the pore structure or emission of gases. It is likely that emission of gases would also cause an opening of the pore structure, but Fairbridge et al. [19] have shown that pyrolysis in air has little or no effect on the surface area of cellulose powder. If it can be assumed that rapid physical expansion is unlikely at this advanced stage of a decomposition process then cross linking is the only remaining explanation.

The general shapes of the TG curves for cellulose under inert atmosphere conditions reported in the literature agree closely with those obtained here (see Table 4). The corresponding temperatures obtained under oxidising conditions are tabulated in Table 5. Except for Fairbridge et al. [19], none of the authors has obtained the curves reported here, showing a slower but initially acceleratory reaction immediately following the main decomposition process. Tang's results [15] obtained from the TG of "ponderosa pine" in oxygen show a constant weight for the next 100°C following the rapid weight loss, and a direct comparison with our results cannot be made in view of the differences in sample and atmosphere. The curves reported by Broido [18] and by Akita and Kase [17] for the TG of cellulose in air are virtually identical in shape to those obtained by the same authors under inert atmosphere conditions. It seems likely therefore that an insufficient air supply was present in these experiments and that most of the decomposition occurred in the non-oxidising atmosphere of the product gases.

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TABLE 4

TG of cellulose under inert atmospheres

| Author(s) | Atmosphere | Heating rate (°C min⁻¹) | Temp. (°C) at which main mass loss: | | | Mass loss at 400°C (%) |
|---|---|---|---|---|---|---|
| | | | Commences | Max. rate | Finishes | |
| Broido [18] | $N_2$ | 6 | 285 | 345 * | 385 | 88 * |
| Shafizadeh and Bradbury [3] | $N_2$ | 15 | 310 * | 360 | 380 * | 90 * |
| Fairbridge et al. [19] | $N_2$ | 7 | 300 | 350 | 370 * | 84 * |
| Akita and Kase [17] | Vacuum | 5 | 290 * | 330 * | 360 * | 100 * |
| Tang [15] | Vacuum | | 275 | 330 * | 360 | >85 * |
| This work | $N_2$ | 10 | 240 | 360 | 385 | 89 |

* Figure not given in original text, but estimated from curves shown.


TABLE 5

TG of cellulose under oxidising atmospheres

| Author(s) | Atmosphere | Heating rate (°C min⁻¹) | Temp. (°C) at which main mass loss: | | | Mass loss at 400°C (%) |
|---|---|---|---|---|---|---|
| | | | Commences | Max. rate | Finishes | |
| Broido [18] | Air | 6 | 265 | 320 * | ~350 * | 85 * |
| Shafizadeh and Bradbury [3] | Air | 15 | 300 * | 345 | 360 * | 90 * |
| Fairbridge et al. [19] | Air | 7 | 300 | 330 | 350 . | 82 * |
| Akita and Kase [17] | Air | 5 | 270 * | 320 * | | 75 * |
| Tang [15] | Oxygen | 18 | 225 * | 285 * | 290 * | >72 * |
| This work | Air | 10 | 240 | 320 | 330 | 89 |

* Figure not given in original text, but estimated from curves shown.

*Additional experiments*

It has been shown that the main weight loss in air coincides with the small endotherm, which commences at 300°C; the first exotherm which immediately follows the endotherm can therefore be ascribed to the flaming combustion of the volatile materials, produced during the rapid weight loss. An explanation of the second and third exotherms may not be so readily obvious, without consideration of some additional data.

Further TG and DTA runs were performed in which the cellulose was first heated in nitrogen to 400°C — beyond the temperatures of the first exotherm seen in air and the rapid weight loss period — and then cooled under nitrogen to room temperature. A second set of TG and DTA experiments was then performed on the partially-decomposed cellulose in flowing air (Figs. 9 and 10). The conditions employed were the "standard" conditions already reported, except that (for DTA) platinum sample cup liners were used.

The TG curve (Fig. 9) for the sample reheated in air shows a recurrence of the same slow but acceleratory weight loss observed for cellulose in air. This reaction can also be seen to terminate (also at 100% weight loss) at the same temperature. These data support the conclusion that the main decomposition reaction of cellulose is largely independent of whether the atmosphere
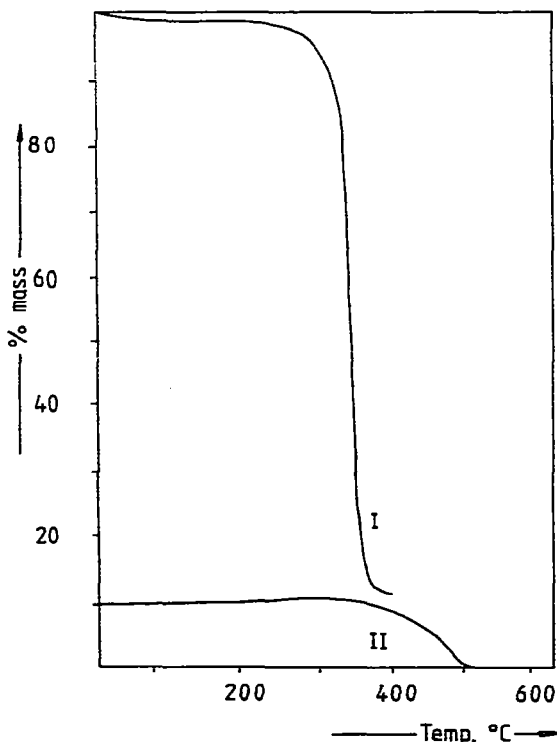


Fig. 9. TG of cellulose in nitrogen to 400°C (I) and subsequent TG in air of the same sample (II).
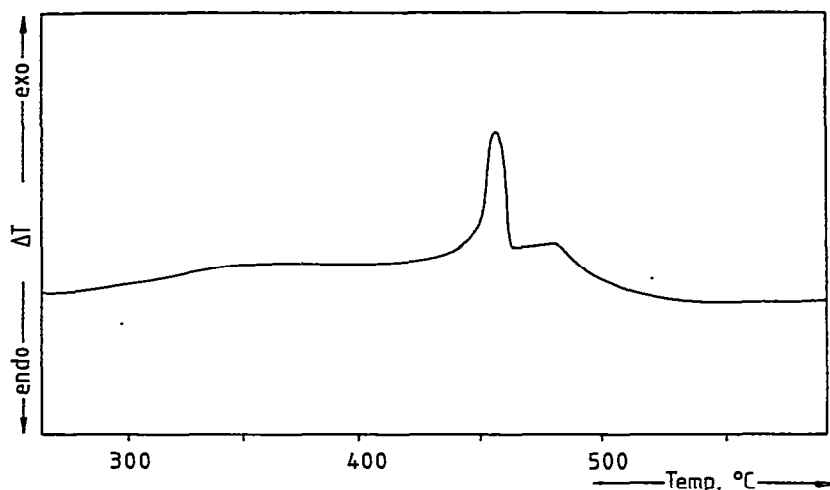
Fig. 10. DTA in air of degraded cellulose previously taken to 400°C in nitrogen.

is air or nitrogen. As expected the first exotherm is absent from the DTA curve of the reheated sample (Fig. 10). However, of the two higher temperature exotherms normally observed, only the lower temperature peak appears. If the atmosphere independence of the main decomposition is assumed, then the disappearance of the third peak is unlikely to be the result of a changed sample composition caused by the pre-treatment. It must also be concluded that, since neither the slow acceleratory weight loss nor the second and third exotherms occur in a nitrogen atmosphere, they are all due to oxidation processes.

It is postulated that the second exotherm [e.g. 458°C in Fig. 5 (II)] represents an oxidation reaction occurring in the charred sample (corresponding to the slow acceleratory weight loss) whilst the third exotherm [e.g. 478°C in Fig. 5 (II)] is caused by subsequent combustion in the gas phase. This theory can be used to explain the appearance sometimes of two and sometimes of three exotherms in the DTA of cellulose in air. The second peak, ascribed to oxidation of the solid residue, is generally squat in shape under static air conditions [Figs. 2 (I), 3 (II) and 4 (I)] due probably to an insufficient air supply retarding the reaction. Lowering the heating rate or using smaller sample weights makes the peak difficult to detect [Figs. 3 (I) and (II), 4 (II) and (III)]. Flowing air enhances this second peak so that it is then always observed irrespective of the other conditions employed and so a total of three peaks invariably appears in this atmosphere. Since static air can allow the product gases to accumulate, prior to their ignition, a strong third exotherm is expected and observed under these conditions. In the case of the pre-treated sample it is concluded that the product gases are slowly evolved during the heating, cooling and reheating cycle, thus preventing the appearance of the third exotherm.

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