# COMPARATIVE THERMAL ANALYSIS STUDY OF TWO BIOPOLYMERS, STARCH AND CELLULOSE

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## Abstract

The degradation of cellulose and starch samples in air and nitrogen has been investigated by thermal analysis techniques. The techniques employed were differential thermal analysis, rising temperature and temperature jump thermogravimetry. Rate data were obtained from these experiments and Arrhenius parameters calculated from these values. This data was used to determine the mechanism by which the cellulose and starch samples degraded. The Arrhenius parameters were also calculated. The behavior of starch and cellulose upon thermal analysis were compared and are reported. $E_{act}$ for corn starch was found to be 474 kJ mol$^{-1}$ and for a cellulose 242 kJ mol$^{-1}$

**Keywords:** cellulose, starch, TG

## Introduction

Both starch and cellulose are biopolymers of glucose. Starch is made up of two types of units, amylose and amylopectin with $\alpha$-(1–4) linkages [1] and highly branched amylopectin with $\alpha$-(1–6) linkages. Cellulose on the other hand is made up of glucopyranose units in $\beta$-(1–4) linkages [2].

Cellulose burns in oxygen and thermally degrades in nitrogen to give a carbon [3]. The general scheme for thermal degradation has been proposed [4–6] to show that combustible volatiles are initially produced. This is an endothermic process but in air, appears as an exotherm because they ignite, this region is termed flaming combustion. The carbonaceous residue produced can also react with oxygen to produce simple gases, CO, $CO_2$ and $H_2O$, this region is termed glowing combustion. In nitrogen the degradation terminates with the production of carbon. Various theories have been used to describe the initial series of changes, all leading to depolymerization, when in nitrogen these depolymerized materials degrade to carbon but the originators of the various schemes are not so clear at this point. Briefly the schemes proposed utilise the formation of 1,6 anhydro rings [7], transglycosylation [8–10] and radical mechanisms [11, 12]. The

work on the thermal degradation of starch is not so detailed, but overall the same degradation pattern might be expected.

In this study an attempt is made to compare the two biopolymers using thermal analysis. In both cases the experiments were performed in an atmosphere of air and nitrogen.

# Materials and methods

## *Materials*

The cellulose used in all the practical work described here is a white granular powder, supplied by the Sigma Chemical Company. This cellulose is manufactured from high purity cotton containing approximately 95% α-cellulose. The manufacturing process consists of acid treatment, which renders the cellulose ashless, followed by controlled grinding which ensures a high packing density. The starch used was corn starch supplied by the Sigma Chemical Company.

The carbon samples from the degradation in nitrogen for both cellulose and starch were analysed to measure their surface area [13, 14]. The cellulose and starch were charred in an oven at 350°C under an atmosphere of nitrogen and the resulting char was analysed for its surface area using a simple adsorption apparatus using nitrogen gas at −170°C.

## *Techniques*

The cellulose and starch samples were analysed using thermal analysis methods. The degradation of cellulose was followed in nitrogen and air using a simultaneous Thermogravimetry (TG) and Differential Thermal Analysis (DTA) unit from TA instruments (model # SDT 2960). A temperature jump method in air was also performed to follow the degradation of the cellulose.

The experimental conditions used for the temperature jump TG curve were: Flowing air, flow rate 10 $cm^3$ $min^{-1}$, temperature jump 10°C, hold time 10 min, sample mass 5–8 mg.

Similar experiments were carried out on starch. The TG equipment was also used in the more conventional mode of 10°C $min^{-1}$ using the rising temperature method. The experiments were repeated 3 times for each sample analysed.

# Results and discussion

Analysis of rising temperature TG: Rising temperature TG has been performed on pure cellulose (under an atmosphere of nitrogen) and corn starch in order to analyse the breakdown that they undergo when subjected to high temperatures. Both cellulose and starch start to undergo degrading at about 250°C. They continue to degrade up until 500°C. This is shown in Fig. 1 which gives the TG–DTA signals for the degradation of alpha cellulose in dry nitrogen (flow
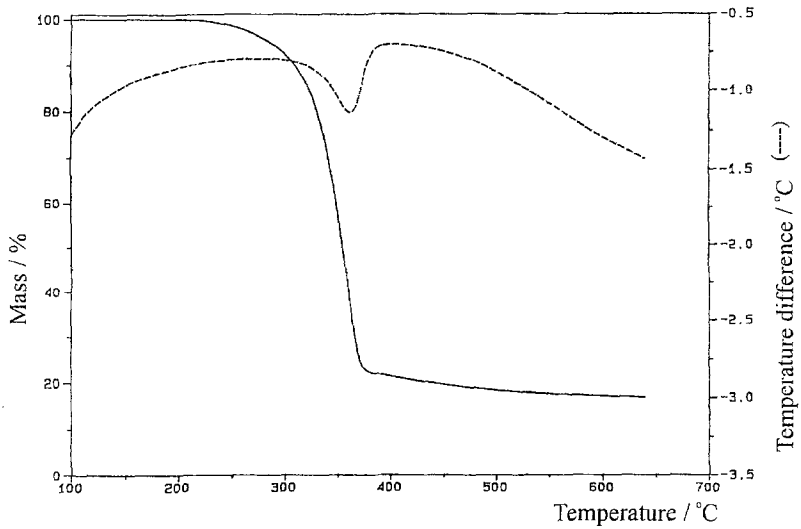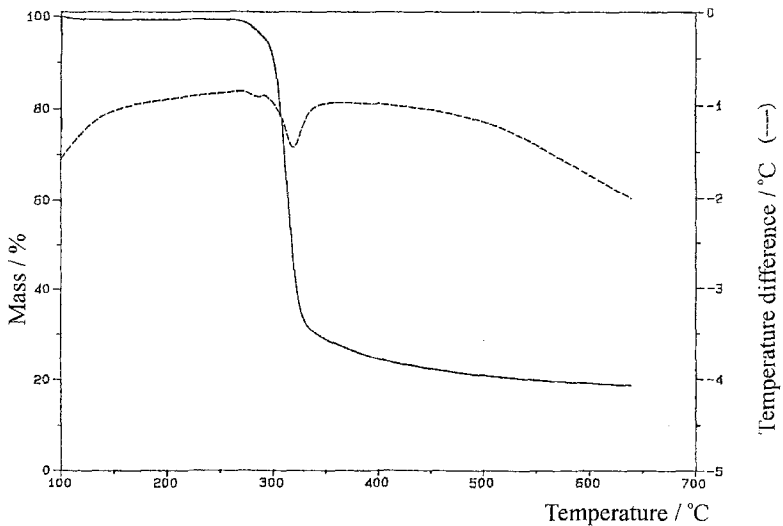
**Fig. 1** TG-DTA plot of α-cellulose in dry nitrogen



**Fig. 2** TG-DTA plot of corn starch in dry nitrogen

rate 10 mL min$^{-1}$) under a temperature regime of 10°C min$^{-1}$ upto 500°C. A similar plot for corn starch is shown in Fig. 2. A two step degradation process occurs under an air atmosphere for both, the cellulose and the starch. The TG-DTA for the cellulose is shown in Fig. 3 and for the starch in Fig. 4. For either atmosphere, the major mass loss, corresponding to the complete breakdown of cellu-
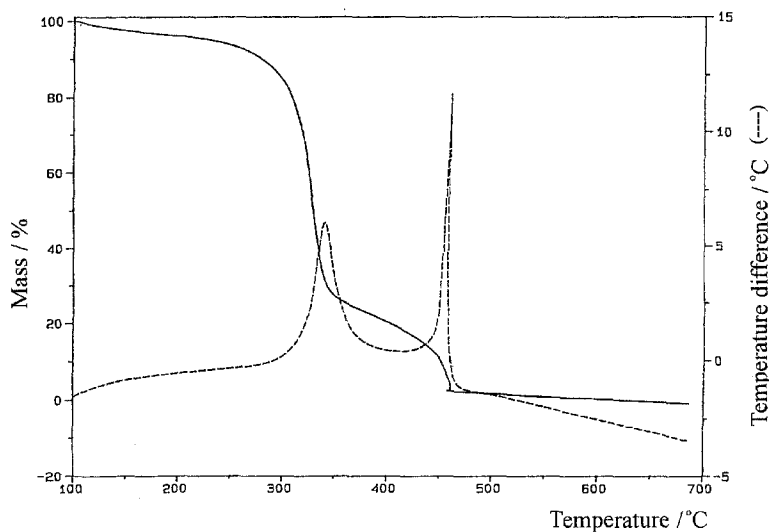
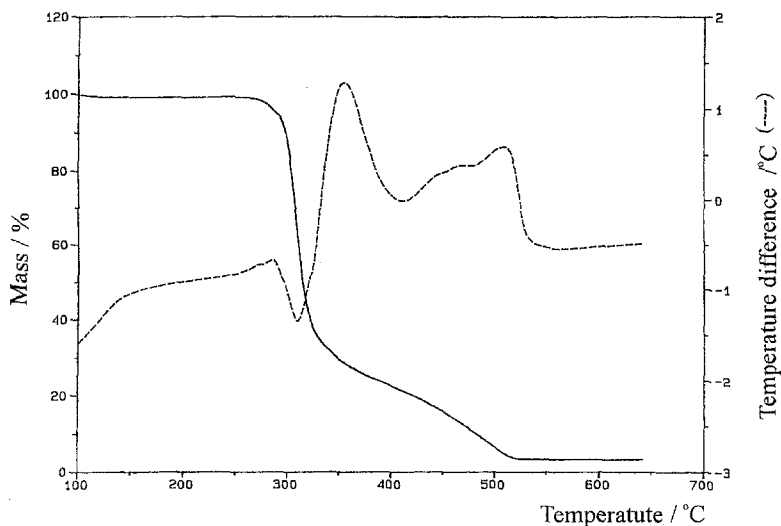**Fig. 3** TG-DTA plot of α-cellulose in dry air



**Fig. 4** TG-DTA plot of corn starch in dry air

lose, starts at approximately 250°C, indicating that initiation of the breakdown is a non-oxidative process. In air, after the initial mass loss, the second slower but acceleratory process starts. This second process does not occur under inert atmospheres and is therefore considered to be the oxidation of the partially decomposed cellulose and starch. It should be noted that the initial breakdown of the cel-

lulose and the corn starch is endothermic (Figs 1, 2) whereas, this is converted to an exothermic change in air due to gaseous combustion, where the gaseous products of degradation ignite. The DTA also demonstrates the exothermic character of the 'glowing combustion', region where the carbonaceous residues burn in air to give simple products such as CO and $CO_2$. An inspection of Fig. 4 shows that the gaseous products initially formed are produced so rapidly that they create a local environment over the sample that prevents them from initially catching fire. The result is, the beginning of an endotherm which is then supplanted by the exotherm normally associated with the gaseous combustion process. The TG data in Figs 3 and 4 clearly indicates where the gaseous combustion is supplanted by the glowing combustion associated with the gasification of the carbonaceous residue.

Kinetic evaluation using the temperature jump method [15]

The steps of 10 min showed a linear mass change with respect to time, so a simple zero order expression for the oxidation in air can be used. For this analysis, the samples were heated for this fixed time at a stated temperature. The temperature was increased by 10°C and then held for 10 min at this new temperature. This process was continued until the reaction was complete. This can be classified as semi isothermal, because the slope of the curve at any given temperature step $(d\alpha/dt)$ allows for the calculations of the specific reaction rate constant, $k$ and from that, $A$ and $E_{act}$ can be determined from a plot of $\ln k$ vs. $1/T$, where $E_{act}$ is the energy of activation, $A$ is the Arrhenius parameter and $T$ is the temperature in Kelvin (Figs 5–7).

The surface area determinations were used to calculate a specific rate of oxidation per unit area. Nitrogen adsorption studies were performed on the chars from cellulose and starch, using a modified single point volumetric apparatus
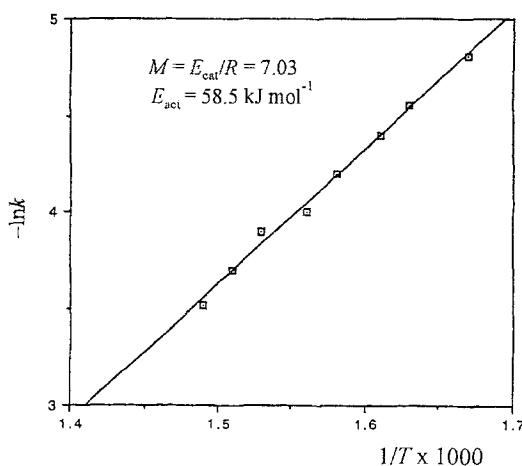


$$M = E_{cat}/R = 7.03$$
$$E_{act} = 58.5 \text{ kJ mol}^{-1}$$

Fig. 5 Arrhenius plot for oxidation of α-cellulose by the jump kinetics

[13, 14]. Both the samples had the same adsorptive surface area, so the specific reaction rate per unit area is also reflected in the specific reaction rate per gram. The surface area for the carbonaceous residue from α-cellulose and corn starch was found to be 29 m$^2$ g$^{-1}$. The specific reaction rate for the carbonaceous residue from α-cellulose was 0.0296 g s$^{-1}$ and the specific reaction rate for the carbonaceous residue from corn starch was 0.031 g s$^{-1}$. The specific rate per unit area for the carbonaceous residue from α-cellulose was found to be 1.02×10$^{-3}$g s$^{-1}$m$^{-2}$ and for corn starch was 1.06×10–3 g s$^{-1}$ m$^{-2}$.

The data on the α-cellulose and corn starch from this temperature jump method is given in Tables 1 and 2. Plots of ln$k$ vs. 1/$T$ are shown in Figs 5 and 6.
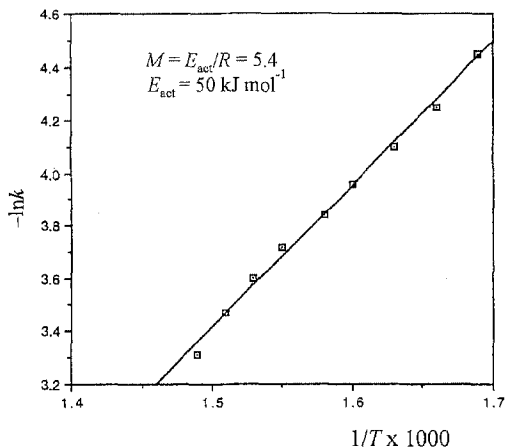


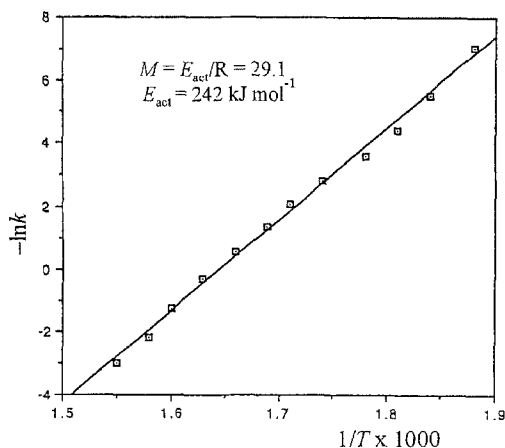Fig. 6 Arrhenius plot for degradation of corn starch by the jump method



Fig. 7 Arrhenius plot for the degradation of α-cellulose in nitrogen

The activation energy ($E_{act}$) and the preexponential values ($A$) for these materials may be noted as follows:

$$\alpha\text{-cellulose } A=992 \text{ s}^{-1}; \; E_{act}=58.5 \text{ kJ mol}^{-1}$$

$$\text{corn starch } A=109.1 \text{ s}^{-1}; \; E_{act}=50 \text{ kJ mol}^{-1}.$$

An inspection of Tables 1 and 2 indicates that this data essentially refers to the oxidation in air of the carbonaceous residues from $\alpha$-cellulose and starch.

**Table 1** The result of the oxidation jump method applied to $\alpha$-cellulose carbonaceous residues

| Mass loss/% | $T$/s | $T$/K | $k$/s$^{-1}$ | $-\ln k$ | $1/T\times10^3$/K$^{-1}$ |
|---|---|---|---|---|---|
| 4.80 | 600 | 602.15 | $8.0\times10^{-3}$ | 4.81 | 1.67 |
| 6.30 | 600 | 612.15 | $1.0\times10^{-2}$ | 4.55 | 1.63 |
| 7.73 | 600 | 622.15 | $1.3\times10^{-2}$ | 4.40 | 1.61 |
| 9.20 | 600 | 632.15 | $1.5\times10^{-2}$ | 4.20 | 1.58 |
| 10.79 | 600 | 642.15 | $1.8\times10^{-2}$ | 4.00 | 1.56 |
| 12.60 | 600 | 652.15 | $2.1\times10^{-2}$ | 3.90 | 1.53 |
| 14.82 | 600 | 662.15 | $2.5\times10^{-2}$ | 3.70 | 1.51 |
| 17.77 | 600 | 672.15 | $3.0\times10^{-2}$ | 3.52 | 1.49 |

**Table 2** The result of oxidation jump method applied to corn starch carbonaceous residues

| Mass loss/% | $T$/s | $T$/K | $k$/s$^{-1}$ | $-\ln k$ | $1/T\times10^3$/K$^{-1}$ |
|---|---|---|---|---|---|
| 8.54 | 600 | 602.15 | $1.4\times10^{-2}$ | 4.25 | 1.66 |
| 10.0 | 600 | 612.15 | $1.7\times10^{-2}$ | 4.10 | 1.63 |
| 11.5 | 600 | 622.15 | $1.9\times10^{-2}$ | 3.96 | 1.61 |
| 12.9 | 600 | 632.15 | $2.2\times10^{-2}$ | 3.84 | 1.58 |
| 14.5 | 600 | 642.15 | $2.4\times10^{-2}$ | 3.72 | 1.56 |
| 16.4 | 600 | 652.15 | $2.7\times10^{-2}$ | 3.60 | 1.53 |
| 18.8 | 600 | 662.15 | $3.1\times10^{-2}$ | 3.47 | 1.51 |
| 22.0 | 600 | 672.15 | $3.7\times10^{-2}$ | 3.31 | 1.49 |

Kinetic evaluation for cellulose and starch degradation using rising temperature data

The samples were heated with a heating rate of 10°C min$^{-1}$ under a nitrogen atmosphere between 50 to 500°C. A differential method of calculating the Arrhenius parameter was adopted. Percent weight and temperature coordinates

were used to determine $\alpha$ and the derivative of function $\alpha$. Where $\alpha$ is the fraction decomposed.

The final expression used in these calculations for the kinetics is

$$\ln k = \frac{\ln d\alpha/dT\, \beta}{f(\alpha)} = \ln A - E_{act}/RT$$

where $k$ is the specific reaction rate constant, $T$ is the temperature in Kelvin, $R$ is the gas constant and $d\alpha/dT$ the slope of the $\alpha$–$T$ plot at the value of $\alpha$ being considered.
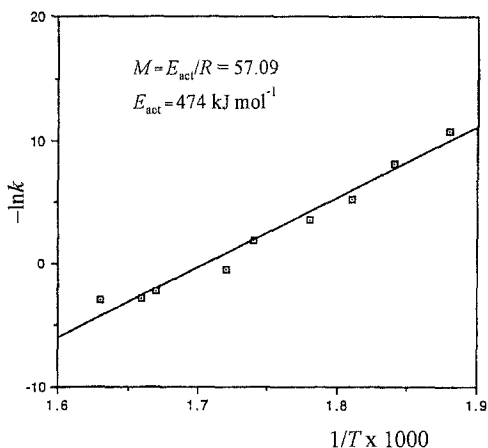


Fig. 8 Arrhenius plot for the degradation of corn starch in nitrogen

A selection process was adopted to identify $f(\alpha)$ which has been described [16, 17] and by this process a D(2) mechanism was selected as the most probable relationship where $f(\alpha)$ was found to be $(-\ln(1-\alpha))^{-1}$. In reporting the rising temperature data, the results are reported based on Arrhenius plots of $\ln k$ *vs.* $1/T$. The $k$ for all regions of $\alpha$ was calculated by a plot of $\alpha$ *vs.* $T$. From plots of $\ln k$ *vs.* $1/T$, the slope represented by $-E_{act}/R$ the intercept represented by $A$ are determined (Figs 7 and 8).

The Arrhenius parameters from this calculation are:

$\alpha$-cellulose $A$=6.3×10$^{20}$ s$^{-1}$; $E_{act}$=242 kJ mol$^{-1}$

corn starch $A$=1.99×10$^{42}$ s$^{-1}$; $E_{act}$=474 kJ mol$^{-1}$.

Analysis of cellulose and starch degradation

Between ambient and 250°C only small or negligible mass loss is apparent. Some loss of adsorbed water occurs. Between 250 and 500°C both cellulose and

starch undergo a dramatic loss in mass according to the rising temperature TG scan. This is due to production of volatile components and formation of chars and tar. Evolution of gases CO and $CO_2$ also occurs in this temperature range. Below 360°C the degradation leads to the evolution of volatiles. In oxygen, these volatile components catch fire (gaseous combustion). This means that the degradation in this temperature region can be studied in a nitrogen environment. The results still have an implication in fire retardancy behavior but the secondary process of the volatiles catching fire in oxygen containing atmospheres obscures some of the details of the basic degradation process. Above 360°C the reaction of the solid carbonaceous residues with oxygen takes place and results in glowing combustion. Under an oxidizing atmosphere, the reaction went to completion at approximately 550°C. Under an inert atmosphere, residual char remained at 750°C. In this way the kinetics of the degradation to the carbonaceous material could be established from the TG plots in nitrogen (Figs 1 and 2) while the subsequent oxidation of the carbonaceous materials could be established for the temperature jump method. The calculation of similar data from the breakdown in air would appear to be more complex as the combustion of the gaseous products turns a basically endothermic process into an exothermic process due to the gaseous combustion of the products. In nitrogen the $E_{act}$ is often reported [18–20] to be around 140–150 kJ mol$^{-1}$. The products of thermal degradation of starches between 200 and 400°C have been studied in detail by gas chromatography techniques. Pyrolysis of starches at 300°C in a stream of nitrogen was shown [21, 22] to give $CO_2$, CO, water, acetaldehyde, furan and 2-methyl furan. The distribution of products formed showed little difference when the pyrolysis was conducted in air or oxygen [23].

**Table 3** Comparison of cellulose and starch degradation in nitrogen

|  | Cellulose | Starch |
| --- | --- | --- |
| In $N_2$ |  |  |
| $T_i^*$ | 220°C | 280°C |
| $T_f^*$ | 380°C | 400°C |
| $T_p^*$ (from DTA) | 360°C | 320°C |
| % mass loss up to 400°C | 80% | 75% |
| % mass loss beyond 400–600°C | 3% | 6% |

\* $T_i$ is the initial temperature, $T_f$ is final temperature, and $T_p$ is the peak temperature.

The degradation of both starch and cellulose may be compared (Table 3). In nitrogen the degradation for cellulose ($T_i$=220°C) occurs before that for starch ($T_i$=265°C) and the other parameters $T_f$, $T_p$ etc. show a similar pattern.

The fast initial reaction to the carbon involves 80% mass loss for cellulose and 75% mass loss for starch but the mass lost above 400°C from the carbonaceous residue for cellulose is significantly less than that from starch. A comparison between starch, cellulose and simple sugars was made previously [24], and it was shown that cellulose has higher thermal stability than starch. Corn starch has a much higher activation energy for degradation to the carbonaceous residue than the cellulose, which would be in accord with the different temperature ranges noted for this carbonization process.

## Conclusions

In this study a comparison between the two biopolymers was attempted using rising temperature data in an atmosphere of dry nitrogen and jump thermogravimetry in dry air. The rising temperature TG curves on cellulose and starch show a degradation to carbon in nitrogen and a continued combustion in air. The initial step in nitrogen to carbon is endothermic but in air is exothermic due to the onset of gaseous combustion. A later exotherm in air is attributed to glowing combustion of the carbonaceous residue. As has been indicated previously [24], for both starch and cellulose, levoglucosan is usually the main constituent of the decomposed products, besides complex gases and water liberated. The kinetics for the production of the carbonaceous residue could be determined from the conventional TG experiments in nitrogen and the activity of the carbonaceous residue determined from temperature jump experiments in air. It was shown that the kinetics of degradation to carbon differed for starch and cellulose, as also did the reactivity of the resultant carbons.

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