Thermal characteristics of the carbohydrate cellulose in relation to fires of buildings and monuments with wood

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ABSTRACT

Cellulose is a carbohydrate present at least in the composition of food, paper, textile and wood. The adaptation of thermal analysis and calorimetric techniques to study exothermic phenomena and self-ignition of cellulose, as well as the use of special tools to characterize fires are mentioned in relation to burning of wood in buildings and monuments especially such as the fire in the cathedral of Notre-Dame de Paris the 15 April 2019.
The main thermodynamic properties of cellulose presented are: specific heat, exothermic decomposition (or pyrolysis) onset temperatures, enthalpy of decomposition (pyrolysis), self-ignition temperatures, heat of combustion of carbohydrate.
Most of the techniques and data presented here were already used with success by the author in the context of occupational safety applied to food processing.

Keywords

Cellulose, wood, high pressure DTA, calorimetry, exothermic phenomena, self-ignition, combustion, pyrolysis, Notre-Dame de Paris, monument fire, building

Introduction

Cellulose (or vegetal fibers) is a polysaccharide present at least in the composition of food, paper, textile and wood. In food, cellulose is part of rice, wheat..., but can also be used as an additive (without taste and flavor). In textile, cotton is a naturally occurring form of cellulose; in wood it is the most abundant (approximately 50%) component, the others being lignin and hemicellulose. It is thus worth to study the thermal characteristics of cellulose in relation to process safety, forest fires but also to safety of buildings and monuments containing wood, in particular in situations of restoration operations.
The measuring techniques used are mainly isothermal calorimetry (Setaram C80), adiabatic calorimetry (Columbia Scientific Industries, Accelerating Rate Calorimeter or ARC) and a differential thermal analysis apparatus with a high pressure autoclave (Netzsch DTA 404H). These instruments are described in the literature (1-3).
Beside our own measured data, some information given here is obtained from data basis in books or on Internet.
The cellulose powder studied by DTA and ARC was from Fluka AG, CH, No.22197. Since all the parameters depend also on particle size, we have performed a particle size analysis: the cellulose used in our measurements presented a median value of 78 micrometers.
Even if these occupational safety studies may concern food, paper, wood and textile industries, one will focus here on buildings and monuments, with wooden elements.

Specific Heat

On the basis of The Engineering Toolbox (4) the specific heat (Cp) of dry cellulose (and cotton) at ambient temperature lies between 1.3 and 1.5 J/g °C. These values increase with temperature and especially with increasing water content.

Exothermic decomposition (or pyrolysis) onset temperatures

According to three types of thermal measurements, the value of cellulose decomposition onset is around 200°C:

- 210 to 220°C from the C80 in scanning mode at 1°C/min, in a sealed cell (3, 5),
- 180°C from the ARC in heat-wait-search mode, threshold at 0.02°C/min heat rate, in a sealed cell (3),
- 210°C from the DTA (Fig.1) in scanning mode at 2.5°C/min, under 25 bar of oxygen (6).

The sealed cells avoid that the exothermic phenomena of decomposition are disturbed by endothermic phenomena such as boiling of water at 100°C (if water would really be present) or by decomposition gases release. In the closed cells, the pressure is always higher than the water vapor pressure due to air compression. In an open situation endothermic and exothermic phenomena will compete.

The 25 bar of oxygen are not a mechanical force, but ensures that there is a great oxygen availability around the sample such as during a strong aeration. In addition it allows to avoid endothermic phenomena up to 220°C. In an open system this high pressure of oxygen simulates in some way strong gas (air) flow rates due to winds or to convective transport during a fire.

Enthalpy of decomposition (pyrolysis)

The enthalpy of decomposition is found by integrating the peak obtained in a closed cell heated with the calorimeter Setaram C80 at 1°C/min: the value is 650 J/g (6) for cellulose. However, in an open system, this phenomenon will be in competition with endothermic phenomena such as water vapor or gases release.

Self-Ignition temperatures

The lowest self-ignition temperature of cellulose we have obtained was determined with the DTA apparatus at 2.5°C/min under 25 bar of oxygen, see below: it was 240°C (Fig. 1, from reference 6). Because of less oxygen availability, this temperature value increases if the pressure is decreased as shown in Fig. 2 (from 6).

As for many gas-solid reactions, self-ignition is a typical reaction occurring at the interface.

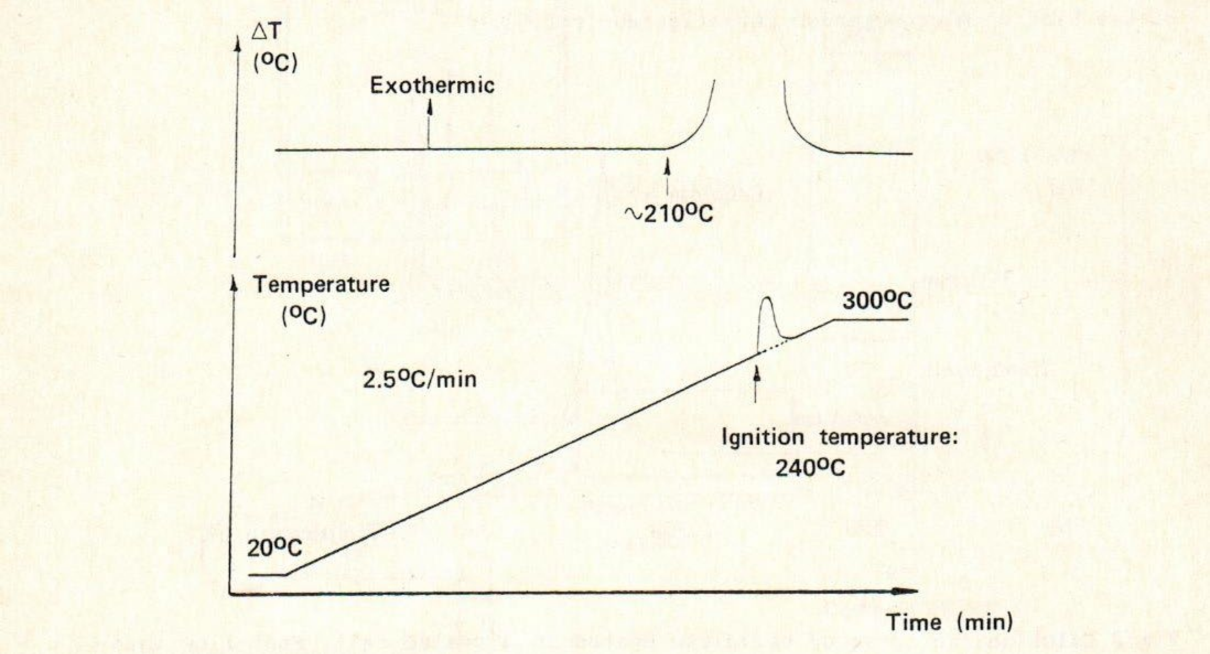

Fig 1. *DTA curves of cellulose heated and burned under 25 bar of oxygen in the high pressure DTA Netzsch instrument*

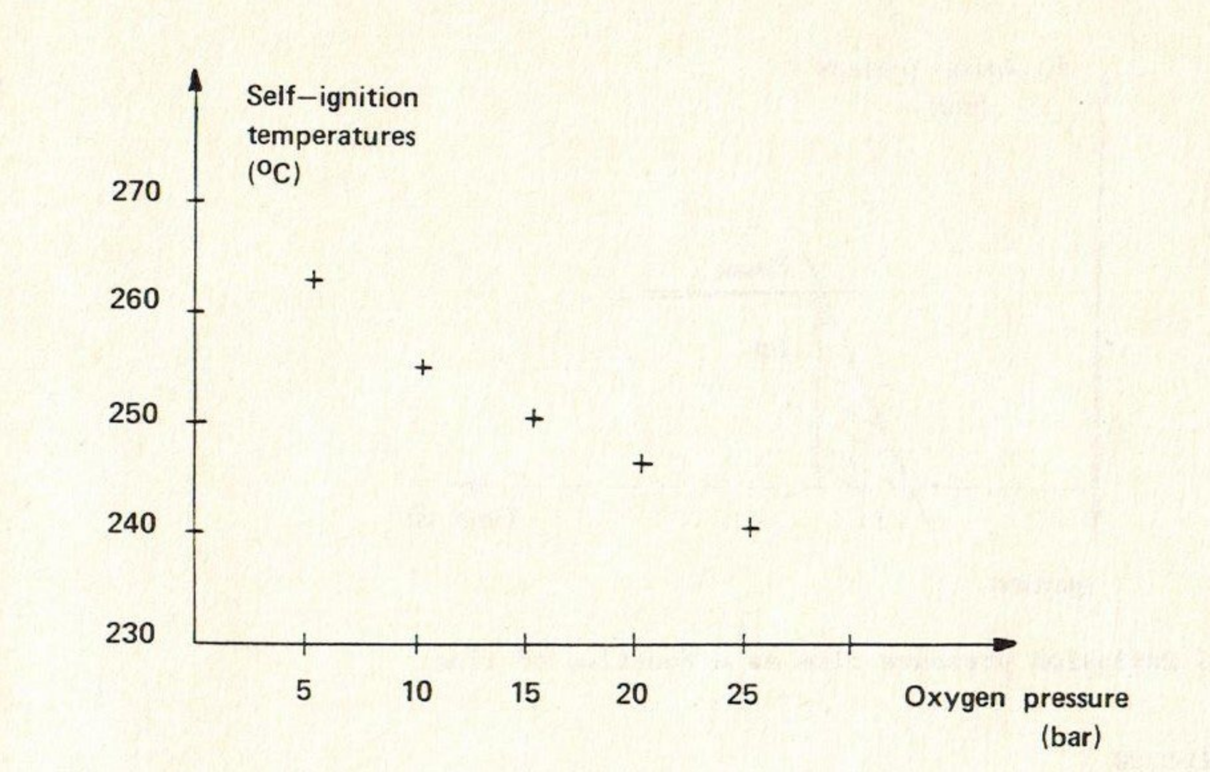

Fig 2. *Self-ignition temperatures of cellulose as a function of oxygen pressure in the Netzsch DTA instrument*

Heat (enthalpy) of combustion

The heat of combustion of carbohydrates determined by combustion calorimetry is known to be 17 kJ/g (7) that means about 25 times the value of 650 J/g obtained for decomposition (without flames) in a sealed cell.

Remark on complementary literature

Many publications performed at too elevated heating rates are mentioned in the scientific literature, they clearly indicate too elevated self-ignition temperatures. However data from thermogravimetry (TG and DTG at 10°C/min) and DSC obtained at relatively elevated heating rates presented in reference 8 are also of interest in this context; thermal characteristics of hemicellulose, cellulose and lignin pyrolysis are shown. Two results have to be especially mentioned: first, xylan used as model for hemicellulose decomposes at an even lower temperature range than cellulose. Secondly, decomposition (pyrolysis) of lignin is very weak in the temperature range of interest.

Fire of monuments with wood

Common sources of wood fires are:
electrical arcs (short-circuits), open flames (welding,…), sparks (static electricity, cutting equipment,…), hot surfaces (electric equipment, metallic tools as motors or generators), smoldering, local gas or dust explosions, chemical reactions (oxidation,…). Thus, it becomes obvious that the probability of a fire increases during maintenance operations and repairs of such buildings containing wood.
Since roofs of large monuments are often covered by metals, the melting temperatures of commonly used metals is of interest in order to assess the consequences. Melting temperatures are:

- Sn	Tin	231.9 °C
- Pb	Lead	327.4 °C
- Zn	Zinc	419.5 °C
- Al	Aluminium	660.3 °C
- Cu	Copper	1083 °C

So melted tin, lead or other metals (see above) spreading on cellulose or wood may cause smoldering that finally results in ignition according to the temperature difference with 200°C (the onset temperature of exothermic effects) after an induction time and depending on the oxygen availability. The self-ignition temperature of cellulose under 25 bar of oxygen measured at 2.5°C/min is 240 °C as shown in Fig. 1.
One recent example, is the fire in the cathedral Notre-Dame de Paris, the 15 April 2019 where large amounts of wood and lead were present in the roof.
Smoldering of wood (dust) has certainly played a role at the begin of this fire; that is probably why it has not been detected earlier by the responsible persons.
As the firefighters received the alarm late, the occurred damages were important.
The appropriate strategies used by the fire fighters saved the stone walls of the monument from collapsing.

The initial causes of the fire of Notre-Dame de Paris are certainly difficult to determine. The author thinks that this short communication may help engineers, scientists and architects concerned to find the reasons of the fire and not to repeat the same errors during the new restoration of the Notre-Dame cathedral. It may also concern other monuments if similar situations happen.

In the literature concerning this event, comparison with other fires of monuments are indicated and fire prevention measures are listed (9). Another article defines the main materials science challenges of post-fire restoration, and discuss them in relation to issues of structural integrity, fire safety and preservation ethics (10).

The quantitative information presented here may also help scientists to complement their models (11).

Conclusions

It is impressive to see how the occupational safety methods applied with success to food processing can be easily adapted to wood in buildings and monuments.

To prevent such fires, we propose to give a greater role to physicists (or physicochemists and material science specialists) in order to find with more efficiency the possible sources of ignition. This is especially important in periods of construction or restoration, also in order to avoid fires or to limit the damages if fire occurs.

Final remarks

Part of this work, especially the instrument used to determine the quantitative data, was presented at the STK (Swiss Society of Thermal Analysis and Calorimetry) Annual Meeting Wednesday May 15th 2019 in Thun (CH). Title: **Thermal characteristics of the carbohydrate cellulose in relation to safety, by Alois Raemy**. See Booklet of the Meeting: Thermal Analysis of Materials.

Slides to be found at:

http://www.stk-online.ch/Thun19.html

Concerning similar data of wood, a review article mentions, in his abstract, ignition temperatures of around 250°C (12); this value corresponds very well to our measurement of self-ignition temperature of 240°C determined for cellulose by high pressure DTA (see also ref. 6).

Acknowledgements

The author thanks Francis Stoessel and Pierre Le Parlouër, former director of Setaram, Lyon (F) for pertinent remarks.

Figure 1 and Figure 2, reprinted from *A. Raemy, P. Lambelet and J. Loeliger, Thermal analysis and safety in relation to food processing, Thermochim. Acta, 95 (1985) 441-446,* **with permission from Elsevier.**

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