

# Influence of metal oxides on the thermal ignition behaviour of woody biomass cellulose

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## Abstract

The reuse and recycling of biomass materials would be useful for minimizing the environmental impact of society, and would help address the strong demand for a safe and sustainable community. Although woody biomass from demolished buildings could be a promising resource for recycling, contaminants are found in recycled wood dust, such as wood preservatives that likely contain metal oxides. These oxides might act as catalysts for the oxidation of organic materials, resulting in the spontaneous ignition of large piles of recycled wood dust.

In order to better understand the influence of a typical wood preservative, CuO, on the oxidation and thermal ignition behaviour of cellulose, a main component of recycled wood dust, we conducted thermal analysis and spontaneous ignition tests of recycled wood dust.

Differential scanning calorimetry (DSC) was used to investigate the influence of the type of metal oxide, and the amount of CuO, on the thermal behaviour of cellulose, and showed that the onset temperature for the exothermic reaction decreased with increasing amount of CuO. Spontaneous ignition tests of various cellulose/CuO samples were used to measure the induction time to ignition, and showed that the induction time decreased as the amount of CuO increased, demonstrating that CuO has a catalytic effect on the thermal behaviour of cellulose.

**Keywords** : thermal ignition, recycled wood dust, cellulose, metal oxides, thermal analysis

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## 1. Introduction

The need for a safer and sustainable society requires the reuse and recycling of biomass materials to minimize our environmental impact. Although waste materials from demolished buildings could be recycled, contaminants such as anti-termite chemicals are found in recycled wood dust. Such compounds, which contain metal oxides, might catalyse the oxidation of organic materials, resulting in the spontaneous ignition of large amounts of wood dust<sup>(1), (2)</sup>. Therefore, in order to better understand the influence of a typical termite control compound, CuO, on the oxidation and thermal ignition behaviour of cellulose, a main component of recycled wood dust, thermal analysis and spontaneous ignition tests were conducted.

## 2. Materials

The materials used in this study were cellulose fiber

from Aldrich Inc., and copper (II) oxide (CuO), copper (I) oxide (Cu<sub>2</sub>O) and zinc oxide (ZnO) from Wako Chemicals Inc. The purity of these materials was more than 90% by weight. The samples were prepared as mixtures of cellulose and metal oxides, and are referred to below as the type of metal oxide and its weight percent (e.g., cellulose/CuO-10).

## 3. Experimental

### 3.1 Thermal analysis

Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo HP827e to investigate the thermal behaviour of cellulose/metal oxide samples. First, 2 mg samples of cellulose with 10 wt.% of each metal oxide was placed in a stainless steel open cell and heated from 30 °C to 500 °C at 5 Kmin<sup>-1</sup> under 0.1 MPa of air flowing at 20 mL min<sup>-1</sup> to determine the influence of the metal oxide.

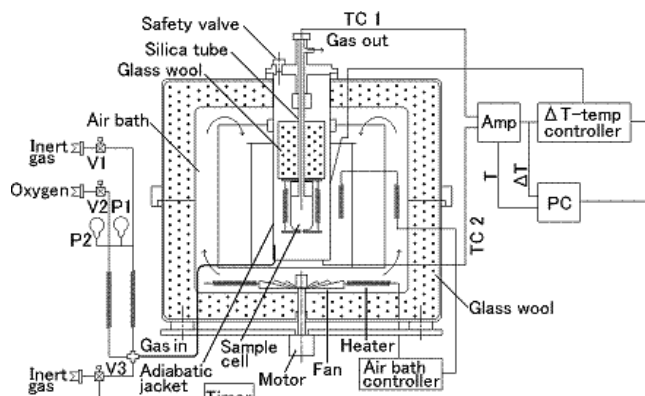


Fig. 1 Block diagram of the SIT apparatus.

Next, to see the influence of atmospheric gas on the thermal properties of cellulose in the presence of different amounts of CuO, DSC was carried out under 0.1 MPa nitrogen at a heating rate of  $10 \text{ K min}^{-1}$ . In addition, isothermal calorimetry was conducted on cellulose and cellulose/CuO-3 under 0.1 MPa air at 260, 270, 280 and 290 °C to see the thermal behaviour of the samples upon prolonged heating at elevated temperatures.

### 3.2 Spontaneous ignition test

Spontaneous ignition tests conducted on a Shimadzu SIT-2 were used to investigate the self-heating behaviour of recycled wood dust under adiabatic conditions and 0.1 MPa air. Figure 1 shows a block diagram of the SIT apparatus; detailed descriptions of this apparatus were given previously<sup>(3), (4)</sup>.

Sample (100 mg) was loaded into a quartz cell and heated to the desired initial temperature under a nitrogen atmosphere, then, following 180 min equilibration, heated air was introduced into the sample cell at  $2 \text{ mL min}^{-1}$  and the adiabatic self-heating curve was measured up to 300°C. When the sample temperature reached 300°C, the SIT apparatus stopped controlling and measuring, and nitrogen gas at room temperature was automatically introduced into the apparatus and sample cell to safely shut down the reaction. If the sample temperature does not change from the initial temperature within 48 h nitrogen gas is introduced to cool and stop the experiment, the sample is evaluated as being “negative”.

## 4. Results and discussion

### 4.1 Influence of the type of metal oxide additive

The influence of the type of metal oxide additive on the thermal behaviour of the cellulose samples under 0.1 MPa air was investigated using DSC. Figure 2 shows DSC curves for cellulose/CuO-10, cellulose/Cu<sub>2</sub>O-10, cellulose/ZnO-10, and cellulose alone; the onset temperature of the exothermic reaction of these samples was 277, 277, 321 and 321 °C, respectively.

To investigate the influence of various amounts of CuO, DSC was conducted on cellulose/CuO-1, cellulose/CuO-3 and cellulose/CuO-10 under 0.1 MPa air; the results are compared to that of cellulose alone in Fig. 3. The onset temperatures of cellulose/CuO-1 and cellulose/CuO-3 were

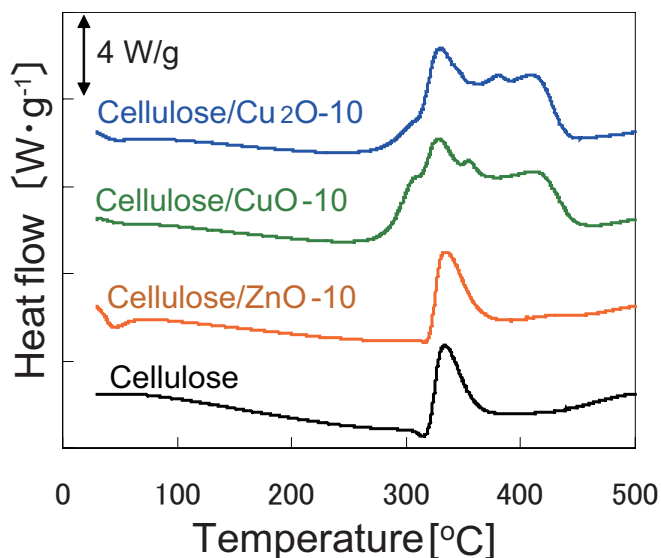


Fig. 2 Influence of the metal oxide on DSC curves of cellulose.

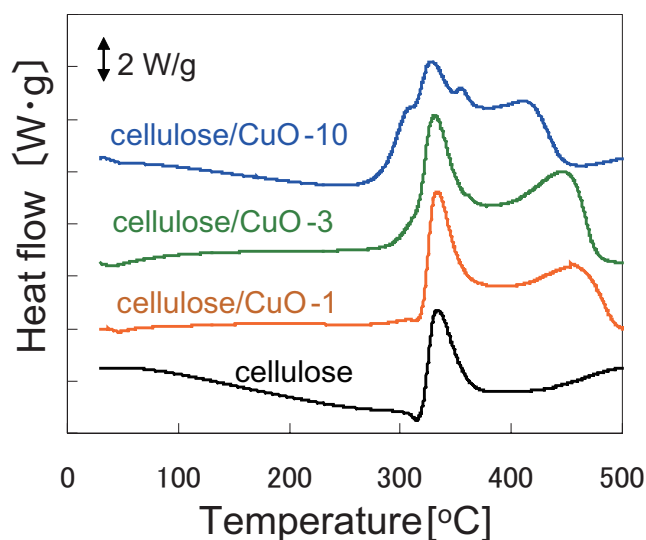


Fig. 3 Influence of the amount of CuO on the DSC curves of cellulose/CuO mixtures in air.

320 °C and 287 °C, respectively, showing that the onset temperature decreased with increasing amount of CuO. Since the thermal diagrams of the cellulose mixtures were similar to that of cellulose alone, CuO and Cu<sub>2</sub>O apparently have a catalytic effect on the thermal oxidation of cellulose.

### 4.2 Influence of atmospheric gas

The influence of atmospheric gas on the thermal behaviour of cellulose samples was investigated with DSC and 0.1 MPa nitrogen. Figure 4 shows DSC curves for cellulose mixed with different amounts of CuO, from 0 to 80 wt.%, under 0.1 MPa nitrogen. The onset temperature of the exothermic reaction was not measured for samples containing less than 40 wt.% CuO, and only endothermic peaks were observed. Cellulose samples containing 40 and 60 wt.% CuO produced both exothermic and endothermic peaks, whereas cellulose/CuO-80 produced only an exothermic peak with an onset temperature of 328 °C. These results suggest that oxygen present in CuO crystals is consumed during the oxidation of cellulose

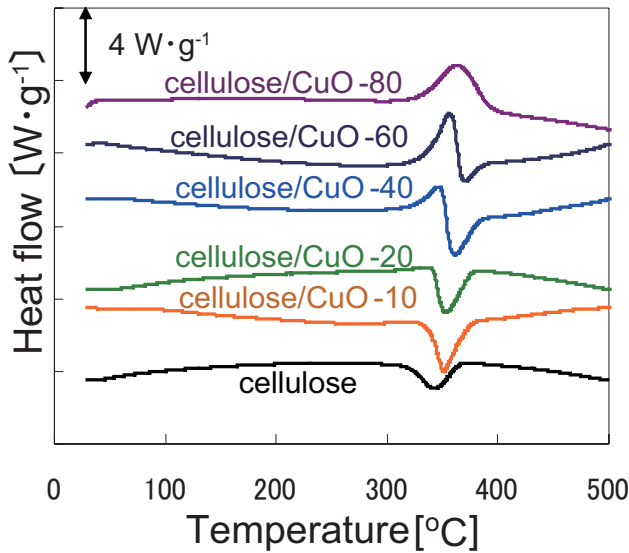


Fig. 4 Influence of the amount of CuO on the DSC curves of cellulose/CuO mixtures in nitrogen.

under a nitrogen atmosphere.

### 4.3 Isothermal calorimetry on DSC

Isothermal calorimetry was conducted on isothermal mode of Mettler Toledo DSC HP827e for cellulose and cellulose/CuO-3 samples under 0.1 MPa air at 260, 270, 280 and 290 °C to see the thermal response of the samples to prolonged exposure to elevated temperatures. With isothermal mode on DSC the temperature of the sample is maintained constant by adjusting the temperature of the surroundings and the advantage is that the temperature effect, exponential variation of the reaction rate, is eliminated during the measurement, which gives direct access to the conversion term of the reaction rate. A series of experiments at different temperature is required for the kinetic analysis<sup>5)</sup>. Figure 5 shows the isothermal curves for cellulose and cellulose/CuO-3 at 260 to 290 °C. All the heat

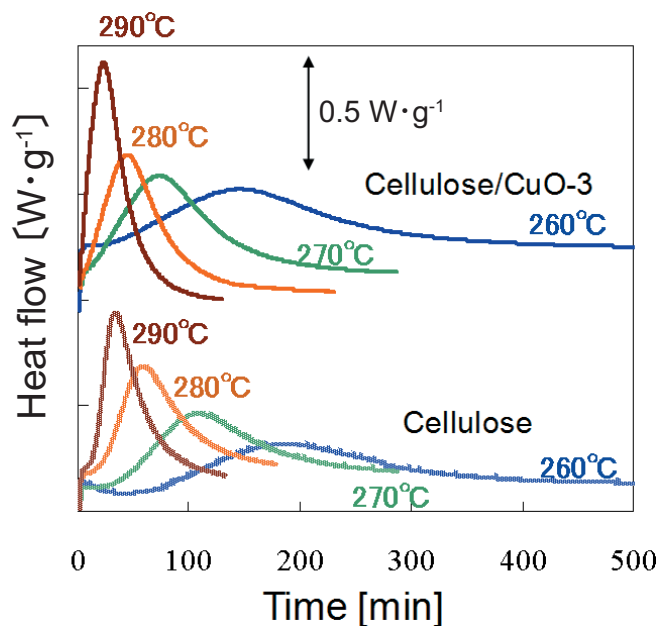


Fig. 5 Isothermal calorimetry curves of cellulose and cellulose/CuO-3.

flow vs. temperature profiles show an autocatalytic reaction, and the induction time of the exothermic reaction for cellulose/CuO-3 is shorter than that of cellulose alone.

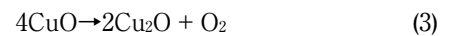
Based on kinetic analysis using an Arrhenius plot with isothermal conversion method, the reaction rate was calculated by the following equation<sup>6),7)</sup>.

$$q = -\Delta H \frac{dC}{dt} = \Delta H \cdot A \cdot f(C) \cdot \exp\left\{-\frac{E}{RT}\right\} \quad (1)$$

where  $q$  is the self-heating rate,  $\Delta H$  is the heat of reaction,  $A$  and  $E$  are the apparent pre-exponential factor and the activation energy, respectively,  $f$  is the model function,  $R$  is the gas constant, and  $T$  is the temperature. If  $\Delta H \cdot A \cdot f(C)$  is assumed to be constant and independent of temperature, the following formula is obtained<sup>6)</sup>.

$$\frac{q_2}{q_1} = \frac{t_1}{t_2} = \exp\left\{\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\} \quad (2)$$

From selected experimental values of time and heat flow, and using eq. (2), the activation energies of cellulose and cellulose/CuO-3 under nitrogen were determined to be 134 - 137 kJ · mol<sup>-1</sup> and 134 - 142 kJ mol<sup>-1</sup>, respectively, at thermal conversions of 0.2 - 0.8. The activation energy of cellulose/CuO-3 and cellulose are the same. This result suggests that CuO does not affect the activation energy of the oxidation of cellulose, but rather increases the reaction rate of the oxidation reaction via catalysis, as shown below. Under a nitrogen atmosphere, CuO is reduced to Cu<sub>2</sub>O and releases oxygen, which in turn oxidizes cellulose, as shown in eq. (3). The oxidation of Cu<sub>2</sub>O to CuO proceeds in air.



### 4.4 Spontaneous ignition test

Adiabatic self-heating with SIT-2 starts at a temperature that is lower than the onset temperature measured with DSC. The adiabatic self-heating curve of cellulose/CuO-3 with SIT-2 starts at 193 °C, whereas no self-heating was observed for cellulose. Figure 6 shows the adiabatic self-heating curves of cellulose, cellulose/CuO-3 and cellulose/CuO-10 measured with SIT-2 at 200 °C, a temperature at which nothing is observed in DSC measurements. Each sample shows self-heating after an

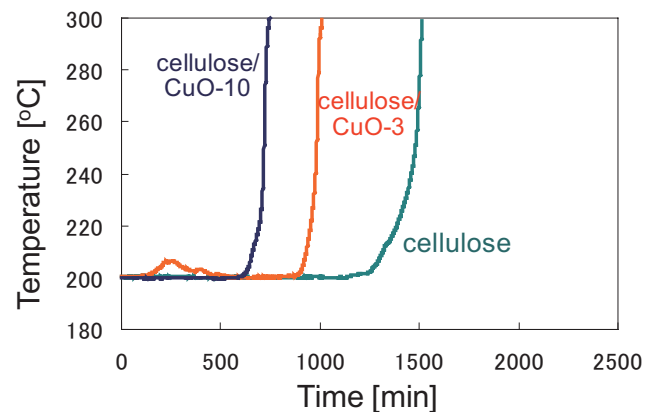


Fig. 6 Influence of the amount CuO on adiabatic self-heating of cellulose/CuO mixtures.

induction period, and finally reaches a temperature of 300 °C. The induction time of each sample was determined to be 1513, 1010 and 746 min for cellulose/CuO-10, cellulose/CuO-3 and cellulose alone, respectively; the induction time clearly decreased as the amount of CuO increased.

Thus, the mixing of CuO strongly influences the thermal stability and oxidation of cellulose, and increases the thermal risk of oxidation processes. This information will be useful for the safe optimization of the reuse and recycling of waste wood dust with a large pile.

## 5. Conclusions

The following conclusions can be drawn from the thermal analysis and spontaneous ignition tests described above on cellulose/metal oxide mixtures :

- [1] Metal oxides have a catalytic effect on the thermal behaviour of cellulose, and CuO and Cu<sub>2</sub>O additives influence the oxidation of cellulose more than ZnO does.
- [2] The onset temperature of the exothermic reaction of cellulose/CuO mixtures decreases with increased amount of CuO under an air atmosphere.
- [3] Oxygen in CuO crystals is consumed during the

oxidation of cellulose under a nitrogen atmosphere.

- [4] CuO does not affect the activation energy of the oxidation of cellulose, but rather increases the reaction rate of the oxidation reaction by the catalytic cycle with CuO.
- [5] Adiabatic self-heating measured with SIT-2 starts at temperature lower than the onset temperature measured with DSC, and mixing CuO with cellulose strongly influences the thermal stability and oxidation of cellulose.

## References

- 1) X-R.Li, H.Koseki, M.Momota, J. Hazardous Materials, 135, 15 (2006).
- 2) T.Watanabe, N.Shirai, H.Okada, Y.Honda and M.Kuwahara, Eur. J. Biochem., 268, 6114 (2001).
- 3) T.Kotoyori, J. Loss Prev. Process Ind., 2, 16 (1989).
- 4) A.Miyake, S.Ando, T.Ogawa and Y.Iizuka, J. Therm. Anal. Cal., 80, 519 (2005).
- 5) F.Stoessel, "Thermal safety of chemical processes", Wiley-VCH (2008).
- 6) T.Grewer, "Thermal hazards of chemical reaction", Elsevier (1994).
- 7) A.Miyake, K.Nomura, Y.Mizuta and M.Sumino, J. Therm. Anal. Cal., 92, 407 (2008).

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# 木質バイオマスセルロースの熱発火挙動に 及ぼす金属酸化物の影響

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バイオマス物質の再利用およびリサイクルは社会への環境負荷を低減する有効な手段であり、安全で持続的社会的構築に大きく貢献する。建築廃材は有望なバイオマス資源であるが、リサイクル木粉には金属酸化物を含む木材保存剤等が不純物として混入されている。これらの金属酸化物は有機物の酸化における触媒として作用し、大量に堆積した木粉の自然発火の原因となる懸念がある。そこで本研究では、代表的な木材保存剤中の酸化銅が木材の主成分であるセルロースの酸化および熱発火現象に及ぼす影響を検討するため、熱分析ならびに自然発火試験を実施した。

金属酸化物の種類、酸化銅の量がセルロースの熱挙動に及ぼす影響を検討するため、示差走査熱量測定 (DSC) を実施したところ、酸化銅の量の増加に伴い、発熱開始温度が低下した。組成の異なるセルロース/酸化銅に対して自然発火試験 (SIT) を実施したところ、酸化銅の量の増加に伴い、発熱誘導時間は短くなり、セルロースの熱挙動に及ぼす酸化銅の触媒効果が明らかとなった。

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