Catalytic effect of copper(II) oxide on oxidation of cellulosic biomass

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Abstract The reuse and recycling of biomass materials can minimize the environmental impact of society, and can help create a sustainable community. Although cellulosic biomass from demolished buildings is a promising resource for recycling, contaminants, such as wood preservatives that likely contain metal oxides, are found in recycled wood dust. These oxides could act as catalysts for the oxidation of organic materials, resulting in spontaneous ignition of large piles of recycled wood dust. Copper(II) oxide (CuO) is major component in wood preservative and plays a catalytic role in the oxidation of cellulose, which could cause spontaneous ignition. The present study focused on the influence of CuO on oxidation of cellulose. The exothermal behavior and mass loss of cellulose/CuO mixtures were investigated. Changes in exothermal behavior and mass loss with an increasing amount of CuO were measured by differential scanning calorimetry and thermogravimetry. In addition, kinetics and spectroanalysis were conducted to determine the catalytic effect of CuO on oxidation of cellulose and help determine the oxidation model of cellulose upon addition of CuO. Results revealed a change in exothermal behavior and increase in mass loss with increasing amounts of CuO. In addition, CuO had a catalytic effect on the oxidation of cellulose, which helped determine the oxidation model of cellulose upon addition of CuO.

Keywords Cellulosic biomass · Copper(II) oxide · Catalytic effect · Thermal analysis · Oxidation model

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Introduction

Biomass, with the except for fossil fuels, is a renewable organic resource. The use of biomass fuels as an alternative to fossil fuels can promote more sustainable and low-carbon societies. Although many types of biomass are available, the utilization of waste materials also contributes to reuse and recycling and reduces the amount of waste materials.

Many studies on the use of cellulosic biomass have been conducted because its use does not compete with foods and can reduce CO_2 emissions than other biomass resources. Cellulosic biomass was converted to various materials and energetic products by physical, thermochemical, and biochemical processes. In particular, pyrolysis of cellulosic biomass during thermochemical conversion produces solid, liquid, and gaseous fuels. Therefore, a comprehensively understanding of the thermochemical properties of cellulosic biomass is needed, which can be obtained through isothermal, non-isothermal, and flash pyrolysis methods.

Most studies involving the use of pure cellulosic biomass are done to the development of energy conversion technology and improve yield and efficiency. However, wood chips from demolished buildings, construction dismantling, and forest thinning in waste materials are likely to contain additives such as wood preservatives, coatings, and fire-retardants. Wood preservatives contain metal oxides that can generally act as a catalyst [1–4]. Copper(II) oxide (CuO) is a major component of wood preservatives and can play a catalytic role in the oxidation of cellulose. Therefore, CuO has the potential to cause spontaneous ignition within large amount of piles of wood chips from constructive waste [5, 6]. This is a problem with waste materials recycling that needs to be solved. Hence, it is important to investigate the safety and thermal risk of waste materials to be used for recycling or reuse.

The main purposes of this study were to investigate the influence of CuO on the thermal behavior of cellulosic biomass and propose an oxidation model upon addition of CuO. To accomplish this, thermal, kinetics, and spectroscopic analyses were conducted using differential scanning calorimetry (DSC), thermogravimetry (TG), and Fourier transform infrared spectrometry (FT-IR).

Materials

The samples used were cellulose, lignin, and xylan, which are the main components of cellulosic biomass, and CuO. Cellulose (Sigma-Aldrich Ltd) and lignin (Tokyo Kasei Kogyo Co., Ltd.) had a particle size of ca. 20 μm. Xylan (Sigma-Aldrich Ltd) had a particle size of ca. 10–200 μm. The CuO (Wako Pure Chemical Industries, Ltd) was of 90% purity and had a particle size of ca. 2 μm.

Experimental

Influence of CuO on thermal behavior of cellulosic biomass

Thermal analysis using DSC (Mettler Toledo, HP DSC827e) was conducted under 0.1 MPa argon and air atmospheres to investigate the effect of CuO on the thermal behavior of cellulose, xylan, and lignin. Samples were cellulose, xylan, lignin, cellulose/CuO mixture, xylan/CuO mixture, and lignin/CuO mixture. The amount of CuO in the mixtures was 10 wt%. Sample amount was ca. 2 mg, which was placed in an open stainless steel cell. Experimental temperature range was 30–500 °C at a heating rate of 5 K min^{-1}.

The DSC curves in argon are shown in Fig. 1. Thermal behavior of cellulose, xylan, and lignin in argon were minimally influenced by CuO. Figure 2 shows the DSC
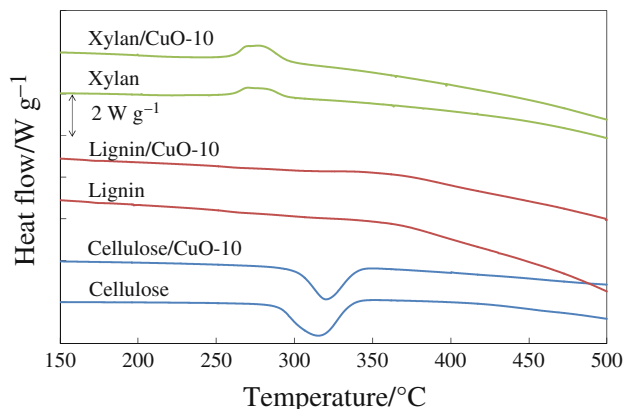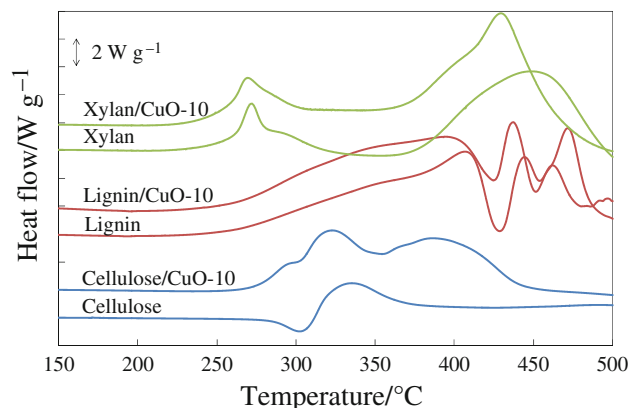

Fig. 2 DSC curves of samples in air

curves in air; Table 1 shows the exothermic onset temperature in air. A comparison of the DSC curves in argon and in air showed that air oxidation occurred. The CuO significantly affected oxidation of cellulose, demonstrated by the observation of new exothermic peaks at ca. 300 and 400 °C. In addition, the exothermic onset temperature of cellulose was lower than those for xylan and lignin (i.e., temperature was reduced 310–262 °C upon addition of CuO. Therefore, CuO had a greater influence on oxidation of cellulose than on xylan or lignin in air.

Influence of CuO amount on thermal behavior of cellulose

Thermal analyses using DSC and TG (Shimadzu, DTG-50) were conducted in air to measure the change in thermal behavior of cellulose with increasing amounts of CuO. Samples consisted of cellulose and cellulose/CuO mixtures of varying proportions (1, 2, 3, 4, 5, and 10 wt%). DSC experimental conditions: sample amount of ca. 2 mg loaded into an open aluminum cell, and an experimental temperature range from 30 to 500 °C at a heating rate of 5 K min^{-1}. TG experimental conditions: sample amount of ca. 5 mg loaded into an open aluminum cell, and experimental temperature range from ambient temperature to 550 °C at a heating rate of 5 K min^{-1} and air flow of 20 mL min^{-1}.

Fig. 1 DSC curves of samples in argon

Table 1 Exothermic onset temperature of samples in air

	T_{onset}/°C
Xylan	202
Xylan/CuO-10	203
Lignin	201
Lignin/CuO-10	198
Cellulose	310
Cellulose/CuO-10	263

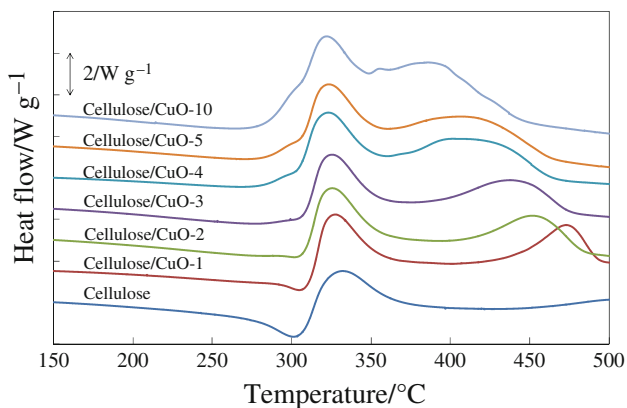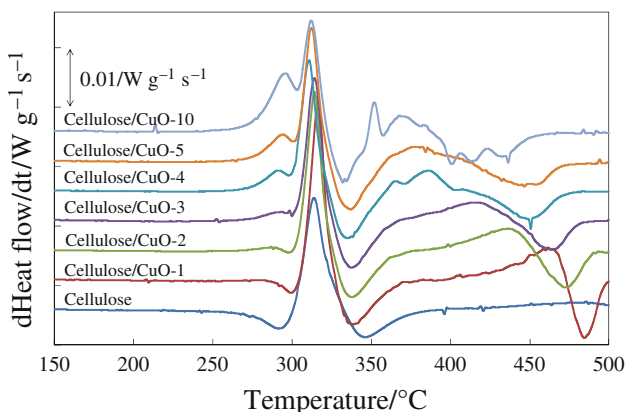**Fig. 3** DSC curves of cellulose and cellulose/CuO mixtures in air

Fig. 4 Derivative DSC curves of cellulose and cellulose/CuO mixtures in air

Figures 3 and 4 show the DSC curves and derivative DSC curves of the samples, respectively. Table 2 shows the first endothermic and exothermic onset temperatures. An endotherm of cellulose at 270 °C was due to amorphous, anhydration, and depolymerization, which involves scission of glucosidic linkages and formation of high boiling volatiles (tar), mainly levoglucosan [7–9]. An exotherm of cellulose at 310 °C was due to air oxidation of tar or cellulose that reduced the degree of polymerization

Table 2 1st endothermic and exothermic onset temperature of samples in air

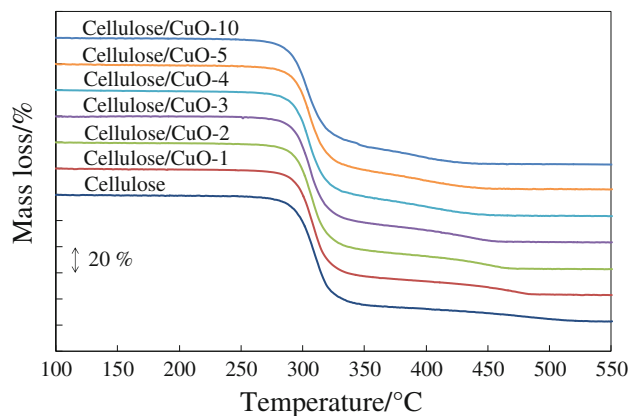|	$T_{Endo-onset}$/°C	$T_{Exo-onset}$/°C
Cellulose	270	310
Cellulose/CuO-1	285	309
Cellulose/CuO-2	295	281
Cellulose/CuO-3	–	279
Cellulose/CuO-4	–	269
Cellulose/CuO-5	–	269
Cellulose/CuO-10	–	263

Fig. 5 TG curves of cellulose and cellulose/CuO mixtures in air

and/or gaseous combustion, where the flammable gaseous products of degradation ignite [10]. Char, which is the residue remaining after high temperature pyrolysis or oxidation of cellulose, was oxidized by oxygen in air at a temperature ca. 500 °C [11, 12]. The endotherm was observed with cellulose, cellulose/CuO-1 and cellulose/CuO-2, but was not observed after addition of CuO at amounts greater than 3 wt%. The exothermic onset temperature decreased with increasing amounts of CuO. An exotherm at ca. 500 °C shifted to lower temperatures with increasing amounts of CuO. The thermal behavior of cellulose/CuO mixtures in air at temperatures near 300 °C was appeared to involve competition between pyrolysis and oxidation reactions. The oxidation reaction dominated when amounts of CuO were greater than 3 wt% because the exotherm of cellulose/CuO-2 at 280 °C was observed before the endotherm at 295 °C and the endotherm of cellulose/CuO-3 disappeared.

The TG curves of cellulose and cellulose/CuO mixtures expect for the amount of CuO are shown in Fig. 5. Mass loss of cellulose upon oxidation involved three steps: a minor mass loss at ca. 270 °C, a major mass loss at ca. 310 °C, and a gradual mass loss at ca. 330 °C [12–14]. The minor mass loss was due to anhydration, the major mass loss was due to gasification of tar and the gradual mass loss was due to oxidation of char. The ending temperature of mass loss shifted to lower temperatures with increasing amounts of CuO, which corresponded to the results of DSC. The third step depends on the concentration of oxygen in the atmosphere [15]. The oxygen in CuO accelerated oxidation of char because the concentration of oxygen in air is constant. The relation between mass loss from 10% to 20% and temperature are shown in Fig. 6. Mass loss was promoted by increasing amounts of CuO, and was associated with an exotherm as indicated by DSC results. The results of DSC and TG revealed that CuO accelerated the exothermal and mass loss of cellulose.
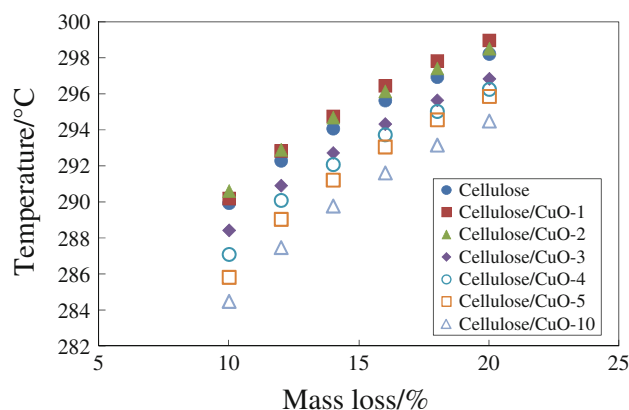
Fig. 6 Relation between mass loss and temperature in air

Fig. 8 IR spectra of residues of cellulose and cellulose/CuO mixtures at 300 °C

Structure analysis of residues after non-isothermal experiments

Spectroanalysis using FT-IR (JASCO, FT/IR-420) was conducted on residues of cellulose and cellulose/CuO mixtures after non-isothermal experiments at a heating rate of 5 K min^{-1} by DSC in air to investigate the effect of CuO on decomposition products of cellulose. FT-IR spectra were obtained using the KBr method in the range of 4,000–400 cm^{-1}. Initial samples were cellulose and cellulose/CuO-10 and their residues at 300 and 350 °C. The temperatures of residues were determined by DSC curves in air (Fig. 3). Next, in order to see the influence of CuO in detail, FT-IR was conducted with samples which were residues of cellulose and cellulose/CuO-1, -2, -3, and -10 at 300 °C.

Results of the first FT-IR analysis are shown in Fig. 7. The glucosidic and ether bonds of cellulose and cellulose/CuO-10 at 350 °C residues at 1,200–900 cm^{-1} disappeared due to depolymerization or ring-opening of the decomposition products of cellulose with a large exotherm and a
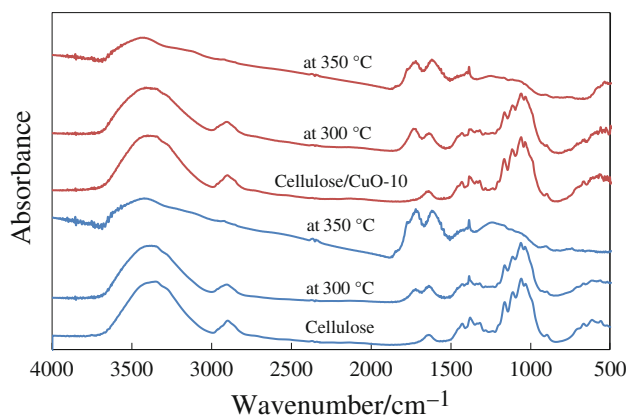

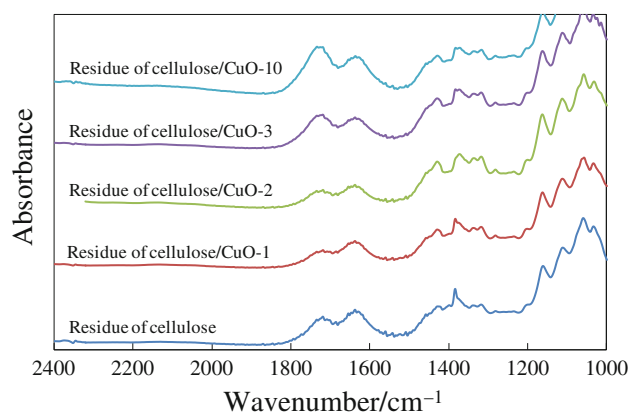**Fig. 7** IR spectra of residues of cellulose and cellulose/CuO-10

major mass loss at ca. 320 °C by DSC and TG [8, 9, 16, 17]. Absorption at 1,630 cm^{-1} was most likely due to absorbed water in cellulose and cellulose/CuO-10 [18]. A carbon–carbon double bond at 1,630 cm^{-1} was observed in cellulose and cellulose/CuO-10 residues at 300 and 350 °C due to structural rearrangement caused by depolymerization and anhydration through pyrolysis and oxidation [16, 19]. In addition, the residue of cellulose/CuO-10 at 300 °C had relatively stronger absorptions compared to the residue of cellulose at 300 °C from the carboxylic bond at 1,700 cm^{-1}. Figure 8 shows FT-IR results from residues of cellulose and cellulose/CuO-1, -2, -3, and -10 at 300 °C. The carboxylic absorptions for cellulose/CuO-3 and cellulose/CuO-10 residues were greater than those of residues of cellulose, cellulose/CuO-1, and cellulose/CuO-2. Those of decomposition products in air were stronger than those in nitrogen because oxygen in air attacked the cellulose chain ends and the oxidation promoted the depolymerization and rearrangements [19, 20]. Therefore, CuO in amounts greater than 3 wt% accelerated the oxidation of cellulose.

Kinetic analysis of oxidation of cellulose and cellulose/CuO mixtures

The most common equation to describe reaction rate in decomposition kinetics is [21–23]:

$$\frac{d\alpha}{dt} = k \times f(\alpha) \tag{1}$$

where α is the extent of conversion, t is time and k is reaction rate. The function $f(\alpha)$ represents the mathematical expression of the kinetic model. Replacing k with the Arrhenius equation and making temperature rate dT/dt a constant β with dynamic technique yields the kinetic equation of non-isothermal reaction:
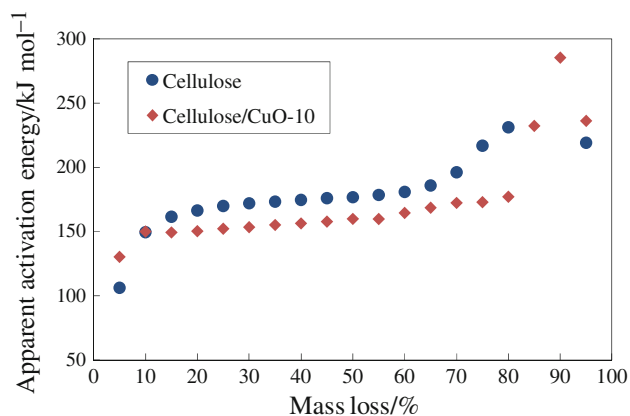
Fig. 9 Relation between mass loss and apparent activation energy

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{Ea}{RT}\right) \times f(\alpha) \qquad (2)$$

where T is temperature, A is pre-exponential factor, β is a heating rate, E_a is activation energy, and R is the gas constant. The apparent activation energy of cellulose oxidation was determined by the Flynn–Wall–Ozawa (FWO) isoconversional equation:

$$\log\beta = \log\left[\frac{AE_a}{Rg(\alpha)}\right] - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \qquad (3)$$

where $g(\alpha)$ is the integral form of $f(\alpha)$. The value of Ea was calculated by a plot of $\log\beta$ versus $1/T$ at constant

conversion obtained from non-isothermal experiments at different heating rates.

Kinetic analysis using TG was conducted not to calculate accurate activation energy, but to investigate the catalytic effect of CuO on oxidation of cellulose as compared to apparent activation energy using cellulose and cellulose/CuO-10. The TG experimental conditions included a sample amount of ca. 5 mg, use of an open aluminum cell, and an experimental temperature range from ambient temperature to 550 °C at four heating rates (0.5, 1, 3, and 5 K min^{-1}) and an air flow of 20 mL min^{-1}.

The kinetics of cellulose pyrolysis under an inert atmosphere has been widely investigated [24–35]. However, the kinetics and mechanism of the thermal degradation of cellulose remained incompletely understood because thermal degradation of cellulose is a complex reaction, which involved competitive and consecutive reactions. The apparent activation energies of cellulose and cellulose/CuO-10 in air at a constant thermal conversion are shown in Fig. 9. The apparent activation energies of cellulose oxidation were not constant because the pyrolysis mechanism of cellulose is multistep, and the apparent activation energies of cellulose pyrolysis were different from the calculation methods and the attitude of pyrolysis mechanisms. The apparent activation energies of cellulose/CuO-10 was 20–30 kJ mol^{-1} lower than that of cellulose at a thermal conversion of 0.2–0.7. The CuO affected the apparent activation energy of cellulose oxidation, but the oxidation mechanism of cellulose/CuO-10 was different
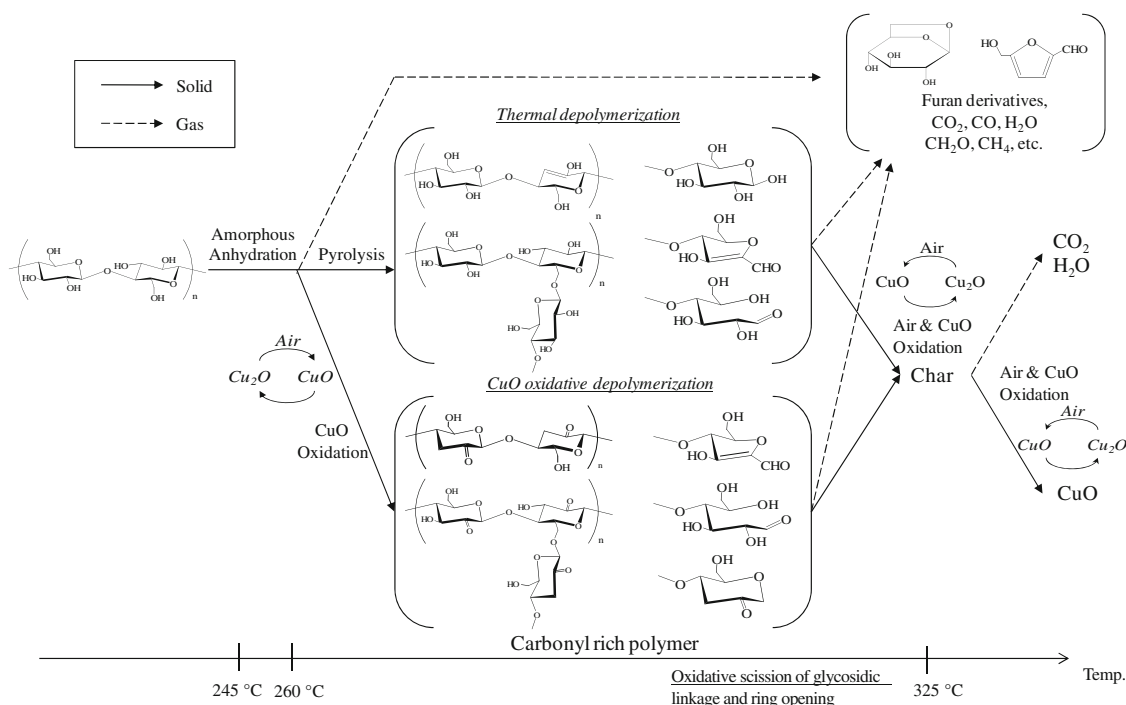

Fig. 10 Oxidation model of cellulose/CuO mixtures

from that of cellulose because the thermal behavior and solid residues of cellulose/CuO-10 were different than those of cellulose, as shown by DSC and FT-IR (Figs. 3 and 8). In addition, CuO affected the pre-exponential factor of cellulose oxidation by the catalytic cycle, during which CuO oxidizes cellulose, CuO is reduced to Cu_2O, and Cu_2O is oxidized by the O_2 in air [6]. Thus, CuO had a catalytic effect on the oxidation of cellulose.

Oxidation model of cellulose/CuO mixtures

An oxidation model of cellulose/CuO mixtures was proposed by DSC, TG, FT-IR, and kinetic analyses results (Fig. 10). Initial pyrolysis of cellulose under an inert atmosphere involves two competitive steps, production and gasification of tar which yields levoglucosan, furan derivatives, flammable gasses, CO_2, and H_2O, and production of residues considered anhydrocellulose, which contains carbon–carbon double bonds (C=C) and carbonyl bonds (C=O) formed through intermolecular and intramolecular anhydration, depolymerization, and rearrangement [13, 18, 19, 36, 37]. The oxidation model of cellulose in air at ca. 300 °C was similar to the pyrolysis model of cellulose under an inert atmosphere because an endotherm at ca. 300 °C in air was due to pyrolysis of cellulose. Upon addition of CuO in amounts greater than 3 wt%, depolymerization, formation of C=C and C=O bonds and gasification were promoted and an exotherm occurred at approximately 300 °C due to accelerated oxidation by CuO. Therefore, oxidation of cellulose by CuO was more predominant than pyrolysis of cellulose at near 300 °C. Char was formed due to oxidation of solid residues at ca. 320 °C, which produced a large exotherm, major mass loss and gasification of tar [37, 38]. The evolved gasses from gasification of tar at ca. 320 °C were similar to those at ca. 300 °C [37, 39]. Their gasses additionally decompose to lower molecular weight products such as furfural, HCOOH, CO_2, CO, etc. in gaseous phase [38]. The CuO accelerated oxidation and gasification of char with increasing amounts of CuO. The evolved gasses from oxidation of char are H_2O and CO_2 [12, 13]. In addition, CuO may have affected, not only the composition of solid residues, but also gaseous composition because K^+ and Fe^{2+} caused a great reduction in levoglucosan and improved the production of hydroxyacetaldehyde, acetol, and small molecule components as well production of H_2 and CO_2, while the production of CO decreased in the presence of iron oxide (Fe_2O_3) [40, 41]. Finally, CuO, which transformed to Cu_2O during the oxidation reaction with cellulose, tar and char, remained after a number of repetitions of the redox reaction with oxygen in air.

This oxidation model requires modification to expand it to include cellulosic biomass because cellulose degradation

and decomposition products of cellulose depend on the experimental condition, such as atmosphere and heating rate, and the major components of cellulosic biomass, respectively, either pyrolyze or oxidize, while the decomposition products of cellulosic biomass react with each other [42].

Conclusions

Thermal, kinetics, and spectroscopic analyses of cellulose/CuO mixtures demonstrated:

(1) CuO affects cellulose oxidation in air more than xylan or lignin oxidation in air.
(2) Heat release and mass loss increase with increasing amounts of CuO.
(3) CuO affects the apparent activation energy of cellulose oxidation by reducing it 20–30 kJ mol^{-1} upon addition of 10 wt% CuO.
(4) The oxidation model proposed involves a predominant oxidative path upon addition of more than 3 wt% CuO at ca. 300 °C; the amount of CuO affects the path to gaseous products.
(5) CuO accelerates thermal decomposition of cellulose/metal oxide mixtures and thermochemical conversion.

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