



Boiling point of levoglucosan and devolatilization temperatures in cellulose pyrolysis measured at different heating area temperatures

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ABSTRACT

Fast heating conditions are known to improve the yields of volatile products in cellulose pyrolysis. The mechanism, however, is not yet well understood. For better understanding of the cellulose fast pyrolysis, the devolatilization temperature was directly measured during the pyrolysis of cellulose. An *in situ* measurement method employing a very fine thermocouple was first developed. A sample in a ceramic boat was pushed into the heating area, preheated at 430–700 °C under the flow of N₂ (150 mL/min). Employing this method, the boiling point (385 °C) of levoglucosan, the major volatile product derived from cellulose fast pyrolysis, was measured directly for the first time, and was found to reduce to 345 and 292 °C under reduced pressures of 0.5 and 0.1 atm, respectively. High heating area temperatures increased the selectivity of levoglucosan evaporation by shortening the period required for the completion of evaporation. With these results in mind, pyrolysis of cellulose powder (Ceolus FD-F20) was studied using a similar procedure. The results obtained under the reduced pressures suggested that the depolymerization of cellulose, not evaporation of the volatiles products, is the rate-determining step for the pyrolytic devolatilization of cellulose. Interestingly, the depolymerization temperature varied depending on the heating area temperature as 360–385 °C (for 430–500 °C) and 400–450 °C (for 500–700 °C) (the values in the parentheses: heating area temperatures). The char morphology also changed; the pyrolysis conditions provided powder-like and film-like char materials, respectively. According to these results, the effects of heating area temperature on the cellulose pyrolysis mechanism are discussed, focusing on the behavior of cellulose crystallites.

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1. Introduction

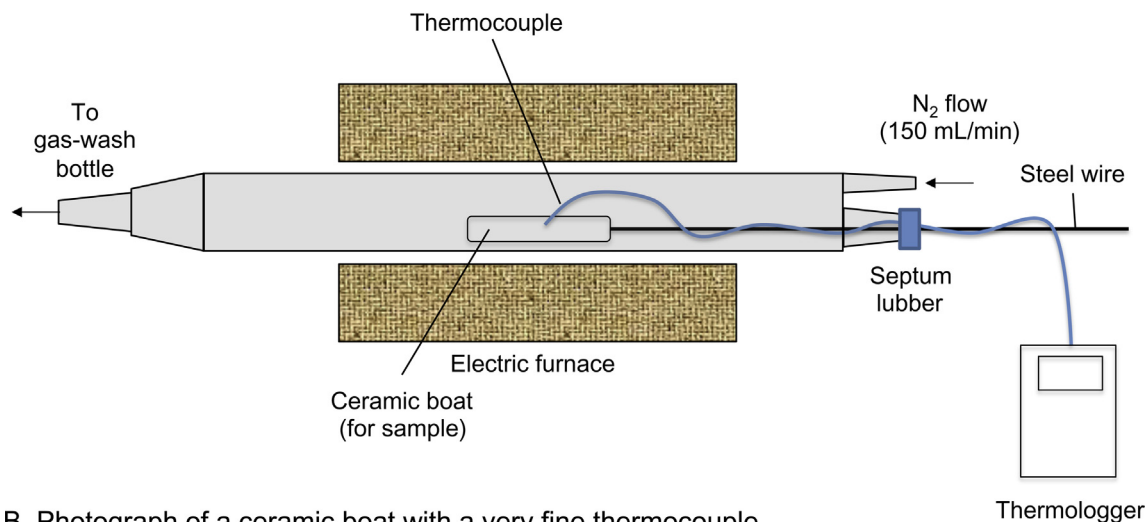
Cellulose is a major chemical constituent of wood and other lignocellulosic biomasses that are expected to be potential renewable resources for fuels, materials and chemicals. Pyrolysis, which is defined as high-temperature decomposition under the limited amount of oxygen, is a promising way to convert biomass effectively to gas, liquid and solid substances. Fast pyrolysis is a technology used to obtain liquid products—so-called “bio-oil”—and is characterized by fast heating and quick quenching of the product vapors [1–3]. During the last three decades, many studies on the fundamentals and applications of fast-pyrolysis processes have been conducted in an effort to obtain liquid fuels and useful chemicals such as levoglucosan (1,6-anhydro-β-D-glucopyranose), anhydro-oligosaccharides, glycolaldehyde, and phenols [2,4,5].

One of the most important findings in this field is the formation of liquid intermediates [6–12]. Boutin et al. [7] reported that cellulose char obtained with an image furnace had no fibrillar structure, and they explained this by the existence of liquid intermediates during pyrolysis. They also estimated the lifetime of these molten species to be lower than 1 s. In a subsequent paper reporting data of mass spectrometry and liquid chromatography/mass spectrometry analyses, Lédé et al. [8] found that the liquid intermediates mainly consisted of anhydro-oligosaccharides. Interestingly, the yields and compositions of liquid intermediates were rather constant during pyrolysis, and the mass loss and char formation started after the yield of liquid intermediates reached a steady state. From these findings, Lédé and his co-workers proposed that the formation of the liquid intermediates is the initial step in the fast pyrolysis of cellulose.

As for the anhydro-oligosaccharide formation, Suzuki et al. [13] identified cellotriosan, cellobiosan and levoglucosan from cellulose pyrolysis products obtained with CO₂ laser irradiation. Because these compounds had only 1 → 4-β-glucosidic linkages,

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A. Schematic diagram of reactor



B. Photograph of a ceramic boat with a very fine thermocouple



Fig. 1. Schematic diagram of the experimental set up used for the boiling point measurement and *in situ* temperature measurement during the pyrolysis of cellulose and levoglucosan.

they concluded that the anhydro-oligosaccharides are formed by cleavage of the glucosidic bonds in cellulose. Radlein et al. [14] also identified cellobiosan in 6–15% yields in syrups obtained from the fast pyrolysis of Avicel cellulose. On the basis of such high yield formation of cellobiosan, they proposed a new pathway in which the depolymerization of cellulose gives cellobiosan as a primary pyrolysis product. Their research group further identified anhydro-oligosaccharides up to heptamer from pyrolysis of cellulose at wall temperatures of 850–1200 °C and very short residence times of 35–75 ms [15]. Anhydro-oligosaccharide formation was also indicated by platinum-filament pyrolysis desorption chemical ionization mass spectrometry of cellulose [16].

Heat and mass transfer limitations relating to the fast pyrolysis of cellulose have been discussed extensively [17–20]. Secondary reactions including the repolymerization of levoglucosan [21–23] as the major primary product from cellulose as well as other gas- and liquid-phase reactions reduce the bio-oil yields by increasing the char and/or gas yield. Thus, mass-transfer efficiencies of liquid- and vapor-phase products are normally important in the high-yield formation of volatile products; i.e., bio-oil.

One of the major problems encountered during the investigation of cellulose fast pyrolysis is the uncertainty of the actual pyrolysis temperature [17,19,20]. Heat-transfer limitations from the reactor to sample, lags in the recordings of the measuring devices and endothermic processes have been considered as the origin of this problem. From theoretical calculation results, Lédé and Villermaux [20] and Narayan and Antal [19] indicated that the true sample temperature remains almost constant during pyrolysis even if the reactor temperature is much higher. This was confirmed by Lanzetta et al. [17], who measured the surface temperature of a thin powdered cellulose layer by direct physical contact with a thin (0.1-mm bead) thermocouple during fast pyrolysis with a radiant heater in the temperature range 250–426 °C. They confirmed that a region existed where the sample temperatures were significantly

lower than the temperature obtained when char was heated in a control experiment. Similar direct temperature measurements have been conducted to obtain the temperature profiles of the surface and interior of wood specimens during pyrolysis [24–30]. In spite of these extensive studies, actual pyrolysis temperature of cellulose has not yet been fully clarified.

This article deals with the devolatilization temperatures of cellulose, along with the boiling point of levoglucosan as the major volatile product. A direct temperature measurement method by contacting a very fine thermocouple to sample was developed first and evaluated by the measurement of the boiling points of some thermally stable aromatic compounds. With this method, the boiling point of levoglucosan was measured for the first time. Temperature of cellulose during pyrolysis was then measured with the same method when cellulose was inserted into the heating area at different temperatures between 430 and 700 °C. Since the devolatilization process lowered the heating up efficiency of cellulose due to its large endothermicity, the resulting temperature profile gave us some insight into the temperatures of cellulose depolymerization and the following volatilization. The heating area temperature may affect the heating up process of cellulose under the influence of these endothermic processes. Finally, according to these experimental results, the paper discusses mechanisms of the volatiles formation during cellulose pyrolysis, focusing on the response of cellulose crystallites at different heating area temperatures.

2. Materials and methods

2.1. Materials

1,3,5-Triphenylbenzene (>99.0%), 1,2-benzanthraquinone (>95.0%), levoglucosan (>99.0%) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), anthraquinone (>98.0%) (Nacalai Tesque,

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