

## Char-free and Flash Pyrolytic Gasification of Cellulose

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### Abstract

Highly crystalline cellulose, microcrystalline cellulose (MCC) was pyrolyzed by heating to the temperature of 445-764 °C at a rate  $> 10^3$  °C /s. Curie-point pyrolyzer, employed for the flash pyrolysis, allowed to investigate the primary pyrolysis of MCC, minimizing the extent of the secondary pyrolysis of volatiles in the gas phase. The primary volatile products were analyzed by using gas chromatography and gas chromatography/mass spectroscopy. The flash pyrolysis with peak temperature over 500 °C gave the yield of char (carbonized residual solid) lower than 3 wt%. The char yield with 764°C was even below 1 wt%. It was thus demonstrated that MCC can be converted into volatiles near completely. Effect of crystallinity of cellulose was examined. MCC was subjected to ball milling to reduce the crystallinity of MCC. It is known that reduced crystallinity enhances the crosslinking of hydrogen-bonded hydroxyls in amorphous moiety, resulting in high char yield. However, the flash pyrolysis of the ball-milled MCC, regardless of the peak temperature, gave product yields very similar to those from MCC, indicating that the flash pyrolysis was also applicable to near-char-less conversion of amorphous cellulose. Some details of the product composition are also reported.

Key words: Cellulose, pyrolysis, gasification

### 1. Introduction

Bioethanol is attracting attention worldwide as environmentally friendly fuel. It is generally produced by fermentation of sugarcane or saccharified starch from corn, followed by purification. Because of availability of the feedstock and technical easiness in the production, it is one of the major vehicle fuels in Brazil. An emerging application of bioethanol is production of ethylene, an important chemical in petrochemistry. Braskem, a leading petrochemical company in Brazil, produces 200,000 tons of polyethylene per year from sugar cane-derived ethylene.<sup>[1]</sup> However, for countries like Japan, large scale production of sugarcane and corn is geographically difficult. Another potential feedstock for the ethanol and ethylene is cellulose in lignocellulosic biomass, such as wood and cellulosic wastes from paper industry, but saccharification of cellulose needs costly enzymes and long reaction time due to its robust chemical structure.

We here propose an alternative approach to produce bioethanol and bioethylene from cellulose, which is consisted of cellulose conversion to

syngas by gasification, catalytic synthesis of ethylene from syngas, and hydration of ethylene to form ethanol. Since gasification of carbonaceous resources generally requires high temperature and thus much energy, it is important for this approach to develop a method to gasify cellulose under milder conditions, following the stoichiometry ( $\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O} \rightarrow 6\text{H}_2 + 6\text{CO}$ ). However, pyrolysis, occurring in gasification as primary reaction, generally produces substantial amount of char, which is hard to be gasified at low temperatures. It is therefore necessary to suppress the char formation in pyrolysis as much as possible.

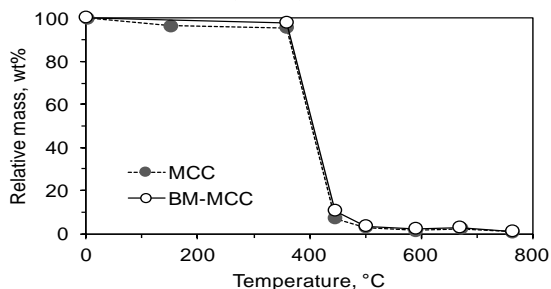
In this study, we employed curie point pyrolyzer (CPP) to investigate characteristics of cellulose pyrolysis with very rapid heating (flash pyrolysis). The rapid heating was considered to be effective to suppress the char formation if it is faster than the reaction rate of crosslinking of hydrogen-bonded hydroxyls in cellulose. Two types of cellulose with different crystallinity were tested to know the influence of cellulose chemical structure on the product.

## 2. Experimental Setup

Microcrystalline cellulose (MCC, Sigma-Aldrich) was used as cellulose sample with high crystallinity. Amorphous cellulose was obtained by ball-milling of MCC for 60 h (BM-MCC). Flash pyrolysis was carried out using CPP (JHP-22). 2 mg of the sample was pyrolyzed at  $>1000$  °C/s with some maximum temperatures (445, 500, 590, 670 and 764 °C). The yield of char was obtained from the mass after pyrolysis, and that of compounds in volatiles were analyzed with GCs.

## 3. Results and Discussion

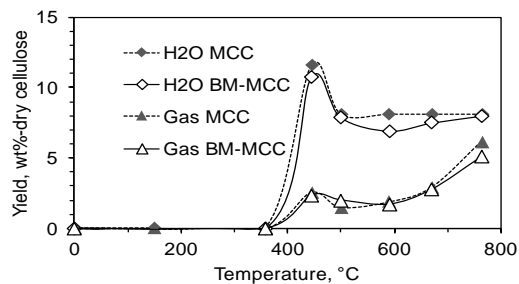
The crystallinity index of cellulose was determined from FT-IR spectrum. Ball-milling for 60 h effectively increased amorphous portion and decreased the crystallinity degree from the initial value of 0.68 (MCC) to 0.2.



**Fig. 1.** Char yield in flash pyrolysis at various maximum temperatures.

**Fig. 1** shows mass decreasing curves for MCC and BM-MCC in pyrolysis. It was clearly seen that higher content of amorphous portion did not influence the mass decreasing curves. More importantly, for both MCC and BM-MCC, the char yields were very low above 590 °C, less than 3 wt%, and decreased as low as 0.8 wt% at 764 °C. Thus, the purpose of this study, near-char-free pyrolytic conversion of cellulose, was achieved by the employment of flash pyrolysis, regardless of the crystallinity of the feedstock cellulose. These results indicate availability of cellulosic wastes, which generally have amorphous nature, as feedstock. There are two potential explanations on these effects of heating rate. The one is, as mentioned above, the effect to suppress crosslinking of hydrogen-bonded hydroxyl groups in cellulose. Another explanation is based on an intermediate liquid mechanism,<sup>[2]</sup> where, in the course of heating, “intermediate liquid” forms over cellulose surface. When the heating rate is high

enough, the intermediate liquid instantly evaporates as volatiles. If this is not the case, it re-polymerizes to form secondary char.



**Fig. 2.** Yields of H<sub>2</sub>O and gaseous products (H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>) in flash pyrolysis at various maximum temperatures.

**Fig. 2** shows formation of substantial amount of water and gaseous products (H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>) in the flash pyrolysis. The highest water yield was observed at 445 °C, which was probably caused by incomplete pyrolysis during heating-up and occurrence of slow pyrolysis in holding time at that temperature (10 s). The yield of gaseous product increased with pyrolysis temperature up to 6.1 wt%. According to a report,<sup>[3]</sup> gaseous products are hardly produced in the primary pyrolysis (< 1 wt%). The formation of these products (water and gaseous product) attributes to the unavoidable secondary reaction of volatiles in gas phase in the device of CPP used in this study. Ideal pyrolysis for realizing cellulose gasification following the stoichiometry above produces only levoglucosan (LGA, C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>), which is a type of anhydrosugar. GC/MS analysis of condensed volatiles from pyrolysis revealed that the main component was LGA, but formations of other compounds such as other anhydrosugars and furanic compounds were also observed, indicating the occurrence of side reactions in pyrolysis as well as gas phase.

## 5. Conclusion

Near-char-free pyrolysis of MCC and BM-MCC was demonstrated using CPP.

## References

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