Improvement of Carbon Fixation Yield from Pulp *via* Pyrolysis with an Additive Agent

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Highlights

- Ammonium dihydrogen phosphate promoted dehydration of pulp and increased carbon fixation yield.
- The effect of ammonium dihydrogen phosphate on dehydration was discussed quantitatively.
- More than 80 % of carbon was fixed as activated carbon product with BET surface area of 730 m^2/g.

1. Introduction

Pulp is a fiber extracted from lignocellulosic biomass. Its main component is cellulose, which is one of the most abundant renewable biomass resources in the world[1,2]. Cellulose is a crystalline polymer with intra- and intermolecular hydrogen bonds, and therefore is highly resistant to chemical treatment. Its development into high value-added products such as liquid fuels[3], activated carbon[4], and synthesis gas[5,6] by pyrolysis has been widely studied. However, the pyrolysis of pulp usually results in a low carbon fixation yield. This study aimed to improve the carbon fixation yield during pyrolysis using an additive agent, and to obtain activated carbon as a product. As an additive agent, ammonium dihydrogen phosphate (ADP) was selected in this study.

2. Methods

ADP solutions were prepared by dissolving 0.005 – 0.03 mol of ADP (FUJIFILM Wako Pure Chemical Co., Japan) into 100 mL of deionized water. 1 g of pulp (Kao Co., Japan) was added into this solution, and the samples were mixed by sonication for 10 min. Samples were dried at 80 °C for 1 day, and vacuum dried for another 1 day. The prepared ADP added pulps were pyrolyzed in a thermogravimetric analyzer (TGA-50, Shimadzu Co., Japan) under a nitrogen atmosphere. At larger scale, the samples were also pyrolyzed in an infrared gold image furnace (RHL-P68, ADVANCE RIKO Inc., Japan). In this case, a quartz tube of 50 cm long with an inner diameter of 50 mm was used for the reaction tube, and the inside of the tube was swept with nitrogen at a flow rate of 500 mL/min. The samples were held at 110 °C for 60 min, and then pyrolyzed at the reaction temperature for 30 min. During the reaction procedure, the temperature rising rate was set as 10 °C/min. After pyrolysis, the product was washed with deionized water at 150 °C for 1 h, to dissolve the P and N contained in the products. The residue was vacuum dried at 80 °C for 1 day and analyzed by elemental analysis and the nitrogen isothermal adsorption system (BELSORP-mini X, MicrotracBEL Co., Japan).

3. Results and discussion

The effect of ADP/pulp ratio [mol/g] was examined by TGA. The ratio was set to 0.005, 0.01, 0.02, or 0.03. The results are shown in **Figure 1**, along with the pyrolysis properties of pulp and ADP alone. The results showed that a notable weight decrease was observed in the temperature range of 200 – 300 °C for all ADP added samples. In addition, for ADP/pulp = 0.005 and 0.01 mol/g samples, the weight decrease in the range of 500 – 600 °C were suppressed and approximately 40% of the sample remained at 800 °C. **Figure 2 (a)** shows the fixed carbon yields of pyrolysis products. At 300 – 500 °C, the carbon yield of pulp alone decreased with temperature, and reached below 30% at 500 °C. One the other hand, all the yields with ADP were over 80%. These results indicated that the dehydration of pulp was promoted at a low temperature by the interaction with ADP, which changed the structure of pulp to prevent decomposition with increasing temperature. Thus, it can be concluded that a significant fixed carbon yield improvement was achieved with ADP addition. Finally, the surface properties of the obtained carbon products by 500 °C pyrolysis were analyzed. The BET surface area was calculated from the nitrogen adsorption isotherm, which are shown in **Figure 2 (b)**. Judging from the results, BET surface area reached a plateau at ADP/pulp = 0.01 mol/g. The surface area at ADP/pulp = 0.01 mol/g was 730 m^2/g, which was a 2.4-fold increase compared to 300 m^2/g without ADP. It was clarified that ADP addition was effective in improving the surface properties of the product carbon.

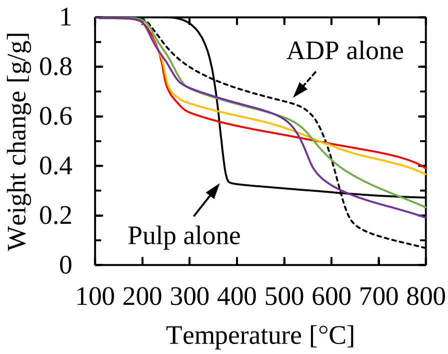

Figure 1. Changes in thermogravimetric profiles with changing ADP/pulp ratio [mol/g]: red – 0.005, yellow – 0.01, green – 0.02, purple – 0.03. Blue – theoretically calculated degradation profile of ADP/pulp = 0.005 mol/g sample.

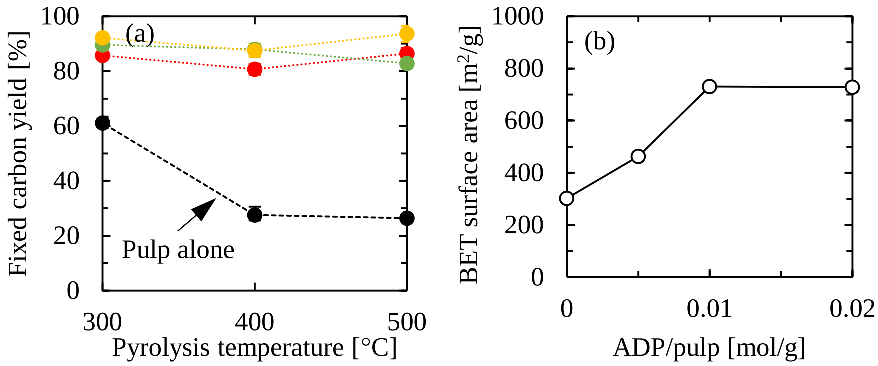

Figure 1. **(a)** Fixed carbon yield change with changing pyrolysis temperature and ADP/pulp [mol/g]: red – 0.005, yellow – 0.01, green – 0.02. **(b)** BET surface area of carbon products by 500 °C pyrolysis.

4. Conclusions

The effect of ADP as an additive agent to the pulp during pyrolysis was examined. By adding ADP, the fixed carbon yield was successfully increased from approximately 30% to greater than 80%. In addition, ADP was also efficient in improving surface properties. The BET surface area increased 2.4-fold compared to that without ADP addition, showing a value of 730 m^2/g. In summary, the addition of ADP during pulp pyrolysis was clarified to be effective, producing high-value-added carbon with high yield.

References

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Keywords
pulp pyrolysis; carbon fixation; activated carbon; ammonium dihydrogen phosphate