Enhancement of sugar char surface area by chemical and physical activation processes

Jidon Janaun and Naoko Ellis*
Department of Chemical and Biological Engineering
University of British Columbia
2360 East Mall, Vancouver, BC Canada V6T 1Z3
Tel: (1) – 604 822 1243
Fax: (1) – 604 822 6003
*nellis@chml.ubc.ca

Introduction

The recent discovery of sugar catalyst gives a new dimension to the biodiesel production [1]. The sugar catalyst (also known as sulfonated carbon catalyst) is prepared by pyrolyzing sugar at low temperature (400°C) and the resultant sugar char is functionalized with sulfonic acid using sulphuric acid. The sugar catalyst shows higher reactivity on esterification and transesterification reactions over conventional solid acid catalysts such as nobic acid and amberlyst [1,2]. These findings are remarkable owing to the fact that the sugar catalyst has a surface area much smaller than any other solid acid catalysts tested for esterification and transesterification reactions (i.e., less than 1 m^2g^{-1}). This unique property (low surface area but high reactivity) leads for further improvement in increasing the catalyst surface area. As the surface area of the sugar catalyst depends on the surface area of the catalyst precursor (sugar char), the enhancement of the sugar char surface area will lead to enhance sugar catalyst surface area.

There are two common techniques to increase the surface area of the sugar char: chemical activation and/or physical activation [5]. Chemical activation involves chemical reagents such as potassium hydroxide, phosphoric acid, or zinc chloride as a dehydrating agent, whereas physical activation involves gasification using CO_2, O_2, or steam [5,6]. Literatures on the parameters affecting the effectiveness of the chemical and physical activations are well established [4,5,6]. However, the effect of combining chemical and physical activations on sugar-based carbon is not yet reported. We report here the enhancement of sugar char surface area as a basis for future sulfonation.

Materials and Methods

Potassium hydroxide and carbon dioxide were used for the chemical and physical activation processes, respectively. Effects of activation temperature (400-800°C) and KOH to sugar ratio (v/w of 1 and 2) on surface area were investigated. The BET surface area was measured using two instruments; by the nitrogen adsorption isotherm at 77K using Micromeritics ASAP 2020, where samples were degassed at 120°C for 3 hours prior to analysis; and the Micromeritics FlowSorb II 2300 using a mixture gas (30% Nitrogen and 70% Helium), where samples were degassed at 150°C prior to analysis.

Results and Discussion

Results of the chemical and physical activation processes on the sugar char are shown in Figure 1. Figure 1 (a) shows that the surface area increases with time for pyrolysis. Furthermore, higher KOH to sugar ratio gives higher surface area. The effect of the pyrolysis temperature on the surface area is shown in Figure 1 (b).

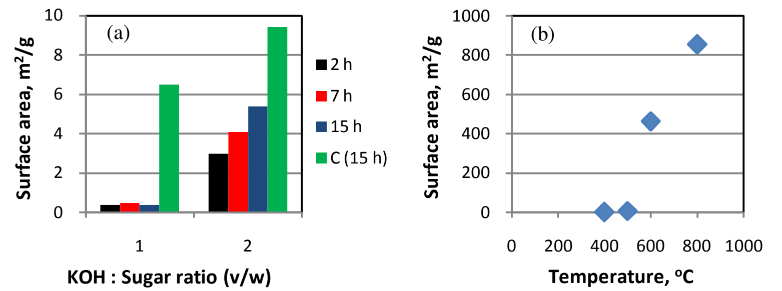

Figure 1: Surface area enhancement by a combined chemical and physical activation processes: (a) Effects of KOH to sugar ratio, and time for pyrolysis (at 400°C). C(15h) is the experimental control with pyrolysis under N_2 (Surface area analysis by FlowSorb II); (b) Effect of pyrolysis temperature on surface area (Surface area analysis by ASAP2020).

Combination of the chemical and physical activation involves simultaneous carbonization and activation processes, unlike in a conventional process where physical activation is done after washing the carbon from the chemical activation step [6]. The large surface area difference between the pyrolysis temperatures at 400-500°C and 600-800°C is due to the fact that physical activation by CO_2 occurs only at high temperatures [4,5,6]. At lower temperatures, only chemical activation takes place, and the surface area enhancement is minimal. The surface area is expected to increase with the increase of KOH to sugar ratio. Higher surface area for the control (C 15h) indicates that CO_2 at 400°C reduces the chemical activation as CO_2 may interfere with the KOH and sugar crosslinking reaction.

Significance

The combined chemical and physical activation processes at high temperatures (600 – 800°C) is effective in enhancing the sugar char surface area. At 400°C, sugar char surface area increased about 9 folds compared with the surface area of the sugar catalyst [1], leading to a possible 9 folds surface area increase of the sugar catalyst once the sugar char is sulfonated. The reactivity of the surface area-enhanced sugar catalyst is now under our investigation.

References

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