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# Reduction of formic acid to methanol under hydrothermal conditions in the presence of Cu and Zn

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ABSTRACT

Formic acid is the main breakdown product of mild hydrothermal treatment of carbohydrates. Further conversion to methanol was achieved using Cu as catalyst and Zn as reductant under hydrothermal conditions of 250–325 °C for 3–12 h. Both Cu and Zn used were commercial Cu and Zn powders with particle sizes of 200 mesh. A methanol yield of 32% was achieved at 300 °C for 5 h with 6.5 mmol of Cu, 12 mmol of Zn and a filling rate of 44%. Thus, this process may provide a promising solution to producing methanol from biomass by converting carbohydrates into formic acid.



## 1. Introduction

Hydrothermal reactions using high temperature water (HTW) as the reaction medium have been proven to be an environmentally friendly technology for the conversion of various types of biomasses into value-added chemicals (Fang et al., 2008; Jin et al., 2010; Jing et al., 2007; Qi et al., 2008; Watchararuji et al., 2008). HTW has unique features compared to ambient liquid water. For example, the ion product ($K_w$) at 250–300 °C is approximately three orders of magnitude greater than that of ambient liquid water, which significantly promotes the organic reactions, such as chemical synthesis, materials synthesis and biomass processing (Akiya and Savage, 2002).

The conversion of biomass into methanol, an important multipurpose base chemical, has been achieved through synthesis gas, which is mainly generated from biomass via pyrolysis or gasification. For example, Güllü and Demirbaş (2001) reported that methanol can be obtained in a yield of 6 gallons per ton of wood with a fractionating column under high temperature of 477–1077 °C, and when injecting air or pure oxygen into the reactor core, the yield could reach 100 gallons per ton of wood. Lv et al. (2007) repored that bio-syngas with a high ratio of $H_2$/CO (1.87–4.45) obtained from pine sawdust via catalytic gasification was favorable for methanol synthesis. The authors also claimed that a high temperature of 750 °C and large amount of catalyst are required for producing synthesis gas of high $H_2$/CO ratio. Although these technologies have been utilized on an industrial scale, high temperatures or expensive catalysts are uneconomical. Therefore, the development of new processes for the production of methanol from biomass via environmentally friendly hydrothermal process is desirable.

Jin et al. (2008) reported that carbohydrates could be efficiently converted into formic acid under mild hydrothermal conditions with yields as high as 75%. In addition to formic acid, only a few low molecular weight carboxylic acids, such as lactic acid and acetic acid, were identified, and the purity of formic acid in the liquid sample produced from carbohydrate biomass was as high as 95%. Processes for the reduction of carboxylic acids including formic acid into alcohols have been described, but these required expensive catalysts or hydrogen sources (Falorni et al., 1999; Manyar et al., 2010). Water can serve as a hydrogen source when in contact with Zn under hydrothermal conditions (Fraga-Dubreuil and Poliakoff, 2006). The use of Zn as reductant has the benefits of producing reactive hydrogen on-site and generating ZnO, which can catalyze the reduction of formic acid since ZnO is traditionally utilized as a hydrogenation catalyst (Chen et al., 1999; Fujitani and Nakamura, 2000).

Cu is frequently used as catalyst for the production of methanol from mixtures of $CO_2$/CO/$H_2$ (Liu et al., 2003; Wainwright and Trimm, 1995), and Cu or Cu-based catalysts exhibit high selectivity for the conversion of carboxylic acids to alcohols (Santiago et al., 2000). In addition, Cu is relatively cheap and easily available compared with noble metals. Thus, Cu was selected as catalyst for the reduction of formic acid to methanol under hydrothermal conditions in the presence of Zn.

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