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# Fractionating pretreatment of sugarcane bagasse by aqueous formic acid with direct recycle of spent liquor to increase cellulose digestibility-the Formiline process

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## HIGHLIGHTS

▶ Biomass pretreatment by formic acid and alkaline deformylation termed as Formiline process.

- ▶ Direct recycle of spent liquid to significantly reduce energy consumption.
- ▶ The pretreated substrates showed excellent enzymatic digestibility and fermentability.
- ▶ A high ethanol concentration was obtained in SSF of pretreated sugarcane bagasse.

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### ABSTRACT

A lignocellulose pretreatment process was developed with formic acid delignification (FAD) followed by alkaline deformylation (AD), which was termed as Formiline process. In FAD, more than 80% of lignin and hemicellulose were removed, but cellulose formylation also happened. Formic acid concentration (FAC) was the most important factor affecting delignification and cellulose formylation. Increasing FAC could enhance degree of delignification but also increased cellulose formylation. The presence of formyl group could inhibit the enzymatic hydrolysis of cellulose; however, removing formyl group with a small loading of alkali well recovered cellulose digestibility. The spent liquor could be directly recycled for delignification thus significantly decreasing energy consumption in solvent recovery. The Formiline-pretreated substrates showed an excellent enzymatic digestibility and could be very well converted to ethanol by simultaneous saccharafication and fermentation (SSF). The final ethanol concentrations were 55.4 and 80.1 g/L respectively at initial solid consistencies of 15% and 20%.

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### 1. Introduction

Lignocellulose is recalcitrant to hydrolyze because that the chemical compositions of plant cell wall with their interactions have constructed a compact structure to protect the carbohydrates from degradation (Himmel et al., 2007). During last decades, a number of pretreatment methods have been developed using various physical, thermal, chemical or biological approaches or their combinations to overcome biomass recalcitrance (Yang and Wyman, 2008; Hendriks and Zeeman, 2009; Zhu and Pan, 2010). These pretreatments improve the direct factor (accessible surface area) by altering the indirect factors thus increasing cellulose accessibility to cellulase enzymes (Zhao et al., 2012). From the point of view to integratedly utilize lignocellulosic biomass,

\* Corresponding author. Tel./fax: +86 10 62772130. *E-mail address:* zhaoxb@mail.tsinghua.edu.cn (X. Zhao). organosolv pretreatment has provided a promising pathway for clean fractionation of biomass feedstock to produce multiple products in a concept of lignocellulose biorefinery (Pan et al., 2006a; Zhao et al., 2009a). Organosolv pretreatment refers to the process to pretreat lignocellulosic biomass in organic solvents or their aqueous solution systems with or without added catalysts in temperature range of 100-250 °C (Zhao et al., 2009a). Organosolv pretreatment yields three separate fractions: highpurity lignin, hemicellulosic syrup and a relatively pure cellulose fraction, all of which show promises for producing high valueadded products. Therefore, organosolv pretreatment can be termed as a "fractionating" process to increase cellulose digestibility and obtain multiple products. Currently, most of the research works on organosolv pretreatment of lignocellulosic biomass are mainly focused on the use of low-boiling point alcohols, particularly ethanol, to delignify biomass feedstocks and increase cellulose digestibility (Pan et al., 2006a, 2007, 2008; Zhao



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