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Pretreatment and fractionation of corn stover by ammonia recycle percolation process

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Abstract

Corn stover was pretreated with aqueous ammonia in a flow-through column reactor, a process termed as Ammonia Recycle Percolation (ARP). The aqueous ammonia causes swelling and efficient delignification of biomass at high temperatures. The ARP process solubilizes about half of xylan, but retains more than 92% of the cellulose content. Enzymatic digestibility of ARP-treated corn stover is 93% with 10 FPU/g-glucan enzyme loading. The SEM pictures and FTIR spectra confirm swelling and delignification effects of the ARP process. The X-ray crystallography data indicate that the basic crystalline structure of the cellulosic component of corn stover is not altered by the ARP treatment. Low-liquid ARP can reduce the liquid throughput and residence time to 3.3 mL/g-biomass and 10–12 min, without adversely affecting the overall effectiveness. The low-water ARP achieved 73.4% delignification and 88.5% digestibility with 15 FPU/g-glucan. The ethanol yield from the SSF of low-liquid ARP-treated corn stover using *Saccharomyces cerevisiae* reached 84% of the theoretical maximum. Successive operation of a hot-water treatment and the ARP was applied as a method of biomass fractionation. The two-stage process separated xylan in the first stage (84%) and lignin in the second stage (75%), resulting treated solid that contains 79% glucan.

Keywords: Aqueous ammonia; ARP; Corn stover; Pretreatment; Fractionation; Digestibility; Ethanol; Fermentation

1. Introduction

A pretreatment method based on aqueous ammonia is being developed in our laboratory. It utilizes aqueous ammonia in a recycle mode, thus termed as Ammonia Recycled Percolation (ARP). Its process flow diagram is shown in Fig. 1. Ammonia is an efficient delignification reagent. The ARP is a pretreatment method that raises the enzymatic digestibility and also achieves high degree of delignification (Kim et al., 2003; Iyer et al., 1996; Kim and Lee, 1996). Lignin is one of the major hindering factors in enzymatic hydrolysis (Chang and Holtzapple, 2000; Cowling and Kirk, 1976; Dulap et al., 1976; Lee et al., 1995; Mooney et al., 1998; Schwald et al., 1988). Lignin and extraneous compounds liberated during pretreatment are also known to inhibit enzymatic hydrolysis and microbial activity, thus limiting the conversion efficiency of ethanol production by fermentation. The ARP can therefore improve the microbial activity and the enzyme efficiency, eventually lowering the enzyme requirement.

The primary factors influencing the reactions occurring in the ARP are reaction time, temperature, ammonia concentrations, and the amount of liquid throughput. Of these, the liquid throughput and the reaction temperature were identified as the factors most sensitively affecting the processing cost. The main interest in early phase of this work was to minimize the liquid input and adjust other conditions so as to attain acceptable levels of digestibility and delignification. During the ARP, a significant fraction of hemicellulose is also removed along with lignin. This partial separation of hemicellulose makes the process of utilizing hemicellulose

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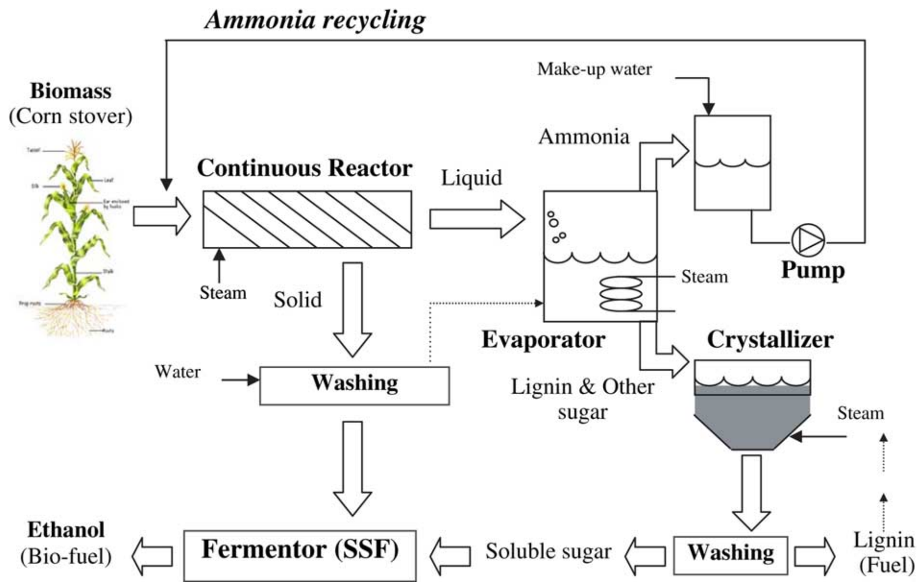

Fig. 1. ARP (Ammonia Recycle Percolation) process diagram.

sugars complicated. To resolve this problem, a two-stage pretreatment was investigated. This process scheme is designed to separate hemicellulose sugars in the first stage by hot water, and separate lignin in the second stage by the ARP. The remaining solid thus contains mostly cellulose. Upon completion of this process, fractionation of biomass is to be achieved. Fractionation of biomass would improve the overall biomass conversion process since each of the biomass constituents are utilized more efficiently.

This paper describes the process conditions of the ARP and the two-stage process, and assesses their performance as a pretreatment method. The samples of these processes were analyzed for composition and the enzymatic digestibilities were determined. Samples were further examined and analyzed by SEM, X-Ray crystallography, and FTIR. The results of the various solid analyses are reviewed in connection with the enzymatic digestibility.

2. Methods

2.1. Material

Air-dried ground corn stover was supplied by the National Renewable Energy Laboratory (NREL, Golden, CO). The corn stover was screened to a nominal size of 9–35 mesh. The initial composition of the corn stover, as determined by NREL, was: 36.1 wt% glucan,

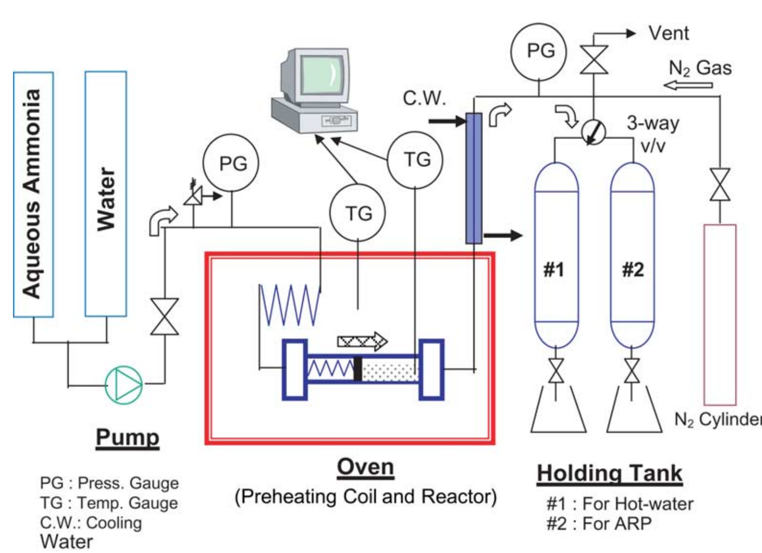

Fig. 2. Experimental set-up of ARP.