Steam gasification of a thermally pretreated high lignin corn stover simultaneous saccharification and fermentation digester residue

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ABSTRACT

Efficient conversion of all components in lignocellulosic biomass is essential to realizing economic feasibility of biorefineries. However, lignin cannot be fermented using biochemical routes. Furthermore, high lignin and high ash residues from simultaneous saccharification and fermentation (SSF) is difficult to thermochemically process due to feed line plugging and bed agglomeration. In this study a corn stover SSF digester residue was thermally pretreated at 300 °C for 22.5 min and gasified in a fluidized bed gasifier to study the effect of thermal pretreatment on its processing behavior. Untreated, pelletized SSF residue was gasified at the same conditions to establish the baseline processing behavior. Results indicate the thermal pretreatment process removes a substantial portion of the polar and non-polar extractives, with a resultant increase in the concentration of lignin, cellulose, and ash. Feed line plugging was not observed, although bed agglomeration occurred at similar rates for both feedstocks, suggesting that overall ash content is the most important factor affecting bed agglomeration. Benzene, phenol, and polyaromatic hydrocarbons in the tar were present at higher concentrations in the treated material, with higher tar loading in the product gas. Total product gas generation is lower for the treated material, although overall gas composition does not change.

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1. Introduction

The current utilization trends for petrochemical fuels is considered unsustainable, with numerous environmental [1], political [2], and economic [3] concerns. According to the 2014 Energy Information Administration reports, 76% of all petroleum consumed by the United States was used to produce liquid transportation fuels, with net imports equal to 5.3 million barrels per day [4]. In order to mitigate the impact the transportation industry has on petrochemical consumption, serious attention is being paid to the use of renewable biomass feedstocks capable of generating liquid transportation fuels [5]. An important concept being developed is the biorefinery. A biorefinery is similar to an oil refinery but uses renewable energy resources such as wood, dedicated bioenergy crops (switchgrass), agricultural residues (corn stover), and industrial residues (pulp and paper mill waste) as feedstocks in conversion processes that generate fuels, chemicals, heat, and power [6]. In order to meet the Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) Bioenergy Technologies Office's (BETO) performance goal of $3 (in 2011 dollars) per gallon gasoline equivalent (GGE) [7], efficient utilization of the three principle biomass components; cellulose, hemicellulose, and lignin, is required. Thermochemical conversion processes, such as gasification, present the opportunity to convert a wide range of whole biomass and waste materials into transportation fuels. Inexpensive, accessible feedstocks in the near term likely include waste (or side-stream) materials such as high lignin, high ash residues from conventional lignocellulosic ethanol production, or residues from pulp and paper manufacturing [8]. The feedstock investigated here is a high lignin corn stover residue (HLCSR) resulting from simultaneous saccharification and fermentation (SSF) of corn stover. Corn stover is an important waste stream from cornstarch based ethanol production,

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and due to its low commercial cost, widespread geographical accessibility, and high volume availability, it is considered an ideal candidate for an integrated biorefinery feedstock [9].

Biomass gasification is a high temperature partial oxidation process to convert lignocellulosic feedstocks to a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4) [10]. The mixture of CO and H_2, often referred to as "syngas", can then be used for synthesis of transportation fuels [11] or for the production of heat [12]. The use of high lignin feedstocks in fluidized bed biomass gasifiers, however, can be problematic, particularly at research/bench scales [13]. One of the issues identified is the tendency of the lignin to soften at elevated temperatures between 90 °C and 190 °C [14]. In the case of a biomass gasifier, where the bed operates at temperatures around 900 °C, the conduction of heat from the reactor into the injection system used to introduce the feedstock to the bed can lead to premature softening, cross-linking, and polymerization reactions [13]. When this happens, the resulting softened material causes agglomeration of the feedstock, and can quickly plug the injection system. Even when plugs are not formed, melting of lignin inside the fluidized bed can cause agglomerations of ash, sand, and charcoal which eventually lead to losses of bed fluidization [15].

The pyrolysis and gasification of lignin rich feedstocks has been the subject of intense research activity [16–21]. For many years, researchers at the University of Western Ontario [22] have studied novel approaches to feed and fluidize lignin rich feedstocks. Their slug injection system has shown promise for feeding lignin and high lignin feedstocks, although an ice water cooling jacket was still necessary on the feed lines. A mechanical stirring device was employed to prevent bed agglomeration [23]. Utilizing the residue from a SSF reactor has shown that pelletization of the feedstock combined with a cooling nitrogen (N_2) co-feed has been successful at overcoming feed line plugging; however the large particle size of the pellets leads to substantial bed agglomeration and a potential loss of bed fluidization [24].

One potential method of overcoming the drawbacks to the use of high lignin materials is to employ a thermal pretreatment (TPT) step to render the feedstock less susceptible to premature melting by increasing the softening point of the material [25]. TPT, also known as torrefaction, slow pyrolysis, mild pyrolysis, roasting, and deep drying [26], involves heating the feedstock in an inert atmosphere at temperatures typically ranging from 200 °C to 300 °C [27]. Studies by Bergman's group have shown that depolymerization of the hemicellulose and cellulose fractions is followed by volatilization of the intermediates [26,28]. The resultant volatiles are composed primarily of acetic acid, methanol, CO, CO_2, and furan derivatives [28]. Hemicellulose, the main reactant in torrefaction, is decomposed via a two-step mechanism starting with depolymerization followed by charring reactions of the remaining solid intermediates. Due to the very low levels of hemicellulose in the SSF digester residue, these reactions are considered minor in relation to the depolymerization and charring of cellulose, a process which takes place at low temperatures (<200 °C). At higher temperatures the decomposition of cellulose occurs faster and to a greater degree [29]. Although mass loss due to the partial devolatilization of the material is unavoidable, the energy content of the starting material is predominantly conserved.

The main goal of this study was to determine the effect of thermal pretreatment on the gasification behavior of a high lignin/ash corn stover SSF residue. It is hypothesized that the removal of a portion of the reactive volatiles during the pretreatment will overcome the tendency of the feedstock to plug within the feed lines, and eliminate the need to pelletize the feedstock and therefore overcome the propensity of the residue to agglomerate in the bed.

2. Materials and methods

2.1. Material characterization

The residue from an SSF [30] process using corn stover as the feedstock was obtained from the National Renewable Energy Laboratory (NREL) in Golden, CO, USA. Approximately half of the material received was then pelletized at the Idaho National Laboratory (INL) to a nominal particle size of −10 + 40 mesh. Pelletization of the SSF residues was necessary due to the fact that the residue as received is a fine powder (−60 mesh). Initial feed system studies showed that the auger feed system employed was unable to consistently meter the unpelletized residue. The feedstock was sent to Microbac Laboratories in Boulder, CO, for compositional analysis including ash, structural protein, polar and non-polar extractives, acid soluble and insoluble lignin, carbohydrates consisting of glucan, xylan, galactan, arabinan, and mannan, and acetyl content using the NREL Laboratory Analytical Procedures (LAP) NREL/TP-510-(42622, 42625, 42619, 42618). Ultimate analysis was performed by Columbia Analytical Services in Tucson, AZ, for C, H, N, O, and S content following the ASTM D5373 and D5291 methods [31,32]. Inorganic species were determined after digestion in a mixture of nitric and hydrofluoric acid, complexed with boric acid, and analyzed by ICP-AES [33].

Proximate analysis (20 mg) was performed via thermogravimetric analysis (TGA) using a Netzsch STA 409 C using a Pt/Rh sample pan from 30 to 600 °C at 10 °C/min under He (100 mL/min). The TGA was calibrated using 8 metals (Au, Ag, Al, Bi, In, Sn, Ni, and Zn). The data generated was used to calculate the proximate analysis for each sample consisting of moisture, volatiles, fixed carbon, and ash. Moisture content was defined as the mass loss up to 160 °C [34]. Volatiles were measured as the dry basis mass loss at 600 °C. Ash content of the starting material was measured separately in a furnace according to the NREL Laboratory Analytical Procedure NREL/TP-510-42622. This value was subtracted from the mass remaining at 600 °C to give the fixed carbon value.

Surface area was determined by the N_2 [35] Brunauer−Emmett−Teller (BET) method on degassed samples (under vacuum at 100 °C for 7 h) in triplicate using an AUTOSORB-6 Surface Area & Pore Size Analyzer (Quantachrome Instruments). Pore size and pore volume were estimated with the Horvath-Kawazoe (HK) method. The specific surface area was also determined by CO_2 adsorption, in triplicate, using a TriStar II plus automatic physisorption analyzer (Micromeritics Instrument Corporation, Norcross, GA) using 0.20 g of degassed sample (vacuum degassed for 4 h at 100 °C). Each isotherm was collected at 0 °C using 75 points between partial pressures of 0.00001 and 0.03. Total surface area and micropore volume (V_{mi}) were determined by the Dubinin-Radushkevick (DR) equation fit to data points between $2 < \log (P_0 P^{-1})^2 < 6$, where P is the equilibrium pressure at temperature T and P_0 is the saturated vapor pressure. Average pore width has been calculated from the characteristic energy given by the DR equation [36].

2.2. Thermal pretreatment

The unpelletized SSF residue was thermally pretreated in a continuous feed auger reactor. A processing temperature of 300 °C and residence time of 22.5 min was chosen based on previous work [25]. Calibration of the residence time was accomplished by filling the void fraction of the reactor with the same unpelletized SSF residue as that to be treated, injecting a spike of material, and recording the time until the material was seen exiting the reactor heating zone. A feed rate of 1.1 kg/hr and N_2 flow rate of 5 L/min were used. Weight loss during the process was calculated by