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Modelling of pretreatment and saccharification with different feedstocks and kinetic modeling of sorghum saccharification

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HIGHLIGHTS

- Data generated for high temperature alkali pre-treatment of 3 feedstocks.
- Effect of parameters studied on delignification extent, X_d & cellulose conversion, X.
- Individual and multi-feedstock models developed for X_d and X prediction.
- Generalized kinetic model developed for sorghum based enzymatic hydrolysis.
- All models shown to be reasonably accurate.

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ABSTRACT

Experiments have been performed for pretreatment of sorghum, wheat straw and bamboo through high temperature alkali pretreatment with different alkaline loading and temperatures, and the data on extent of delignification in terms of the final compositions of cellulose, hemicellulose and lignin have been generated. Further, enzymatic saccharification has been carried out in all the cases to find the extent of conversion possible after 72 h. The effect of different operating parameters on the extent of delignification and cellulose conversion are evaluated. This data is employed to develop a generalized multi-feedstock and individual feedstock based models which can be used to determine the extent of delignification and cellulose conversion for any and specific biomass respectively with alkaline pretreatment and similar enzyme conditions as considered in the present study. Also, a kinetic model is developed and validated for sorghum for cellulosic conversion.

1. Introduction

Second generation biofuels are the most sought-after today, given the drastic after-effects of extreme exploitation of fossil fuels in the past. The economic growth in India has been about 7 percent per annum since 2007 (ESI Web source, 2016), and simultaneously the demand for alternate forms of biofuel has also been growing. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. Bioethanol, as an alternative fuel energy resource, has been a subject of great interest since the oil crisis in the 1970s. Therefore, the second generation bioethanol, by utilizing non-edible biomass, is gradually attracting worldwide attention (Karimi et al., 2014). Hence other sources of fuels such as renewable surplus lignocellulose materials are under tremendous scrutiny to make them economically viable assets for commercial scale utilization. Studies are being conducted on non-edible crops such as sorghum straw, switch grass, poplar, silver grass, corn stover, wheat straw, rice straw, sugarcane bagasse, cotton stalk etc., to meet industrial and domestic energy requirements by enhancing their energy conversion efficiency (Liu et al., 2012). Tremendous potential of the non-edible crops grown in India has been identified, and efforts have been directed towards their growth. Sorghum, wheat straw and bamboo are some such prospective non-edible crops (Petti et al., 2013). Maharashtra, Karnataka, Madhya Pradesh and Andhra Pradesh have been reported to be the highest producers of sorghum in India, which in turn contributes largely to commercial

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Nomenclature

X_d	extent of delignification (%)
L_0	lignin content in raw biomass sample (% mass)
L_i	lignin content in biomass sample after pretreatment (% mass)
X	cellulosic conversion (%)
$(C/L)_{in}$	initial cellulose to lignin ratio
$(H/L)_{in}$	initial hemi-cellulose to lignin ratio
A	alkaline loading (%)
T	temperature (°C)
E	enzyme loading (FPU/gm cellulose)
$X_d^{\max}$	observed maximum extent of delignification (%)
$X_{\max}$	observed maximum cellulosic conversion (%)
k_1^d, k_2^d	parameters in individual and multi-feedstock based delignification models
k_1, k_2	parameters in individual and multi-feedstock based models for cellulosic conversion
AAD	average absolute deviation (%)
t	time (h)
τ	time constant (h)
k	first order rate constant (1/h)

scale production of second generation biofuels (Purohit and Fischer, 2014).

Production of biofuel from these non-edible plants essentially consists of three phases. They are pre-treatment, saccharification and fermentation. The major components of plants are cellulose (38–50%), hemicellulose (23–32%), and lignin (10–25%). Lignin is covalently linked to hemicelluloses, and it fills the spaces in the cell wall between cellulose and hemicelluloses giving the plant tissues vigor. Lignin thus forms a barrier during saccharification wherein the polysaccharides are acted upon by cellulosic enzymes and are broken down to their respective monosaccharides (Hu and Ragauskas, 2012). Hence, the biomass is pre-treated to structurally modify some lignocellulosic features such that it ensures increased xylan and glucan accessibility to the enzymes, and then subjected to saccharification, after which the products are fermented to synthesize ethanol. Many pre-treatment methodologies have been implemented over the years to enhance the yield of fermentable sugar during saccharification which include biological, physical, chemical and physico-chemical pre-treatments. The choice of pre-treatment greatly influences the effectiveness of the subsequent enzymatic hydrolysis during saccharification. Economically viable processes require less severe pre-treatment options but have reduced yields (Alvira et al., 2010).

Alkali pretreatment has been reported to have significant effect on the final composition of lignin, cellulose and hemicelluloses. Also, it is described to cause less sugar degradation than acid pre-treatment and it was shown to be more effective on agricultural residues than on wood materials (Sambusiti et al., 2013; Si et al., 2015). Studies have established the effectiveness of pairing up of alkali treatments with high temperatures in order to determine critical output biomass composition which might be apt for further saccharification treatments in case of different biomass feedstocks (McIntosh and Vancov, 2011; Yamashita et al., 2010). Although, presently a rise in numerous studies on the use of microwave assisted and ultrawave assisted pretreatment methodologies has been observed, the economic prospect of such approaches is questionable for large scale operations. Alkali pretreatment at high temperature, on the other hand, has been projected to have a more desirable ethanol yield when compared to other approaches such as acid treatment, hot water treatment or steam explosion treatment with a judicious economic front (Deepak and Murthy, 2011).

Two approaches reported in literature for the next two steps in bioethanol production are simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermentation (SHF) approaches. Although SSF approach has the advantage of reduction in operating time and less capital cost, the optimal temperature for the yeast and the cellulolytic enzymes differ, hence the conditions used in SSF cannot be optimal for both the enzymes and the yeast, and might therefore result in lower efficiency and lower product yield. Hence, for better efficiency of enzymatic hydrolysis, the SHF approach is preferred (Karin et al., 2007; Mehmood et al., 2009).

Modeling and simulation studies on conversion of lignocellulosic biomass to bioethanol have ranged from process level to kinetic and parametric effect models over the last few years. While the process level models have focused on evaluating techno-economically feasible options and energy efficient configurations, the unit level models have focused on performance evaluation with respect to the specific unit for a selected biomass feedstock or with a chosen pretreatment method (Rodriguez et al., 2011; Zhang et al., 2009; Mosier et al., 2005). Kinetic modeling studies have focused on specific biomass and/or specific pretreatment method, and have employed theoretical or empirical techniques for model development (Esteghlalian et al., 1997; Silverstein et al., 2007; Kadam et al., 2004).

The literature review indicates that although alkali pretreatment has been reported to result in very high delignification and cellulose conversions, the modeling studies for this pretreatment method are limited to a single biomass feedstock of cotton stalks (Silverstein et al., 2007). Further, simple kinetic models for cellulose hydrolysis with alkaline pretreatment are also not available in literature. Therefore, in the present study, experiments are conducted for alkali pretreatment using three different feedstocks of sorghum, wheat straw and bamboo, and also for their enzymatic hydrolysis. The effect of different parameters on the extent of delignification and cellulose conversion are evaluated. Multi-feedstock models are developed for pretreatment and final cellulose conversion, and kinetic model is developed for hydrolysis based on sorghum feed stock and the prediction performance of the models is illustrated.

2. Materials and methods

2.1. Chemicals

Raw material sorghum straw, bamboo and wheat straw biomass, procured from ICRISAT, Hyderabad were milled to get a size between 4 mm to 6 mm. Commercial biomass hydrolyzing enzyme complex, *Sacchari SEB*, gifted by Advanced Vital Enzymes Ltd, Thane was used for saccharification. Other AR grade chemicals, Sodium hydroxide (NaOH), Sodium citrate and citric acid were purchased from Sigma–Aldrich.

2.2. Biomass characterization

The compositional analysis of biomass (moisture, ash, extractives, cellulose, hemicellulose, and lignin) were quantified before