Solar assisted alkali pretreatment of garden biomass: Effects on lignocellulose degradation, enzymatic hydrolysis, crystallinity and ultra-structural changes in lignocellulose

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ABSTRACT

A comprehensive study was carried out to assess the effectiveness of solar assisted alkali pretreatment (SAAP) on garden biomass (GB). The pretreatment efficiency was assessed based on lignocellulose degradation, conversion of cellulose into reducing sugars, changes in the ultra-structure and functional groups of lignocellulose and impact on the crystallinity of cellulose, etc. SAAP was found to be efficient for the removal of lignin and hemicellulose that facilitated enzymatic hydrolysis of cellulose. FTIR and XRD studies provided details on the effectiveness of SAAP on lignocellulosic moiety and crystallinity of cellulose. Scanning electron microscopic analysis showed ultra-structural disturbances in the microfibrils of GB as a result of pretreatment. The mass balance closer of 97.87% after pretreatment confirmed the reliability of SAAP pretreatment. Based on the results, it is concluded that SAAP is not only an efficient means of pretreatment but also economical as it involved no energy expenditure for heat generation during pretreatment.

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1. Background

Bioprocessing of lignocellulosic biomass generally involves several sequential steps including lignocellulose pretreatment, enzymatic hydrolysis, and fermentation. Presently, the biggest technological and economic challenge in biomass processing is the cost-effective release of fermentable sugars from biomass materials (Himmel et al., 2007). The conversion of lignocelluloses into glucose is through hydrolysis for which lignin is the recalcitrant compound (Lawoko et al., 2006). Pretreatment is therefore necessary for the removal of lignin and to make cellulose amenable for enzymatic hydrolysis. It is one of the most expensive processing steps in bioethanol production with costs as high as 30$/gal ethanol produced which comprises 19% of total cost of cellulosic ethanol production (Mosier et al., 2005). Pretreatment processes which are in practice today are usually energy intensive or require hazardous chemicals which warrant the need of cost effective, and environmentally benign technologies for cellulosic ethanol industry.

Pretreatment of lignocellulosic substrates using acid or alkali is considered as effective for lignocellulosic pretreatment (Girio et al., 2010). However, requirement of high amount of acid or alkali along with the requirement of heat makes it cost intensive. Alternative technologies which are economic but efficient than conventional methods was therefore, formulated by various researchers such as Alkali-microwave (Hu and Wen, 2008), Alkaline wet oxidation (Martın et al., 2007), Autohydrolysis (Gullon et al., 2010), Ammonia fiber/freeze explosion (Sendich et al., 2008), Organosolv (Zhao et al., 2009), pH-controlled liquid hot water (Mosier et al., 2005), Ionic liquids (ILs) (da Costa Lopes et al., 2013; Tan et al., 2011) and High pressure CO_2–H_2O (Morais et al., 2014).

Supply of heat (thermal energy) is crucial for pretreatment process as it mediates bond breaking between molecules during chemical action (Gabhane et al., 2011). Generally, conventional heating devices such as burners, electric heaters, gas burners, and ovens are being employed to generate heat for pretreatment purposes. Utilization of such energy consuming devices in pretreatment is one of the reasons for the increased production cost of cellulosic ethanol.

Solar energy, radiant light and heat from the sun, has been harnessed by humans since ancient times using a range of ever evolving technologies. With the use of some devices such as solar concentrator, radiation collector, and wave length shifting radiation converters applicability of solar energy is increasing.

Nowadays, solar energy is widely used in water heaters, solar lights, solar cookers, milk and wine pasteurization as well as photocatalytical degradation of lignin in paper industries (Kansal et al., 2008). In the same manner, solar energy can also be used for the pretreatment of lignocelluloses. However, as the availability and intensity of sunlight is variable, solar mediated pretreatment cannot be a replacement for conventional technologies but it offers an alternative and cost effective means of lignocellulosic pretreatment in places where good amount of sunlight is available.

Solar energy consists of UV and visible radiation wherein UV is capable of breaking molecules. It has been reported that upon excitation with UV radiation, phenolic compounds in aerated aqueous solutions, undergo degradation yielding quinines, dimers and sometimes oligomers as major products (Mazelier et al., 1998). So, it is not surprising to note that photolysis of lignin conduces to similar degradations observed for phenols, even though non-phenolic elements are absorbing the excitation light. The wavelength range required for lignin degradation is generally of lower energy (between 300 and 400 nm) than for phenols (<300 nm). As the primary task of pretreatment is to remove lignin from lignocellulosic moiety, we tried SAAP pretreatment with a major objective of understanding the efficacy of alkali pretreatment under the influence of UV radiation.

2. Materials and method

2.1. Collection and processing of GB

GB consisting mostly of grasses, weeds and fallen leaves was collected from the garden area of National Environmental Engineering Research Institute (NEERI), Nagpur, India. It was sun dried initially for 2–3 days followed by oven drying at 70 °C for about 92 h in a hot air oven. The dried GB was powdered in a pulverizer to pass a 0.250 mm sieve and stored in polythene sample containers for further experiments. A minimum of three replicates were maintained for all analysis and the mean values are reported.

2.2. Solar concentrator

A parabolic solar concentrator was procured from PRINCE, Suman Foundation, Dhule, India. The heating capacity of the solar concentrator was 4.744 kJ/min, calculated by $Q = m * cp * \Delta T$. where Q = heat capacity, cp = specific heat, and ΔT = change in temperature. The intensity of UV radiation at the focal point (apex) of concentrator was 25 μW/cm^2 (measured using UV light meter, Lutron, UV 340 A). The positioning of parabola was adjusted time to time (approximately 10 min interval) to fix the apex at the center of reactor.

2.3. Pretreatment of GB using different means of heating

For solar assisted alkali pretreatment (SAAP),10 g of powdered substrate (GB) was taken in a 500 ml conical flask and added with 100 ml of 0.25%, 0.5%, 1%, 2%, 4%, 6%, 8% and 10% of NaOH (W/V). The contents were mixed well and placed on a parabolic solar concentrator for heating at different (0, 15, 30, 60, and 90 min) durations. Simultaneously, other means of pretreatments such as hotplate assisted alkali pretreatment (HAAP), autoclave assisted alkali pretreatment (AAAP) and microwave (Ethos 900, Italy) assisted alkali pretreatment (MAAP) were also carried out. The reaction temperature for SAAP and HAAP was 100 °C, whereas AAAP was performed at 121 °C and MAAP performed at 200 °C. The reaction temperature for autoclave and microwave was fixed on the basis of our previous experiments (Gabhane et al., 2011, 2014a,b). The content was neutralized after cooling using 1–10%

H_2SO_4 to pH 7. The neutralized mixture was filtered through Whatman filter paper 42. The solid retained on filter paper was repeatedly washed with de-ionized water, dried at 50 °C and subjected to compositional analysis using standard protocols as per Section 2.4.

2.4. Estimation of cellulose, hemicellulose and lignin degradation rates

Pretreated substrate (GB) was analyzed for cellulose content by HNO_3 ethanol method (Liu, 2004). The lignin and hemicellulose contents were estimated by Liu method (Liu, 2004). The actual degradation (%) of cellulose, hemicellulose and lignin was calculated on the basis of solid recovery:

$$\text{Solid recovery}(\%) = \frac{\text{Dry weight of sample after pretreatment}}{\text{Dry weight of raw sample used for pretreatment}} \times 100 \tag{1}$$

The cellulose, hemicellulose, and lignin in recovered solid after pretreatment were calculated as:

$$\text{Cellulose recovery} = \frac{\text{Conc.(\%) of cellulose after pretreatment} \times \text{solid recovery}}{\text{Dry weight of raw sample used for pretreatment}} \tag{2}$$

Similarly hemicellulose and lignin recovery rates were also calculated.

The actual loss of cellulose was calculated by subtracting cellulose recovery from initial cellulose concentration of substrate

$$\text{Actual loss of cellulose} = \text{Initial conc. of cellulose} - \text{cellulose recovery} \tag{3}$$

$$\text{Actual cellulose loss}(\%) = \frac{\text{Actual loss of cellulose}}{\text{Initial conc. of cellulose}} \times 100 \tag{4}$$

Similarly, actual loss% of hemicellulose and lignin was calculated.

2.5. Crystallinity measurements on raw and pretreated GB samples

Both raw and pretreated GB samples were subjected to X-Ray Diffraction (XRD) analysis using X-ray diffractometer [Rigaku (Miniflex-ll), Japan]. Approximately 50 mg of sample was pressed in a specified sample holder and scanned at 2°/min from $2\Theta = 10–30°$. The crystallinity index (Cr) was calculated from the XRD patterns by the empirical method proposed by Nelson and O'Connor (1964) using the following equation:

$$\text{CrI} = \frac{I_{002} - Iam}{I_{002}} \tag{5}$$

where CrI is the crystallinity index, I_{002} is the maximum diffraction intensity at peak position $2\Theta \sim 22.6°$ and Iam is the intensity at $2\Theta = 18.7°$.

2.6. FTIR analysis of pretreated GB samples

The properties of reaction products were characterized by Fourier Transform Infrared Spectroscopy (FTIR) (Bruker, Vertex 70, Germany). The analysis was carried out using a diffuse reflectance accessory with KBr as standard. For sample preparation 20 mg of KBr was ground with 1 mg of sample and kept in a sample holder and used for analysis. The sample mixture was scanned in the MIR (Middle infrared) range from 4000 cm^{-1} to 400 cm^{-1} at a spectral resolution of 4 cm^{-1}.

2.7. SEM analysis of GB samples

Scanning electron microscope (SEM) studies were conducted to analyze ultrastructural changes and surface characteristics of