Applied Energy 113 (2014) 97–105

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Eco-friendly dry chemo-mechanical pretreatments of lignocellulosic biomass: Impact on energy and yield of the enzymatic hydrolysis ☆

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HIGHLIGHTS

- Innovative dry NaOH chemo-mechanical pretreatment was developed.
- Dry (TS_{dry}) and dilute (TS_{dilute}) NaOH chemo-mechanical pretreatment were compared.
- TS_{dilute} consumed higher amounts of water and energy compared to TS_{dry}.
- Energy efficiency obtained for TS_{dilute} was 0.417 kg glucose kW h^{-1} and 0.888 for TS_{dry}.

ARTICLE INFO

Article history:
Received 22 March 2013
Received in revised form 6 June 2013
Accepted 4 July 2013

Keywords:
Lignocellulosic biomass biorefinery
Dry pretreatment
Size reduction
Energy efficiency

ABSTRACT

In this study, we developed an eco-friendly dry alkaline chemomechanical pretreatment of wheat straw without production of waste and liquid fractions with objective to save energy input, to decrease the environmental impact and to increase enzymatic hydrolysis.

Wheat straw was pretreated with NH_3, NaOH—H_2O_2, NH_3—H_2O_2 and NaOH at high materials concentration (5 kg/L) equivalent to biomass/liquid ratio of 1/5 (dry chemomechanical) and at low materials concentration (0.2 kg/L) equivalent to biomass/liquid ratio of 5/1 (dilute chemomechanical). Untreated and chemical treated wheat straw samples were subjected to grinding and milling following by enzymatic hydrolysis with commercial cellulases.

NaOH and NaOH—H_2O_2 dry chemomechanical pretreatments were found to be more effective in decreasing the particle size and energy consumption and increasing the surface area. However, alkaline dilute-chemomechanical treatments consumed higher amounts of water (5 L water/1 kg biomass) and energy compared to dry-chemomechanical treatments. In point of fact, the lowest energy efficiency obtained was 0.417 kg glucose kW h^{-1} for dilute-chemomechanical treatments compared to 0.888 kg glucose kW h^{-1} glucose kW h^{-1} for dry-chemomechanical treatments.

Alkaline dry-chemomechanical pretreatments approach appears more attractive and efficient in terms of glucose, energy efficiency and environmental impact, compared to conventional alkaline chemomechanical pretreatments.

1. Introduction

The pretreatment of lignocellulosic biomass prior to enzymatic attack is an essential step in order to increase cellulose and hemicelluloses accessibility and biodegradability [1,2]. Application of pretreatment steps allows modifying the supramolecular structures of cellulose–hemicellulose–lignin matrix, thereby changing the natural binding characteristics of lignocellulosic materials and increasing the holocelluloses accessibility for enzymatic or biological action.

A large number of pretreatment methods have been developed until now [3–7]. Some chemical, physico-chemical, physical and mechanical pretreatments are known to be effective, but that these methods have some disadvantages in terms of energy consumption or energy input, corrosion of processing tools, introduction of inhibiting effects, the number of separation and purification steps, etc. The performance of pretreatments step mainly depends on the energy input and output and the environmental impact. The current use of a high amount of water, solvents are in part responsible for the cost of pretreatment steps in lignocellulose biorefineries and a negative environmental impact [2].

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0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.07.015

The mechanical pretreatments allow in an improved depolymerization of saccharides during hydrolysis and improved total digestibility without production of wastes. For example, studies have shown that particles sizes must be reduced to 0.5–2 mm in order to decrease heat and mass transfer limitations and to reach a well-accepted level of digestibility. Unfortunately, mechanical size reduction steps are not cost-effective because of too high energy requirements [2]. Alkaline and acidic ones have been more studied for many years in order to increase enzymatic accessibility. Acid pretreatment is used for removing hemicelluloses and solubilize cellulose [8–10]. Among chemical reagents, sulfuric acid is the most applied acid. Acid pretreatment can be performed either at low temperature with concentrated acids or at high temperature with diluted acids. Concentrated acids (typically 72% H_2SO_4 at low temperature) usually lead to the conversion of at least 90% of the potential glucan in the biomass into glucose. However, they are corrosive and toxic and need to be recovered after pretreatment to make the process economically feasible. Dilute acids (2–5% H_2SO_4) at high temperature (120–200 °C) for a few minutes are typically employed but consume more the energy compared to concentrated acids. Alkaline pretreatments, performed by using bases such as sodium, potassium, calcium are effective in altering the structure of lignin, thus increasing the enzymatic accessibility to cellulose and hemicelluloses [11–14]. Calcium hydroxide or sodium hydroxide pretreatments were shown to be effective at a lower temperature than that used in acid treatment but the time required is of the order of hours or days rather than the minutes or seconds needed for acid pretreatment. In general, these conventional pretreatments conducted at low materials concentration (biomass/liquid ration varied between 1/5 and 1/20) consumed more the energy especially at high-temperature, and high quantity of water and generate many toxic effluents.

To overcome the limitations of the individual operations, the pretreatment procedure can be conducted by a duplex mode combining mechanical size reduction with moderate chemical or physicochemical co-treatments. This dual pretreatment procedure may reduce energy consumption, and increase enzymatic accessibility. Some studies indicate clearly that the coupling of chemical- or physicochemical co-treatment with mechanical size reduction is very important for the reduction of the energy consumption in plants biorefinery [2,14–18].

To reduce mechanical energy consumption for wood size reduction through milling, Zhu and Pan [18] proposed an approach of post-chemical pretreatment size-reduction (post-chemical pretreatment → size reduction → saccharification). The benefits in energy savings achieved using this post chemical pretreatment size-reduction approach is significant (50 Wh/kg wood) compared to (150–850 Wh/kg wood) for conventional size reduction-chemical pretreatment (size reduction → chemical pretreatment → saccharification).

The total energy consumption during post-chemical pretreatment size-reduction approach also includes thermal energy used for thermochemical pretreatments, drying and mechanical energy. The thermal energy depends on the liquid/biomass ratio and pretreatment temperature [18]. As a consequence, the thermal energy consumption for pretreatments is almost linearly proportional to liquid/biomass ratio; thus, reducing liquid/biomass ratio is very much needed in order to improve energy efficiency and to reduce waste production and water consumption. The biomass are mostly wet after chemical or physicochemical co-treatment conducted at dilute concentration or at high moisture content (>50%). Drying energy is the energy need to dried wet biomass to about 8–15% of moisture content before grinding and milling. Milling or grinding biomass at high moisture content is very difficult and consume more the energy compared to dry biomass. Therefore, drying to low moisture contents is problematic and has not been optimized for biomass conversion [19]. Drying biomass from high moisture (biomass chemically co-treated at low materials concentration) to low moisture contents require more energy, which increased energy input and decreased energy efficiency.

Such problems open a significant opportunity for dry physicochemical and chemical "solid state" pretreatments (high moisture content and high materials concentration) combined with mechanical size reduction, because the liquid/biomass ratio is very low in this case. Moreover, dry physicochemical and chemical pretreatments may be used directly in a downstream process without separation, washing and drying led to decrease of dried and thermal energy and as a consequence in decrease of energy input for lignocellulosic biomass pretreatments without waste production.

In this article, we report on the development of an innovative dry chemomechanical pretreatment of biomass by coupling alkaline co-treatment conducted at high concentration (5 kg/L) with mechanical treatment. The objectives of this study was to investigate the effect of alkaline pretreatment (25 °C) at high materials concentration (5 kg/L) coupled to mechanical treatment on energy efficiency compared to conventional or dilute chemo-mechanical treatment realized at low materials concentration (0.2 kg/L).

2. Materials and methods

2.1. Raw material

Wheat straw was obtained from a local farm (Languedoc-Roussillon region, France). Wheat straw was coarsely cut to less than 2 mm by knife milling (Retsch SM 100, Germany). The cut wheat straw was pretreated by NaOH, NH_3, and a mixture of NaOH—H_2O_2 and NH_3—H_2O_2.

2.2. Chemical treatment

Sodium hydroxide (NaOH), ammoniac hydroxide (NH_3OH) and a mixture of NaOH—H_2O_2 (hydrogen peroxide) and NH_3—H_2O_2 were dissolved in distilled water to adjust the alkaline concentration at 5% w/w (5 g of catalyst/100 g of wheat straw). The alkaline solutions were also made with amounts of water required to adjust the moisture content of 100 g of wheat straw to 30% (dry basis) equivalent to biomass/liquid ratio of 5/1 and a high materials concentration of 5 kg/L called "dry chemical treatment". Two control samples (T_0 and TS_{dilute}) were used in this study (Table 1). For T_0 sample, wheat straw was treated with water at high material concentration (5 kg/L) in the same condition and TS_{dilute} sample was treated with 5% w/w of NaOH at dilute concentration (0.2 kg/L) equivalent to biomass/liquid ratio of 1/5 called "dilute chemical treatment". The treated biomass were equilibrated for 5 h at ambient conditions (25 °C) and then dried at 105 °C to 8–10% moisture content and the drying energy (E_{DY}) requirement was calculated.

2.3. Mechanical treatment

Untreated and chemical treated cut milled wheat straw samples (1–4 mm) at moisture content of 8–10% were subjected to centrifugal milling (Retsch, ZM 200) using 0.25 mm screen size. Five grams of untreated and chemical treated centrifugal milled wheat straw was then added to a 20-ml milling cup containing 2 stainless steel balls (diameter 2 cm) and milled (Retsch, MM 400) for 2 min at room temperature. After centrifugal and ball milling, the size of control and pretreated wheat straw was analyzed by laser granulometry (MASTERSIZER 2000, Malvern Instrument). Density of particle was determined using a pycnometer (ULTRA PYCNOMETER 1000, Quantachrome Instrument).