Bioresource Technology 226 (2017) 9–17

Contents lists available at ScienceDirect

Bioresource Technology

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

Techno-economic comparison of centralized versus decentralized biorefineries for two alkaline pretreatment processes

Ryan J. Stoklosa [a,b], Andrea del Pilar Orjuela [a], Leonardo da Costa Sousa [a,b], Nirmal Uppugundla [a,b], Daniel L. Williams [a,b], Bruce E. Dale [a,b], David B. Hodge [a,b,c,d,*], Venkatesh Balan [a,b,*]

[a] *Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA*
[b] *Great Lakes Bioenergy Research Center, Michigan State University, USA*
[c] *Department of Biosystems and Agricultural Engineering, Michigan State University, East Lansing, MI 48824, USA*
[d] *Division of Sustainable Process Engineering, Luleå University of Technology, Luleå, Sweden*

HIGHLIGHTS

- A techno-economic analysis (TEA) compared two biorefinery processing scenarios.
- Decentralized biorefineries employing AFEX require the highest capital cost.
- A centralized biorefinery using AHP has lower capital cost but higher water use.
- The best-case AFEX scenario yields the lowest minimum ethanol selling price (MESP).
- Biomass cost and alkali recovery exert a significant impact on MESPs.

ARTICLE INFO

Article history:
Received 1 October 2016
Received in revised form 21 November 2016
Accepted 22 November 2016
Available online 30 November 2016

Keywords:
AFEX
AHP
Pretreatment
Enzyme hydrolysis
Biorefinery
Techno-economic analysis

ABSTRACT

In this work, corn stover subjected to ammonia fiber expansion (AFEX™)[1] pretreatment or alkaline pre-extraction followed by hydrogen peroxide post-treatment (AHP pretreatment) were compared for their enzymatic hydrolysis yields over a range of solids loadings, enzymes loadings, and enzyme combinations. Process techno-economic models were compared for cellulosic ethanol production for a biorefinery that handles 2000 tons per day of corn stover employing a centralized biorefinery approach with AHP or a decentralized AFEX pretreatment followed by biomass densification feeding a centralized biorefinery. A techno-economic analysis (TEA) of these scenarios shows that the AFEX process resulted in the highest capital investment but also has the lowest minimum ethanol selling price (MESP) at $2.09/gal, primarily due to good energy integration and an efficient ammonia recovery system. The economics of AHP could be made more competitive if oxidant loadings were reduced and the alkali and sugar losses were also decreased.

1. Introduction

Over the past years the quest for energy security has led to the search for alternative sources of fuels, and as a response to this, liquid biofuels such as corn starch and sugar cane-derived bioethanol and plant oil-derived biodiesel have emerged as alternatives to fossil fuels. Corn ethanol is the predominant biofuel produced in the United States; but its future growth is now sharply limited, given that ethanol production now consumes over one-third of the U.S. corn crop and that the blend wall of 10% of U.S. domestic gasoline has been reached (Hess et al., 2015). An alternative approach to producing liquid biofuels involves a chemical pretreatment of lignocellulosic feedstocks followed by enzymatic hydrolysis of the cell wall polysaccharides to monomeric sugars and fermentation to a metabolite such as ethanol. These renewable liquid biofuels generated from lignocellulosic biomass offer the potential to achieve a lower net greenhouse gas generation relative to fossil-derived fuels and contribute to rural economic development (Souza et al., 2015). Identified challenges to the widespread deployment of cellulosic biofuels include technological challenges such as feedstock logistics (Hess et al., 2009), solids handling during pretreatment and hydrolysis (Lamers et al., 2015), and mixed sugar fermentation in the presence of inhibitors (Sato et al., 2014), while economic challenges include a substantially higher

---

* Corresponding authors at: Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA.

E-mail address: hodgeda@egr.msu.edu (D.B. Hodge).

[1] AFEX™, is a trademark of MBI International.

http://dx.doi.org/10.1016/j.biortech.2016.11.092
0960-8524/

capital cost per unit of biofuel produced relative to sucrose or starch-derived biofuels (Humbird et al., 2011).

A diverse range of pretreatment chemistries have been investigated over the past several decades (Ong et al., 2014), while all of the recently built cellulosic ethanol plants use either dilute acid or hydrothermal pretreatment, with the exception of DuPont's Nevada, Iowa plant, which employs a dilute aqueous ammonia pretreatment. Pretreatment technologies under investigation at the Great Lakes Bioenergy Center (GLBRC) include alkaline pretreatments such as Ammonia Fiber Expansion (AFEX™) pretreatment (Dale, 1986) and alkaline hydrogen peroxide pretreatment (AHP) (Banerjee et al., 2012). In the AFEX process, biomass with different moisture content (20–60% dry weight basis) is contacted with gaseous ammonia at approximately 1:1 (kg/kg) ammonia to biomass loading, temperatures between 40 and 120 °C and residence times between 10 and 60 min followed by rapid pressure release (Balan et al., 2010). During pretreatment, ammonolysis and hydrolysis reactions cleave the ester crosslinks between cell wall biopolymers (Chundawat et al., 2010, 2011), while the sudden pressure release also relocates lignin onto the biomass surface resulting in four to five fold improvements in the hydrolysis yields (Jin et al., 2013).

AHP pretreatment employed as a one-stage delignifying pretreatment has been demonstrated to be highly effective at improving the subsequent enzymatic hydrolysis yields of grasses such as corn stover, wheat straw, and switchgrass (Banerjee et al., 2012, 2011; Gould, 1984; Li et al., 2012). For conventional AHP pretreatment, biomass is treated with H_2O_2 at ambient temperature and pH 11.5 which primarily targets the removal of cell wall lignin. However, a drawback limiting economic efficacy of this as a one-step process is that H_2O_2 loadings of greater than 0.10 kg per kg biomass must be employed to realize any incremental improvement over low temperature NaOH-only pretreatment (unpublished data), presumably due to non-productive oxidation of lignins already solubilized by the alkali. We've recently adapted a two-stage pretreatment whereby alkali pre-extraction using NaOH at mild temperature and low alkali loadings is followed by solid-liquid separation to remove a fraction of the pre-extraction liquor. This pre-extraction liquor contains inorganics derived from the pretreatment and organics solubilized from the biomass that include extractives, acetate, *p*-hydroxycinnamic acids, lignins, and xylan. Options for utilization of this stream include concentration and combustion for generation of process heat and alkali recovery, recovery of soluble cell wall biopolymers for further valorization, utilization as a carbon source for anaerobic digestion, or animal feeds. This pre-extraction is followed by a second stage AHP delignification at low H_2O_2 loadings (Liu et al., 2014). This approach substantially improves the sugar hydrolysis yields (>95% hydrolysis yields of glucose) from corn stover at low enzyme loadings (15 mg protein per g biomass) and requires relatively low alkali loadings for pre-extraction (<100 mg NaOH per g biomass at 80 °C), and substantially lower H_2O_2 loadings in the subsequent AHP pretreatment step (25 mg H_2O_2 per g biomass) than a comparable single-stage AHP pretreatment (Liu et al., 2014). This approach can be considered as comparable to the existing commercial practice of soda pulping of non-woody agricultural residues followed by oxygen delignification or bleaching (Mohta et al., 1998). Recently constructed commercial lignocellulosic biorefineries employing these conversion pathways in the U.S., Europe, and Brazil operate at the scale of 12–30 M gal ethanol per year (Davison et al., 2015), processing from 65,000–375,000 dry tons of biomass per year (~200–1000 dry tons per day). It is envisioned that large, centralized biorefineries may need to operate at the scale of up to 2000 tons per day to obtain greater benefit from the capital investment due to economies of scale (Humbird et al., 2011). Decentralized biomass aggregation and pre-processing facilities feeding larger centralized biorefineries have also been proposed as solutions to the challenges associated with feedstock logistics (Egbendewe-Mondzozo et al., 2013). As one example, decentralized, depot-scale pre-processing employing AFEX pretreatment and densification via pelletization could provide feedstock-associated benefits that include increased bulk density by 8–10-fold, facilitating transportation, storage, and subsequent year-round supply as well as decreasing the sensitivity to supply chain disruptions and potentially yielding a product with additional applications (e.g., a high-digestibility ruminant feed) (Campbell et al., 2013; Lamers et al., 2015).

Techno-economic analysis (TEA) has been applied to compare AFEX with other pretreatments such as dilute acid, ammonia recycle percolation (ARP), liquid hot water and lime (Eggeman and Elander, 2005; Kazi et al., 2010), while recently the economic benefits of de-centralized AFEX pretreatment and pelletization have been assessed (Campbell et al., 2013; Lamers et al., 2015; Sarks et al., 2016). While no TEA has been done for AHP pretreatment, other work has investigated the integration of alkaline pre-extraction followed by dilute acid pretreatment of corn stover and identified economic benefits associated with this two-stage process (Tao et al., 2012). As such, the scope of this work includes both an experimental assessment of the effects of enzyme and solids loading on enzymatic hydrolysis yields for AFEX and AHP pretreated corn stover and a TEA for these two pretreatments in a biorefinery processing 2000 tons of corn stover per day to ethanol. For the AFEX pretreatment a de-centralized biorefinery approach was used, where the biomass is pre-processed and pretreated at depots and then sent to a centralized biorefinery for saccharification and fermentation. The AHP pretreatment on the other hand was modeled in a centralized biorefinery scheme. The costing of equipment required for enzymatic hydrolysis, fermentation, ethanol recovery and waste water treatment was performed based on the NREL model (Humbird et al., 2011). Results obtained from the enzymatic hydrolysis of the pretreated biomass at different solid and enzyme loadings determines the minimum ethanol selling price (MESP) for both processes. Finally, a sensitivity analysis investigated the relationship between the costs of the biomass, alkali, oxidant, and alkali recovery on the MESP. As a result, we have identified the MESP required for each of these pretreatments and have also identified bottlenecks for both the pretreatment process that must be addressed in order to develop cost-effective pretreatment processes at commercial-scale biorefinery facilities.

2. Methods

2.1. Biomass

Low cob corn stover (*Zea mays* L. Pioneer hybrid 36H56) was used for both pretreatments. The biomass was grown and harvested in 2009 on Field 570-C Arlington Research Station, (Arlington, WI) and milled to pass a 5-mm screen (Circ-U-Flow model 18-7-300, Schutte-Buffalo Hammermill, LLC). The composition of the untreated biomass was determined using NREL/TP-510-42618 (Crocker, 2008).

2.2. Pretreatment

AFEX pretreatment of the corn stover was conducted at 100 °C with a 1:1 ammonia to biomass loading and 60% moisture (dry basis) for 30 min residence time in a packed bed reactor system as reported previously (Campbell et al., 2013). AHP pretreatment with alkaline pre-extraction of corn stover was performed in a stationary stainless steel vessel with initial mixing only. Pre-extraction was performed at 80 °C for 1 h using 80 g of NaOH with 1 kg of biomass and a total liquid volume of 5 L (20% w/v). Follow-