Bioresource Technology 271 (2019) 218–227

Contents lists available at ScienceDirect

Bioresource Technology

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

# Simultaneous application of predictive model and least cost formulation can substantially benefit biorefineries outside Corn Belt in United States: A case study in Florida

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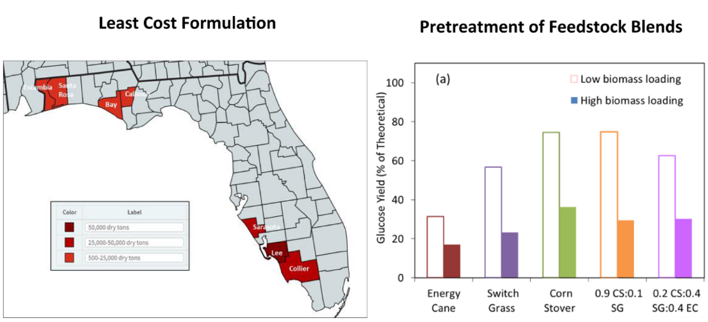
## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Keywords:*
Predictive model
Least Cost Formulation (LCF)
Biomass blends
Impact analysis
Fermentation

## ABSTRACT

Previously, a predictive model was developed to identify optimal blends of expensive high-quality and cheaper low-quality feedstocks for a given geographical location that can deliver high sugar yields. In this study, the optimal process conditions were tested for application at commercially-relevant higher biomass loadings. We observed lower sugar yields but 100% conversion to ethanol from a blend that contained only 20% high-quality feedstock. The impact of applying this predictive model simultaneously with least cost formulation model for a biorefinery location outside of the US Corn Belt in Lee County, Florida was investigated. A blend ratio of 0.30 EC, 0.45 SG, and 0.25 CS in Lee County was necessary to produce sugars at high yields and ethanol at a capacity of 50 MMGY. This work demonstrates utility in applying predictive model and LCF to reduce feedstock costs and supply chain risks while optimizing for product yields.

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https://doi.org/10.1016/j.biortech.2018.09.103
Received 3 July 2018; Received in revised form 17 September 2018; Accepted 18 September 2018
Available online 21 September 2018

## 1. Introduction

Bio-based manufacturing in the United States, thus far, has relied heavily on optimizing processing conditions for a single feedstock source, such as corn stover. This approach limits establishing biorefineries in geographical areas that have access to substantial lignocellulosic biomass, but from varying feedstock sources. For example, more than 1 million dry tons of orchard and vineyard prunings were available in Florida for biofuel production in 2016 (Langholtz et al., 2016). INEOS Bio was the first commercial-scale cellulosic ethanol plant established in 2013 to convert Florida's different sources of feedstocks including vegetative wastes, agricultural wastes, and municipal solid wastes (Jose and Bhaskar, 2015; Lubowski et al., 2002). The Idaho National Laboratory (INL) has been developing a Least Cost Formulation (LCF) model to identify geographical areas across the United States that present such increased availability of low-cost feedstocks and thereby opportunities of biomass blending (Ray et al., 2017; Sun et al., 2015; Williams et al., 2016). Researchers at the Advanced Biofuels Process Development Unit (ABPDU), Lawrence Berkeley National Laboratory (LBNL) further investigated recommendations from LCF, but from a bio-processing point-of-view, by optimizing feedstock ratios in blends and the associated conversion conditions to achieve high yields and/or lower costs. A collaboration among researchers from ABPDU, INL, and Sandia National Laboratories (SNL) helped develop a predictive model that could rapidly identify optimal feedstock ratios in tandem with optimal deconstruction parameters in a given geographic area (Narani et al., 2017).

The geographical area chosen for this predictive model development was Lee County in Florida, primarily because it is situated further away from the Corn Belt and has access to an abundant but recalcitrant feedstock, energy cane (EC). Per LCF, switchgrass (SG) was also abundantly available in the region and could be easily incorporated into a blend. Corn stover (CS) was chosen to also be a part of the blends as it was assumed it to be representative of a high-quality feedstock in this study. The singular feedstocks and biomass blends were pretreated with either dilute acid or dilute alkali or ionic liquid (IL) followed by enzymatic hydrolysis and then measured for sugar yields. When pretreated with dilute alkali, we observed that a 1:9 biomass blend of EC and CS led to glucose yield of 71.22% (of theoretical). This yield was similar to that from CS alone, at 74.6% (of theoretical), making the blend more preferable in lowering feedstock costs for lignocellulosic sugar production in a biorefinery (Narani et al., 2017). Similarly, a 0.4: 0.4: 0.2 blend of EC, SG, and CS led to a sugar yield of 62% (of theoretical), higher than those observed from EC or SG alone, at 31.46% and 56.78% (of theoretical). Based on these and other results, we developed a predictive model and presented it through an interactive ternary chart that enabled rapid and simultaneous optimization of biomass blends and associated pretreatment conditions. The model itself was validated by independent studies. The ability to instantaneously access predictions from a valid model that can substantially reduce biomass costs also reduces supply chain risks for a biorefinery. The petroleum industry has long been utilizing such models to be able to promptly tune their processing parameters per feedstock variability (Hsu and Robinson, 2007; Hu et al., 2002).

This predictive model was generated from deconstruction studies conducted only at a low biomass loading (LBL); 10% (w/w) dry untreated biomass in slurry during pretreatment and approximately 4% (w/w) dry untreated biomass in hydrolysis slurry. Many lab-scale deconstruction studies are conducted at LBL (Li et al., 2010; Lloyd and Wyman, 2005; Uppugundla et al., 2014; Wyman et al., 2005a; Wyman et al., 2005b), but for this model to be useful in real-world scenarios, it is necessary that the model's predictions are applicable in commercial scale setting for bio-based manufacturing (Li et al., 2013; Sadhukhan et al., 2014; Tao et al., 2014). High biomass loading (HBL) of 30% (w/w) during pretreatment and 20% (w/w) enzymatic hydrolysis are commonly applied in commercial scale bio-based manufacturing (Humbird et al., 2011). Lower water concentration and consequently reduced heat capacity and reactor volume requirements coupled with higher sugar concentrations in hydrolysates are necessary for economical operation of a biorefinery (Humbird et al., 2011). To ensure that this model is applicable in real-world scenarios, in this study, some of the model's predictions were tested at higher biomass loading (HBL) of 30% (w/w) during pretreatment and 12% (w/w) enzymatic hydrolysis. Further, the quality of sugars in these HBL hydrolysates was tested through fermentation to ethanol.

The 0.4:0.4:0.2 EC, SG, and CS blend, comprised mostly of local feedstocks – EC and SG, will have lowered feedstock transportation costs. These lower upfront costs could possibly negate the lower sugar yield of 62% (of theoretical) from this blend, compared to 74.6% (of theoretical) from CS. To investigate this possibility, which compares feedstock quality and transportation costs, in this study, the predictions from this model were integrated with those from LCF by performing an impact analysis. Without such an analysis, we are unable to determine the value of employing the models. This manuscript also briefly probes process economic implications of these models by simulating the results from downstream fermentation studies into a techno-economic analysis (TEA) model. Performing HBL deconstruction studies, testing hydrolysates in fermentations, integrating LCF and predictive model, and performing TEA was necessary to establish a robust modeling platform for commercial-scale bio-based manufacturing.

## 2. Materials and methods

### 2.1. Feedstocks and high solid loading pretreatment

Information on feedstocks used in this study was provided in Narani et al. (2017). Experimental details associated with LBL pretreatment and enzymatic hydrolysis conducted for model development were also provided in Narani et al. (2017). The 10 best sugar yielding feedstock and treatment combinations observed during model development, five each with dilute alkali and IL pretreatment catalysts, were applied for HBL pretreatments and enzymatic hydrolysis; treatment conditions and biomass blends are listed in Table 1. Reaction temperatures were scaled for each pretreatment: Dilute alkali (1–100%) 55–120 °C, IL (1–100%) 120–160 °C. as per Narani et al. (2017). Similarly, reaction times were also scaled: Dilute alkali (1–100%) 1–24 h, IL (1–100%) 1–3 h (Narani et al., 2017).

HBL was administered at 30% (w/w) untreated dry biomass in slurry during pretreatment. HBL alkali slurries were prepared by mixing, in 250 mL Pyrex Erlenmeyer flasks, 30 g of dry biomass with 70 g of water containing 1% (w/w) sodium hydroxide. All pretreatments were conducted by placing the flasks either in an autoclave (Primus Sterilizer, Omaha NE, Model# PSS5-G.1-MSSD) to reach 120 °C or a convection oven for the two other reaction temperatures of 65 and 107 °C (Binder, Bohemia, NY). Enzymatic hydrolysis was then performed on alkali pretreated residual solids without any washing, but diluted to 2.5× on mass basis, thereby making solids loading in the hydrolysis step equivalent to 12% (w/w) untreated dry biomass. The hydrolysis procedure and the ratio of other reagents were the same as described in Narani et al. (2017), except hydrolysis was conducted in larger 250 mL Erlenmeyer flasks. An enzyme loading of 11 mg protein/g glucan in untreated biomass, same as in Narani et al. (2017), was administered.

IL biomass slurries at 30% (w/w) were prepared by mixing 30 g of dry biomass with 70 g of 1-ethyl-3-methylimidazolium acetate (EmimAcetate or [C2mim][oAc]) in pure form in a 500 mL Globe reactor (Syrris, UK). The reactor was stirred at 200 rpm with overhead anchor impeller that held a shaft with blades made of Polytetrafluoroethylene. Once the slurry appeared homogeneous, oil from an oil bath was circulated in the reactor jacket to maintain the slurry at desired pretreatment reaction temperature. Julabo temperature control unit (Allentown, PA) was used to regulate the temperature