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Impact of hardwood species on production cost of second generation ethanol

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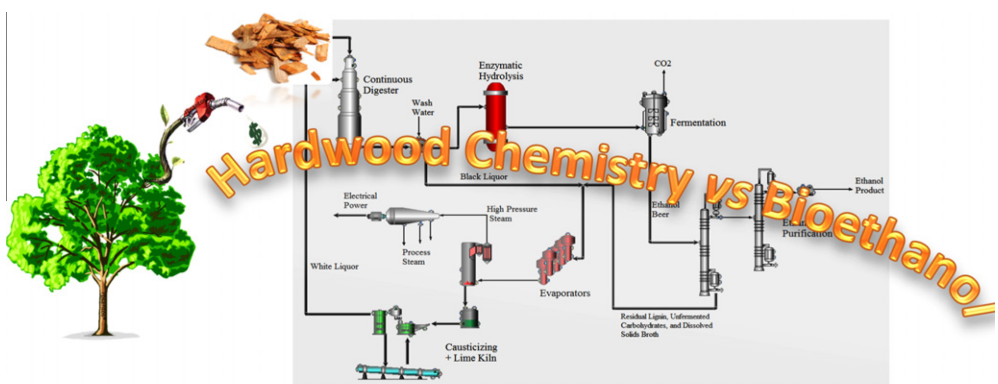
HIGHLIGHTS

- ▶ Study targeted the influence of different hardwood species on ethanol production yield and costs.
- ▶ Minimum ethanol revenue was lower for extended kraft-pretreated samples.
- ▶ The influence of species characteristics remained restricted to high residual lignin content.
- ▶ Species such as maple, globulus and sweet gum presented the lowest variation in relative MER.
- ▶ Sensitivity analysis showed that ethanol yield has the largest influence in MER followed by CAPEX.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work targeted the understanding of the influence of nine different hardwood species as feedstock on ethanol production yield and costs. It was found that the minimum ethanol revenue (MER) ($ per gallon to the producer) to achieve a 12% internal rate of return (IRR) on invested capital was smaller for low lignin content samples and the influence of species characteristics remained restricted to high residual lignin content. We show that if the pretreatment being applied to the feedstock targets or is limited to low lignin removal, one can expect the species to have a significant impact on overall economics, playing important role to project success. This study also showed a variation of up to 40% in relative MER among hardwood species, where maple, globulus and sweet gum varied the least. Sensitivity analysis showed ethanol yield per ton of feedstock had the largest influence in MER, followed by CAPEX.

1. Introduction

The availability of cellulosic polymers (cellulose and heteropolysaccharides) on the planet in the form of biomass gives them the prominent position of one of the most promising feedstocks for conversion into liquid and solid fuels (Aden et al. 2002; Gonzalez et al., 2011a–c; Wu et al., 2010). However, the conversion of lignocellulosic biomass is challenged by its recalcitrant structure which is demonstrated by its virtual immutability to almost any chemical and enzymatic hydrolysis attempts (Mosier et al., 2003, 2005; Gonzalez et al., 2011c).

Because carbohydrates in natural wood are not amenable to enzymatic hydrolysis, the use of some type of pretreatment is essential for the ultimate production of liquid biofuels. Pretreatments target wood structure by opening up pathways in the microstructure to facilitate enzyme hydrolysis of the carbohydrates. A variety of pretreatments have been tested over the past years including ozonolysis, organosolv, AFEX, auto hydrolysis, alkaline hydrolysis as well as integrated process with hemicellulose extraction prior to pulping and power generation (Treasure et al., in

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press), and the development of the concept of repurposing a kraft pulp mill for ethanol production (Gonzalez et al., 2011d; Carroll and Somerville, 2009; Ye and Jiayang, 2009; Chirat et al., 2010; Lee et al., 2010b; Santos et al., 2012). Currently, dilute sulfuric acid is the most widely studied pretreatment method to process cellulosic raw materials.

Pretreatment steps have a significant impact on the design and efficiency of the conversion process and the overall profitability. Pretreatment accounts for 25–35% of the cost of converting lignocellulosic biomass to ethanol (Eggeman and Elander, 2005) in which feedstock composition and subsequent chemical reactivity will dictate the necessary pretreatment stage for conversion to ethanol.

So far, most of the studies related to biofuel have focused on the development of a process that is economically viable, particularly with respect to pretreatment and enzymatic hydrolysis. Not many studies have discussed the impact of raw material and its characteristics on the production of ethanol.

From a practical perspective, it has been conjectured that the resistance of lignocellulosics to component separation/processing arises primarily from high residual lignin quantity and distribution, low lignin reactivity (low syringyl/guaiacyl (S/G) ratio), high cellulose crystallinity, accessible surface area, fiber dimensions, degree of polymerization and others (Mansfield et al., 1999; Mooney et al., 1998; Ohgren et al., 2007; Yu et al., 2011; Lee et al., 2010b). Also, the presence of phenolic residues has been reported as one of the major barriers to efficient enzymatic hydrolysis of carbohydrates in lignocellulosic biomass (Martin and Akin, 1988; Ximenes et al., 2010; Zhu et al., 2008). In the case of enzymatic hydrolysis, lignin acts as a physical barrier protecting cellulose from enzymes. Studies have demonstrated how complex the cell wall structure is with covalent bonds between lignin and all major polysaccharides, (arabinoglucuronoxylan, galactoglucomannan, glucomannan, pectins, and cellulose), and also cross-links among those components (Li and Khraisheh, 2010; Lawoko et al., 2005). Phenyl glycosides, benzyl ethers and gamma esters have been suggested as the main types of lignin-carbohydrate bonds found in wood (Balakshin et al., 2007).

Because of the distinct chemical and structural composition of different species, pretreatment selectivity (carbohydrates preservation *versus* lignin removal) and enzymatic hydrolysis efficiency are of large impact on the amount of carbohydrates recovered that can be processed into fermentation. Therefore, the use of different hardwood species as process feedstock to ethanol production may result in large variation on ethanol yield and cost, depending upon structural and chemical features of the raw material utilized.

In this work, we targeted the understanding of the influence of the use of different hardwood species as feedstock materials on ethanol production cost.

2. Methods

2.1. Materials

Feedstocks used in this research are *Eucalyptus nitens* (EN), *Eucalyptus* globulus (EG), *Eucalyptus* urograndis (URO), sweet gum (*Liquidambar styraciflua*, SG), red maple (*Acer rubrum*, MA), red oak (*Quercus rubra*, RO), red alder (*Alnus rubra*, RA), cottonwood (*Populus trichocarpa*, CW), acacia (*Acacia mangium*, ACA); in the form of clean wood chips. The estimated moisture content for all feedstocks were about 45%. The average feedstock delivered cost was assumed at \$71 per dry short ton (\$78.3 per dry metric ton) for all feedstocks (Gonzalez et al., 2011a–c). The estimation of the feedstock based on several reports (Gonzalez et al., 2011a,b,d) include payment to the forest landowner, harvesting and transportation. Though several of these species do not occur in the U.S. naturally or planted, the assumed delivered cost is representative for clean wood hardwood chips. Later on in the sensitivity analysis, a variation of ±25% in the cost of feedstocks will be considered to understand impact on the economics of the biorefineries.

The chemical composition of the feedstocks used for this study is a normalized version of compositional analysis data collected in the laboratory (Table 1). The original compositional analysis was determined at the Department of Forest Biomaterials at North Carolina State University and is explored in greater detail by Santos et al. (2011). Normalization of the data to satisfy mass balance constraints within the process model was applied only to carbohydrates present in the original wood. Since lignin content is the most accurate analysis its content did not participate in the normalization. Extractive (includes extractives, uronic acids and acetyl groups) was assumed to be 7% for all the species and ash was assumed to be 1% (Sjöström 1981).

2.2. Wood pretreatments

Kraft pretreatment of wood chips was performed at 150 °C. An M&K digester was filled with 150 g (dry weight) of samples including excess of white liquor, (liquor: wood ratio of 10:1) with an active alkali charge of 40% with 25% sulfidity. Such a high alkaline charge and wood to liquor ratio was used to avoid compositional (consumption of reagents by carbohydrates and extractives) and structural (wood density) interference from the different species. As shown in the literature (Smook, 2002), significant amounts of the alkali charge is consumed by reactions with carbohydrates and also neutralization of acetyl groups present in the hemicelluloses. Also, structural characteristics (wood density) will determine how fast penetration and white liquor diffusion occurs which may impact wood component dissolution. Pretreatment times were set to be 20, 30, 45, and 60 min. After the desired reaction time, the whole apparatus was cooled by running cold water through the digester. The samples were removed from the digester and washed with deionized water until a neutral pH was reached.

2.3. Enzymatic hydrolysis

One gram (dry weight) of pretreated sample was subjected to enzymatic hydrolysis. The samples were placed into a 50 mL centrifuge tube with enough buffer solution (pH 4.8) to bring the consistency to 5%. Three commercial enzymes were used: cellulase (*Trichoderma reesei*, NS-50013), xylanase (NS-50014), and β-glucosidase (*Aspergillus niger*, NS-50010). Cellulase was added at a dose of 20 FPU (filter paper unit)/g of substrate. Xylanase and β-glucosidase were dosed at 30% of the weight of the cellulose solution charged (Lee et al., 2009). The tubes were placed in an incubator shaker (180 rpm) for 48 h at a temperature of 50 ± 2 °C.

Table 1
Feedstock chemical composition.

Specie	Component (%)					
	Glucose	Xylose	Lignin	Ext	Ash	Total
Sweetgum (SG)	49.3	15.5	27.2	7.0	1.0	100
Acacia (ACA)	51.8	13.4	26.8	7.0	1.0	100
Red alder (RA)	48.4	17.9	25.7	7.0	1.0	100
E. Urograndis (URO)	53.6	11.8	26.6	7.0	1.0	100
E. Nitens (EN)	48.6	17.9	25.5	7.0	1.0	100
E. globulus (GLO)	52.7	15.4	23.9	7.0	1.0	100
Cottonwood (CW)	54.6	15.9	21.5	7.0	1.0	100
Red oak (RO)	46.2	18.4	27.4	7.0	1.0	100
Maple (MA)	52.1	15.6	24.3	7.0	1.0	100