Improving economics of lignocellulosic biofuels: An integrated strategy for coproducing 1,5-pentanediol and ethanol

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HIGHLIGHTS

- An integrated strategy for coproducing 1,5-pentanediol and bioethanol is proposed.
- An experimentally based model is developed to determine economic potential.
- Sensitivity analysis identifies the most important process and economic parameters.
- 1,5-pentanediol coproduct plays a paramount role in improving economics.
- The coproduction strategy leads to a promising biorefinery strategy.

ARTICLE INFO

ABSTRACT

A biorefinery strategy for the coproduction of ethanol and 1,5-pentanediol (1,5-PDO), which can be used as polyester and polyurethane component, from lignocellulosic biomass is proposed. This strategy integrates biomass fractionation with simultaneous conversion of hemicellulose and cellulose constituents into 1,5-PDO and ethanol, respectively. An experimentally-based process model is developed to determine the economic potential of the integrated strategy. The coproduction strategy becomes competitive with the ethanol-only strategy when 1,5-PDO can be sold at $1140/ton, which is well below the market price of 1,5-PDO. The most important process parameters include biomass loading for biomass fractionation, enzyme loading for enzymatic hydrolysis and fermentation, and overall achievable yields from C5 sugars to 1,5-PDO.

1. Introduction

Lignocellulosic biomass feedstocks are available on a scale that other solid or liquid renewable resources cannot match. The United States has enough domestic feedstocks to potentially supply 30–45 billion gallons of fuel [1], which would lessen the nation's dependence on petroleum and reduce greenhouse gas emissions. Yet, while biofuels seem an appealing choice over conventional fuels, the low price of crude oil and the challenges with economically producing biofuels on a commercial scale impede the production of biofuels. Creating high-value coproducts along with biofuels is a promising approach for improving the economics of biomass utilization [2–20], in a manner similar to the petroleum refining industry [19]. A variety of value-added chemicals have been identified for production from lignocellulose, either "drop-in" petroleum hydrocarbons (mainly simple alcohols and acids) or oxygenated platform chemicals (*e.g.*, 5-hydroxymethyl furfural

(HMF), vinyl and furyl glycolic acid) [10,17,20]. The remaining major polymeric component (~20 wt%) of lignocellulose, lignin, is generally burnt to generate heat and power, as its conversion into additional coproducts remains challenging [18,21,22]. Lignocellulosic biomass contains 40–60% oxygen which makes technologies for producing hydrocarbon fuels economically challenging [23]. The oxygen functionality makes biomass an attractive feedstock for high value oxygenated commodity chemicals that are expensive to synthesize from petroleum-derived feedstocks [18,24]. Nevertheless, the integration of a downstream scalable cost-effective separation and recovery processes associated with utility and waste treatment subsystems is required to ensure high quality products which can replace chemicals (*e.g.*, polymer and specialty chemical precursors) currently derived from petroleum [2,8,10,19].

1,5-Pentanediol (1,5-PDO), along with two other conventional α,ω-diols (*e.g.,* 1,6-hexanediol (1,6-HDO) and 1,4-butanediol (1,4-BDO)),

are widely used in the chemical industry as building blocks for polyurethane and polyesters. These α,ω-diols are currently derived from petroleum and, as a group, represent an annual market over $7 billion with a nearly 7% annual growth rate [25,26]. The current worldwide consumption of 1,5-PDO is about 3000 tons per year but at a high price of $6000/ton due to limited readily accessible C5 petrochemical feedstocks. However, C5 platform chemicals from hemicellulose component of lignocellulose, such as furfural and xylose, have been produced at industrial scale and can be converted to 1,5-PDO. 1,5-PDO based polyester polyols have similar properties as 1,4-BDO and 1,6-HDO based polyester polyols and can be formulated into polyurethanes without extensive re-work, while they are different enough to give unique and versatile polyurethane systems (*e.g.*, low thermal transition temperature). 1,4-BDO and 1,6-HDO have larger market sizes of 3200000 and 138000 tons per year, respectively [26,27]. A new approach has been recently developed for producing 1,5-PDO at cost lower than $2000/ton with a commercial-scale plant (37000 tons per year) at current furfural starting-material price ($1000/ton) [28,29]. To fully utilize other polymeric components of lignocellulose, this technology could be integrated with cellulosic ethanol production to improve cellulosic biorefinery economics. From a process perspective, such integration requires cheap fractionation of lignocellulose into its major components (cellulose, hemicellulose, and lignin), which remains challenging due to the different chemical structures of the biomass constituents [30]. A recently proposed biomass fractionation approach, using a γ-valerolactone (GVL)/H_2O solvent [31], leads to the production of high purity solid cellulose, and a soluble hemicellulose and lignin stream, which enables further conversion of hemicellulose and cellulose into 1,5-PDO and ethanol, while the remaining lignin could be combusted to produce high-pressure steam for electricity production and process heat.

Multiple technoeconomic studies have been conducted for various configurations of industrial lignocellulosic fuels production [19,32–58]. The results of some representative biochemical and thermochemical technologies are presented in Table 1. Though we note that directly comparing the results from different studies is challenging due to differences in the assumptions and parameters used. Specifically, the wide range of minimum selling price (MSP) values is, partly, due to differences in feedstock cost, plant size, coproduct values, process parameters, and economic assumptions. However, the study by Biddy et al. [19] demonstrated that renewable diesel blendstock (RDB) cost could be substantially reduced by nearly $3/GGE if hemicellulose is diverted to succinic acid coproduct. Later, we will use minimum ethanol selling price (MESP) as an evaluation criterion since ethanol already has an established market with a traceable market value. Accordingly, to better understand the technical and economic challenges of the coproduction strategy, we first synthesize the corresponding process, then develop a process simulation model based on experimental data, and perform technoeconomic analysis to determine the economic potential of the process.

2. Methods

2.1. Process synthesis

The process described here uses organosolv fractionation of lignocellulosic biomass [31], followed by catalytic conversion of the hemicellulose fraction to 1,5-PDO [29,31] and enzymatic hydrolysis and fermentation of the remaining cellulose to ethanol [41]. The process also includes wastewater treatment, lignin combustion, product storage, and required utilities. The process is divided into 7 areas (see Fig. 1) with the key process parameters of each unit given in Table 2.

Area 100: Biomass fractionation: Corn stover was used as a feedstock to remain consistent with the design of the National Renewable Energy Laboratory (NREL) cellulosic ethanol process [41]. Corn stover is conveyed directly to the biomass fractionation reactor. The composition of

corn stover is given in Table A.1 with 20% moisture content. This step is carried out at low temperature (130 °C) and low pressure (< 3 bar) for 45 min using a 80:20 GVL/H_2O mass ratio and 0.1 M sulfuric acid as a catalyst. The fractionation reactor produces a GVL/H_2O soluble fraction that contains over 90% of the hemicellulose and 95% of the lignin at 30 wt% biomass loading. Two solid/liquid separation stages (filters) are combined to recover the solid cellulose from the liquid solution. The liquid fraction, containing the soluble C5 sugars and lignin, is transferred to the furfural reactor, while the solid cellulose is sent to Area 300 to carry out enzymatic hydrolysis upon removal of the GVL solvent by conventional evaporation. GVL enables excellent yields of furfural (90%) by dehydration of xylose with 30 s residence time at 225 °C using the upstream C5 sugars and lignin solution as the feed. A small amount of NaCl is added to take advantage of the chloride ion effect for furfural production [31]. After neutralization of the acid, furfural and water are evaporated from the high-boiling point solvent (GVL, 208 °C). The furfural/H_2O azeotrope has a boiling point of 98 °C, which makes it easy to distill from GVL. Lignin and other heavy components are soluble in GVL. GVL is then separated from lignin by evaporation. Upon evaporation of GVL, lignin will become insoluble, be separated and sent to a combustor to produce steam and electricity in Area 600. The remaining furfural/H_2O azeotrope is distilled to obtain high purity furfural. This is similar to the furfural purification step currently used in the commercial production of furfural [60].

Area 200: Furfural upgrading: In this area, the purified furfural (> 99 wt%) from Area 100 is converted to 1,5-PDO using a catalytic approach that involves hydrogenation, dehydration, hydration, hydrogenation, and associated separation and recovery steps [29]. First, furfural is hydrogenated into tetrahydrofurfuryl alcohol (THFA) at high yield (> 90%) in gas phase over Ni/SiO_2 catalyst [59]. The gaseous mixture of hydrogenation products is condensed to recover excess hydrogen and then purified by conventional distillation. The purified THFA (98.5 wt%) is further converted to 1,5-PDO via dihydropyran (DHP) and 2-hydroxytetrahydropyran (2-HY-THP) as subsequent intermediates [28]. Finally, conventional vapor-liquid separation and distillation are employed for the excess hydrogen recovery and 1,5-PDO purification. All the wastewater generated in this area is sent to wastewater treatment (Area 400).

Area 300: Cellulose upgrading: This area follows the NREL's design for cellulosic ethanol production [41]. Enzymatic hydrolysis of cellulose is initiated at a 20 wt% total solids loading in a high-solid continuous reactor using a cellulase enzyme prepared on-site from purchased glucose (corn syrup). The partially hydrolyzed slurry is then fed to one of several parallel bioreactors. Hydrolysis is completed in the batch reactor, and then the slurry is cooled and inoculated with the cofermenting microorganism *Zymomonas mobilis*. After a total of five days of sequential enzymatic hydrolysis and fermentation, most of the cellulose has been converted to ethanol. The resulting beer is sent to the product recovery train to be separated into ethanol, water, and residual solids by distillation and solid-liquid separation. Ethanol is distilled to a nearly azeotropic mixture (7.5% H_2O in ethanol) and then purified to 99.5% using vapor-phase molecular sieve adsorption. Solids recovered from the distillation bottoms are sent to the combustor (Area 600) while the liquid is sent to wastewater treatment (Area 400).

Area 400: Wastewater treatment: Plant wastewater streams are treated by anaerobic and aerobic digestion. The methane-rich biogas from anaerobic digestion is sent to the combustor (Area 600), where sludge from the digesters is also burned. The treated water is suitable for recycling.

Area 500: Storage: This area provides bulk storage for chemicals used and produced in the process, including GVL, corn steep liquor (CSL), ammonia, sulfuric acid, nutrients, water, 1,5-PDO, and ethanol.

Area 600: Heat and power generation: The solids from distillation and wastewater treatment and the biogas from anaerobic digestion are combusted to produce high-pressure steam for electricity production and process heat. The majority of the process steam demand is in the