Energy Conversion and Management 138 (2017) 511–517

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Process systems engineering studies for catalytic production of bio-based platform molecules from lignocellulosic biomass

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ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form 9 February 2017
Accepted 10 February 2017

Keywords:
Levulinic acid
Furfural
Propyl guaiacol
Lignocellulosic biomass
Process designs
Economic feasibility

ABSTRACT

This work presents a process-system engineering study of an integrated catalytic conversion strategy to produce bio-based platform molecules (levulinic acid (LA), furfural (FF), and propyl guaiacol (PG)) from hemicellulose (C_5), cellulose (C_6), and lignin fractions of lignocellulosic biomass. A commercial-scale process based on the strategy produces high numerical carbon yields (overall yields: 35.2%; C_6-to-LA: 20.4%, C_5-to-FF: 69.2%, and Lignin-to-PG: 13.3%) from a dilute concentration of solute (1.3–30.0 wt.% solids), but a high recovery of these molecules requires an efficient separation system with low energy requirement. A heat exchanger network significantly reduced the total energy requirements of the process. An economic analysis showed that the minimum selling price of LA as the highest value-added product (42.3×10^3 t of LA/y using 700×10^3 dry t/y of corn stover) is US$1707/t despite using negative economic parameters, and that this system can be cost-competitive with current production approaches.

1. Introduction

Derivatives of lignocellulosic biomass have the potential to replace many petroleum-based products (*e.g.*, fuels, plastics, pharmaceuticals) [1]. Lignocellulosic biomass is mainly composed of polysaccharides (30–50% cellulose, 20–35% hemicellulose, 15–30% lignin) [1,2], which can be converted to useful products *via* several intermediate molecules (*e.g.*, levulinic acid (LA), furfural (FF)) [3–6]. Most synthesis routes to produce these platform molecules involve an initial process to depolymerize the polysaccharides to soluble C_5 (xylose derived from hemicellulose) or C_6 sugars (glucose derived from cellulose), followed by upgrading processes. The insoluble lignin is separated from the sugars after the initial process, then passed to additional hydrogenolysis or oxidation processes to yield monomers. Use of dilute acid pretreatment (DAP) and enzymatic hydrolysis as the initial process achieves 82–91 mol% cellulose/hemicellulose-to-C_6/C_5 yields.

The major challenge in the initial process is to extract the hemicellulose and lignin fractions of biomass from the pretreated state to increase accessibility to the cellulose by enzymes added in the subsequent hydrolysis stage. Moreover, to cut the cost of producing platform molecules and other products, the cost of enzymes must be reduced. Recently, non-enzymatic hydrolysis that uses dilute acid catalyst instead of enzymes to break down the cellulose to C_6 sugars has been reported [7].

After fractionating the biomass by the initial process C_5 and C_6 fractions can be then catalytically converted to platform molecules (FF, LA) by catalytic upgrading. Many recent studies of homogeneous catalysis have reported that in the absence of C_6, high yields of FF can be achieved by using pure C_5 at low concentrations (0.1–6 wt.%) with large quantities of solvent and dilute acid (HCl, H_2SO_4) catalyst [1,8–10]. The catalytic upgrading process should be followed by effective separation of high-purity platform molecules from the diluted acid-containing aqueous solution. Two-phase (organic/aqueous) separation using lignin-derived alkylphenols can extract platform molecules (FF, LA) effectively from the diluted acid-containing aqueous solution [11]; most of the acid catalyst in the aqueous phase can be reused in this upgrading process.

The many recent studies have focused on increasing yields during each reaction, but few studies have evaluated the cost of producing platform molecules within an integrated process that entails DAP, catalytic upgrading, and separation systems. Thus, based on the data presented in these studies we present a process-system engineering study (with large-scale design, energy analysis, and economic analysis of integrated process) to evaluate the techno-economic feasibility of the strategy for catalytic coproduction of FF, LA, and PG from lignocellulosic biomass.

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http://dx.doi.org/10.1016/j.enconman.2017.02.027
0196-8904/

2. Methods

2.1. Experimental studies of conversion subsystems

The strategy combines four catalytic reactions for (1) production of xylose from hemicellulose [12], (2) production of FF from the xylose [9], (3) production of LA from cellulose [13], and (4) production of propyl guaiacol (PG) from lignin [9]. Data (*e.g.*, reaction conditions and yields) for the four reactions have been validated experimentally (Table 1) in the literature [9,12,13].

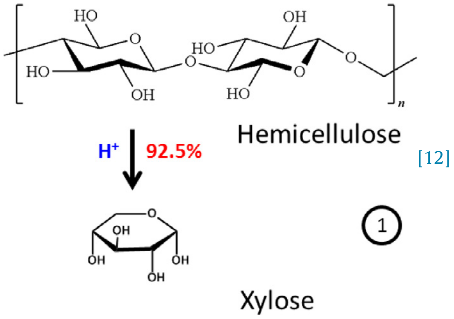
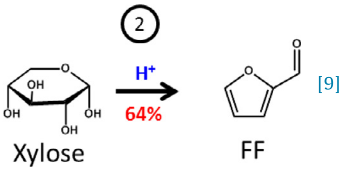
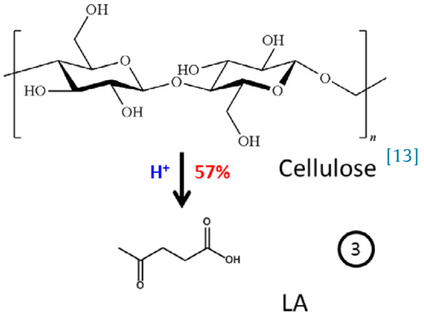
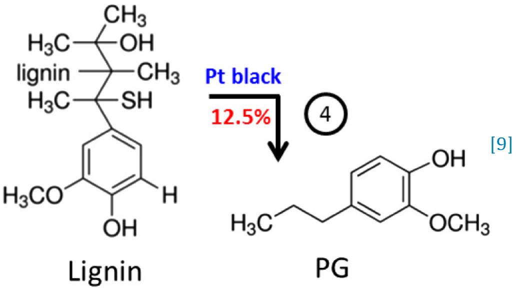
Reaction 1 (Table 1) produces xylose from hemicellulose with 92.5% molar yield in a catalytic reactor that contains 30 wt% biomass loading and 1.1% sulfuric acid (SA) catalyst loading in H_2O solution at 463 K and 12.1 atm. This reaction converts 5% of the remaining hemicellulose to FF. Most of the xylose and FF is solubilized; the remaining insoluble materials are cellulose, lignin, and unconverted hemicellulose.

The xylose can be converted to FF with 64% molar yield in a catalytic reactor that contains 1.3 wt% xylose loading and 0.1 M HCl catalyst loading in biphasic solution (aqueous: organic (PG) mass ratio = 6.67:1); 15% of the xylose is degraded to humins (Reaction 2 in Table 1). Here, the biphasic reaction leads to high partitioning (75%) of FF into the organic (PG) phase because the NaCl-saturated aqueous phase increases the polarity difference between the aqueous and organic phases.

The cellulose can be converted to LA and formic acid (FA) (Reaction 3 in Table 1) with 52% molar yield in a catalytic reactor that contains 28.1 wt% cellulose loading and 0.5 M SA catalyst loading in H_2O solution at 423 K and 35 atm; the remaining cellulose is degraded to humins.

The lignin can be converted to phenolic monomers with 28% molar yield (12.5% PG, 1.3% propyl syringol (PS), 0.3% syringyl propanol (SP), and 13.8% guaiacyl propanol (GP)) under H_2-rich atmosphere in a catalytic reactor that contains 9.1 wt% lignin loading

Table 1
Reaction conditions and yields for the catalytic production of bio-based platform chemicals (P: pressure; T: temperature).

Reactions	Conditions	Yield (mol%)
	30 wt% biomass and 1.1% SA catalyst in H_2O solution, P: 12.1 atm, T: 463 K	xylose: 92.5; FF: 5
	1.3 wt% xylose in biphasic (6.67:1 aqueous/organic mass ratio) solution (aqueous phase: 0.1 M HCl catalyst in saturated NaCl solution, organic phase: PG), T: 443 K	FF: 64, (75% of this in PG phase)
	28.1 wt% cellulose in H_2O solution containing 0.5 M SA catalyst P: 35 atm, T: 423 K	LA and FA: 52
	9.1 wt% lignin and 0.45 wt% Pt black catalyst in H_2O solution, P: 39 atm, T: 473 K	PG: 12.5, PS: 1.3; GP: 13.8; SP: 0.3

Abbreviations: formic acid (FA), fufural (FF), guaiacyl propanol (GP), levulinic acid (LA), pressure (P), propyl guaiacol (PG), propyl syringol (PS), sulfuric acid (SA), syringyl propanol (SP), and temperature (T).