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Process design and techno-economic evaluation for catalytic production of cellulosic γ-Valerolactone using lignin derived propyl guaiacol

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ABSTRACT

This paper presents an integrated strategy to produce cellulosic γ-Valerolactone (GVL) using lignin derived propyl guaiacol (PG) from lignocellulosic biomass. A commercially large-scale process that was designed based on the strategy achieves 12.3% carbon yields at low (9.1–30.0 wt%) concentrations of reactants, and requires an efficient separation system to obtain high recovery of products with low energy requirements. A heat exchanger network is designed to significantly decrease the total energy requirements of the process. Techno-economic evaluation results assuming nth commercial plant and negative economic parameters show that this process ($US 3,805/t GVL) can be cost-competitive with current production approaches.

Introduction

Lignocellulosic biomass has been evaluated as a resource for production of chemicals to replace petroleum derivatives [1–7]. γ-Valerolactone (GVL) which is the one of value-added platform chemicals derived from lignocellulsic biomass is primarily used as an intermediate in the production of jet-fuel-range alkenes, fuel additives, and polymers [5,8,9]. GVL is commonly produced from levulinic acid (LA) by selective hydrogenation using molecular H_2 as the reducing agent, supported metals (Ir, Rh, Pd, Ru, Pt, Re or Ni) as heterogeneous catalysts, and H_2O and alkylphenols as solvents [10].

Lignocellulosic biomass contains 15–30% lignin, 30–50% cellulose, and 20–35% hemicellulose [5,11]. Lignin can be converted to alkylphenols, i.e., propyl guaiacol (PG), which can be used as a reactive solvent in the production of GVL from LA as well as an organic extractive solvent to extract LA effectively from the diluted acid-containing aqueous solution [12]. Cellulose can be converted to LA with high yields (>50 mol%) using dilute acid catalysts under homogeneous conditions. Before PG production from lignin or LA production from cellulose, an initial pretreatment process to remove the hemicellulose is the key step in large-scale use for industrial applications [13]. Most pretreatment processes use dilute acid (HCl, H_2SO_4) catalysts to degrade the hemicellulose to soluble xylose, which can be separated from insoluble cellulose and lignin [14]. The major challenges in the catalytic process for cellulosic GVL production are design of effective separation steps after catalytic conversion; i.e., effective recovery of high-purity biomass derivatives (LA, GVL), solvents (H_2O, PG), and acid catalysts at low reactant concentrations.

Most previous studies have focused on increasing yields during each catalytic conversion step, but few studies have evaluated the cost of producing cellulosic GVL within an integrated process that entails catalytic conversion and separation steps. Several researchers have process synthesis and technoeconomic evaluation of producing cellulosic GVL using 2-sec-butyl phenol (SBP) as an alkylphenol solvent [15,16] and biomass-derived GVL as a reactive solvent [11,17–19]. Thus, based on the experimentally validated data presented in those studies, the present work develops a large-scale design of an integrated process to produce cellulosic GVL catalytically using PG from lignin in lignocellulosic biomass, and evaluates the techno-economic feasibility of the process. The results identify the major cost drivers and technical bottlenecks of the process.

Methods: experimental studies

The strategy combines four catalytic conversion routes for production of (1) xylose from hemicellulose [20], (2) LA from cellulose [21], (3) GVL from LA [12], and (4) PG from lignin [12].

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Details of experimental parameters and results for the four conversion routes, which were investigated in the literature, are expressed below.

In route 1, hemicellulose is converted to xylose and FF with 92.5% and 5.0% molar yields respectively in a monophasic aqueous solution containing 30 wt% biomass and 1.1% sulfuric acid (SA) catalyst at 12.1 atm and 463 K. Most of the xylose and FF can be solubilized and separated from the remaining insoluble materials containing cellulose, lignin, and unconverted hemicellulose. In route 2, the cellulose is converted to LA and formic acid (FA) at 52% molar yield in a monophasic aqueous solution containing 28.1 wt% cellulose and 0.5 M SA catalyst at 35 atm and 423 K; the remaining cellulose is degraded to humins. In route 3, the LA is hydrogenated to GVL with a 93% molar yield in a packed bed flow reactor using PG solvent and 5 wt% RuSn(1:4)/C catalyst with 10.0 wt% LA at 13.8 atm and 453 K. In route 4, the lignin is converted to the phenolic monomers PG (12.5%), propyl syringol (PS, 1.3%), syringyl propanol (SP, 0.3%), and guaiacyl propanol (GP. 13.8%) with a 28% molar yield in a one-pot reactor using aqueous solution containing 9.1 wt% lignin and 0.45 wt% Pt black catalyst under moderate hydrogen pressure (39 atm) and 473 K.

Based on these experimental studies, the four conversion routes show maximum yields with low concentrations of reactants (9.1–30.0 wt%) when a large amount of solvents is used. Especially, routes 1 and 2 use dilute SA as a homogeneous catalyst; this strategy has a potential drawback of separation of the catalyst from the product solution. In addition to recycling catalysts, effective design of separation systems to achieve high recovery of solvents and products with high purity is crucial. Details of the separation systems combined with the catalytic conversion systems at optimized feed and product concentrations will be presented in Section “Results and discussion: process systems engineering studies”.

Results and discussion: process systems engineering studies

Process design

An integrated process that consists of conversion and separation systems was designed to produce cellulosic GVL using lignin derived PG from corn stover. The process exploits the results of the experimental studies, The feedstock processing rate was selected to be 700 × 10^3 t/y of dry corn stover (Table 1), which is the same rate used in previous process systems engineering studies for large-scale catalytic production of biomass derivatives [15–19,22]. The integrated process consists of 11 main systems: biomass handling, pretreatment (including conversion route 1), LA production (including conversion route 2), LA recovery, GVL production (including conversion route 3), GVL recovery, PG production (including reaction 4), PG recovery, wastewater treatment (WWT), heat and electricity generation, and storage. A process flow diagram (PFD) of the integrated process was developed (Fig. 1). Simulation models of major units (e.g., reactors, separators, distillation towers, heat exchangers, pumps) for six systems (LA production, LA recovery, GVL production, GVL recovery, PG production, and PG recovery) in the integrated process were developed using the ASPEN Plus Process Simulator [23]; input data for simulation models were selected to the experimentally optimized ones among various parameters (e.g., reaction conditions; temperature, pressure, catalyst, solvent, and concentration) determined according to the best experimental results (e.g., the highest reaction yields) described in the previous Section “Methods: experimental studies”. The simulation results of the other systems were scaled based on models in previous studies [15–19,22].

Table 1
Feedstock composition [20].

Component	% Dry basis
Glucan	37.4
Xylan	21.1
Lignin	18.0
Ash	5.2
Acetate	2.9
Protein	3.1
Extractives	4.7
Arabinan	2.9
Galactan	2.0
Mannan	1.6
Unknown soluble solids	1.1
Moisture	15.0

The corn stover is shredded in the biomass handling system, then fed to a pretreatment system to separate the soluble hemicellulose-derived xylose from the insoluble cellulose and lignin. In the pretreatment system, an aqueous stream (1,939 × 10^3 t/y) that

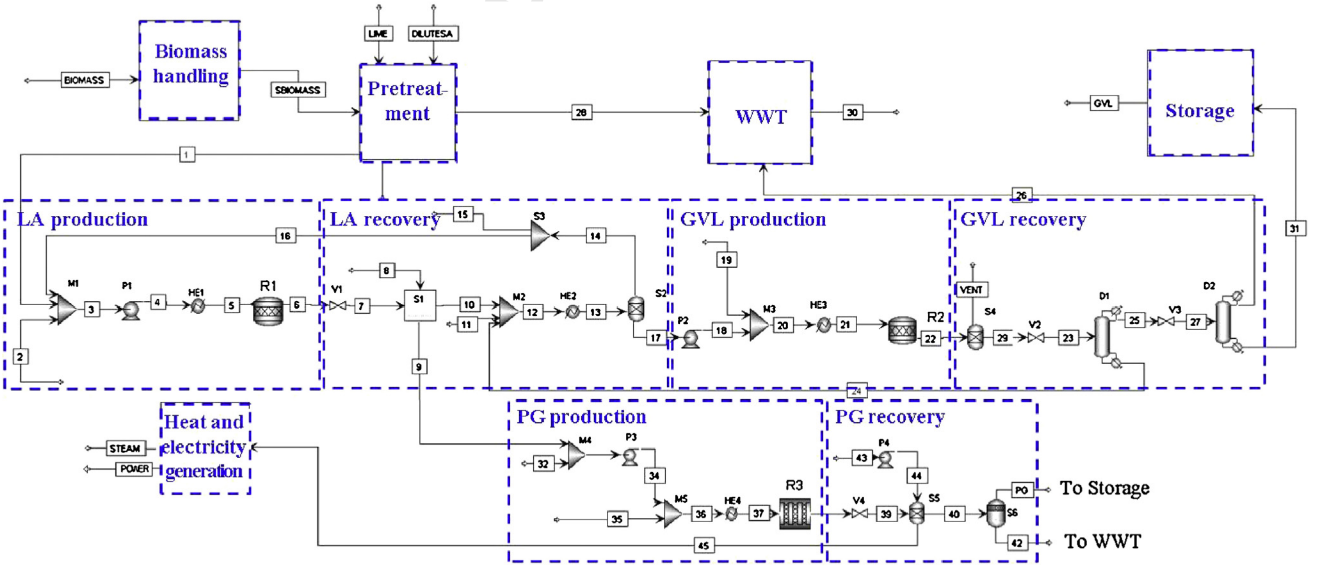

Fig. 1. Process flow diagram of an integrated process for producing cellulosic GVL using lignin derived PG from corn stover.

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