Simulation study of a strategy to produce gamma-valerolactone from ethyl levulinate

Juyeon Kim [a], Jeehoon Han [b], *

[a] School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeon-ju 54896, South Korea
[b] School of Chemical Engineering, Chonbuk National University, Jeon-ju 54896, South Korea

ABSTRACT

This work presents a strategy to produce gamma-valerolactone (GVL) from ethyl levulinate (EL) by heterogeneous catalytic reaction and vapor-liquid equilibrium separation. This approach has the advantages of achieving a high yield of GVL and of using easily recycled catalyst and solvent. Based on experimental results, this work presents a large-scale process simulation study including process design, energy analysis, and economic analysis to show the economic feasibility for the proposed strategy. This strategy is very sensitive to EL price and highly depended on an off-site supply of heating energy. Results of our study suggest that the strategy is an economically-competitive alternative to current GVL production approaches.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Gamma-valerolactone (GVL) is a value-added chemical derived from lignocellulosic biomass [1]. GVL can be used as an precursor for production of biofuels, pharmaceuticals, food ingredients, and environmentally-benign solvents for biomass processing [2]. The wide range of its application has led to extensive studies on GVL production from various lignocellulosic biomass derivatives [3]. The catalytic hydrogenation of levulinic acid (LA) or its esters such as ethyl levulinate (EL), into GVL is the main route to synthesize GVL from biomass derivatives [4,5].

A number of studies on GVL production by hydrogenation of LA or EL using homogeneous catalysts, such as sulfuric acid and formic acid, have been actively conducted over the last years [6]. The homogeneous catalysts such as Ru-based catalysts [7] and acid catalysts [8] present high activity and yields under mild conditions. However, they are difficult to be separated from the reaction mixture, which results in high separation cost and extra catalysts loading cost [9]. Recently, to overcome these potential drawbacks, several studies for GVL production from EL focused on heterogeneous catalysts, which can be easily separated and reused [10],

especially, metal nanoparticle supported catalysts like Pd [11], Au [12], Ni [13], Pt [14], a and Zr [15]. Compared to the LA obtained at yields of 40–70 wt % from lignocellulosic biomass treated with homogeneous acid catalysts (sulfuric acid and hydrogen chloride), EL could achieve at the higher yield and more easily separated due to its lower boiling point and weaker-acidity leading to less corrosion-related problems [16]. Thus, these findings suggest that EL has a potential of alternative to the LA for production GVL.

Recently, it was reported that EL can be hydrogenated to GVL with a high yield (99 mol%) by using commercial zeolite supported Pt catalyst in alcohol solvent in the presence of a hydrogen donor [17]. The EL-based GVL process was conducted on a laboratory scale, but industrial-scale production entails additional processes such as separation of the product, recovery of solvent, and regeneration of catalyst [18], so the technical and economic feasibility of the whole process must be determined. Several techno-economic feasibility studies of the LA-based process have focused on production of GVL using solvents based on 2-sec-butyl phenol [19], propyl guaiacol [20] or GVL-water [21]; they determined that the economics of the whole process is strongly affected by the design of the separation subsystems [22], and provided possible directions for future research to find optimal conversion methods. However, few techno-economic studies have considered EL-based GVL production. Therefore, the goal of this simulation study is to develop a

---

* Corresponding author.
E-mail address: jhhan@jbnu.ac.kr (J. Han).

new strategy for the production of GVL from EL and to show this approach has a techno-economic feasibility.

In this work, we design a process for GVL production from EL over zeolite-supported Pt catalyst, and evaluate techno-economic feasibility of the process which shows potentially achieve at the higher yield and more easily separated than the previous GVL production studies. To design a conversion process based on conversion experimental results, we analyzed reaction condition parameters and results of previous studies and determine of the optimized condition. To improve the reliability of separation process, the modified property model applied to obtain accurate parameters using data regression of vapor-liquid equilibrium (VLE) experimental data. An experimentally-based simulation study is conducted to determine the economic potential of the strategy. The simulation study considered process design, energy analysis, and economic analysis. We develop a whole process including conversion and separation subsystems based on the experimental results of investigations, and designed a heat exchanger network (HEN) to minimize the total requirements of energy for the whole process. Lastly, we evaluate the economics of the proposed process, and perform a sensitivity analysis of the minimum selling price (MSP) of GVL.

2. Method

This section presents experiment results on reactions to convert EL to GVL and on separation of binary ethanol/gamma-valerolactone (EtOH/GVL) systems by VLE, then presents how a simulation model can be developed using these results.

2.1. Conversion of EL to GVL

EL is hydrogenated to GVL at high yield by using commercial zeolite-supported Pt/ZSM 35 [17] (Fig. 1). In the study, the effect of oxygen-containing solvents on GVL yield was investigated using several organic solvents (EtOH, propanol, isopropanol, and tetrahydrofuran). Under the optimized condition, the experiment results show high conversion rates of EL in all the organic solvents. Especially, the higher yield of GVL (99.0 mol %) was obtained in EtOH solvent than the others (81.0−86.6 mol %). Moreover, during the reaction EtOH was produced as a by-product, resulting in simplifying separation of solvent from product as a binary EtOH/GVL system. Temperature (180−220 °C) and pressure (10−60 bar) were examined as important parameters for the catalytic hydrogenation reaction. First, the high reaction temperature could accelerate the conversion rate of EL, but at above temperature of 210 °C the opposite results were obtained. Furthermore, the yield of GVL increased linearly with the increasing of hydrogen pressure, because the higher pressure of hydrogen makes the higher hydrogen concentration on the surface of the catalyst that accelerates the reaction rate. At the 60 bar, the production of GVL reached the maximum (99 mol %) yield. Under optimized conditions (200 °C, 60 bar, EtOH solvent), the reaction of GVL production can achieve 100 mol % conversion of EL with a high selectivity (99 mol %) for GVL. For reliable simulation of the reaction, these optimized experiment conditions (temperature, pressure, and

solvent) and results (yields and by-product) were applied to design of catalytic conversion subsystem, including reactor modeling (mass and energy balance) and sizing (volume), and the details will be presented in Section 3.1.

2.2. Separation of GVL from EtOH

Reaction of EL yields at a low concentration of GVL in EtOH solvent, so recovery of GVL from EtOH is important as the subsequent separation step in GVL production. Therefore, this study introduces phase-equilibrium separation of a binary EtOH/GVL system. The non-random two liquids (NRTL) [23] model was used to estimate physical properties of component, including the vapor-liquid equilibrium (VLE) of the binary EtOH/GVL system. To improve the accuracy of VLE unit operation, the NRTL model was modified using data regression in Aspen Plus Properties, using experimental VLE data [24]; The blue lines are VLE prediction of before regression, while the green lines are after regression. The modified NRTL model (green line) estimates experimental results (points) well (in Fig. 2). The modified NRTL model can give reliable simulation of separation and will be applied to modeling (mass and energy balance) and to sizing the stages of the distillation column in a separation unit.

3. Results and discussion

3.1. Process design

A large-scale process that produces GVL from EL was developed based on the experimental investigation, by using the Aspen Plus Process Simulator. The feedstock processing rate of EL was chosen to be 133 kiloton per year (kt/y), assuming that the lignocellulosic biomass is fed into a biorefinery at 1 dry kt/days for 350 days per year and converted to GVL with a 38% efficiency [25]. The process consists of four processing subsystems: GVL production, GVL recovery, Storage, and Utilities.

A liquid mixture of 1.15 wt% EL in EtOH solution (8877 kt/y) was sent to a GVL production subsystem, and EL was hydrogenated to GVL with a 99 mol % yield in a batch reactor using Pt-ZSM catalyst at 60 bar and 200 °C (reaction in Fig. 1; R-1 in Fig. 3). Modeling and sizing of the reactor proceeded as follows. The process was split into two identical processing trains. To build a simulation of the process at steady state, multiple batch reactors were connected in parallel to a continuous GVL recovery subsystem. One train consists of six reactors that executed their processes sequentially. The GVL was produced in the final-stage reactor during 6.0 h of total residence time. The same steps were used in each processing train. Based on the experimental reaction results (Section 2.1), the total volume for the reaction in each processing train was determined to 518.4 m^3 and was partitioned into six reactors, each with a volume of 86.4 m^3. Each reactor was operated in each stage for only 0.5 h, but concurrent operation of all reactors enabled continuous production of 1.3 wt% GVL in EtOH solution (8877 kt/y) in each processing train.

The resulting rich EtOH mixture containing GVL was sent to a subsystem to recover the GVL. This subsystem consists of one flash
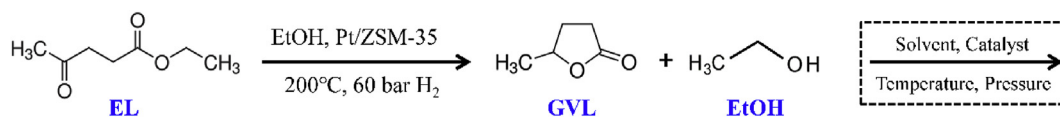

Fig. 1. Reaction route of the production GVL from EL.