Simulation Study and Sensitivity Analysis of Gamma-Valerolactone Production from Ethyl Levulinate

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ARTICLE INFO	ABSTRACT
	Gamma-valerolactone (GVL) is emerging as a promising renewable fuel because it can be produced from renewable materials such as biomass. This article presents a conceptual design and simulation of the conversion of ethyl levulinate into GVL biofuel by hydrogenation process using ChemCAD 7.1.2 software. The process simulation method involves selecting a thermodynamic model, defining component chemicals, selecting suitable operating units and identifying operating conditions. The NRTL thermodynamic model was used for the liquid phase modeling and SRK for the vapor phase fugacity calculation. The binary interaction parameter of NRTL thermodynamic model was regressed from experimental vapor-liquid equilibrium (VLE) data. A sensitivity analysis of the effect of feed temperature on the GVL purification distillation column was carried out to obtain the optimum value for the distillation column configuration.

1. Introduction

The exploitation of fossil resources not only resulted in rapid development but also in environmental pollution and an energy crisis as industrialization has progressed [1]. Water pollution, the greenhouse effect, a lack of energy, and reduced biodiversity have all become major issues [2,3]. To alleviate the current state of environmental pollution and the global energy crisis, researchers continue to investigate and develop a new green renewable energy resource such as wind, solar, and biomass power [1,4,5]. Among these alternatives, using biomass energy as a clean renewable energy source has the advantages of widespread availability, abundant reserves, and low prices [6-8]. Waste biomass has the potential to replace traditional fossil energy by serving as a feedstock for the production of high-value-added fuels and chemicals [9]. Most countries around the world, including

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the European Union, the United States, China, and India, have made renewable bioenergy development a policy priority [10].

Biomass is derived from various organisms and is produced in nature through photosynthesis [11]. Plants and animals are predominantly composed of cellulose, hemicellulose, and lignin. Hemicellulose is an amorphous polymer with a branched structure that is made up of five different sugar groups: D-xylose, D-galactose, D-glucose, D-mannose, and L-arabinose [12]. The xylose content accounts for the majority of the total. Hemicellulose can generate Gamma – Valerolactone (GVL) [13] when alcohol such as 2-butanol is used as a hydrogen donor. Brønsted acid hydrolyzes hemicellulose to form a five-carbon sugar, and xylose can form Furfural (FAL) via a three-step continuous dehydration reaction. The transfer hydrogenation reaction reduces FAL to furfuryl alcohol (FA). Part of the FA is etherified to form furfuryl ether (FE) in the presence of a solid acid catalyst and 2-butanol, and Brønsted acid converts FA and FE to a mixture of levulinic acid (LA) and acetic acid [14,15]. Furthermore, LA esterification with alcohol is gaining popularity because this levulinate or ester is a versatile chemical feedstock with numerous potential applications in the flavoring and fragrance industry, as well as as a blending component in biodiesel fuels. Among them, ethyl levulinate (EL) is one of the most important esters, as a 5% by weight EL mixture in diesel causes significant changes in fuel properties such as increased lubricity, flash point stability, reduced sulfur content, and increased viscosity[16]. Traditional catalysts, such as strong Brønsted liquid acids (such as H_2SO_4, HCl, and polyphosphoric acid) or metal catalysts, can be used to efficiently produce EL by esterifying LA with ethanol.

The primary starting materials for GVL synthesis are biomass-derived LA and its esters. One of synthetic technique for producing GVL is the catalytic hydrogenation of levulinic acid (LA). The former can be produced by dehydrating C6-sugars in an acidic medium [17]. Piskun *et al.,* [18] reported a kinetic investigation on the hydrogenation of levulinic acid (LA) to 4-hydroxypentanoic acid (4-HPA) and the subsequent intramolecular esterification to GVL in water utilizing Ru/C (3 wt. percent Ru) as the catalyst in a batch setup. Calculated results from experiments show that LA and hydrogen intra-particle diffusion have an impact on the total reaction rate. Delgado *et al.,* [19] studied the hydrogenation of butyl levulinate (BL) and levulinic acid on top of Ru/C and Amberlite IR-120. It is possible to speed up the production of GVL by enhancing the kinetics of the cyclization stages in the presence of LA and Amberlite IR-120. In recent years, extensive catalytic routes for GVL synthesis from LA/levulinate esters using ethanol as H donor have been continuously improved as shown in Figure 1 [20,21]. Although isopropanol appears to be a good H donor, secondary alcohols are known to form their corresponding ketones, which may favor unwanted side effects [22]. Metal catalysts, as is well known, have high catalytic activity in hydrogenation reactions. The common noble metals used for hydrogenation of LA/levulinate esters to GVL are Pd, Pt, Ru, Ir, and Rh, and they exhibit quite satisfactory catalytic performance under optimal reaction conditions [23,24]. In this study, we design a process for producing GVL from EL that has the potential to give a greater yield. Recently, it was revealed that utilizing a commercial zeolite-supported Pt catalyst in alcohol solvent in the presence of a hydrogen donor allows EL to be hydrogenated to GVL with a high yield (99 %mol) [25]. We examined reaction condition parameters and findings from earlier investigations in order to build a conversion procedure based on experimental data. Vapor-liquid equilibrium (VLE) experimental data were used in data regression to acquire correct parameters, which improved the separation process's reliability.
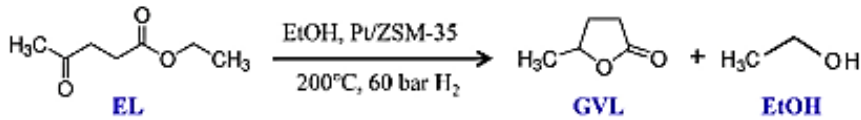
Fig. 1. GVL Synthesis Reaction with Hydrogenation of Ethyl Levulinate

2. Methodology

CHEMCAD 7.1.2 software is used for process design and simulation, which includes selecting and defining components, determining the appropriate thermodynamic model, selecting the necessary equipment, and determining operating conditions. Using CHEMCAD software, the work was completed by determining the operating conditions for the simulation. To gain a better understanding of the separation of GVL and ethanol using a distillation column, convergent simulation operating conditions were used to begin a sensitivity analysis.

2.1 Thermodynamic Model

The NRTL activity coefficient model was utilized to model the liquid phase, and SRK was used to calculate the vapor phase fugacity. The binary interaction parameters for the NRTL model were obtained by regressing from the available VLE experimental data for the system involved in the simulation , and are presented in table 1. The Eq. (1) is the NRTL equation used in ChemCAD software.

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_i^N G_{ij} x_i} + \sum_j^N \frac{x_j G_{ij}}{\sum_i^N G_{ij} x_i} \left[\tau_{ij} - \frac{\sum_i^N x_i \tau_{ij} G_{ij}}{\sum_i^N G_{ij} x_i} \right] \qquad (1)$$

where

$\tau_{ji} = A_{ji} + \frac{B_{ji}}{T} + C_{ji} \, x \ln(T) + D_{ji} * T$, in the NRTL equation only B_{ij}, B_{ji} and α. are used
$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji})$
$\alpha_{ji} = \alpha_{ij}$
T = temperature in Kelvin

Table 1
Binary Interaction Parameter for NRTL Model

Component 1	Component 2	Bij	Bji	α	Source
Ethanol	EL	350.4	-19.11	0.398	Regressed from Experimental Data [26]
Ethanol	GVL	754.04	-318.19	0.224	Regressed from Experimental Data [9]
EL	GVL	-282.8	419.11	0.339	Regressed using UNIFAC

Our approach for comparing experimental vapor pressure data to the ChemCAD Library equation for vapor pressure Eq. (2) has been completed. It is based on modern computer technology and our understanding of the options for fit optimization. Table 2 displays the regression coefficients together with an acceptable root mean square deviation (RMSD). Figure 2 to Figure 4 compares the experimental results with the data produced when vapor pressure was predicted using Eq. (2) and the regressed coefficient. Since the temperature range of the employed data already corresponds to the temperature range in the simulation, the choice of experimental data is appropriate.

$$P = \exp(A + \frac{B}{T} + C \ln(T) + D\, T^{E} \tag{2}$$

where
P = vapour pressure in Pascal
T = temperature in Kelvin
A, B, C , D ,E = Coefficient for vapor pressure equation

Table 2
Coefficient for Vapor Pressure Equation (Eq. 2)

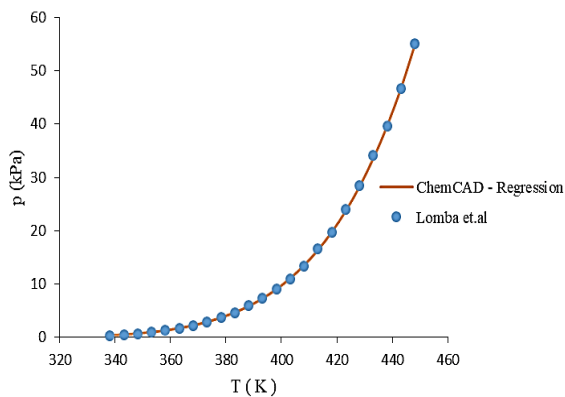| Component	A	B	C	D	E	RMSD P	Source
EL	348.13	-20956	-48.91	0.00	2.00	4.34×10^{-7}	Regressed from Experimental Data [27]
GVL	36.76	-7534.20	-1.17	0.00	2.00	9.97×10^{-7}	Regressed from Experimental Data [28]
Ethanol	122.52	-9236.7	-14.656	9.72×10^{-6}	2.00	1.51×10^{-10}	Regressed from Experimental Data [29]

Fig. 2. Comparison of Ethyl Levulinate Vapor Pressure used in the simulation and experimental data [27]
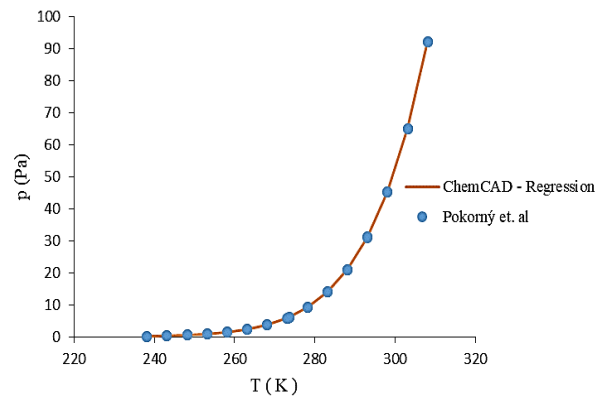

Fig. 3. Comparison of GVL Vapor Pressure used in the simulation and experimental data [28]
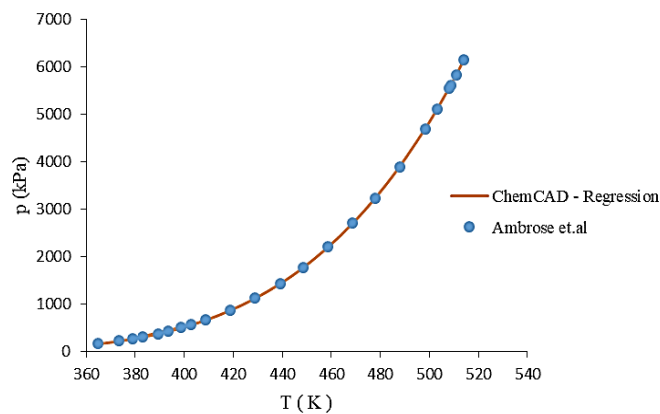

Fig. 4. Comparison of Ethanol Vapor Pressure used in the simulation and experimental data [29]

2.2 Process Description

Figure 5 illustrates the process simulation used in this study. At a temperature of 25 °C and a pressure of 101.3 kPa, the feed consists of 99 % mole Ethyl Levulinate (1 % mole ethanol) with a flow rate of 10 kmol/hour and hydrogen 60 bar (13 kmol/hour). The hydrogen flow rate is increased to

ensure maximum ethyl levulinate conversion [20]. The reactor used was a stoichiometric reactor operating at 200 °C and converting 99% ethyl levulinate based on experimental data [20,21,25]. To separate the remaining hydrogen from the reaction, the product pressure is reduced to 101.3 kPa and a heat exchanger is installed to adjust the flash tank temperature. A pre-heater is installed in the distillation column to regulate the temperature of the distillation column feed. The distillation column operates at a pressure of 101.3 kPa, with the top product being vapor. The vapor distillate is then cooled to 25°C for hydrogen separation in flash tank. Thirty percent of the distillate's liquid ethanol is recycled as a solvent in the hydrogenation reaction of ethyl levulinate. The distillation column's bottom product is GVL with a purity of 99.76 % mole.
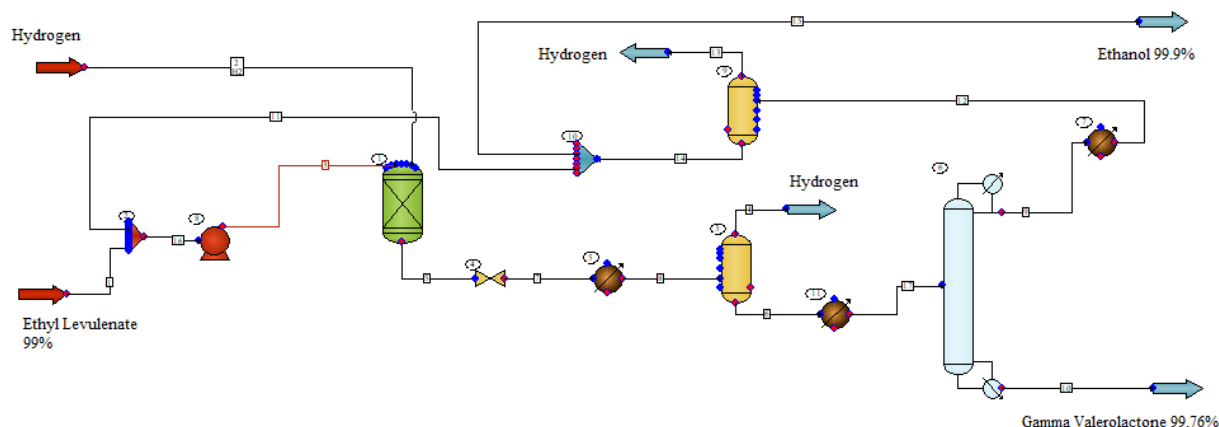

Fig. 5. Process flow diagram for simulating GVL production from EL using hydrogenation reaction and shortcut distillation column

3. Results

The vapor-liquid equilibrium (VLE) for several components involved in the purification of GVL using distillation was well represented by the NRTL activity coefficient model used in this simulation. Figures 6 and Figure 7 show a comparison of the VLE data generated by the NRTL equation and the experimental results for several components [9]. Table 3 displays the results of the simulation using the initial input specified in the process description. The results show that the two products are extremely pure. This demonstrates that the NRTL model can be used to accurately estimate the required VLE value. In the initial simulation, GVL and Ethanol were separated using a shortcut type distillation column, where it would be simple to conduct a sensitivity study on the effect of column feed temperature on the required column design and its effect on product quality. Design sensitivity studies can be performed to determine the importance of key design parameters as well as to recommend an optimal setup.
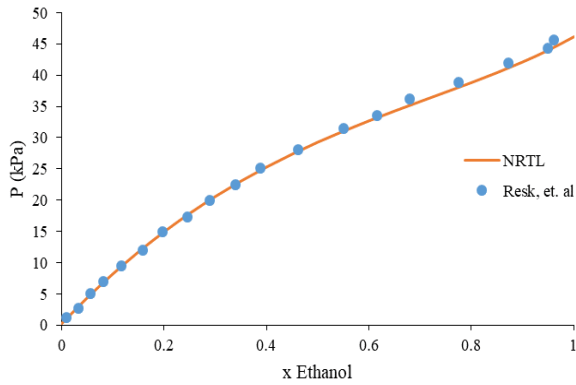
Fig. 6. P-x diagram of Ethanol – Ethyl Levulinate experimental data and NRTL model at 60 °C [9]
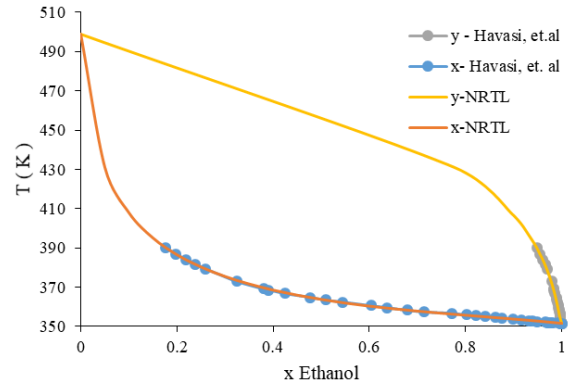

Fig. 7. T-xy VLE diagram of Ethanol – GVL experimental data and NRTL model and at 101 kPa [26]

Table 3
Simulation product from EL

Product	GVL	Ethanol
Temperature (°C)	221.632	25
Pressure (kPa)	101.3	101.3
Vapor Fraction	0	0
Mass Flow Rate (kg/ hr)	991.442	452.164
Composition (Mol Fraction)		
Ethyl Levulinate	0.000968	2.665×10^{-6}
Hydrogen	0	1.21×10^{-5}
GVL	0.9976	0.00071
Ethanol	0.001415	0.9993

By modifying design parameters, this work proposes a systematic approach for design sensitivity analysis of a distillation column. With the increase in the temperature of feed, a change in the outlet concentration of product and reboiler load of the distillation column has been observed. The temperature of the feed has a significant impact on the overall thermal balance of a distillation column system. At the same degree of separation, changes in the feed enthalpy can assist lower the required energy input from the reboiler [30]. The operating conditions achieved in the distillation column in the convergent state are shown in Table 4.

To gain a better understanding of the GVL – Ethanol separation process, sensitivity analysis was performed. The variables chosen for the sensitivity analysis for the GVL-Ethanol separation process are the distillation column feed temperature, with the GVL product flow rate, GVL product purity and reboiler load as the dependent variables. The outcomes are shown in Figures 8 and Figure 9. In Figure 5 can be seen that changing the feed temperature with constant convergence parameters from Table 4 does not affect the purity and flow rate of the GVL product. This is due to the fact that the simulation is based on the split fraction of LK and HK, so the resulting separation is constant. However, it will most likely have an impact on the reboiler load. As a result, the sensitivity analysis is extended in Figure 6 to examine the effect on the reboiler load. As shown in Figure 8, the change in feed temperature does not affect the reboiler load as a heat supplier to the column. As a result, the feed temperature was set at 25 °C for the rigorous distillation column operating conditions for the GVL – EL separation by removing the preheater and one flash tank in Figure 5. Figure 10 depicts the new process flow diagram for optimal simulation. The results of this new process are not significantly different from the initial simulation using the distillation column shortcut. The outcomes of the new

simulation are shown in Table 5. The ethanol produced from the separation of GVL – Ethanol is partially reused in the reactor as a solvent for the hydrogenation reaction.

Table 4
GVL – Ethanol separation distillation column shortcut configuration

| Colum Specification		Feed		Convergence Specification	
Number of Stages	12	Total Flow Rate (kmol/hr)	23.924	Light Key (LK)	Ethanol
Feed Stage	6	Temperature (°C)	70	Light Key Split	0.999
Reflux Ratio	0.086	Pressure (kPa)	101.3	Heavy Key (HK)	GVL
Operating Pressure	101.3	Component Molar Flow Rate in Feed (kmol/hr)		Heavy Key Split	0.001
		Ethyl Levulinate	0.0099	R/Rmin	2
		Hydrogen	0.0004		
		GVL	9.892		
		Ethanol	14.021		
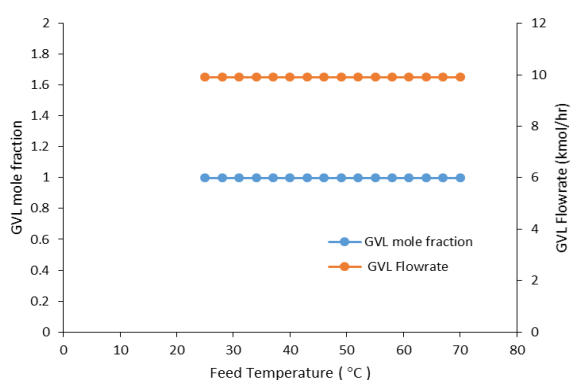
Fig. 8. Sensitivity analysis of the effect of column feed temperature on GVL purity and product flow rate
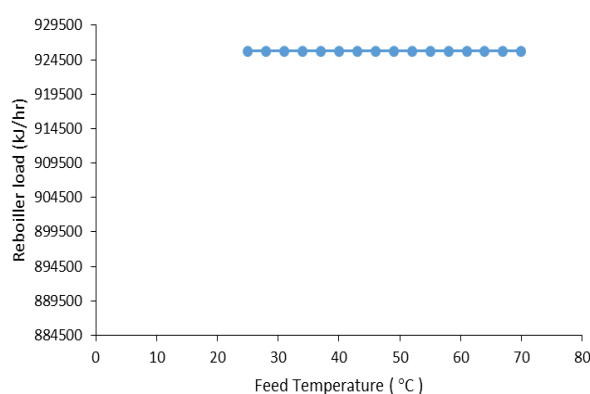

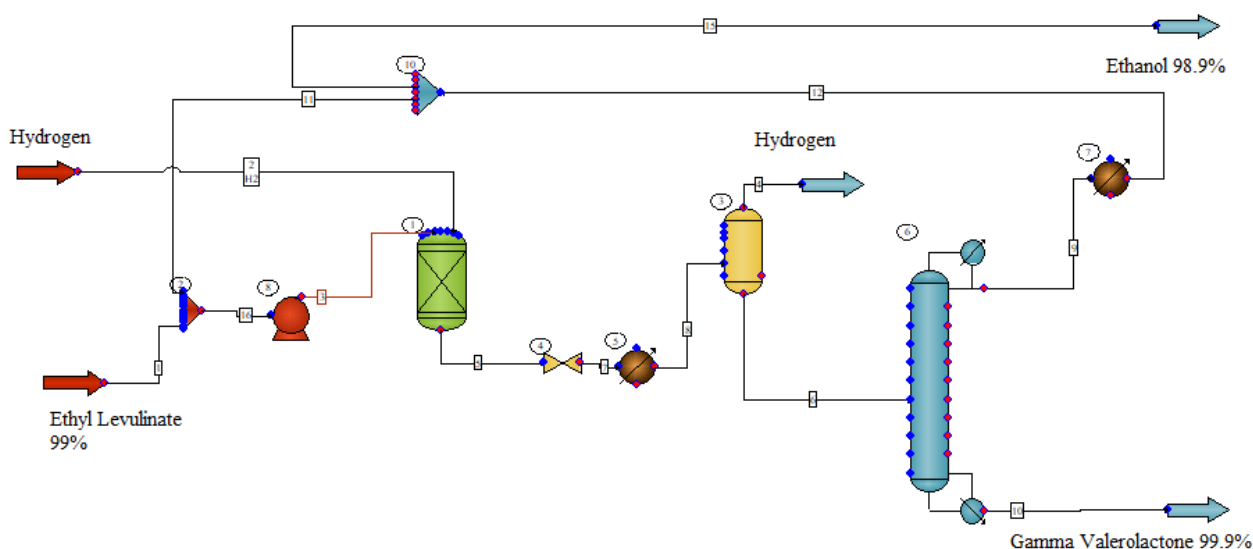**Fig. 9.** Sensitivity Analysis of the effect of column feed temperature on reboiler load

Fig. 10. Process Flow Diagram for simulation of GVL production from EL with hydrogenation reaction after optimization

Table 5
SCDS distillation column configuration for GVL - Ethanol separation

Specification	
Number of Stages	12
Feed Stage	6
Reflux Ratio	0.0866
Operating Pressure (kPa)	101.3
Condensor Type	Partial
Feed	
Molar Flowrate (kmol/hr)	23.8136
Temperature (°C)	25
Pressure (kPa)	101.3
Component Flow Rate in Feed (kg/hr)	
Ethyl Levulinate	1.413125
Hydrogen	0.00059
GVL	980.3615
Ethanol	639.101
Top Product	
Molar Flowrate (kmol/hr)	14.01487
Temperature (°C)	78.5413
Pressure (kPa)	101.3
Ethanol Mole Fraction	0.989
Bottom Product	
Molar Flowrate (kmol/hr)	9.79873
Temperature (°C)	279.562
Pressure (kPa)	101.3
GVL Mole Fraction	0.999
Reboiler Duty (kJ/hr)	1.223×10^6 J

The liquid phase distribution from the Ethanol – GVL distillation column shows two distinct areas: rectifying at the top of the feed stage (stage 5) and stripping at the bottom of the feed stage. In trays 5–7, the accumulation of the liquid phase is dominated by ethanol (Figure 8), the amount of which decreases as the tray position approaches the reboiler. The high heat of vaporization of the components of separated mixtures is linked to the energy intensity of the rectification process [31]. Starting with tray 6 (feed stage), the temperature drops (Figure 12), causing the amount of steam above the feed stage to be dominated by ethanol according to the VLE curve in Figure 7. In tray 1, the temperature is close to the boiling point of ethanol, and the mole fraction of ethanol has reached 0.989, allowing for proper separation of GVL and ethanol.
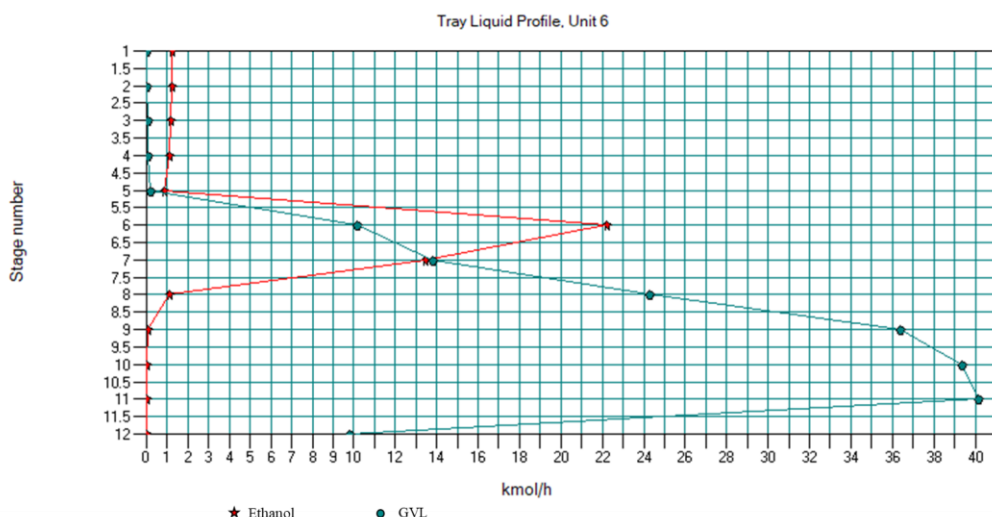
Fig. 11. Liquid phase flow rate profile of Ethanol and GVL components in the distillation column
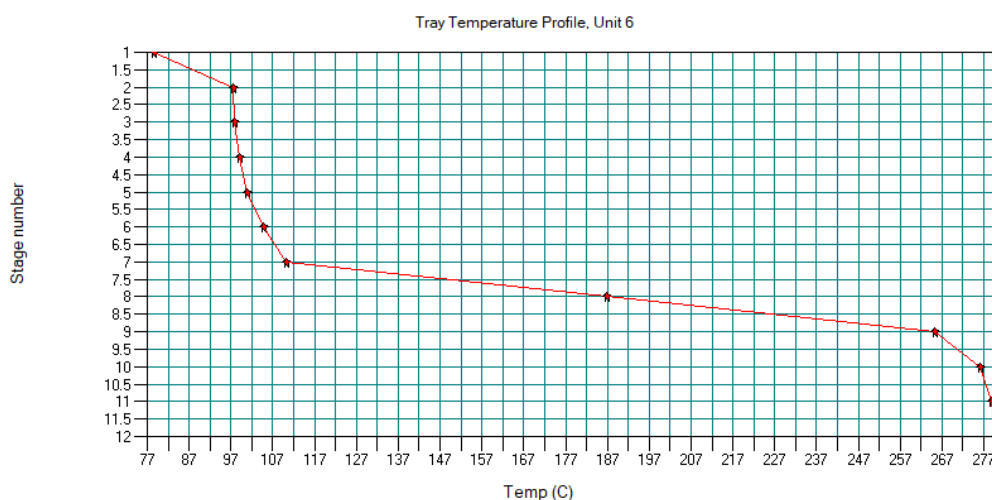

Fig. 12. The equilibrium temperature profile of Ethanol – GVL separation column

4. Conclusions

The NRTL activity coefficient model accurately models the vapor-liquid equilibrium for the system involved in the hydrogenation of ethyl levulinate to produce GVL. In order to produce GVL from EL, this work presented a simulation study of a method using EtOH solvent and heteregenous catalyst. High conversion of EL (99 mol%) were demonstrated in heterogeneous catalytic reaction based on experimental data. To find any unit operations where the operating conditions may be changed to enhance the process, sensitivity studies were carried out. Sensitivity analysis on the shortcut distillation column revealed that changes in column feed temperature did not affect the number of stages required for GVL – ethanol separation. Because the hydrogen fraction are so small when mixed with the feed stream that the vapor fraction of the mixture becomes 0 after SCDS column optimization, a flash tank for separating Hydrogen from the ethanol stream to be recycled is no longer required. The suggested PFD demonstrated efficient separation of GVL from Ethanol.

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