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Reparameterization of Binary Interaction Parameters for The Gamma-Valerolactone Purification Process

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ABSTRAK

Selain produksi biodiesel, bioetanol, biometana dan biohidrogen dari sumber terbarukan, gamma-valerolactone (GVL) muncul sebagai bahan bakar terbarukan potensial lainnya yang dapat diproduksi dari biomassa. GVL menunjukkan karakteristik yang sesuai sebagai sumber energi cair berkelanjutan yang menjanjikan. Dlaam kegiatan produksi GVL murni jumlah besar pastinya melibatkan proses pemisahan/ pemurnian, salah satunya adalah distilasi. Dalam perancangan proses distilasi diperlukan data kesetimbangan Uap – Cair (VLE), dan untuk akurasi perancangan biasanya digunakakan software simulasi proses seperti ChemCAD. Dalam penelitian ini, data VLE yang tersedia akan direparamterisasi sehingga bisa digunakan sebagai parameter model thermodinamika di Software ChemCAD. Pada penelitian ini dilakukan reparemeterisasi parameter interaksi biner (BIP) model NRTL untuk data VLE komponen yang terlibat dalam produksi GVL dari literature yang tersedia. Kemudian BIP hasil reparemterisasi digunakan untuk analisis sensitivitas pada shortcut kolom distilasi. Hasil analisis sensitivitas menunjukan bahwa perubahan suhu umpan berpengaruh terhadap konvigurasi kolom, tetapi tidak pada kualitas GVL yang dihasilkan.

***Kata kunci*:** Biofuel, Gamma-valerolactone,Distilasi, Kesetimbangan Uap-Cair, Reparameterisasi.

ABSTRACT

In addition to producing biodiesel, bioethanol, biomethane, and biohydrogen from renewable sources, gamma-valerolactone (GVL) is emerging as a potential renewable fuel from biomass. As a promising long-term liquid energy source, GVL possesses the necessary characteristics. The production of pure GVL in large quantities involves a separation/purification process, one of which is distillation. In designing the distillation process, Vapor-Liquid equilibrium(VLE) data is needed, and process simulation software such as ChemCAD is usually used for design accuracy. In this study, the available VLE data will be reparameterized to be used as a thermodynamic model parameter in ChemCAD Software. The binary interaction parameter (BIP) NRTL model reparameterization for the VLE data of the components involved in the creation of GVL was carried out in this work using data from the literature. The reparameterized BIP was then applied to the distillation column shortcut for sensitivity analysis. The findings of the sensitivity study reveal that changing the feed temperature changes the column arrangement but not the quality of the GVL produced.

***Keywords*:** Biofuel, Distillation, Gamma-valerolactone, Reparameterization, Vapor-Liquid Equilibrium.

1. INTRODUCTION

The majority of total energy consumption worldwide (about 80%) is generated from fossil fuels with global consumption projected to increase at an average annual rate of 0.9% through 2030, according to the

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International Energy Agency (IEA) [1], [2]. Renewable energy sources are reported as the fastest-growing sector of the world's energy resources, with consumption expected to increase by 3.0% per year by 2030. The transportation sector is the world's largest consumer of fossil energy (about 40%) indicating the importance of reducing fuel consumption in this sector [3]. Biomass is the most abundant renewable feedstock on Earth, for this reason, its use for producing renewable products such as chemicals, fuels and energy has been widely promoted in recent years. Biomass can be an ideal substitute for fossil resources as oil for producing various commodities. In this case, processes that convert biomass into high-value products are commonly called biorefineries [4]. Many researchers discover chemical varieties of biomass and various possible synthesis routes to produce major industrial chemicals and fuels [5], [6]. As the demand for chemicals and fuels increases while fossil resources will run out, it is imperative to find sustainable alternatives to petroleum-based products. Gamma-valerolactone (GVL), a natural molecule found in fruits and a commonly used food additive, demonstrates the most significant properties of an ideal renewable material and can be used to manufacture energy and carbon-based consumer products [7],[8]. Due to its excellent physical and chemical properties such as high boiling point, low volatility, easy degradation, and low toxicity, gamma-valerolactone (GVL) is an important compound derived from renewable biomass that can be used as an environmentally friendly solvent, fuel additive, alkene-based transportation fuel precursor, or intermediate compound to prepare other materials [9]. GVL, on the other hand, can be regarded as a sustainable liquid fuel for global transportation as well as a renewable hydrocarbon [10].

2. RESEARCH METHODS

Significant effort has been expended in the last decade to identify and characterize new renewable platform chemicals that can replace industrial chemicals or fossil base materials as renewable feedstocks for production. [11]. In this regard, lignocellulosic biomass (LCB) has piqued the interest of many because it is carbon-neutral, renewable, cost-effective, and abundantly available. Furthermore, advances in biorefinery technology may be able to meet future demand for bio-based fuels, chemicals, and other value-added products [12]. Among these chemicals is gamma-valerolactone (GVL), which was first proposed as a feedstock and renewable liquid energy by Horvat et al [13]. Recently, GVL has received significant interest, and several innovative applications for its utilization have been demonstrated. GVL can be easily obtained from biomass via levulinic acid and can be used to produce alkanes and alkenes for transportation fuels, ionic liquids, monomers for the polymer industry, etc. GVL has also been extensively accepted as an environmentally acceptable, aprotic, and dipolar solvent for synthesis and catalysis [14–16]. In terms of supporting data on the GVL production process, several studies have been carried out that focus not only on the synthesis route but also on the purification of GVL.

Pokki, et al.[17] determined isobaric vapor-liquid equilibrium (VLE) data from the GVL furfural system and examined the GVL as a binary mixture with water including its isothermal VLE data, the properties measured included excess enthalpy and solution density. In addition, measurements of the GVL-water solution were also carried out for the enthalpy property of evaporation and the heat capacity of the saturated solution. The study by Ceriani et al. [18] reported liquid-liquid equilibrium data for three n-tetradecane-based ternary mixtures from GVL. Ceriani et al [18] have suggested that gamma-valerolactone (GVL) can be considered a sustainable liquid because it is renewable and has environmentally friendly physical and chemical properties. Shen et al. [19] conducted a study on the use of GVL as a solvent in AGET ATRP, a type of polymerization technique that is very good for controlling the molecular weight of the polymer produced. The manufacture of Polymethyl methacrylate using GVL as a solvent yields conversion of 70.1% with a Polydispersity (PDI) of 1.27.

2.1. DATA COLLECTION AND PARAMETERIZATION METHOD

This research was initiated by collecting vapor-liquid equilibrium data for mixed binary systems involved in the GVL production process. After that, the vapor-liquid equilibrium data that has been collected is correlated with the NRTL activity coefficient equation to obtain binary interaction parameters using ChemCAD [1], [2], [20] software. The binary interaction parameters were calculated as a function of temperature in this work so that they could be accurately applied throughout a wide temperature range. The following is the NRTL model used in ChemCAD software.

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

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 $\alpha.$ are used

$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji})$

$\alpha_{ji} = \alpha_{ij}$

T = temperature in Kelvin

2.2. SIMULATION OF THE GVL SEPARATION PROCESS USING DISTILLATION COLUMN

The results of BIP reparameterization will be used to model the separation of GVL from the impurities. A distillation column shortcut is employed in this simulation. The effect of changes in feed temperature on the number of stages and the position of the feed stage required in the column is investigated in a sensitivity analysis. In this simulation, the feed is used at a temperature of 60 °C, a pressure of 101.3 kPa, a mass rate of 631. 68 kg/h and the composition in mole fraction is as follows:

1. GVL 0.3
2. Water 0.1
3. Levulinic Acid 0.001
4. Furfural 0.01
5. Furfuryl Alcohol 0.01
6. Ethanol 0.5789

The selection of feed composition were based on consideration of the conversion of furfural and levulinic acid of more than 99%, as well as the use of excess ethanol to ensure optimal conversion to GVL.

3. RESULTS AND DISCUSSION

The separation method is the most energy-intensive process in the chemical industry, although separation methods are prevalent in the chemical industry since most processes produce mixes of many components. Designing a suitable separation unit necessitates a thorough understanding of thermodynamic data as well as adequate modeling. While many reaction paths can be used to make compounds, environmental factors, simplicity of production, and energy consumption must all be considered. This comparison should include not just the reaction process but also the separation process because, in most situations, the separation process consumes the greatest energy and hence accounts for roughly 40% of the total production cost. [21]. Therefore, this study aimed to investigate the process of separating GVL from a mixture of components that may occur during the production process. [22].

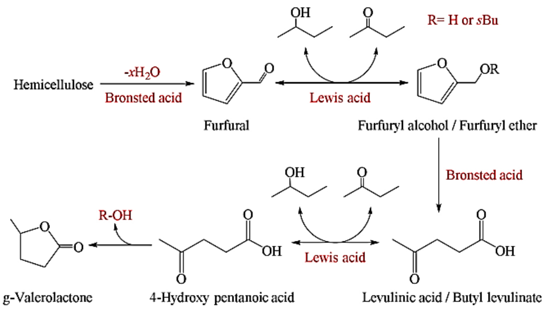

Figure 1. The process of synthesizing GVL from hemicellulose-containing materials. [16].

Theoretically, a bio-refinery is equivalent to a petroleum refinery producing oil fuel and chemicals. In the same way, effective biomass conversion technologies and separation and purification technologies, which represent about 20-50% of the total production costs, play an essential role in the thriving commercial implementation of bio-refinery. As a result, substantial advancements in separation and purification technologies can lower total production costs while also resulting in an environmentally friendly and economical process [4]. Knowledge of the thermodynamic data of the mixture is required for the proper design of the thermal separation unit for liquid mixtures. The essential data needed to construct a distillation unit are the vapor pressure of the pure component and the vapor-liquid equilibrium data. For a mixture that can produce azeotropes, the latter is critical. Without experimental data, we can only rely on calculating the vapor pressure of the pure component or on the calculation of the group contribution [23]. GVL can be produced in several ways, including hydrogenation of levulinic acid (LA) [24–26], hydrogenation of levulinate esters [27–29]. Meanwhile, the production of LA and levulinate esters can be derived from the breakdown of cellulose and hemicellulose (Figure 1).

Table 1. Availability of VLE data for binary mixtures in GVL production through hemicellulose pathway

Component	GVL	Water	Linulivic Acid	Furfural	Furfuryl Alcohol	Ethanol
GVL		V	X	V	X	V
Water	V		X	X	X	V
Linulivic Acid	X	X		X	X	X
Furfural	V	X	X		X	X
Furfuryl Alcohol	X	X	X	X		V
Ethanol	V	V	X	X	V	

Note: V = Experimental VLE data available, X = no experimental VLE data available.

Table 2. Availability of VLE data for binary mixtures in GVL production through hemicellulose pathway

Component 1	Component 2	Bij	Bji	α	Source
Water	Furfural	1310	220	0.3958	Database ChemCAD
Water	Furfuryl Alcohol	1134.03	-341.222	0.2207	Database ChemCAD
Water	Ethanol	670.441	-55.1681	0.3031	Database ChemCAD
Furfural	Furfuryl Alcohol	101.068	43.8876	0.3015	Database ChemCAD
Furfural	Ethanol	328.316	510.442	0.7771	Database ChemCAD
Furfuryl Alcohol	Ethanol	-323.236	594.055	0.2899	Database ChemCAD
Gamma-Valerolactone	Water	4865.466	1031.109	0.385519	Reparamterisasi (Havasi, et.al, 2016)
Gamma-Valerolactone	Furfural	15663.27	24941.81	0.203762	Reparamterisasi (Pokki, et.al,2018)
Gamma-Valerolactone	Ethanol	24627.21	3693.57	0.397018	Reparamterisasi (Havasi, et.al, 2018)
Levulinic Acid	Furfural	-432.347	954.3394	0.296021	Predicted using UNIFAC VLE
Levulinic Acid	Ethanol	-372.83	739.7252	0.296835	Predicted using UNIFAC VLE
Furfural	Furfuryl Alcohol	101.068	43.8876	0.3015	Predicted using UNIFAC VLE
Furfural	Ethanol	328.316	510.442	0.7771	Predicted using UNIFAC VLE
Furfuryl Alcohol	Ethanol	-323.236	594.055	0.2899	Predicted using UNIFAC VLE

In the production of GVL from hemicellulose as shown in Figure 1, several components are involved, namely:

a. GVL
b. Water
c. Linulivic Acid
d. Furfural
e. Furfuryl Alcohol
f. Ethanol (solvent)

If there is a partial conversion in the reaction, the final product will be a mixture of the above components, which must be separated by distillation. Distillation requires vapor-liquid equilibrium data, which can be presented using the NRTL model with Binary Interaction Parameters (BIP). The availability of VLE data for binary mixtures in GVL production for this simulation were presented in Table 1.

The binary pairs of each of the above components were reparameterized in this study. To obtain the NRTL BIP from experimental data that is not yet available, an estimation method using the UNIFAC equation [2] is performed. The results of reparameterization are presented in Table 2.

The following are the results of VLE prediction using the NRTL model for some of the available VLE data in the form of experimental data.

Figures 2–4 show that the reparameterization results are very accurate, with an average deviation of 0.4%. Based on these findings, it is possible to conclude that the BIP parameterization results can be used for simulation and optimization of the GVL purification process via distillation. Figures 5–10 show the results of simulations and case studies for optimizing GVL purification by distillation.

Figures 5 and 6 show that increasing the feed temperature of the distillation column reduces the number of stages required to achieve the desired product purity. It can be seen that the energy required to boil the mixture decreases as the mixture enters the column close to its boiling point, so that the amount of volatile components that evaporates is greater in the feed stage, shifting the equilibrium to a better separation state.

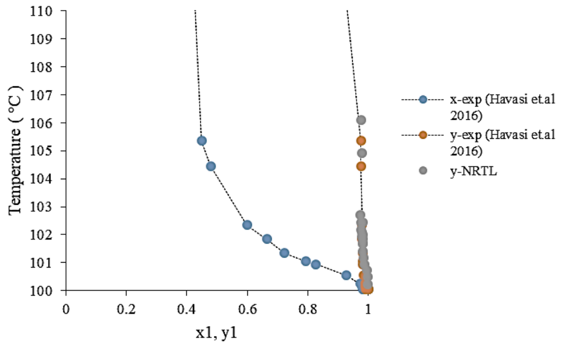

Figure 2. VLE Txy curve for the Water – GVL system at a pressure of 101.325 kPa [30].

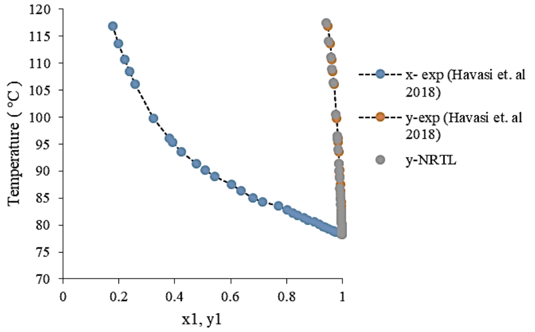

Figure 3. VLE Txy curve for the Ethanol – GVL system at a pressure of 101.325 kPa [22].

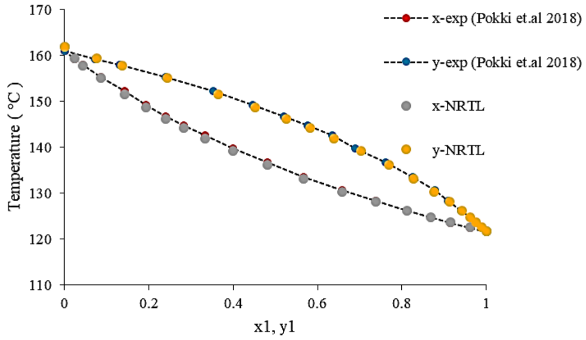

Figure 4. VLE Txy curve for Furfural - GVL system at 30 kPa [17].

Figures 7 and 8 show that changing the feed temperature does not affect the GVL recovery results at the bottom product.

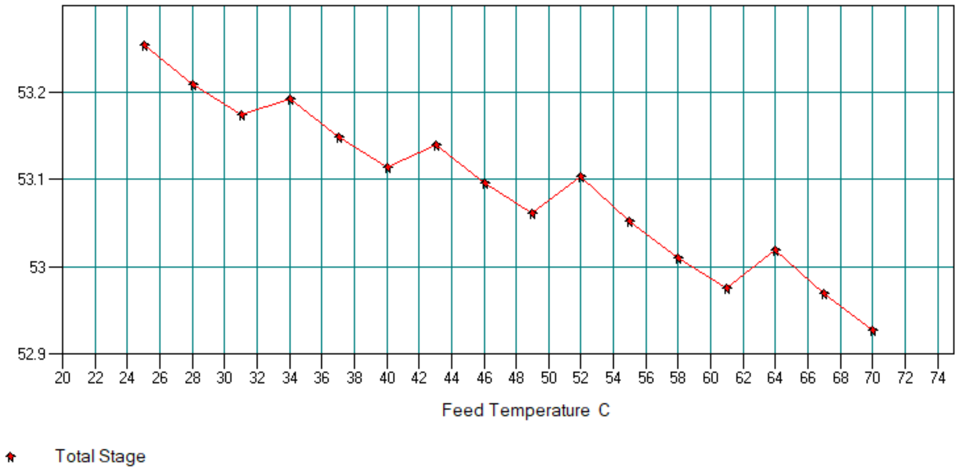

Figure 5. The number of stages required in GVL purification column.

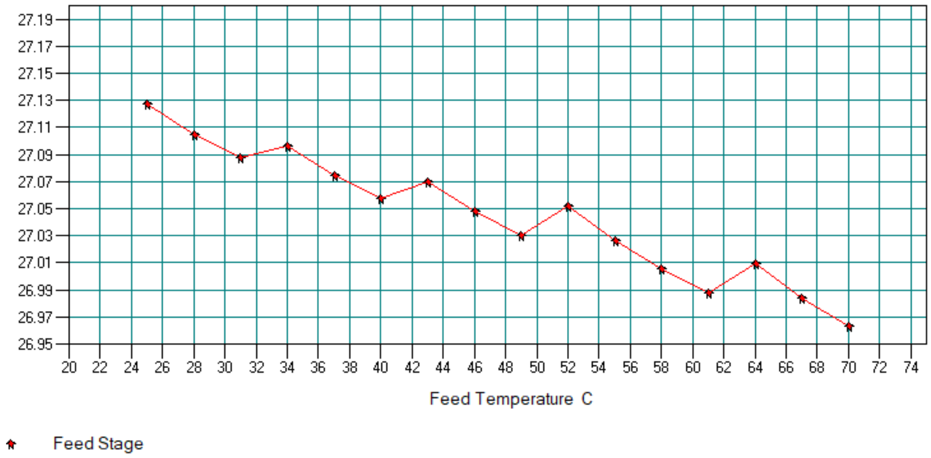

Figure 6. Position of feed stage in distillation column for GVL purification.

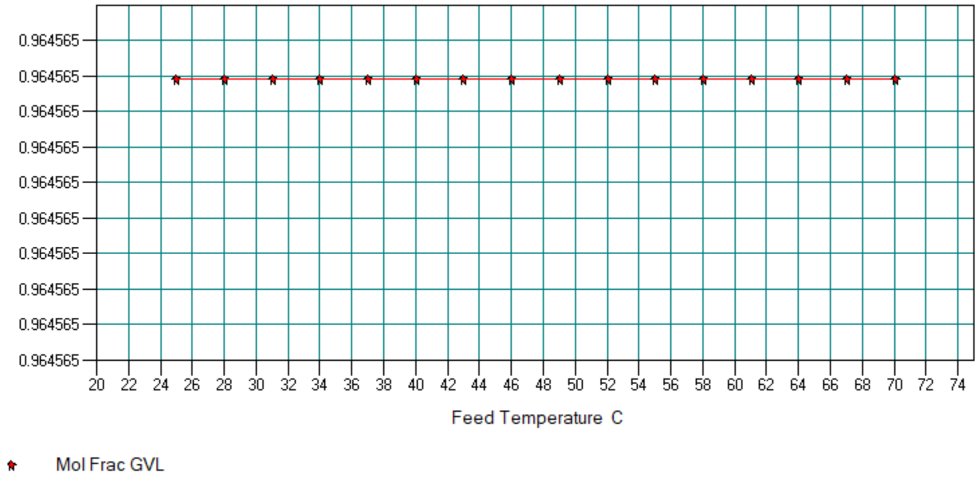

Figure 7. Purity (mole fraction) of the GVL product in the distillation column.

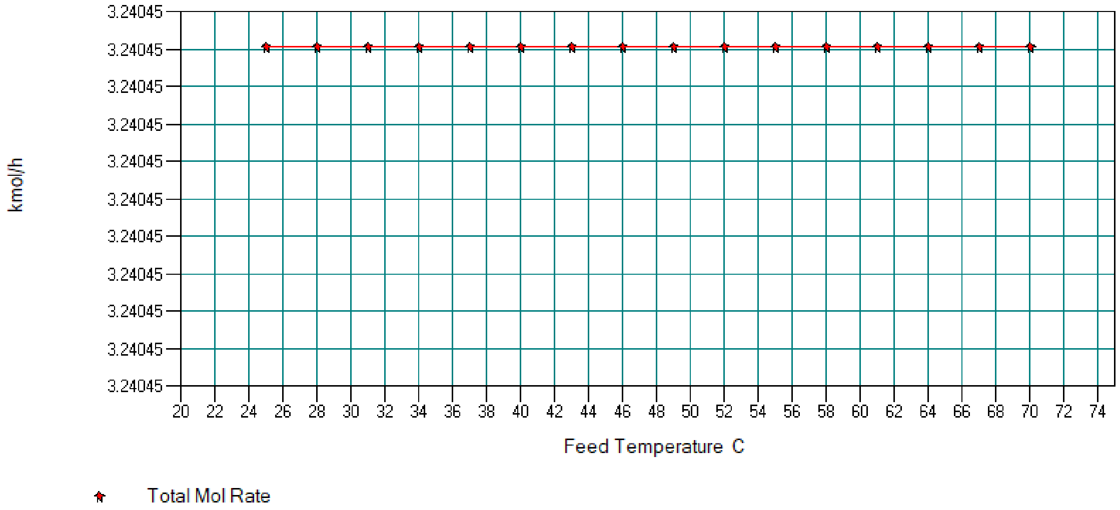

Figure 8. Product flow rate of GVL distillation column (Bottom Product).

CONCLUSSION

It can be observed that the results for systems involved in GVL production are well defined. The UNIFAC model was used to calculate the baseline VLE data for some components that lacked experimental data. Sensitivity analysis in the simulation of the GVL separation process from the mixture reveals that changes in column feed temperature affect the number and position of the feed stage but do not affect purity or product flow rate.

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