

Downstream Processing of 1,3-Propanediol: Thermodynamic Analysis and Simulation

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In recent years, as a result of the transition from the “hydrocarbon economy” to the “carbohydrate economy”, the chemical industry has accepted the fermentation process as an economical path for producing many compounds. 1,3-propanediol is one of them, since it is one of the oldest known fermentation products that was reliably identified in 1881 in glycerol fermentation.

This work focuses on the separation of the 1,3-propanediol+water mixture that, to the authors’ knowledge, is poorly investigated in the literature. This separation is encountered in the microbial production of 1,3-propanediol, as well as in the downstream processing of the aqueous mixture obtained in the production of biofuels in which heavy by-products are often present. In particular, the system comprising water+1,3-propanediol+glycerol has been considered representative of the fermentation broth to be subject to further separation. Since no parameters of the Non-Random Two-Liquid (NRTL) model are available in the Aspen Plus® V11 process simulator for two of the three pairs of compounds involved in this system, a thermodynamic analysis has been performed to properly calibrate such a model for a reliable representation of the Vapour-Liquid Equilibrium data that have been collected from the literature. The resulting thermodynamic model has been used in the Aspen Plus® V11 process simulator for studying the recovery and purification of 1,3-propanediol produced by glycerol fermentation, paying attention not only to its purity but also to the quality of the removed water (maximum theoretical oxygen demand of 10 g_{O₂}/l) in order to avoid a water treatment step.

1. Introduction

Many challenges, such as the depletion of fossil fuels, environmental concerns and the concept of sustainability, have recently led to a growing interest in processes being able to produce fuels and chemicals from alternative, renewable resources. In this context, the case of biobutanol can be mentioned to show how, in response to the transition from the “hydrocarbon economy” to the so-called “carbohydrate economy”, its production by fermentation (the well-known acetone-butanol-ethanol or ABE fermentation) has gained renewed attention in the last years (Lodi et al., 2018), despite the limits it has for an industrial-scale production that are related to the high costs of the downstream processing. To overcome these drawbacks, numerous techniques have been investigated and integrated with ABE production by fermentation, including integrated product recovery (IPR) techniques like gas stripping (De Guido et al., 2019).

Also the chemical industry is now accepting the fermentation process as an economical means for producing bulk chemicals from bio-based or renewable feedstocks. For example, iso-propanol can be produced by fermentation of cellulosic materials (Moioli et al., 2021), or ethylene can be obtained from biomass-derived ethanol by means of a sustainable route alternative to the petrochemical one (Rossetti et al., 2017), which requires the development of strategies for the downstream processing and purification for the production of biofuels. In this context, there is a paramount interest in producing 1,3-propanediol by fermentation using microorganisms. Among bulk chemicals, this compound has attracted worldwide attention due to its numerous applications in different fields. The reader can refer to the work by Saxena et al. (Saxena et al., 2009) for a comprehensive review of this. Conventional processes for 1,3-propanediol production are those by Degussa and by Shell, which respectively start from acrolein and ethylene oxide. Some drawbacks related to these

processes are the severe operating conditions, the use of catalysts, and the release of toxic intermediates. However, 1,3-propanediol is one of the oldest known fermentation products that was identified in 1881 by August Freund in a glycerol fermentation mixed culture containing *Clostridium Pasteurianum* as an active organism. Thus, much attention has been recently devoted to the microbial production of 1,3-propanediol, either based on glycerol or on glucose. Glycerol, which is a major by-product of the biodiesel industry, promises to be a good substrate for the production of 1,3-propanediol, which may change the perception of glycerol as an industrial waste (Saxena et al., 2009).

This work focuses on the downstream processing of 1,3-propanediol produced by glycerol fermentation, which requires the development of an efficient purification strategy. To this purpose, the mixture water+1,3-propanediol+glycerol has been considered, which has been first subject to a thermodynamic analysis aimed at the set-up and calibration of the Non-Random Two-Liquid (NRTL) model (Renon and Prausnitz, 1968) for a correct representation of the thermodynamic phase behaviour. Then, it has been used for the simulation of the separation process based on two distillation columns: in the first one, water (i.e., the most abundant component in the mixture) is separated paying attention to its quality (a maximum theoretical oxygen demand of 10 g_{O2}/l has been considered) to avoid its further treatment; in the second one, 1,3-propanediol at the desired purity (99.5 wt.%) is separated from glycerol, which can be recycled to the fermentation step.

2. Methods

Given the components that are involved in the system under investigation in this work, the NRTL model has been considered suitable for the representation of the thermodynamic behavior of the system. Such a model calculates the activity coefficient according to Eq(1):

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (1)$$

where:

$$\begin{aligned} G_{ij} &= \exp(-\alpha_{ij} \tau_{ij}) \\ \tau_{ij} &= a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \\ \alpha_{ij} &= c_{ij} + d_{ij} (T - 273.15K) \\ \tau_{ii} &= 0 \\ G_{ii} &= 1 \end{aligned} \quad (2)$$

However, when using the Aspen Plus® V11 (AspenTech, 2019) process simulator, no Binary Interaction Parameters (BIPs) are available for the two pairs water+1,3-propanediol and 1,3-propanediol+glycerol. One may use the BIPs presented in a previous literature work (Sanz et al., 2001), but this was considered not the best choice since they were regressed using Vapor-Liquid Equilibrium (VLE) experimental data presented in the same work for the ternary system at 0.3 bar, rather than using VLE data for each pair of compounds in a wider range of conditions. Therefore, in this work BIPs of the NRTL model have been regressed, when missing, based on VLE data available in the literature for each pair of compounds. The parameters a_{ij} , a_{ji} , b_{ij} , and b_{ji} have been assumed as adaptive ones; c_{ij} has been fixed at 0.3 (i.e., the typical recommended value) and all the remaining BIPs in Eq(2) have been set to zero. The collection of VLE data has been carried out using the NIST (National Institute of Standards and Technology) database. In particular, for the system water+1,3-propanediol isobaric data sets have been found covering the range 0.08 - 1.01 bar (104 points), which have been used for regressing the missing BIPs of the NRTL model. As for the water+glycerol system, many isobaric VLE data (195 points) are available in the literature in the range 0.01 - 1.01 bar, which have been used to check if the BIPs available in Aspen Plus® V11 (AspenTech, 2019) for the NRTL model allow to satisfactorily represent the thermodynamic behaviour of this system. As for the pair 1,3-propanediol+glycerol, only one dataset is available in the NIST database, which consists of P-T-x data (48 points) at different pressures and temperatures in the range 0.0001 - 0.34 bar and 361.80 - 462.28 K, respectively. Such data have been used for the regression of the BIPs of the NRTL model.

3. Results and discussion

In this section, the results of the calibration of the NRTL model are presented and discussed (section 3.1), as well as the results of the simulation of the process for 1,3-propanediol recovery and purification (section 3.2).

3.1 NRTL model parameters

The BIPs of the NRTL model regressed for the binary system water+1,3-propanediol are reported in Table 1. The good agreement of the results of calculation (solid line) and the experimental data is shown in the T-x-y plots in Figure 1 for the pressures of 0.30, 0.40 and 1.01 bar (T-x-y plots at the other pressures are not shown due to the limited length of the paper), at which the bubble-point temperature is predicted with a deviation within ± 2 K. Moreover, as shown in Figure 1, the NRTL model with the regressed BIPs (solid line) performs better than the NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (dashed line) that, in comparison to other values ($c_{ij} = 0.3$ and $c_{ij} = 0.47$) gave them a slightly better fit of their VLE data at 30 kPa for the ternary system water+1,3-propanediol+glycerol.

Table 1: Regressed NRTL parameters for the system water(i)+1,3-propanediol(j)

a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}
2.8322	-0.6386	-187.5894	-220.6440	0.3

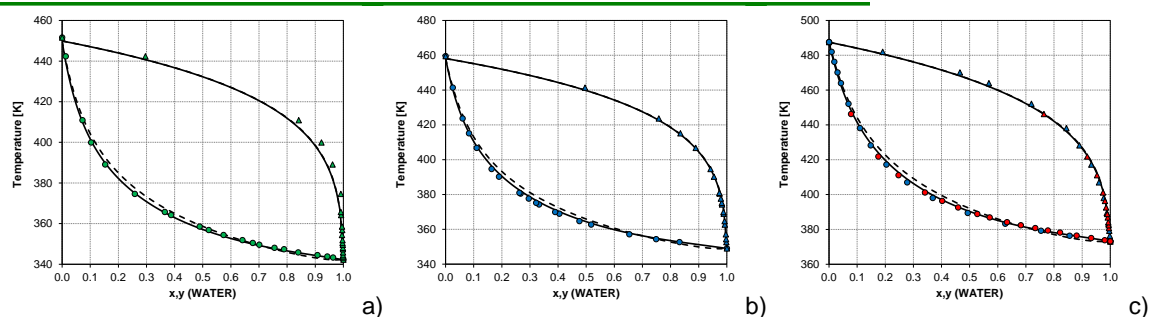


Figure 1: T-x-y diagram for the system water+1,3-propanediol at: a) 0.30 bar; b) 0.40 bar; c) 1.01 bar. Experimental data taken from the literature (green, (Sanz et al., 2001); blue, (Mun and Lee, 1999); red (Lai et al., 2014)). NRTL model with the regressed BIPs (solid line); NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (dashed line)

As for the water+glycerol system, the BIPs of the NRTL model that are available in Aspen Plus[®] V11 (AspenTech, 2019) are reported in Table 2. The results (solid line) are illustrated in the T-x-y diagrams in Figure 2, which show a good agreement with the experimental values, with an average absolute deviation for the bubble-point temperature of 0.16 - 6.25 % in the pressure range 0.01 - 1.01 bar. However, a deviation from the experimental data is observed along the dew-point curve at atmospheric pressure (Figure 2c). Since only one literature source (Chen and Thompson, 1970) reports the composition of the vapour phase in addition to that of the liquid phase, it is not possible to check the reliability of these data that deviate from the calculated ones at temperatures higher than 450 K. Moreover, the NRTL model with BIPs that are available in Aspen Plus[®] V11 (AspenTech, 2019) performs better than the NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (dashed line), especially at the lowest pressures. At atmospheric pressure, a slightly wider lens is obtained with the latter model and it is more difficult to understand which model is more reliable because of the scatter in the available experimental data along the bubble-point curve. More VLE data are planned to be measured for this system at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano to shed some light on this.

Table 2: NRTL parameters available in Aspen Plus[®] V11 (AspenTech, 2019) for the system water(i)+glycerol(j) in the temperature range 298.15 - 563.15 K

a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}
-1.2515	-0.7318	272.6075	170.9167	0.3

The BIPs of the NRTL model regressed for the system 1,3-propanediol+glycerol are summarized in Table 3 and the results (filled dots) are illustrated in Figure 3, which shows that the maximum deviation, obtained at the

lowest temperatures, is within 3.5 K (Figure 3b) and is much lower than the one obtained with the NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (empty triangles).

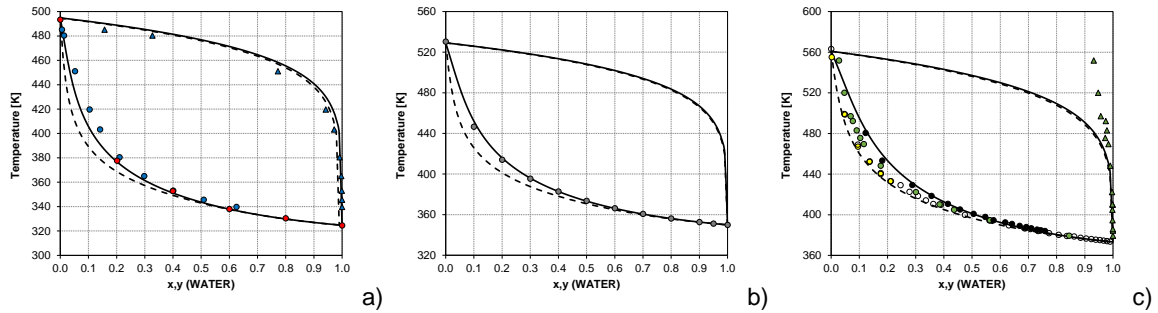


Figure 2: T-x-y diagram for the system water+glycerol at: a) 0.13 bar; b) 0.42 bar; c) 1.01 bar. Experimental data taken from the literature (blue, (Sokolov et al., 1972); red, (Veneral et al., 2013); grey, (Sokolov et al., 1972); yellow, (Gruen and Wirth, 1919); white, (Lewis, 1922); green, (Chen and Thompson, 1970); black, (Oliveira et al., 2009)). NRTL model with BIPs that are available in Aspen Plus® V11 (solid line); NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (dashed line)

Table 3: Regressed NRTL parameters for the system 1,3-propanediol(i)+glycerol(j)

a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}
-0.9094	-0.6155	900.0619	10.5235	0.3

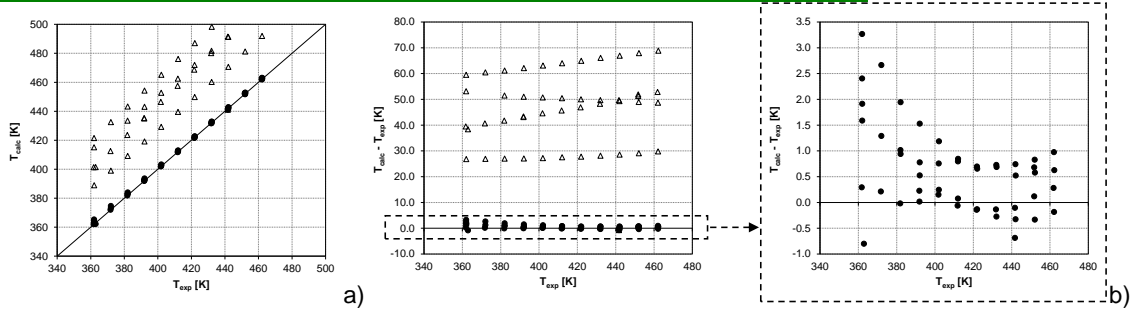


Figure 3: Calculated temperature using the NRTL model for the system 1,3-propanediol+glycerol: a) parity plot; b) error. Experimental data taken from the literature (Mokbel et al., 2012). NRTL model with the regressed BIPs (filled dots); NRTL model with the BIPs presented by Sanz et al. (Sanz et al., 2001) with $c_{ij} = 0.8$ (empty triangles)

3.2 1,3-propanediol recovery and purification process

A simulation has been carried out for the recovery and purification of 1,3-propanediol contained in a fermentation broth having the following composition (Sanz et al., 2001): 80 wt.% water, 9 wt.% 1,3-propanediol and 11 wt.% glycerol. Aspen Plus® V11 (AspenTech, 2019) has been used for this purpose and the NRTL model with the BIPs reported above for each pair of compounds has been selected as thermodynamic package. First, the separation by flash expansion has been considered for water removal in order to assess the performances that can be achieved using a single stage of separation. The feed (100 kg/h) enters the flash chamber at its bubble-point temperature at the operating pressure of the vessel. In order to saturate the two degrees of freedom that characterize this unit operation, the pressure and the vaporization ratio (V/F) have been specified. The pressure has been fixed at 0.3 bar, whereas the vaporization ratio has been varied in the range 0.6 - 0.99. As shown in Figure 4, as the vaporization ratio increases, the duty and the recovery of water both increase (since more water is evaporated), but its purity decreases from 99.97 mol.% / 99.85 wt.% at V/F = 0.6 down to 95.75 mol.% / 83.08 wt.% at V/F = 0.99. This latter aspect is not desired since it has an impact on the downstream water treatment (De Guido et al., 2021) by making it more demanding. Thus, the same mixture has been subject to separation by distillation in order to assess the performances that can be achieved by means of a multi-stage separation. First, a preliminary short-cut calculation has been carried out with the DSTWU column available in Aspen Plus® V11 (AspenTech, 2019), which makes use of the Winn-Underwood-Gilliland method. The column has been considered to be operated at the same pressure of 0.3 bar and pressure drops have been neglected.

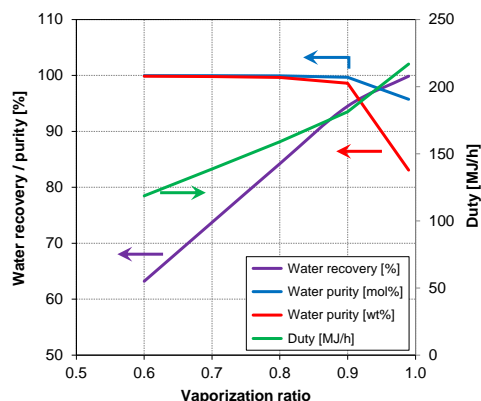


Figure 4: Results of the sensitivity analysis on the vaporization ratio for the removal of water by flash expansion

By specifying the recovery of water (i.e., the light-key component) in the top product, set equal to 99.99 %, and the recovery of 1,3-propanediol (i.e., the heavy-key component) in the top product, set equal to 0.01 %, the minimum reflux ratio, R_{\min} , has resulted to be 0.026, whereas the minimum number of stages has turned out to be equal to 4.84. Assuming a reflux ratio $R=2 \cdot R_{\min}$, the number of ideal stages is obtained, which has been, then, specified in the simulation of the rigorous distillation column, thus, equipped with 24 ideal stages (including the bottom reboiler) and a total condenser, with the feed entering the column on the 10th stage from the top. In addition to that, in the rigorous distillation the same reflux ratio has been specified together with the mole fraction of 1,3-propanediol in the top product stream. This value has been determined by finding the maximum content of 1,3-propanediol that is allowable to limit the theoretical oxygen demand to 10 g_{o2}/l, considering that 1,3-propanediol is the only oxygenated compound that is found in the top product stream. This allows recovering all the water in the top product at a high purity (99.85 mol.%, 99.37 wt.%). As shown in Figure 5, the bottom product consists of an almost equimolar mixture of 1,3-propanediol (48.31 mol.%) and glycerol (51.69 mol.%), which is further separated in the second column for recovering the desired product 1,3-propanediol.

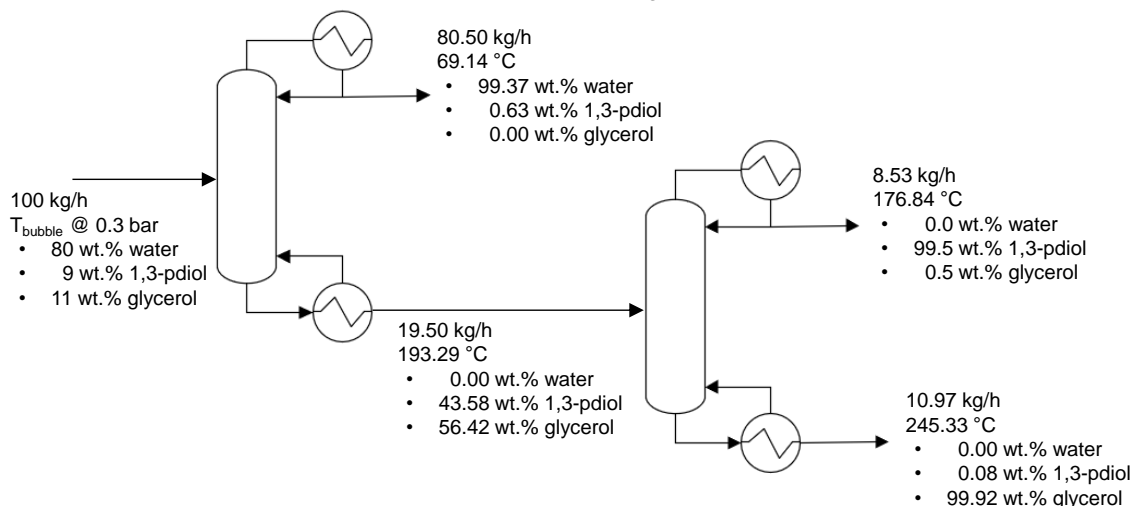


Figure 5: Simulation of the process for the recovery and purification of 1,3-propanediol from a fermentation broth containing water (80 wt.%), 1,3-propanediol (9 wt.%) and glycerol (11 wt.%)

Also in this case, a preliminary short-cut calculation has been performed first. In order to recover 99.9 % of 1,3-propanediol at 99.5 wt.% purity, R_{\min} has resulted to be 0.253, whereas the minimum number of stages has turned out to be equal to 5.75. Assuming $R=2 \cdot R_{\min}$, the number of ideal stages is obtained, which has been, then, specified in the simulation of the rigorous distillation column, thus, equipped with 11 ideal stages (including the bottom reboiler) and a total condenser, with the feed entering the column on the 6th stage from the top. As a result, 1,3-propanediol is separated at the desired purity from glycerol, recovered in the bottom product at a purity of 99.92 wt.%, which can be recycled to the fermentation step.

4. Conclusions

Considering the importance of a transition towards sustainable processes, 1,3-propanediol may be obtained by fermentation of renewable substrates, as an alternative to the conventional production processes. Glycerol-rich streams generated by the biofuels industry have the potential to be used to this purpose. This poses the problem of separating 1,3-propanediol from the fermentation broth, that can be assumed to consist of water+1,3-propanediol+glycerol. In this work, a thermodynamic analysis has been carried out for a reliable description of the phase behaviour of this system. To this purpose, the Binary Interaction Parameters of the Non-Random Two-Liquid (NRTL) model have been regressed, when missing, based on VLE data collected from the literature. The model so calibrated, which allows obtaining a good agreement between calculated and experimental values, has been implemented in the Aspen Plus® V11 software for the simulation of 1,3-propanediol recovery and purification from a fermentation broth containing 80 wt.% water, 9 wt.% 1,3-propanediol and 11 wt.% glycerol. It has been shown that, by using two distillation columns, it is possible to recover all water in the first one, meeting the target theoretical oxygen demand of 10 g_{o2}/l, and to recover 1,3-propanediol at the desired purity (99.5 wt.%) in the second one.

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