

# Downstream Processing of Butanol Produced by Fermentation: Thermodynamic Measurements and Modelling

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Several factors, including environmental concerns and the concept of sustainability, are leading to an increased interest in processes able to produce fuels and chemicals from alternative, renewable resources. In this context, the interest in the Acetone-Butanol-Ethanol (ABE) fermentation of lignocellulosic biomasses has been intensified in the last years as a route alternative to the petrochemical one for producing butanol both for the chemical industry and as a biofuel. This work focuses on the downstream separation process of the ABE fermentation, which represents a key challenge due to its high energy demand. The attention is devoted to the thermodynamic framework in order to properly describe the phase equilibrium conditions involved in the process. To this purpose, new experimental data, collected at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano, are presented as for Vapour-Liquid Equilibria (VLE) for the binary system ethanol+water and for Liquid-Liquid Equilibria (LLE) for the pair 1-butanol+water. The collected data show good agreement with the experimental data available in the literature. Then, the performances of the Non-Random Two-Liquid (NRTL) thermodynamic model, coupled with the Redlich-Kwong (RK) Equation of State for the calculation, respectively, of the activity coefficient in the liquid phase and of the fugacity coefficient in the vapor phase, are discussed to assess its reliability in the thermodynamic characterization of the systems of interest. The model can predict the vapour-liquid equilibrium temperature with a percent Average Absolute Deviation (AAD%) in the range 0.17 – 0.26 %, the mole fraction of ethanol and water in the vapor phase with an AAD%, respectively, of 23.3 – 31.6 % and 4.3 – 12.1 %. Concerning the LLE measurements for the system 1-butanol+water, the model predicts the mole fraction of water with an AAD% of 2.4 % and 0.17 %, respectively, in the organic and in the aqueous phases.

## 1. Introduction

The search for green chemicals and fuels is getting increasing interest towards a more sustainable future. In this scenario, the Acetone-Butanol-Ethanol (ABE) fermentation is a promising green route for the biological production of butanol, which finds application both as a biofuel and as a reactant.

The ABE fermentation is a process that uses bacterial fermentation to produce acetone, 1-butanol and ethanol from starch-rich, sugar-rich or lignocellulosic materials (García et al., 2011). This process has been known since the beginning of the 20<sup>th</sup> century (Schiel-Bengelsdorf et al., 2013) and its industrial exploitation started in 1916 during the First World War (Weizmann, 1919). However, the market penetration of biobutanol is still today limited due to its higher production costs in comparison with those for petrobutoanol (Veza et al., 2021). In particular, the downstream separation of the three obtained products represents a major challenge to be addressed in the next years due to its high-energy demand. In this scenario, the collection of new thermodynamic equilibrium data under different operating conditions for the binary mixtures of interest for the ABE downstream separation process is essential to properly assess phase equilibrium conditions and to check the predictability of thermodynamic models in the characterization of the systems under investigation.

This work presents new experimental data collected in the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano for the systems ethanol+water (VLE data at 103.5, 150.0 and 200.0 kPa) and 1-butanol+water (LLE data at atmospheric pressure in the temperature range 313.15 – 353.15 K), both of interest in the context of the ABE fermentation process (De Guido et al., 2019).

## 2. Experimental Setup

In this section, the apparatus and the procedure used for performing the VLE and LLE measurements are described. The experiments were carried out in the PT lab, which is located at Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta” and has been created within the “Ingegneria Chimica – Energia (ICE)” collaboration with the aim of collecting experimental data of phase equilibria (Vapour-Liquid-Equilibrium (VLE), Vapour-Liquid-Liquid-Equilibrium (VLLE) and Liquid-Liquid-Equilibrium (LLE)) of mixtures of interest for which there is a lack of data in the literature or in other existing databases.

The PT lab comprises a unit (Fischer Labodest VLLE 602, Figure 1a) for these types of measurements that is a recirculating still in Borosilicate Glass 3.3, operating from vacuum to 400 kPa and from ambient temperature to 453.15 K. For the operation under vacuum, it is connected to a vacuum rotary pump (Edwards E2M5), provided with a trap upstream. For the operation with two liquid phases at atmospheric pressure, it is equipped with an ultrasound generator that enhances the mixing of the condensed phases to achieve the equilibrium with the vapor phase. Further details on the unit are reported in Moiola et al. (Moioli et al., 2021). The PT lab is also equipped with a gas chromatograph (GC) Agilent 7820A with a TCD detector, and has been recently improved with a thermostatic bath (Huber CC304) for the study of LLE at different temperatures.

Ethanol (denatured with about 1% methyl ethyl ketone, with molecular weight of 46.07 g/mol and density of 0.79 kg/l), 1-Butanol (with molecular weight of 74.12 g/mol and density of 0.81 kg/l) and demineralized water (ISO 3696 Q3, ASTM D 1193 TYPE 4) were used for the measurements presented in this work. Table 1 summarizes information about the supplier and the purity of these chemicals. Nitrogen (> 99.99 mol.%) from Sapio, coming from a tank storing it in the liquid phase, is used for pressurizing the VLLE unit up to the desired pressure and as a carrier for the GC. The latter one was calibrated to determine the response factors for each component.

*Table 1: Purities and suppliers of the chemicals used in this work*

Chemical	Supplier	Purity
Ethanol (CAS 64-17-5)	Merck KGaA	99 %
1-Butanol (CAS 71-36-3)	Sigma-Aldrich	99.9 %
Demineralized water	Idrochimica	ISO 3696 Q3, ASTM D 1193 TYPE 4

### 2.1 VLE Measurements

VLE measurements for the system ethanol+water were performed using the Fischer Labodest VLLE 602 unit (Figure 1a) and following the same experimental procedure described in a previous work (Moioli et al., 2021), to which the reader can refer for more details. In this work, a more detailed description of the LLE unit is given in the following section. For the system ethanol+water, measurements were performed at 103.5, 150.0 and 200.0 kPa to cover the range of conditions in which data are missing in the literature (indeed, data at sub-atmospheric pressures and at pressures above 200.0 kPa are already available). It was decided to start the measurements at 103.5 kPa (i.e., at a pressure close to the ambient one) to validate the apparatus and the experimental procedure for this system by comparison with literature data. The experiments started with pure ethanol and were continued by gradually adding water to the mixture to be charged into the unit so to cover the full range of composition from one pure component to the other one. As the pressure and the water content increased (> 80 mol% on a molar basis), it was necessary to set a higher duty value (40-50 %) for heating up the mixture while keeping the temperature stable. For this system, to deal with the more rapid evaporation of the feed inside the heater, the loading of the same feed mixture was more frequent to avoid leaving the resistance uncovered.

### 2.2 LLE Measurements

For LLE measurements for the system 1-butanol+water, the device used for charging the mixture (denoted by the term “equilibrium cell” (EC) in the following) to be analyzed was one of the two receivers (Figure 1b) the Fischer Labodest VLLE 602 unit is equipped with for sampling the liquid and vapor (in its condensed state) phases at equilibrium. This choice was made aiming at setting up a proper procedure for future VLLE measurements with that unit, which requires analyzing the two liquid phases in a separate equipment. At the beginning of each measurement, the thermostatic bath filled with silicone oil (SilOil P20.275.50) was switched on and the temperature at which the measurement had to be carried out was set. Then, in the EC a mixture of

known composition (total volume of about 4 ml) of the two compounds was prepared under the hood. The EC was inserted in a flask to keep it firm during the weighting procedure.



Figure 1: Pictures of: a) the Fischer Labodest VLLE 602 unit; b) one of the two receivers of the Fischer Labodest VLLE 602 unit; c) the thermostatic bath used for LLE measurements and the support properly designed to submerge the EC in it

A properly design support, made up of stainless steel, was used to submerge the EC in the thermostatic bath (Figure 1c). The temperature inside the EC was monitored by means of a digital thermometer (Hanna Instruments) until it reached a constant value (oscillations within 0.1 K). At this point, the cap was removed from the EC for stirring the mixture for about 5 min. The closed system was, then, left undisturbed for a period of time necessary for the two phases to settle. Such a time was evaluated for each temperature by performing some preliminary measurements aimed at determining the time interval required for obtaining a stable composition for the upper phase. It was found that 1 hour was enough for reaching equilibrium at the highest temperatures in the investigated range (i.e., 333.15 - 353.15 K), whereas a longer time (> 4 h) was necessary at the lowest temperatures (i.e., 313.15 - 323.15 K).

Once stable conditions were reached, the sampling phase began, starting from the upper organic phase. The analyses for each phase were repeated at least three times to guarantee the repeatability of the measurements. All measurements were performed at atmospheric pressure. At the end of each set of measurements at a certain temperature, the thermostatic bath was switched off. Once the ambient temperature was reached, the EC was removed from it, using the support, and was carefully cleaned to make it ready for further measurements.

### 3. Results

#### 3.1 VLE Measurements

Figure 2 shows the VLE data measured in the PT lab at 103.5 kPa (Figure 2b), 150.0 kPa (Figure 2c) and 200.0 kPa (Figure 2d) for the system ethanol+water. An analysis of errors was performed following the approach described by Taylor and Kuyatt (Taylor and Kuyatt, 2009), which resulted in uncertainties related to molar fractions within 5 %.

In Figure 2a the most recent data available in the literature (Al-Rub et al., 1999; Alvarez et al., 2011; Arce et al., 1996; Iwakabe and Kosuge, 2001; Kamihama et al., 2012; Kurihara et al., 1993; Lai et al., 2014; Li et al., 2012; Liu et al., 2012; Orjuela et al., 2010; Rojas et al., 2016; Tsanas et al., 2014; Wang and Yang, 2002; Xu et al., 2011; Yang and Wang, 2002) at atmospheric pressure are also reported for comparison purposes. Experimental data presented in this work are slightly shifted to the right with respect to the other ones available in the literature. This is due to the fact that the system pressure (103.5 kPa) is a little higher than the atmospheric pressure at which the other literature data are available. By comparing Figure 2b-d it can be observed that, as the pressure increases, the amplitude of the VLE region decreases.

Lines in Figure 2b-d refer to the results obtained using an indirect  $\gamma/\varphi$  method (NRTL-RK) with the default parameters available in Aspen Plus<sup>®</sup> V11 (AspenTech, 2019), since they have been reported (Lodi et al., 2017) to be suitable for satisfactorily reproducing experimental data.

For a quantitative assessment, the percent Average Absolute Deviation (AAD<sub>%</sub>) has been taken into account, which has been calculated according to Eq(1), where “n” stands for the number of data, “v<sub>calc</sub>” and “v<sub>exp</sub>” refer, respectively, to the calculated and experimental value of the generic variable (namely, the temperature or the mole fraction of each component in the vapor phase).

$$AAD_{\%} = \frac{100}{n} \sum_{i=1}^n \frac{|v_{calc,i} - v_{exp,i}|}{v_{exp,i}} \quad (1)$$

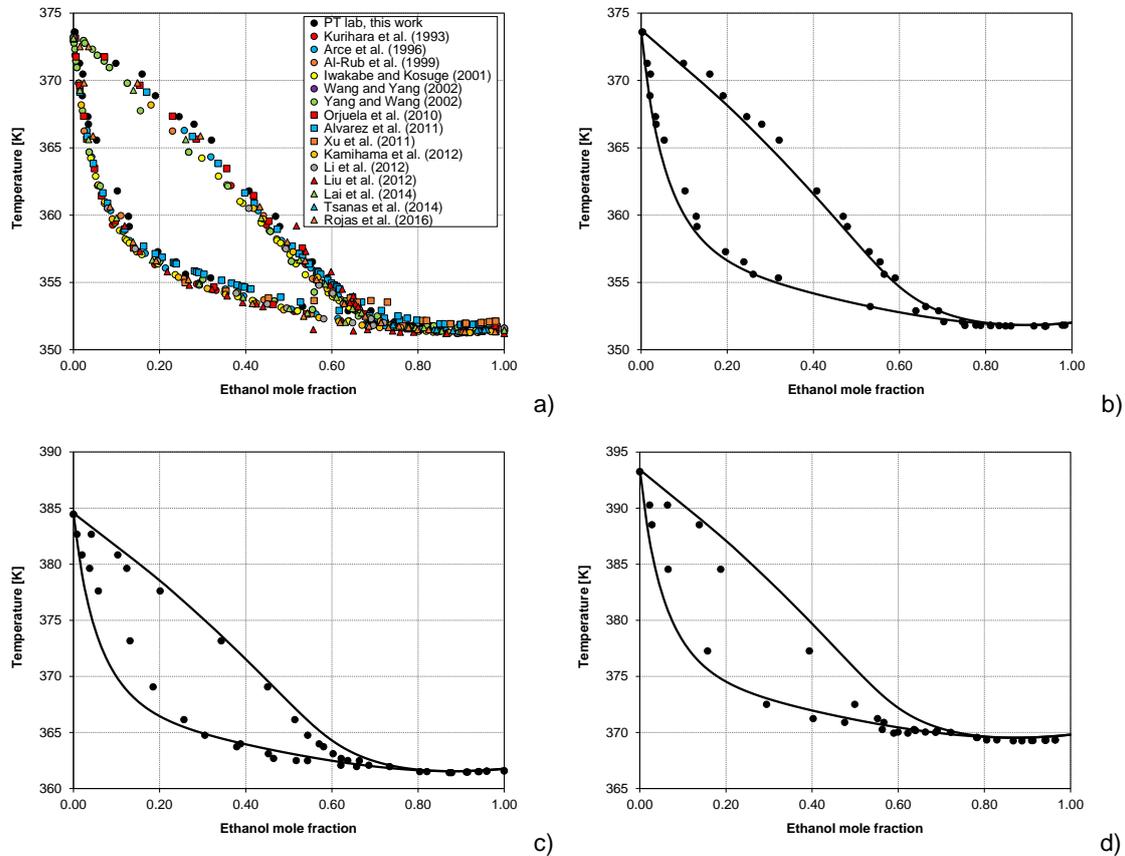


Figure 2: VLE data for the ethanol+water system at: a), b) 103.5 kPa; c) 150.0 kPa; d) 200.0 kPa. Filled black symbols refer to the data measured in the PT lab; the other symbols in Figure 2a refer to data available in the literature, as specified in the legend; lines refer to predictions by the NRTL-RK model

If a bubble-point calculation is performed, at given pressure and composition of the liquid phase equal to the experimental ones presented in this work, the model is able to predict the equilibrium temperature with an AAD% of 0.17 – 0.26 %, and the mole fraction of ethanol and water in the vapor phase with an AAD%, respectively, of 23.3 – 31.6 % and 4.3 – 12.1 %, with the highest deviations obtained at the highest pressures, as shown in Figure 2.

### 3.2 LLE Measurements

Figure 3 is the temperature-composition diagram illustrating the LLE measurements carried out in this work for the system 1-butanol+water together with the data available in the literature. Of the many data that can be found in the NIST database, those which belong to a complete set (i.e., for which pressure, temperature and composition of both phases are all given) and consist of more than 3 points have been selected (Drouillon, 1925; Erichsen, 1952; Hill and Malisoff, 1926; Jones, 1929; Mueller et al., 1931; Ruiz et al., 1984; Stephenson and Stuart, 1986; Wannachod et al., 2016; Zhang et al., 1986), though some of them reach temperatures higher than the temperature of the heterogeneous azeotrope at atmospheric pressure, which occurs at 364.6 K with a composition of 76.33 mol. % water according to Luyben (Luyben, 2008). It is possible to observe that the new data collected in this work are in good agreement with the ones presented in previous literature works, to a lesser extent at the lowest investigated temperature. It is also interesting to notice, with reference to Figure 3b, that the data presented in this work exhibit the trend observed by Stephenson and Stuart (Stephenson and Stuart, 1986) as for the solubility curve of the alcohol that goes through a minimum at about 332.15 K.

Lines in Figure 3 refer to the results obtained using an indirect  $\gamma/\phi$  method (NRTL-RK) with the parameters for the NRTL model reported by Lodi et al. (Lodi et al., 2018), which were properly regressed to improve model

predictions. By performing a flash calculation at given temperature and pressure, set equal to the experimental values, the model results to predict the mole fraction of water with an AAD% of 2.4 % and 0.17 %, respectively in the organic and in the aqueous phases.

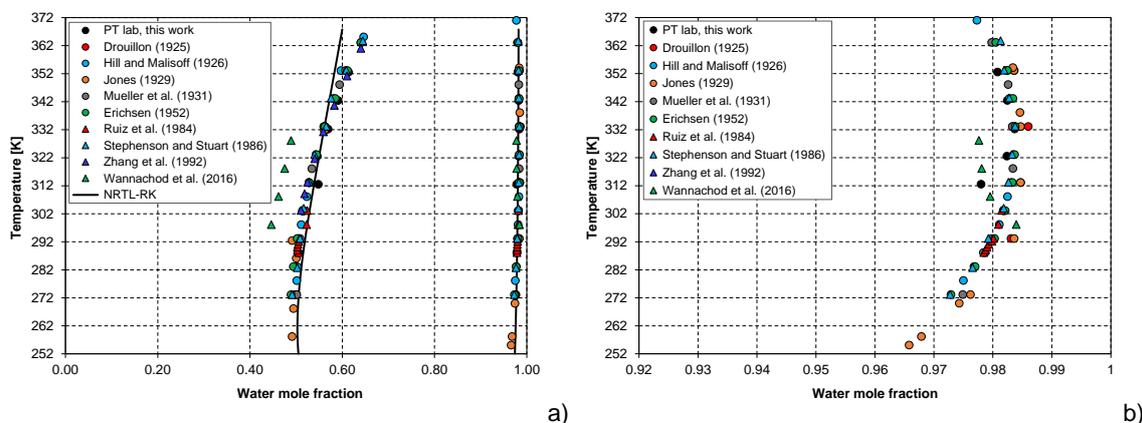


Figure 3: Temperature-composition diagram illustrating the LLE measurements carried out in this work (PT lab series, black symbols) and available in the literature (as specified in the legend, other symbols) for the system 1-butanol+water: a) entire composition range; b) zoom on the composition of the water-rich phase

#### 4. Conclusions

This work presents new VLE data for the system ethanol+water and new LLE data for the system 1-butanol+water, both of interest considering the renewed attention devoted to the ABE fermentation process. The VLE measurements fill the gap existing in the literature as for data between atmospheric pressure and 287 kPa, whereas the LLE measurements have allowed to set-up the procedure in view of, then, using that unit for VLLE measurements. Comparison with literature experimental data suggests the new data are in good agreement with them. Satisfactorily results have been also obtained from the modelling point of view using the NRTL-RK property package, with parameters available by default in the Aspen Plus® V11 process simulator (for ethanol+water) or properly regressed in a previous literature work (for 1-butanol+water). As for the VLE measurements for the system ethanol+water, if a bubble-point temperature calculation is performed, the model is able to predict the equilibrium temperature with an AAD% of 0.17 – 0.26 %, and the mole fraction of ethanol and water in the vapor phase with an AAD%, respectively, of 23.3 – 31.6 % and 4.3 – 12.1 %, with the highest deviations obtained at the highest pressures. As for the LLE measurements for the system 1-butanol+water, by performing a flash calculation at given temperature and pressure the model predicts the water mole fraction with an AAD% of 2.4 % and 0.17 %, respectively in the organic and in the aqueous phases.

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