

## Experimental Study on the Extractive Distillation Based Purification of Second-Generation Bioethanol

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Among the steps of the transformation chain to produce second generation bioethanol, this work addresses experimental aspects of the final step of bioethanol purification with real fermentation broths whose reducing sugars come from wheat straw. The initial bioethanol diluted broth was preconcentrated up to a concentration close to the azeotropic point with a distillation column of 15 stages in continuous operation, following a process previously designed on Aspen Plus®. In comparison with the process carried out with a synthetic mixture, bioethanol preconcentration required a longer settling time, but reflux ratio and reboiler duty were slightly lower. This difference motivated the construction of an equilibrium curve based on bioethanol, through a batch distillation system, in which a smaller boiling point is seen in comparison with the one of a pure ethanol-water mixture. With respect to the ethanol dehydration using glycerol as entrainer, experimentation in the same batch distillation system was carried out with both preconcentrated bioethanol and synthetic ethanol, and different glycerol-ethanol ratios. The experimental outcomes show that although with bioethanol the distillation temperature is slightly lower than the one with synthetic ethanol, the experimentation time is much longer. In other hand, it is demonstrated that a glycerol-ethanol of 0.8:1 is enough to get a fuel grade ethanol, which is a ratio different resulting from an Aspen Plus® based study. These outcomes show that current studies based on ethanol-water mixture are just an approximation to real bioethanol systems and real fermented broths would be needed to obtain more accurate data.

### 1. Introduction

The constant increase of the world population has resulted in an increase in the demand of energy and fuels from fossil sources. The use of this kind of energy makes an increase in pollution due to greenhouse gases, and the research for new kinds of renewable energy has gained importance (Volynets et al., 2017). One of the most studied biofuels is bioethanol because it can be used as a substitute or an additive of gasoline. This is an oxygenated fuel and its use potentially makes the emission of greenhouse gases decrease (Cardona et al 2009). Most bioethanol is produced from cereals and sugarcane. The production of these raw materials constitutes between 40-70 % of the bioethanol production costs; therefore, the production of a large scale of ethanol as a fuel may be feasible if raw materials are cheaper and more abundant. Then, using forest, agroindustrial waste, the cost of raw materials can be reduced (Cardona et al., 2010). Wheat straw is one of the most important crops worldwide, and only a small percentage of wheat straw is used as livestock feeds, leaving a significant amount of waste that is not used at all (Alemdar & Sain, 2008). Although lignocellulosic materials are abundant, producing ethanol from them is complicated, because fermentable sugars are found within large cellulose chains that are protected with hemicellulose and lignin chains. Due to this, it is necessary to bring under a process of four main stages the lignocellulosic materials, which are: pretreatment, enzymatic hydrolysis, fermentation and purification (Brienzo et al., 2016).

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Purification step is indispensable because ethanol composition in fermentation broths is lower than 12 %wt, being water the component of greatest content, and for use as fuel, bioethanol must be anhydrous (99.5 %wt) (Baeyens et al., 2015). The main problem of bioethanol purification is that ethanol forms an azeotropic mixture with water, and it is impossible to obtain anhydrous ethanol by a single distillation. Due to this the implementation of non-conventional separation processes is resorted to, such as extractive distillation in which a third component is added to the mixture in order to move out the azeotrope (Navarrete-Contreras et al., 2014). In a simulation framework, Gil et al. (2012) studied the design of an extractive distillation process to produce anhydrous ethanol using glycerol as an extractant, concluding that glycerol can be used in the production of high purity ethanol taking advantage of its low cost, high availability and low toxicity. Later, Navarrete-Contreras et al. (2014) experimentally verified the effectiveness of glycerol to separate a synthetic ethanol-water mixture.

To the extent of purification process is concerned, there is a large amount of work developing its design and even proposing advanced alternatives in which dehydration and recovery of the extractant are carried out in a single equipment. However, most of the works are developed in a simulation framework, and just a few experimental works exist in the open literature, majorly based on a synthetic ethanol-water mixture, that does not really come from a real fermentation process. Although the separation of ethanol-water is a problem already solved, it does not mean that bioethanol purification is, since fermentation broths contain components that likely bring additional challenges.

Aimed to distinguish additional challenging issues on bioethanol purification, in this work, in an experimental framework, purification of second generation bioethanol was carried out through a distillation process based on extractive distillation, and compared with the one of a synthetic ethanol-water mixture.

## **2. Materials and methods**

### **2.1 Fermentation broths**

Initially fermentation broths had an ethanol composition of less than 5 %w/w. These were obtained through *S. cerevisiae* yeast and reducing sugars coming from enzymatic hydrolysis of pretreated wheat straw. The wheat straw was pretreated with high-pressure steam to avoid the use of another chemicals. In order to remove solids, firstly a preconcentration was carried out in a batch distillation system bringing the fermentation broth up to an ethanol composition of 32.2 %v/v. Additionally to the above mentioned, wheat straw was considered because is one of the most abundant agroindustrial waste in the center of Mexico.

### **2.2 Design of preconcentration process with Aspen Plus®**

Experimentation of the preconcentration process was previously designed through Aspen Plus® by considering an ethanol-water mixture, and constructing a distillation column of similar characteristics to an experimental system described below (PIGNAT® DVI/3000). The thermodynamics model considered was NRTL because it has given a precise description of ethanol-water system (Carlson, 1996); in addition, a non-equilibrium consideration was used because it is better for a small size distillation column (Seader et al., 1998; Meirelles et al., 1992). The design started with the use of the operating conditions of the preconcentration stage according to the characteristics and capabilities of the laboratory equipment. The geometric aspects of the column were necessary for the simulation, so the rate-based model was used. In this model, it can be specified the number of plates, the feeding plate, the type of plate and the spacing between stages. After this, it was continued with the design of the operating conditions of the process. A 92.75 % w/w distillate composition near the azeotropic point was specified (Kiss et al 2014), with a recovery of ethanol feed of 99.5 % w/w. To achieve these design specifications, the distillate composition was related to the reflux ratio and the recovery of ethanol to the reboiler duty. It is worthy to highlight that the process pressure specified corresponds to the local pressure of 11.32 psia.

### **2.3 Preconcentration of the bioethanol in an experimental continuous distillation system.**

A distillation column DVI/ 3000 by PIGNAT® (Figure 1a) was used in continuous operation. It has 15 plates with bubble caps, a dosing pump for feeding, preheater with electric resistance, a boiler with electric resistance, serpentine condenser, and storage tanks for bottoms and distillation part. The bioethanol used for the first stage had an initial concentration of 32.2 % v/v and the volume was of 17.5 L. The resulting process conditions from the previous task of design (Table 1) were introduced in the control panel of the distillation system to start up experimentation, which lasted up to 7 h. The process goal was to go from an ethanol composition of 32.2 % v/v up to one close to 95 %v/v, which is the azeotropic point for ethanol-water system (Seader et al. 1998). Along experimentation, samples were frequently taken out, and its ethanol content was measured with a refractometer, and the sample at the end of experimentation was analyzed with an alcoholmeter and HPLC.

## 2.4 Dehydration of ethanol in a batch extractive column

In this part, the bioethanol recovered from the preconcentration step with a concentration near to 95 %v/v was used. The extractive distillation was made in a conventional batch distillation system of laboratory scale as shown in Figure 1b. Since theoretical studies (Uyazán et al., 2006) indicate different entrainer-ethanol ratios, experiments with different glycerol-ethanol ratio were explored: from 0.8:1 up to 1.6:1.

The measurements of samples were made in situ by a refractometer  $r^2$  mini Reichert®, and the more representative samples were analyzed by HPLC and alcoholmeter Anton Paar to be able to exactly know the concentration of ethanol, as well as being able to know if the samples contained some other fermentation subproducts.

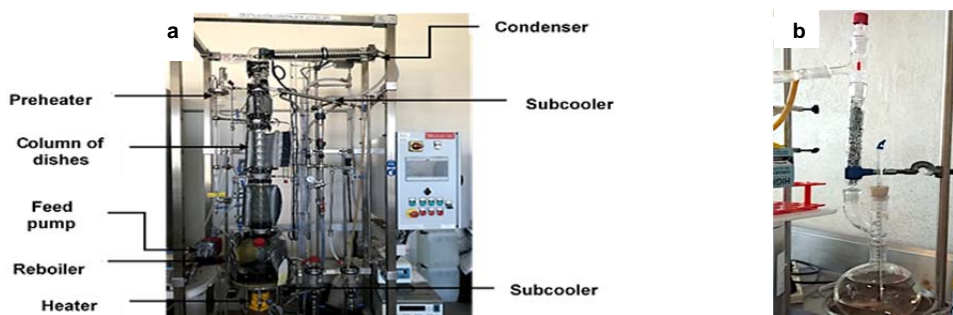


Figure 1: a) Distillation column DVI/3000 by PIGNAT®, b) Batch system for extractive distillation.

## 2.5 Construction of the equilibrium curve

In order to distinguish a basic difference between bioethanol-water and ethanol-water mixtures, corresponding equilibrium curves were constructed.

The ethanol-water equilibrium curve was constructed with the simulator Aspen Plus®. The binary module for equilibrium analysis was used and the thermodynamic model NRTL was considered. It should be dustcart that to obtain the curve according to the ambient conditions was made a modification to the pressure thus calculating each boiling point.

The bioethanol-water equilibrium curve was made in the conventional batch distillation system shown in Figure 1b. Diverse mixtures of different bioethanol composition were prepared. Once the bioethanol-water mixture has been charged in the flask, the content was boiled, and the temperature of vapor and liquid condensed were registered. On the basis of these data, the curve of temperature vs composition on the liquid (x) and vapor (y) phase was constructed.

## 3. Results and discussion

### 3.1 Design of preconcentration process with Aspen Plus®

From the model based design in Aspen Plus® of the preconcentration process, the initial conditions for the reflux ratio and reboiler duty were obtained (Table 1). These data are just an approximation of the conditions to which the distillation column should be operating because it was necessary to adjust them to achieve the desired composition while maintaining mass balances along experimentation, as described below.

Table 1: Process conditions of continuous preconcentration process.

Data used in the Design with Aspen Plus®				Process Conditions in experimental system	
Initial Data		Results			
Feeding (g/s)	0.5	Reboiler Duty (W)	670	Reboiler Duty (W)	560
Xb (Bioethanol)	0.28	Feed(ml/h)	5809.53	Feed (mL/h)	3776.19
Thermodynamic method	NRTL	Reflux Ratio	6.44	Reflux Ratio	4.1

### 3.2 Preconcentration of bioethanol in a continuous distillation system.

With the operating conditions given by the previous design task, the ethanol composition in distillate and the ethanol recovery were a little close to the desired values; then, further adjustments were carried out in the reflux ratio and in the reboiler duty. In Table 1 are given the adjusted operating conditions, which are in magnitude order with the initial ones. This difference can firstly be attributed to the nature of the bioethanol-water mixture in the sense that real bioethanol has more components from fermentation process than just ethanol and water.

In other hand, along experiments, a temperature record was made to analyze the temperature profile and thus to observe if the column reaches its stationary state. Figure 2 shows the trajectories of temperature on different column plates. It can be observed that after 6 hours of operation, the process begins to stabilize. This time is longer than the time needed for a synthetic mixture of ethanol-water.

The volume of bioethanol obtained after the preconcentration stage was 3.8 L with a final concentration of ethanol of 94.6% v/v measured with refractometer. The results of the HPLC analysis showed that, in addition to ethanol and water, the mixture also contained other organic compounds shown on Table 2. On this basis, it is worthy to highlight that ethanol composition measured with refractometer is pretty different to the one of alcoholmeter and HPLC, which reflects that the other components provides a considerable difference between a bioethanol-water mixture and an ethanol-water mixture.

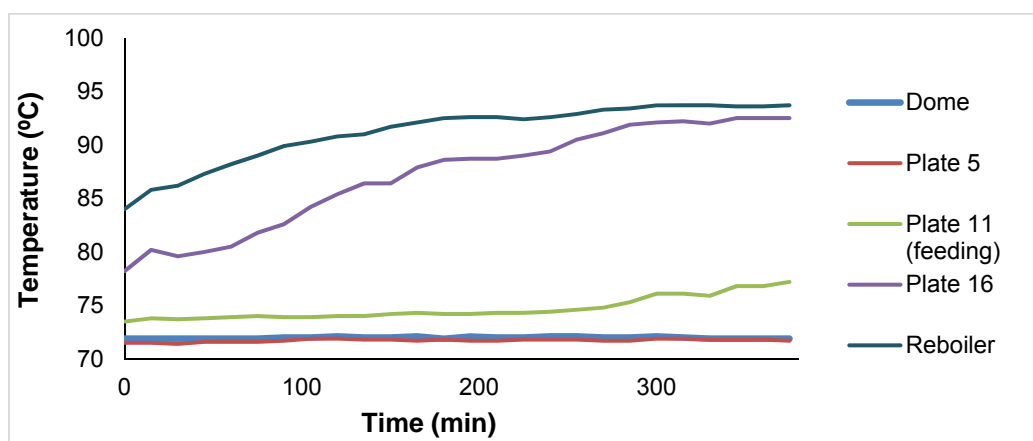


Figure 2: Temperature profile for preconcentrated column (6h of operation).

Table 2: Concentration of the different compounds in the bioethanol sample measured with refractometer, alcoholimeter Anton Paar and HPLC.

Measuring instrument	Component	Bioethanol initial	Bioethanol concentrated
Refractometer	Ethanol (%v/v)	32.2	94.6
Alcoholometer Anton Paar	Ethanol (%v/v)	26.6	90.5
	Isobutyraldehyde (g/l)	----	0.0666
	Ethyl acetate (g/l)	0.23976	1.04514
	Methanol (g/l)	0.3545	11.9592
HPLC	Ethanol (g/l)	275.16	750.1
	1-propanol (g/l)	0.1205	0.28852
	Isobutanol (g/l)	0.10312	0.22744
	Isoamyl alcohol (g/l)	0.22742	0.06624
	Furfural (g/l)	0.79806	----

### 3.3 Dehydration of ethanol in a batch extractive column

The experiments for the extractive distillation were carried out by duplicate for every glycerol-ethanol ratio, obtaining different distillate volumes but all of them with an anhydrous bioethanol (Table 3). The ethanol composition measured by refractometer indicated that samples had 99 %v/v of ethanol, while the analysis carried out with the Anton Paar Alcoholmeter showed a little lower concentration. Even more, among the five glycerol-ethanol ratios explored, the one of 0.8:1 yielded the lowest ethanol composition (96 %v/v), and this composition is even greater than the azeotropic point (95 %v/v). In this sense, with every glycerol-ethanol ratio the azeotropic point was broken.

Along the experiments, a collection of samples were taken out at different times and analyzed. The results are shown in Table 4 where it can be observed that other components are contained in the bioethanol-water mixture. Probably to remove these compounds, a separation step in a batch system after the preconcentration step would be necessary.

Table 3: Volume and concentration of anhydrous bioethanol with different glycerol ratio.

Glycerol ratio	Volume obtained (ml)	Refractometer (%v/v)	Anton Paar Alcoholmeter (%v/v)
0.8	46.5 6±2.12	99.56±0.47	96.1±0.3
1.1	77.5 6±2.12	99.53±0.44	97.05±0.05
1.3	80 6±7.07	99.9±0.1	97.1±0.1
1.4	87.5 6±3.53	99.9±0.1	97.2±0.1
1.6	57.5±7.5	99.9±0.1	97.35±0.05

Table 4: Components in anhydrous bioethanol with different glycerol ratio.

Component/ Glycerol ratio	Concentration (g/l)				
	0.8	1.1	1.3	1.4	1.6
Ethyl acetate	1.61±0.81	1.70±0.06	0.14±0.01	0.077±0.001	0.031±0.025
Methanol	1.71±0.37	1.65±0.02	0.783±0.08	0.706±0.09	0.846±0.14
Ethanol	744.78±0.50	728.76±43.2	763.22±33.15	691.07±25.77	740.61±16.43
1-propanol	0.29±0.1		0.14±0.007	0.136±0.009	0.15±0.036
Isobutanol	0.072±0.007		0.066±0.007	0.072±0.007	0.089±0.019

### 3.4 Equilibrium curves

The equilibrium curve based on bioethanol that was made experimentally is shown in Figure 3, in this figure also represents the equilibrium curve obtained from the ASPEN PLUS® simulator. In these curves, we can see that the points differ between the theoretical curve and the experimental one at approximately 10°C, this can be deviated from the fact that bioethanol is not only an ethanol-water mixture, this mixture contains other components that are more volatile which can affect the boiling and condensing temperature of the bioethanol mixture.

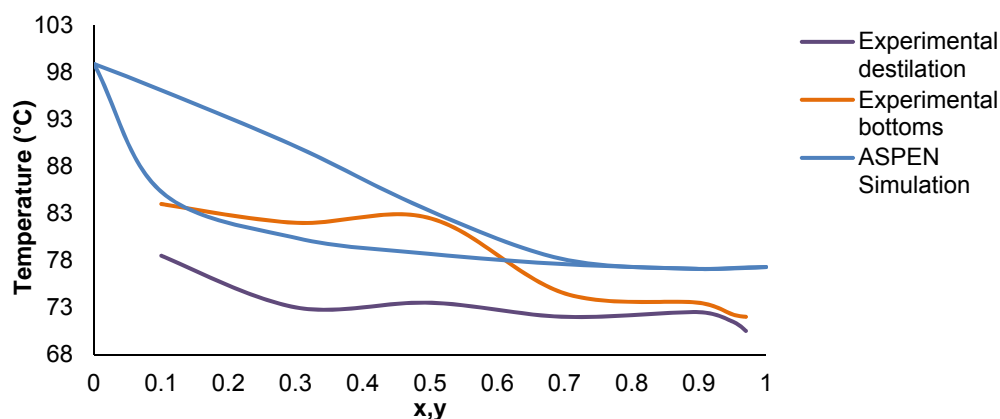


Figure 3: Equilibrium Curves

#### 4. Conclusions

The purification of bioethanol from lignocellulosic biomass was achieved, starting from a mixture of ethanol composition of 32.2 %v/v. The model-based framework in ASPEN PLUS® provided an approximation of the process and operation conditions to be used for the experimentation in a continuous distillation column to preconcentrate the fermentation broth, and further but little adjustments were required. Analysis of samples along distillation processes show the presence of other components, majorly lighter alcohols, that made the bioethanol-water mixture to behave a little different as expected according to theoretical estimations based on ethanol-water mixture; even in the dehydration step, where the effective amount of entrainer differs from the one given by a study based on synthetic ethanol-water mixture. Then, although the problem of ethanol-water has been already solved, the purification of bioethanol still requires further study.

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