ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
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UNIVERSIDAD DE CANTABRIA

***Trabajo Fin de Grado***

# Recuperación de butanol de mezclas ABE mediante pervaporación. De membranas planas a fibras huecas. (Butanol recovery from ABE model solutions by pervaporation. From flat-sheet membranes to hollow fibers)

**Para acceder al Título de**

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# INDEX

# FIGURES INDEX

# GRAPHICS INDEX

# TABLES INDEX

# 1. INTRODUCTION

## 1.1 Lifetime problems of classic fuels.

There is an increasing of interest in the obtention of biofuels from renewable resources because of the pollution problems and high price of fossil fuels. A high consumption of fossil fuels during last decades produced big environmental changes and problems such as the greenhouse effect and the acidification of rain and fresh water sources.

Some studies have predicted that the life limit of fossil fuels. In Figure 1, they are represented the values of Recovering/Production ratios (R/P) of fossil fuels and nuclear source as energy source. Useful life is not older than 150 years for coal. It is the main source of energy production, but values for oil are more restrictive. It is not possible to use it for more than 40 years.

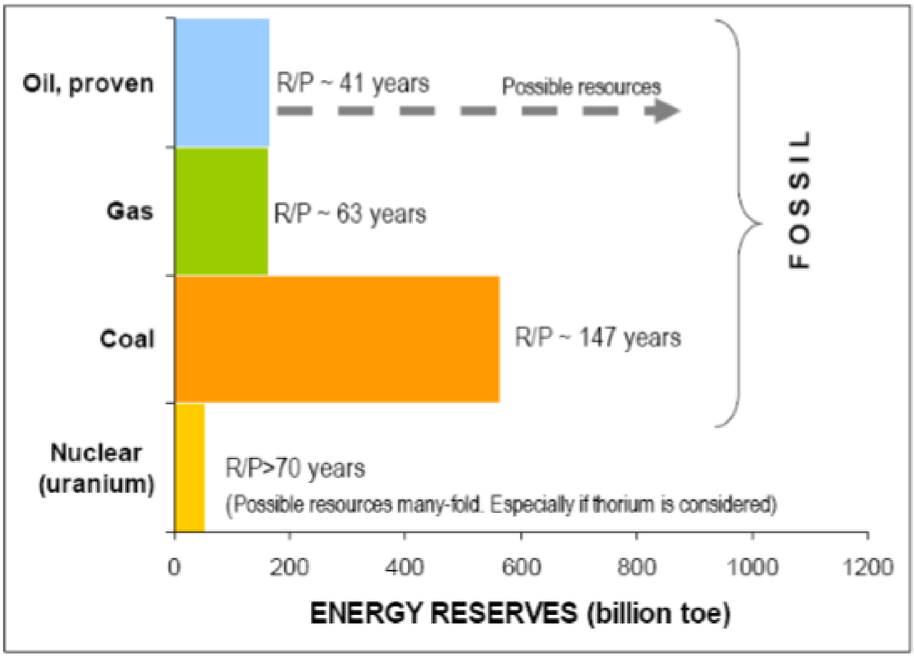


**Figure 1. Total energy reserves and current R/P ratios (BP 2007, Johansson & Goldemberg 2005).**

Some European studies of the energy origin determined that from 2006 to 2016, there was a reduction of global consumption of non-renewable energy resources of almost a 15%, but it is not enough to solve the problems (Figure 2).

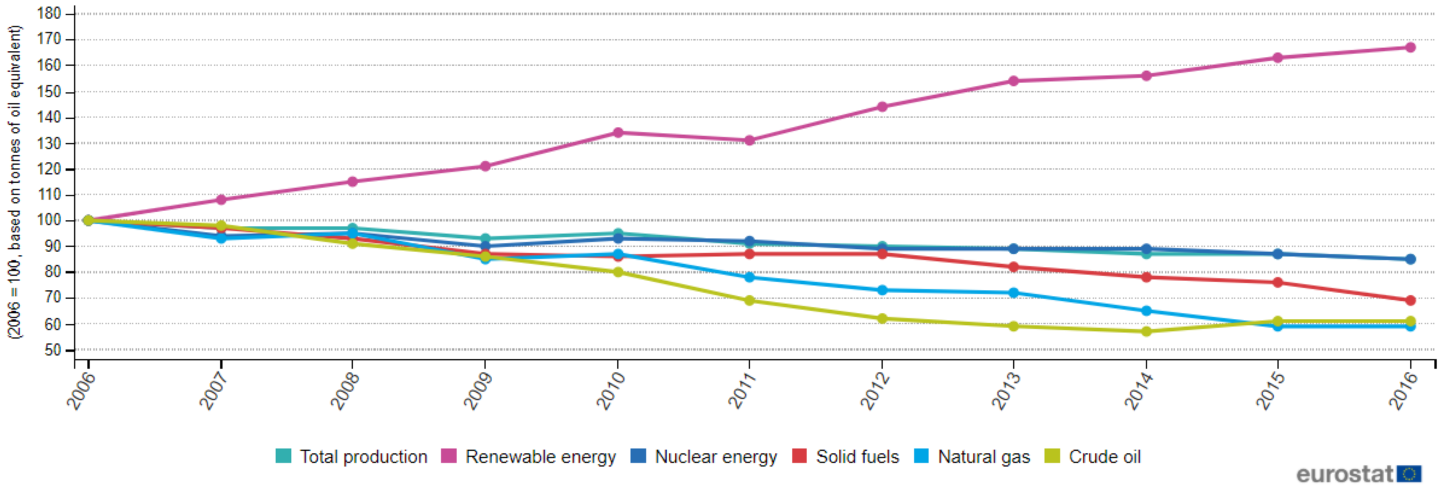


**Figure 2. Energy sources evolution [1].**

Because of that, there is an increasing interest on the study of production of chemicals and renewable resources [1].

Liquid biofuels are of particular interest because of the vast infrastructure already in place to use them, especially for transportation. The liquid biofuel in greatest production is ethanol (ethyl alcohol), which is produced by fermenting starch or sugar. Brazil and the United States are among the leading producers of ethanol. In the United States ethanol biofuel is made primarily from corn (maize) grain, and it is typically blended with gasoline to produce "gasohol," a fuel that is 10 percent ethanol. In Brazil, ethanol biofuel is made primarily from sugarcane, and it is commonly used as a 100-percent-ethanol fuel or in gasoline blends containing 85 percent ethanol [2]. Unlike the "first-generation" ethanol biofuel produced from food crops, "second-generation" cellulosic ethanol is derived from low-value biomass that possesses a high cellulose content, including wood chips, crop residues, and municipal waste. The second most common liquid biofuel is biodiesel, which is made primarily from oily plants (such as the soybean or oil palm) and to a lesser extent from other oily sources (such as waste cooking fat from restaurant deep-frying). Biodiesel, which has found greatest acceptance in Europe, is used in diesel engines and usually blended with petroleum diesel fuel in various percentages. The use of algae and cyanobacteria as a source of "third-generation" biodiesel holds promise but has been difficult to develop economically.

Biofuels are a good alternative for extended fuels but depending on the source that is used to produce them, it is possible to create additional environmental problems. For instance, biofuels distillation generates more carbon dioxide compared to fossil fuels. As a renewable energy source, plant-based biofuels in principle make little net contribution to global warming and climate change; carbon dioxide that is produced in the combustion is almost consumed by algae during the fermentation. These kind of productions are called ‘carbon neutral’. Some estimates state that algae and cyanobacteria could yield between 10 and 100 times more fuel per unit area than second-generation biofuels [2].

## 1.2 Biobutanol.

N-Butanol corresponds to the third generation of biofuels because of using cyanobacteria to obtain it. It exhibits good properties as solvent. It can be used as a component of detergents, paints, natural resins or dyes. It is also an intermediate substance for obtaining medicines, chemical compounds and it has also different applications at industrial scale. For biobutanol production, the most used method is ABE fermentation [3].

**Table 1. Properties of most used fuels [4,5]**

| Property | Butanol | Gasoline | Ethanol | Methanol | Diesel |
|---|---|---|---|---|---|
| Molecular Formula | $C_4H_9OH$ | $C_4$-$C_{12}$ | $C_2H_5OH$ | $CH_3OH$ | $C_{12}$-$C_{25}$ |
| Cetane number | 25 | 0-10 | 8 | 3 | 40-55 |
| **Octane number** | **96** | **80-99** | **108** | **111** | **20-30** |
| **Energy density ($MJ \cdot L^{-1}$)** | **27-29.2** | **32** | **19.6** | **12.8** | **39-46** |
| Oxygen content (%weight) | 21.6 | - | 34.8 | 50 | - |
| Density (g/mL) at 20°C | 0.808 | 0.72-0.78 | 0.79 | 0.796 | 0.82 (-0.86) |
| Autoignition temperature (°C) | 385 | ~300 | 434 | 470 | ~210 |
| Flash point (°C) at Closed cup | 35 | -45 to -38 | 8 | 12 | 65-88 |
| Lower heating value (MJ/kg) | 33.1 | 42.7 | 26.8 | 19.9 | 42.5 |
| Boiling point (°C) | 117.7 | 25-215 | 78.4 | 64.5 | 180-370 |
| **Air to fuel ratio** | **11.21** | **14.7** | **9.02** | **6.49** | **14.3** |
| Latent heating (kJ/kg) at 25°C | 582 | 380-500 | 904 | 1109 | 270 |

| | | | | | |
|---|---|---|---|---|---|
| Flammability limits (%volume) | 1.4-11.2 | 0.6-8 | 4.3-19 | 6 (-36.5) | 1.5-7.6 |
| Saturation pressure (kPa) at 38°C | 2.27 | 31.01 | 13.8 | 31.69 | 1.86 |
| Viscosity (mm$^2$/s) at 40°C | 2.63 | 0.4-0.8 (20°C) | 1.08 | 0.59 | 1.9-4.1 |

As it can be seen on Table 1, butanol energy properties are so closed to the most used fuels. Comparing with methanol and ethanol, butanol is a more complex alcohol, possessing several advantageous characteristics: higher heating value, lower volatility, less ignition problems, higher viscosity and is safer for distribution. Moreover, n-butanol can be blended with petrol at any ratio. Biobutanol has lower water miscibility, flammability, and corrosiveness than ethanol, and has the enviable advantage to be able to directly replace gasoline in car engines without requiring modifications. Furthermore, using butanol as a fuel enables reduction of NOx emission and soot creation in exhaust gases. Its energy heating value is closer than ethanol or methanol from conventional fuels. To have high values in energy aspects is one of the most important characteristics referred to biofuels because of the need of using them as extended fuels.

### 1.2.1 ABE process.

Acetone–butanol–ethanol (ABE) fermentation is a process that uses bacterial fermentation (*Clostidria*) to produce acetone, n-Butanol, and ethanol from carbohydrates such as starch and glucose. The main difference between this fermentation and the others is that it is used an anaerobic bacteria. Most used are Clostridium family microorganisms. It was developed by the chemist Chaim Weizmann and it was the primary process used to make acetone during World War I to produce cordite, a special substance for British guns. After World War II, ABE fermentation became generally non-profitable, compared to the production of the same three solvents from petroleum.

In order to make ABE fermentation profitable, many product recovery systems have been developed. These include gas stripping, pervaporation, membrane distillation, adsorption, and reverse osmosis. It is produced a mixture of solvents in a ratio of 6 parts of butanol, 3 parts of acetone and only 1 part of ethanol (Figure 3).

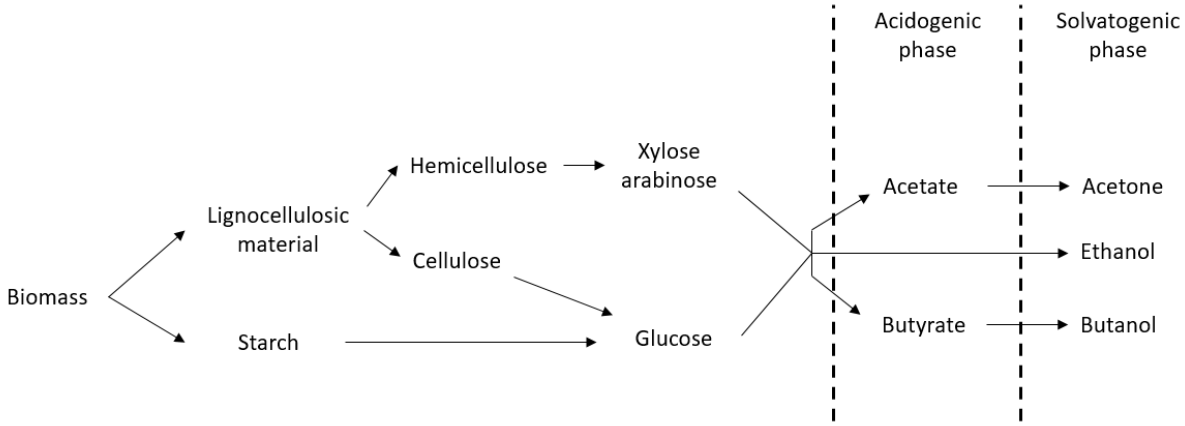


**Figure 3. Simplified product formation pathway by ABE process using Clostridium species [6].**

Currently, modification of some aspects of the original ABE process are being tested; such as the use of different bacteria or microorganisms. Not genetically modified bacteria are being tested in order to favor butanol production during the fermentation (Optinol). Other enterprises, like Green Biologics, are working on metabolic engineering and optimization of the global process. Other option is to use other kind of microorganisms like yeasts to convert sugars into isobutanol. Escherichia Coli genetically modified is also an alternative (Gevo).

Actual studies are focused now in the development of photobiologic production from carbon dioxide using cianobacteria (Phytonix) and catalytic condensation of butanol from Guerbet reaction (Abengoa) [7].

The main problem associated with the ABE fermentation by bacteria is the self-inhibition of the process due to n-butanol toxicity to the microorganisms. An added problem to that is the depletion of nutrients during fermentation that often cause the really fast termination of the process. The highest butanol productivity by the strain fermentation reported in literature is 3.0 wt.% [7]. As it has been said before, the problem of extended biofuels is that they are more expensive than the common fuels and also its energetic density is lower too. Most of the problems are related with the separations methods of organic mixtures with water. N-Butanol can solve the problem of energetic density because energy values are so similar to fossil fuels, but the separation step continues to be a problem. N-Butanol and water forms an azeotropic mixture (42.4 wt.% water) and it is not possible to separate them by conventional methods as distillation. In order to obtain almost a pure concentration of n-butanol from this mixture, there are several techniques to achieve it [7, 8].

### 1.2.2 Different separation methods of butanol.

As a general overview, Table 2 contains data about techniques main advantages and disadvantages. After that, analyzed techniques are described and explained more detailed.

**Table 2. Summary of principal advantages and disadvantages of each technology that is analyzed.**

| Process | Advantages | Disadvantages |
|---|---|---|
| Distillation | Easy to operate | High energy consumption and low values of efficiency |
| Gas stripping | No fouling, easy to operate, no harm to the culture | Low selectivity, low efficiency |
| Liquid-liquid extraction | High selectivity | Emulsion, extractant cost, toxic to culture, extractant recovery and loss |
| Adsorption | Easy to operate, low energy requirement | High material cost, low selectivity, adsorbent regeneration |
| Pervaporation | High selectivity | Fouling problem, membrane material cost, medium energy costs |

- **Double distillation.**

Azeotropic distillation (Figure 4) consists of the addition to the mixture of a different component in order to displace the azeotropic point. Several economic disadvantages appear because of the costs of distillations. It is required a distillation for the separation of the desired component and the agent from the undesired component. Second distillation is required to separate the desired compound from the agent. The main disadvantage is the economic cost of both distillations [9].

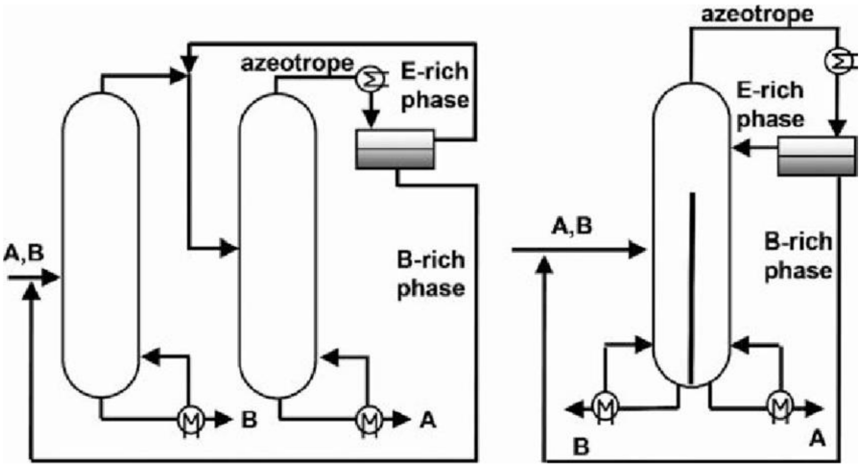


Figure 4. Azeotropic distillation in a two-column setup (left) and combined [10].

- **Gas stripping.**

Gas stripping is a simple technique that can be used to separate butanol from product solutions. In this method, oxygen free nitrogen or fermentation gases (hydrogen and carbon dioxide) are bubbled through the fermentation broth to strip away acetone, butanol and ethanol (Figure 5). The performance of the gas stripping process depends on the gas flow rate, antifoam and the presence of other components in the fermentation broth.

Based on the literature results, it can be concluded that although gas stripping may increase the productivity and sugar utilization in butanol fermentation, the selectivity for butanol separation is still low. In some recent investigations, different processes such as two-stage gas stripping or two stage fermentation coupled with gas stripping have been studied to achieve higher performances [9].

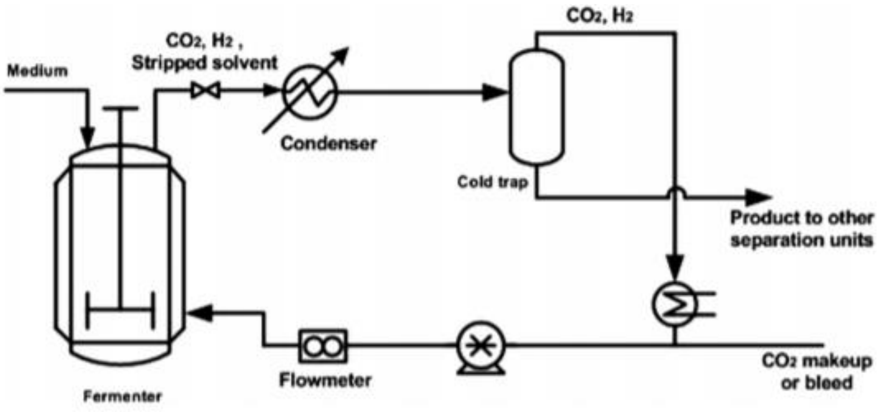


Figure 5. Gas-stripping technology schema for butanol removal from fermentation [9].

- **Liquid- liquid extraction.**

Liquid-liquid extraction (LLE) is another technique used for the removal of butanol or ABE from fermentation broths (Figure 6). In this process, a water-insoluble organic extractant, with a low toxicity to the microorganism, is mixed with the fermentation broth to selectively remove butanol. Due to the immiscibility of the extractant in the fermentation broth, the organic phase can be easily separated to recover a fraction of the butanol and other miscible solvents. It is desired to have an organic solvent that would preferentially separate butanol without significantly removing substrates, water and nutrients.

Until now, extractants with high butanol distribution coefficients were found to be toxic to butanol producing microorganisms. Oleyl alcohol is one of the extractants used for butanol separation because it possesses good extraction ability and a relatively low toxicity to bacteria.

There are however some potential problems with using extractants. Problems such as loss of extractant, toxicity to culture, emulsion formation and sometimes accumulation of biomass in the extractant can be problematic in an LLE process [9].

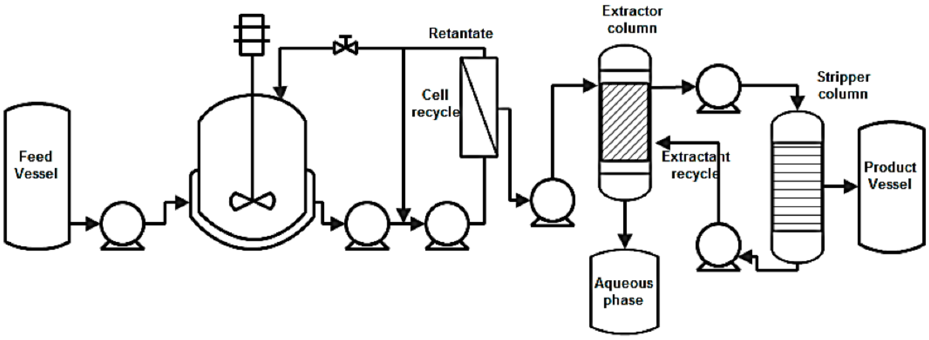


**Figure 6. Fermentation integrated with liquid- liquid extraction [11].**

- **Adsorption.**

Adsorption is an energy-efficient process that can be used to selectively separate butanol from fermentation broths. In this technique, butanol is adsorbed onto the surface of a suitable adsorbent and subsequently desorbed by increasing the temperature and/or using displacers to produce a concentrated butanol solution (Figure 7).

In selecting a suitable adsorbent, many factors need to be considered: adsorption rate, adsorption capacity, ease of desorption, selectivity for the desired product and cost of the adsorbent. The adsorption kinetics directly impacts the contact time required between the solution containing the adsorbate and the adsorbent. A fast kinetic is desirable since it allows the fermentation broth to circulate more rapidly and decreases its concentration below the inhibitory range. For slow adsorption rate, a larger amount of adsorbent is needed to achieve the product removal in the desired time. Materials such as activated carbon, polymeric resins, polyvinylpyridine (PVP), and zeolites are commonly used as butanol adsorbents for model solutions and fermentation broths.

Based on the results of different investigations of butanol separation by adsorption, it can be concluded that this energy efficient technique could be integrated economically to industrial butanol bioproduction processes [6].

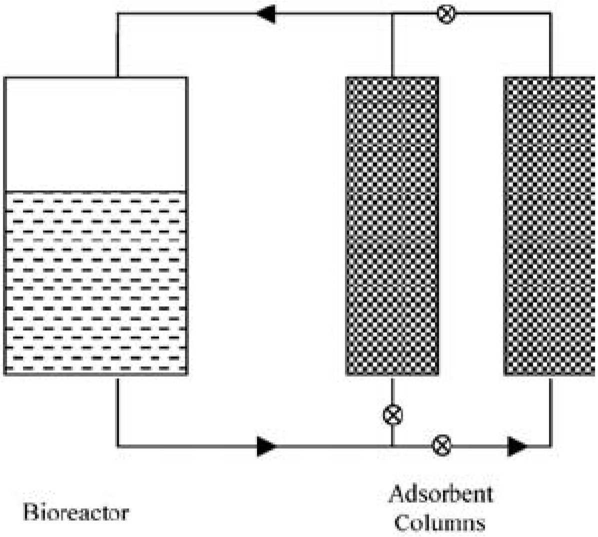


**Figure 7. A schematic diagram of butanol or ABE removal by adsorption with recirculation [12].**

### 1.2.3 Pervaporation.

Pervaporation is a rapidly developing membrane technology as an energy-efficient process for separating liquid mixtures (e.g., azeotropic mixtures and mixtures with similar volatilities) that are difficult to separate by conventional methods. Pervaporation can be used for the purification of chemicals. Depending on the type of membranes used, pervaporation can be applied for dehydration of organic solvents, recovery of organic compounds from aqueous solutions, and the separation of organic mixtures. Pervaporation consists of a liquid mixture feed that is placed in contact with one side of a membrane and the permeated product will be removed using low pressure from the other side of the membrane. Due to the low values of pressure in the permeate side, the vapor pressure is reached and the product is in vapor phase but it can be processed and transformed into liquid. It is needed a driving force to induce liquid to pass through the membrane (Figure 8) [6, 13, 14].

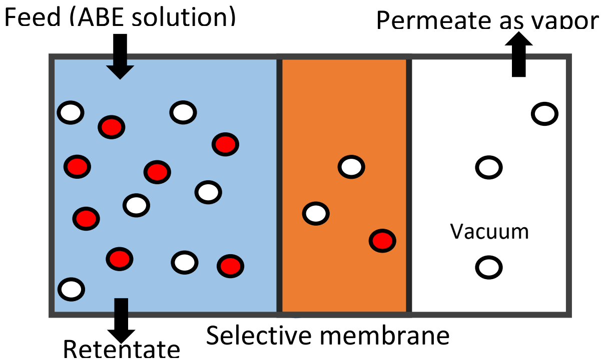


**Figure 8. Pervaporation schema.**

An important parameter on this method of separation is the affinity of different compounds of the feed with the membrane. This separation is based on the rate of different compounds through the membrane, so it is a kinetic separation. Due to that, it is possible to obtain so high concentrated permeates from low concentrated feeds. For instance, if the membrane is hydrophobic, organic compounds will permeate faster than water. Opposite, if the membrane is hydrophilic, permeate will be enriched in water.

This process can be explained in the stages:

1. Sorption of the permeant from at the feed liquid to the upstream side of the membrane.
2. Diffusion of the permeant through the membrane.
3. Desorption at the downstream side of the membrane under a low-pressure.

The component solubility/sorption and diffusivity dictate the selectivity and the permeability of the membrane. The solubility/sorption of a component in a membrane is determined by permeate-membrane interaction, and its diffusivity depends on its molecular size, shape and mass. Pervaporation efficiency may be limited by some factors including low fluxes, membrane swelling and concentration polarization. To develop membranes with a high permeate flux, efforts have been made to modify the membrane structure from a dense thick film to an asymmetric or composite structure. It has been observed that by reducing the membrane thickness, the flux increased, but the selectivity decreased. The reduction in membrane thickness is limited by the pore size, porosity and surface roughness of the membrane and the support.

Pervaporation possesses strong attributes for butanol separation from fermentation broths since, in addition to low energy requirement, it does not affect microorganisms, and losses of nutrients and substrates are prevented. Other advantages of pervaporation are the high selectivity, low operating temperature, reasonable performance to cost ratio, possibility of modular design and the absence of a separating agent that could cause product contamination [6, 13, 15- 17].

- **Membranes for pervaporation and butanol recovery.**

There are three major types of pervaporation (PV) hydrophobic membranes that may be applied to separate biobutanol, namely polymeric, inorganic, and composite membranes. PV membranes are often made with a thin non-porous selective layer (hydrophobic) on a porous substrate that allows the separation of organic compounds from an aqueous solution. Inorganic substrates exhibit the advantages of the chemical, mechanical and thermal stabilities. However, the use of polymeric materials is more desirable for industrial scale because they are easy to fabricate and provide good performance at low cost [18, 19]. Different hydrophobic- organophilic polymeric membranes have been tested for the recovery of n-butanol by PV such as polyether block amide (PEBAX); polyvinylidene fluoride (PVDF); poly(1-trimethylsilyl-1-propyne) (PTMSP); as well as polyoctylmethyl siloxane (POMS) membranes [6].

Ionic liquids (ILs) have been investigated and are widely used in numerous separation processes. They are organic salts with melting points around or below the ambient temperature and relatively low viscosity. Their unique properties make polymer membranes containing ionic liquids (PM-ILs) have many advantages such as high fluxes and faster separation because molecular diffusion is much higher in ionic liquids than in polymers and it can be enhanced by a proper choice of IL components. In addition, only small amounts of ILs are necessary to form the membrane making them more viable in terms of cost. However, the use of ILs in membrane-based technologies is limited due to the gradual release and leakage of unbound ILs from the membrane during its utilization [20-22].

Recent studies evaluated the combination of various ILs with the polymers PEBAX 2533 and PVDF for the synthesis of membranes in pervaporation. PEBAX 2533/ [HMIm][FAP] offered the highest selectivities. However, the ratio in the composition between polymer /ionic liquid that provides better results for pervaporation performance must still be optimized [23]. Together, these studies indicate that there is room in the PV separation of butanol with Polymer/IL membranes to improve the process. In this way, this work focuses on the development of polymeric inclusion membranes, and incorporating different amounts of IL and polymer, for the separation of butanol-ethanol- acetone aqueous solutions by PV. Moreover, a methodology for the manufacture of dense membranes with polymeric inclusion using the technique of phase inversion by evaporation of the solvent is used. The influence of the composition of the membranes in the separation of butanol-water mixtures is also studied and finally a comparison of the performance of the IL membranes with a commercial membrane is discussed.

# 2. OBJECTIVES

## 2.1 Main objective.

- Development of new membranes for butanol recovery from complex ABE solutions by pervaporation.

## 2.2 Partial objectives.

- PEBAX 2533/ [HMIm][FAP] composed flat-sheet membranes production with an improved performance for butanol recovery from ABE model solutions by pervaporation.
- Characterization of system mass transfer parameters. Evaluation of different mass transfer resistance on the system (liquid phase resistance, membrane resistance, vapor phase resistance).

- Kynar 740/ PEBAX 2533/ PDMS composed hollow fiber production for butanol recovery from ABE model solutions by pervaporation.

# 3. METHODOLOGY

## 3.1 Materials.

In order to prepare flat-sheet membranes, different devices are required:

- Accurate pipettes.
- Analytic balance.
- Syringe.
- Vacuum oven.
- Controlled heater and stirrer.
- Petri dish.

Regarding on the materials:

- PEBAX 2533.
- Ionic liquid [HMIm][FAP].
- Butanol.

Hollow fiber membranes used devices are:

- Analytic balance.
- Controlled heater and stirrer.
- Bore liquid and polymeric solution pumps.
- Test tubes.
- Loom.

Hollow fiber necessary materials that are going to be used:

- Kynar 740/NMP solution at selected concentration.
- Isopropanol.
- PEBAX 2533 solution at desired concentration.
- PDMS solution.
- Epoxy resin.

## 3.2 Preparation of flat-sheet membranes.

The aim of the study is to analyze pervaporation results varying mass of 90/10 composition plane membranes. Membrane mass values are 0.15g, 0.30g, 0.40g, 0.50g and 0.60g. Tested membranes are made of two components: PEBAX 2533 and ionic liquid [HMIm][FAP]. It means that 90% of the membrane will be PEBAX polymer and the other 10% corresponds to the ionic liquid.

At first, ionic liquid required quantity is weighted. After that, PEBAX 2533 polymer is also added in pellet form. Then, 5 mL of butanol are introduced into the flask being helped by a syringe. When the three component mixture is prepared (ionic liquid- PEBAX- butanol), it is stirred and heated at 60ºC until de polymer is completely dissolved. Finally, when membranes are totally dissolved and cooled, they are poured into a Petri dish and they are introduced into a vacuum oven (VO200 model, supplied by Mermmet). Selected conditions for controlled evaporation of the solvent are 30ºC and lowest value of pressure as possible for 24 hours (Figure 9).

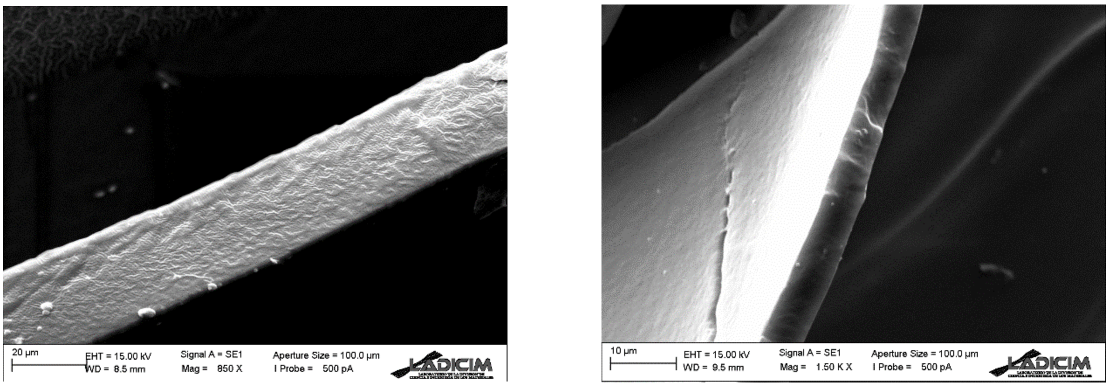


**Figure 9. SEM picture of flat-sheet membranes transversal section.**

## 3.3 Preparation of hollow fibers.

- **Morphology of hollow fiber**

In this work, the designed composite hollow fiber membrane consists of an outer dense selective layer, a highly permeable gutter layer and an inner porous Kynar 740/NMP hollow fiber support. Feed solution is introduced into the shell side and the butanol enriched stream is collected in the lumen side of the module. (Figure 10) [24].

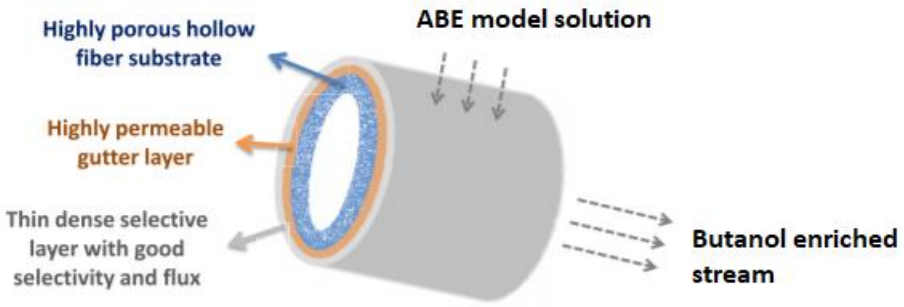


**Figure 10. Configuration of the composite hollow fiber membrane [24].**

Surface and substructure morphology of the substrate play important roles on the overall flux of the composite membrane. The ideal substrate should possess a low substructure resistance, a high surface porosity but a small mean pore size with a narrow pore size distribution.

- **Selection of gutter layer**

The gutter layer plays a critical role because it not only serves as an adhesive medium between the selective layer and the hollow fiber substrate, but also prevents the intrusion of the selective material into the porous substrate. Therefore, the candidates of gutter layer materials must possess characteristics such as:

1. The ability to provide good adhesion between the selective layer and the substrate.
2. High permeability to minimize mass transport resistance.
3. Minimum solution intrusion into the substrate. It is the main important aspect and this is why this method can obtain better results than the 2 layer model.

For gas separation, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and PDMS are the commonly used gutter layer materials in separation membranes owing to their high gas permeability. In this work, PDMS layer is tested as a protective coating in order to prevent the dilution of the PEBAX 2533 layer with feed contact. Isopropanol has the role of gutter layer.

- **Selection of selective layer**

The permeability increases with increasing ionic liquid content, especially when the ionic liquid content is more than 50%. In this study, for butanol separation by using hollow fibers, it was used a solution only of butanol and PEBAX 2533 [24,25].

A 18 wt.% Kynar 740/NMP solution is prepared in order to use it to produce hollow fibers. It is well stirred and heated at 40ºC during almost a day. When it is properly mixed, it is removed and cooled at room temperature.

Plant of Figure 11 is the one that is used for carrying on hollow fibers creation experiments. Two pumps are needed in order to introduce into the spinneret Milli-Q water as bore liquid and polymeric solution Kynar740/NMP 18 wt.%.

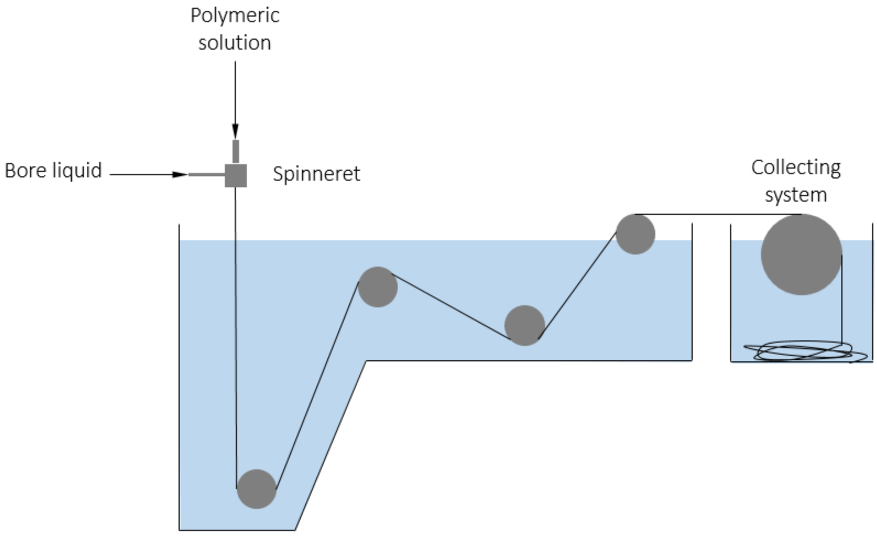


**Figure 11. Used plant for hollow fiber production.**

Due to the high viscosity of the polymeric solution, this kind of pumps are required. Pump rate will be constant at 4 ml/min for Kynar 740/NMP solution, but it will change from 1 to 3 ml/min for Milli-Q water.

When the equipment and water level is ready to start the experiment, Kynar 740/NMP pump is turned on. The polymeric solution will pass through the spinneret and it will start to fall down to the water in the form of a solid coil. When the first drop of Kynar 740/NMP is falling down, it is time to turn on the Milli-Q water pump. When both components are present on the spinneret device, it introduces the Milli-Q water into the solid fiber, forming here a hollow fiber. When the Kynar 740/NMP solution is in contact with water, it coagulates, so finally when the hollow fiber falls down to the tank water, it passes from liquid phase to solid phase. The hollow fiber is threaded through pulleys and recovered on the collector.

Mechanical properties of the fiber can be affected by the temperature of the tank water, temperature of the spinneret, height of the spinneret and composition of the initial polymeric solution.

It is also prepared PEBAX 2533 solution at different testing concentrations. Required quantities of butanol and polymer are introduced into a flask to be heated and stirred. After enough time, it is perfectly mixed and cooled at room temperature. 30 hollow fiber units are put on a loom to prepare them for the double/triple coating process. It is done into two/three test tubes (one for each solution), at first isopropanol, secondly PEBAX 2533 and finally PDMS (Figure 12).

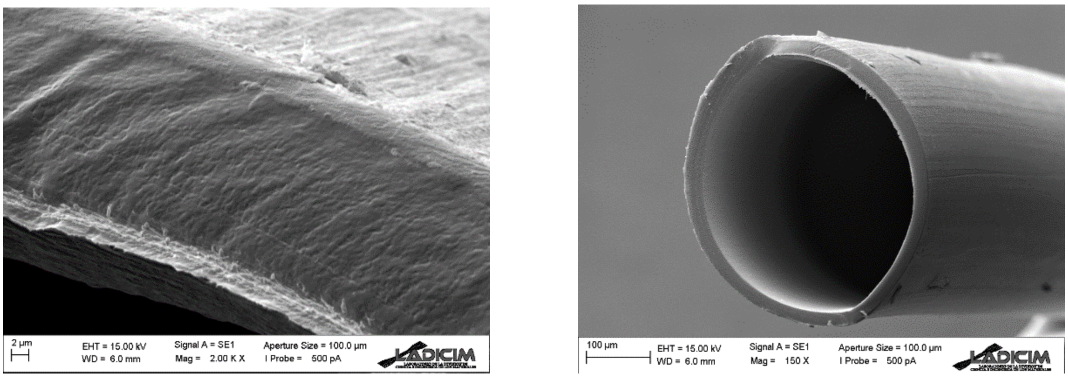


**Figure 12. SEM picture of hollow fiber membranes transversal section.**

## 3.4 Experimental setup.

### 3.4.1 Experimental procedure for both membranes.

Pervaporation plant of Figure 13 is being used for the study. It is composed by:

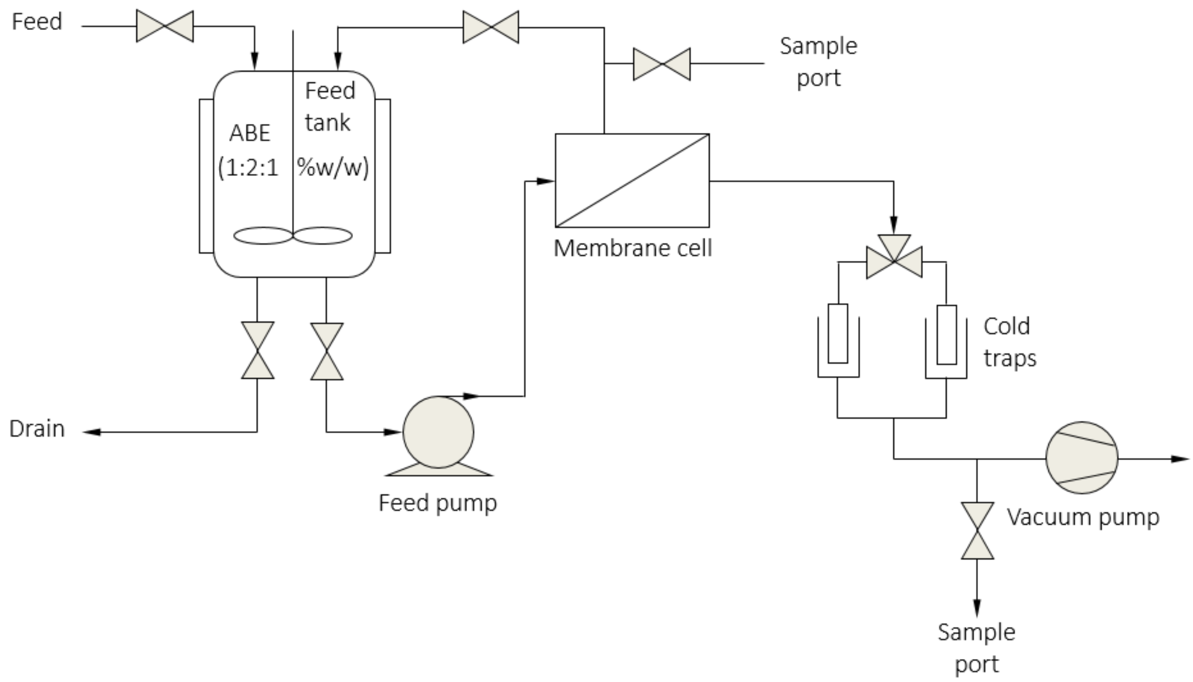


**Figure 13. Experimental plant for testing both kind of membrane cells.**

At first, ABE model solution is prepared. For this experiment, it is required a solution of 2 L that is composed by 2 wt.% butanol, 1 wt.% of acetone and 1 wt.% of ethanol. The rest of the volume is filled with Milli-Q water. The solution is introduced into the tank and the glycol bath is turned on selecting the operation temperature.

Separation membrane is introduced into the pervaporation module. Experiments are being performed without using a ceramic support. In this case, two filter papers are used as supports in order to fix the membrane. The flat-sheet membrane is disposed hugging the filter paper and keeping it to feed side, ensuring that permeate will pass first through the membrane. There is also a rubber ring to reach the vacuum condition inside the cell. For each flat-sheet membrane, tested temperatures are 30, 40 and 50ºC.

Hollow fibers are introduced into a module (Figure 14) and tested in the plant showed in Figure 13. Hollow fibers need to be dried before testing. Then, the procedure that is followed for experiment performing is the same that was explained before.

**Figure 14. Hollow fiber membranes module.**

When the temperature of ABE solution and separation membrane are ready to start the experiment, vacuum conditions and the pump are turned on. In order to prevent a hole formation on membrane surface, feed flow is increased slowly with a controlled valve. If there is anything wrong on it (problems on the membrane condition or accommodation), liquid from the feed will pass directly through the cell without perform a pervaporation process.

The experiments have a duration of 4 hours in which measurements are taken each 30 minutes. When experiment is started and operation temperature is reached on the module, first measurement is carried out. For each measurement, it is required to take samples of feed and permeate. Due to the serpentine shape of feed extractor, 10 mL are discarded for each sample. Then 5 mL are taken and introduced on a proper flask for a later analysis. Regarding on the permeate, extracted quantity that is recovered on the permeate flask is diluted 20 times with water. Then 5 mL of sample are taken form the diluted one and they are introduced on a proper flask for a later analysis.

### 3.4.2 Analysis of obtained samples.

Gas chromatography is a term used to describe the group of analytical separation techniques used to analyze volatile substances in the gas phase. In gas chromatography, the components of a sample are dissolved in a solvent and vaporized in order to separate the analyzed compounds by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyzed compounds through the heated column. Gas chromatography is one of the sole forms of chromatography that does not use the mobile phase for interacting with the analyzed sample. The stationary phase is either a solid adsorbent, termed gas-solid chromatography (GSC), or a liquid on an inert support, termed gas-liquid chromatography (GLC) [26].

# 4. RESULTS

Several important parameters are going to be analyzed and compared during results summary. **Permeate flux** is defined by Eq.1:

$$J_i = \frac{P_i}{\delta}\left(p_i^0 \cdot x_i \cdot \gamma_i - p_p \cdot y_i\right) \tag{1}$$

Where:

- $P_i$ is the permeability of component *i* [kg·h$^{-1}$·bar$^{-1}$·m$^{-2}$].
- $\delta$ is the thickness of the membrane [m].
- $p_i^0$ is the vapor pressure of component *i* [bar].
- $x_i$ is the molar fraction of component *i* [-].
- $\gamma_i$ is the activity coefficient of component *i* [-].
- $p_p$ is pressure value on permeate side [bar].
- $y_i$ is vapor fraction of component *i* [-].

**Separation factor** is defined by Eq. 2:

$$\beta = \frac{{}^{y_i}/_{y_j}}{{}^{x_i}/_{x_j}} \tag{2}$$

Where:

- ${}^{y_i}/_{y_j}$ is the ratio between molar concentration of the components on permeate side [-].
- ${}^{x_i}/_{x_j}$ is the ratio between molar concentration of the components on feed side [-].

**Resistance** of each component through the membrane is also analyzed and it is defined by Eq. 3:

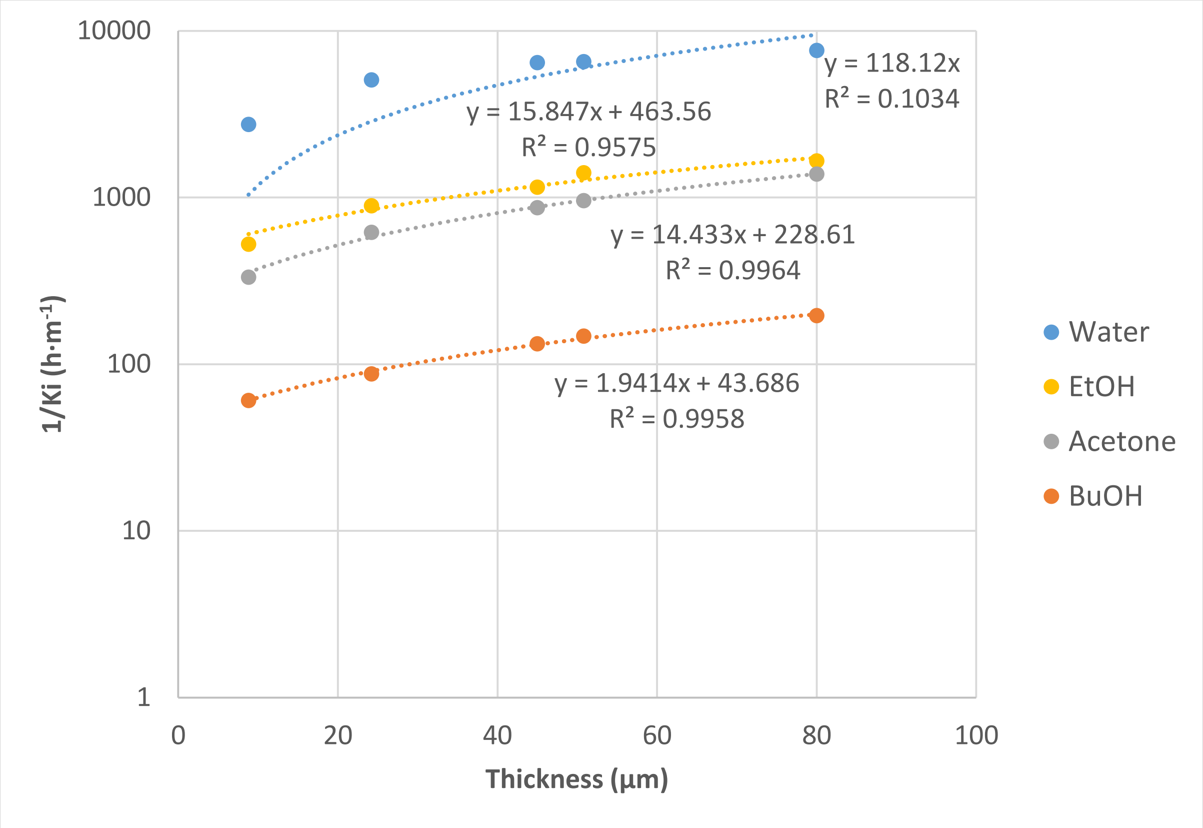
$$K_i = \frac{J_i}{x_i} \tag{3}$$

Where:

- $J_i$ is the permeate flux of component *i* [kg·m$^{-2}$·h$^{-1}$].
- $x_i$ is weight fraction of component *i* in the feed side [kg·m$^{-3}$].

## 4.1 Flat-sheet membranes.

Flat-sheet membranes from 0.15g (8.8 μm) to 0.60g (80 μm) were tested. It was analyzed what are the effect of the mass (thickness) or operation temperature on membrane resistance values for each component. It is desired to obtain low resistance values for acetone, butanol and ethanol (especially butanol) because of their usage as final or intermediate products. High resistance values for water are also desired in order to obtain a final organic mixture as pure as possible. Variables effects are shown in Graph 1:



**Graph 1. Flat-sheet membranes experiments results at 40ºC.**

As it can be seen, membrane mass transfer resistance is a parameter strongly influenced by thickness. A positive slope is appreciated on represented functions. Highest trend corresponds to water and lowest one is referred to butanol. Because of the characteristics of the membrane and the separation values for butanol, water always has the higher values of resistance in comparison with the others. Butanol has a value of membrane resistance around 100 times lower than water. It means that studied composite membrane is working at a good performance (Graph 3). It can be also seen that temperature affects membrane mass transfer resistance. Butanol resistance at 30ºC is over 100 h·m$^{-1}$ and when the temperature is increased to 50ºC, this value is almost a half. The others follows the same rule. It means that total permeate will be higher (total production is increased), but the separation will be worst. Better butanol permeate fluxes results were obtained for 40g membrane (73 µm).

## 4.2 Hollow fiber membranes.

Regarding on hollow fiber membranes results, it is possible to say that obtained permeate flux of butanol is almost five times higher than the same conditions for flat-sheet membranes.

Due to the cylindrical disposition of the selective layer, separation possibilities increases. Different thickness for each component of the external layers of hollow fibers were tested: 0.75-7.5% PEBAX 2533 + 0.5-2% PDMS. They were also tested hollow fibers with only selective PEBAX 2533 layer at different concentrations.

Layer thickness on hollow fibers has the same effect than on flat-sheet membranes. Thicker PEBAX 2533 layers will obtain less quantity of permeate but it will have a better value of separation. PDMS layer, that is used to prevent dilution of PEBAX 2533 with the feed, also works as an additional resistance.

Total resistance contribution among the system is distributed as 30% for selective membrane and 70% for fluid conditions when values of thickness are extremely low. For thin enough membranes (less than 5 $\mu$m), membrane resistance is negligible, so total resistance corresponds to the fluid. In order to analyze this resistance and try to optimize working conditions for a better system performance, inlet flow to modules were varied from 0.18 L/min to 6.352 L/min. All the experiments are collected on Graph 3, in which is represented total permeate flux in front of separation.

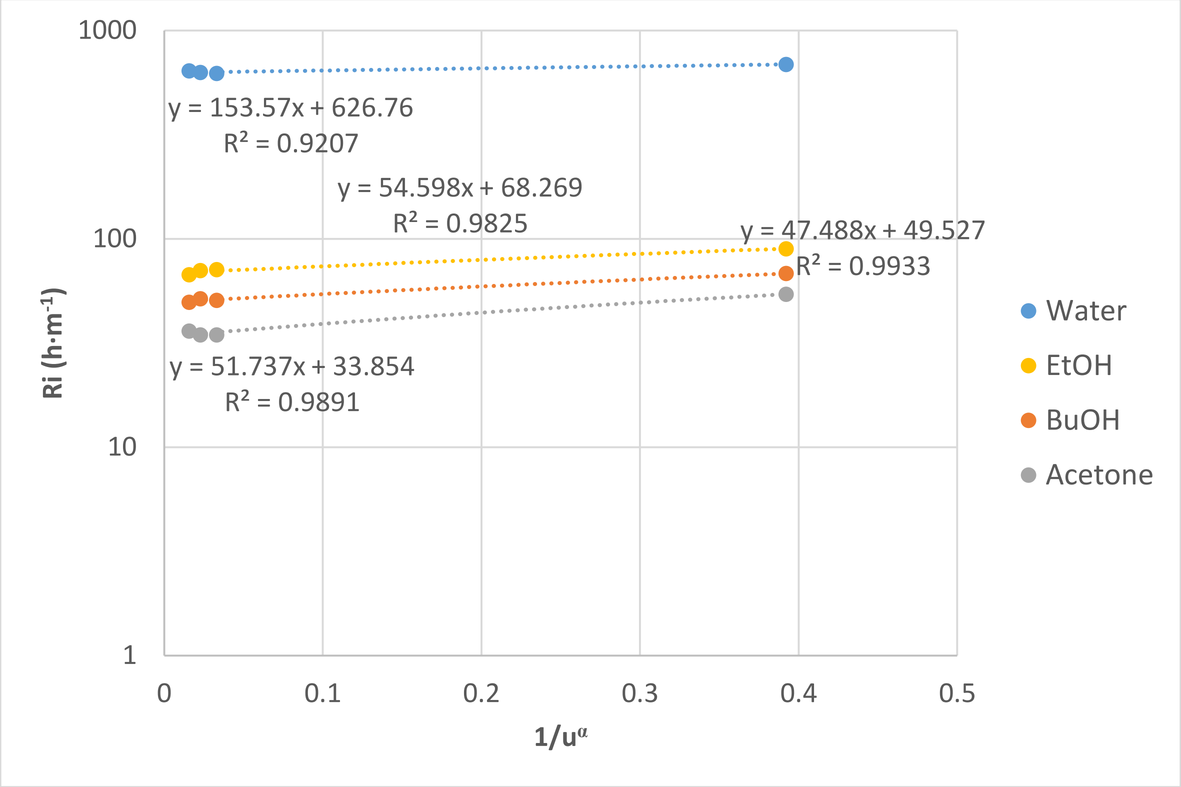
It was also developed a Wilson plot method that provides an outstanding tool for the analysis and design of mass transfer processes. It deals with the determination of the dependence of the mass transfer coefficients with the operational conditions based on measured experimental data (Eq.4). [27].

$$Ji = f(K_i, Re^{\alpha}, Sh) \tag{4}$$

Where:

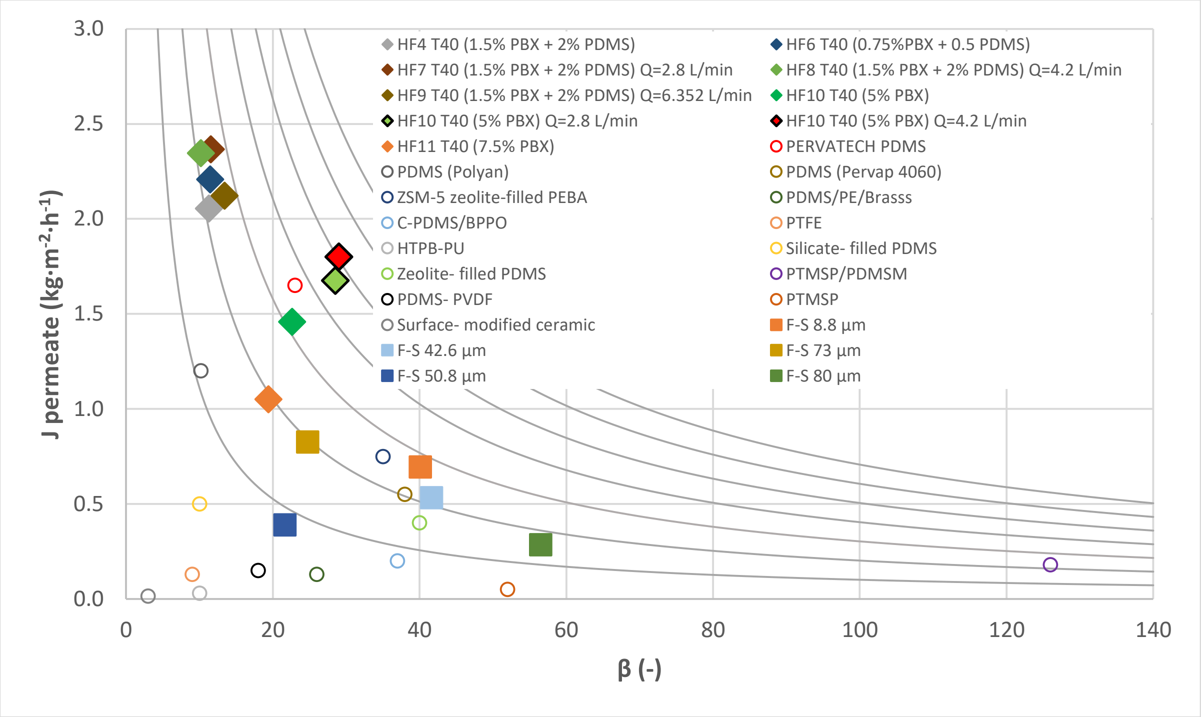
- $Sh$ is Sherwood number [-].
- $\alpha$ value is an estimated parameter for the correlation between 0 and 1. In this work, it was used $\alpha$=0.9 [-].
- $Re$ is Reynolds number [-].
- $K_i$ is the resistance of each component [m/h].

Ji values can be obtained by calculating velocities through the module's membranes. Results of this method are collected on Graph 2:



**Graph 2. Wilson plot of the experimental mass transfer.**

By using slope and independent term of functions equations, it is possible to estimate new performance for new working conditions. HF10 results with inlet flow variation were obtained by using this procedure.



**Graph 3. Comparison of various membranes performance in n-butanol recovery by PV [4].**

It can be seen on Graph 3 that most of hollow fiber results are located over 1.5 $kg \cdot m^{-2} \cdot h^{-1}$ of total permeate. If it is compared HF4 with HF6, for half concentration of both layers, results are quite closed. Separation factor has the same value and the total permeate increased. It is a good conclusion because its materials optimizing meaning. A 0.5% PDMS layer is enough to prevent PEBAX 2533 dilution.

HF7, HF8 and HF9 compare the same membrane conditions but inlet flow variation. For higher values of flow, separation factor increases and total permeate values remain constant. It is the same case for HF10. 5% PEBAX 2533 layer allows highest values of separation and also a total permeate flux increase is reached varying the inlet flow. PSI value (Eq.5) for PERVATECH PDMS (best performance from literature [4]) membrane is between 30 and 40. PSI values for 5% PEBAX 2533 hollow fibers are closed to 50.

$$PSI = J \cdot (\beta - 1)] \qquad (5)$$

Where:

- J is permeate flux [$kg \cdot m^{-2} \cdot h^{-1}$].
- $\beta$ is separation factor value [-].

# 5. CONCLUSIONS

Extremely thin flat-sheet membranes (10 μm) were successfully prepared. As it was demonstrated, permeate flux is higher for thinner membranes. Because of that, it is necessary to develop new studies to improve process results by optimizing membrane thickness. Addition of small amounts of ionic liquid [HMIm][FAP] improves the membrane separation performance. For thin enough membranes (less than 5 μm) membrane resistance is negligible in comparison with operation conditions resistance. PVDF/ PEBAX 2533/ PDMS hollow fibers presented promising results were permeate fluxes higher than 1.5 $kg \cdot m^{-2} \cdot h^{-1}$. PDMS has a positive effect as a coating layer, covering protection for PEBAX 2533 selective layer. On the other hand, it works as an additional resistance for separation process. Flowrate conditions variation allows a better system performance, increasing total permeate and also separation factor.

# 6. FUTURE CHALLENGES

Several values of thickness were tested during experiments. Basic ideas of how process variables affect to the process were obtained. Future studies should be focused on optimization of these variables vs. separation factor values.

Optimize membrane thickness at the same time than working variables. Materials optimization is also important because of its direct relation with the economic part of the process. Better working conditions and membrane characteristics, higher the production and separation.

Ionic liquid addition to selective layer improved mass transfer phenomena on flat-sheet membranes butanol recovery at 90/10 proportion. Next studies should be focused on new ionic liquid proportionalities for hollow fiber structure separation.

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