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# Transport of Lignin and other Lignocellulosic Components Through Supported Ionic Liquid Membranes

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Wood can be considered as the main renewable raw material. Until now, the production of cellulose has been the main target of wood transformation. However, the other components, mainly hemicellulose and lignin, must be taken into account for sustainable implementation of bio-refineries. The transition from low to high value added applications, specifically for lignin, requires the development of new separation processes. Supported ionic liquid membranes can be a promising option to separate and purify lignocellulosic components. The extraction from the feed phase to the stripping phase in only one stage allows the compaction of the system, without high energy demand. The main objective of this work was the analysis of the potential of supported ionic liquid membranes for lignin extraction and purification. [BMIM]$MeSO_4$, [EMIM]$EtSO_4$ and CYPHOS 108 were the ionic liquids chosen to impregnate PVDF membranes. The obtained results demonstrated that lignin can be extracted, but the SILMs were not selective and further study is required to determine their stability and the transport mechanisms involved.

## 1. Introduction

Wood can be considered as the main renewable raw material for aromatic chemicals, so the forest industry must be managed according to sustainable principles. Until now, the production of cellulose has been the main target of wood transformation, but the other components (lignin and hemicellulose) must be taken into consideration for the successful implementation of bio-refineries (Liebmann et al., 2012). The transition from low to high value added applications for lignin (from dispersants and emulsifiers to aromatic compounds) requires the development of new separation processes, including alternatives based on ionic liquids (ILs) (Keskar et al., 2012).

ILs are organic salts that usually melt below 100ºC. They are widely considered to be a green class of solvents due to their negligible vapor pressure, limited reactivity, high thermal stability and their ability to be easily recycled (Fu et al., 2010; Burns et al., 2014).

Different ILs have been reported in the literature for application in lignocellulosic biomass pretreatment, fractionation and separation. The case of imidazolium based ILs has been deeply investigated and some of these ILs have demonstrated a great potential for the selective dissolution of lignin without undesired modification of cellulose and hemicellulose. Different radicals in the main imidazolium ring have been reported, including methyl, ethyl, allyl, butyl, hexyl or benzyl. The selected anions can be simple (chloride, bromide, acetate...) or more complex (tetrafluoroborate, trifluoromethanesulfonate o methylsulfate). The butylmethylimidazolium methylsulfate ([BMIM]$MeSO_4$) can be highlighted as an example of a suitable solvent for dissolution of lignin and its posterior recovery (Pu et al., 2007; Prado et al., 2013).

Nevertheless, imidazolium-based ILs can suffer some drawbacks. They might be unstable under alkaline conditions or incompatible with the presence of ozone, a chemical often employed in the processing of lignin. Therefore, alternative ILs, based on ammonium, phosphonium and pyrrolidinium, which show higher tolerance to alkaline and ozone, must be more deeply investigated for their application in biomass fractionation (Glas et al., 2015). Moreover, their higher thermal stability and commercial availability can provide some advantages over imidazolium-based ILs. However, economic limitations are common to all ILs, as their high price greatly limits the economic competitiveness of the processes that use ILs.

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Membrane separation systems allow drastic process improvements thanks to low energy consumption, waste generation and capital investment (Abejon et al., 2012). Supported ionic liquid membranes (SILMs) can be a promising option to separate and purify lignin. The extraction from the feed phase to the stripping phase in only one stage favors the compaction of the system, without requirements of high energy demand (no heating or pressure to be applied). The reduced amount of ionic liquid (IL) required for SILMs minimizes the economic drawback that characterizes the use of such expensive chemicals.
The main objective of this work was the analysis of the potential of SILMs for fractionation and separation of lignocellulosic biomass components, with special attention to lignin extraction and purification. The flow of the lignin from the feed compartment to the stripping one was characterized and compared with the flow of other component (glucose in this case) to determine the selectivity of each membrane.

## 2. Materials and methods

### 2.1 Materials

Two imidazolium-based ILs ([BMIM]$MeSO_4$ from Iolitec, and [EMIM]$EtSO_4$ from Sigma-Aldrich) and a phosphonium-based IL (CYPHOS 108 from Cytec) were used as supplied. Alkali lignin (low sulfonate content) and D-(+)-glucose (>99.5%) were provided by Sigma-Aldrich.

### 2.2 SILMs preparation

The SILMs were prepared using hydrophobic PVDF membranes (47 mm diameter with 0.45 μm pores). Firstly, the membrane and the IL were introduced in a vacuum oven (< 35 mbar) separately to eliminate the water, gases and any other traces of volatile compounds. Later, the membrane was soaked in the ionic liquid, keeping the vacuum for 24 hours to favour a proper impregnation by removal of air from the membrane pores. Finally, the liquid excess over the membrane surface was removed by allowing to drip overnight. This way, the membrane was ready to be placed in the membrane cell.

### 2.3 Experimental tests

The experimental tests were carried out in a membrane cell designed for this specific project (Figure 1). The cell is composed of two identical compartments (volume lower than 300 ml) separated by the SILM. Two different types of experiments were performed. On the one hand, the feed and stripping solutions were poured into the cell at the same time and the compartments were closed without inlet or outlet streams in the system. On the other hand, the feed and stripping solutions were poured into the cell at the same time and two tubes were introduced in each compartment to allow inlet and outlet streams. These streams were connected to an external reservoir (about 100 ml) under continuous agitation. The flowrate of these streams was 1 ml/s, so a quick replacement of the fluid in the cell compartments by the fluid from the reservoirs was assured.

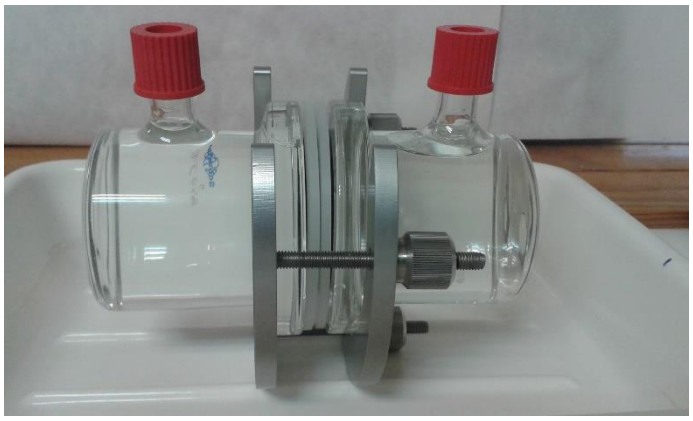

*Figure 1: Image of the cell where the SILMs tests were carried out*

In both cases, samples were taken at regular time intervals from both compartments. All the experiments were carried out at room temperature. It was decided to stop the experiments after the capture of enough samples to characterize the trend.
Lignin and glucose concentrations were determined by a UV-VIS spectrophotometer DR 5000, using a wavelength of 280 nm for the lignin (Alén and Hartus, 1988) and of 575 nm for glucose, according to the dinitrosalicylic acid method for determination of reducing sugars (Miller, 1959).

## 3. Process modelling

The amount of a solute (lignin or glucose) that passes through a SILM and per unit of time and surface is called flux *J* and it is proportional to the gradient of concentration C between both solutions:

$$J = k * \Delta C \quad (1)$$

where k is the proportionality constant that can be defined as the permeability. To model the evolution of the concentration of the solute in the feed compartment $C_F$, a mass balance to the feed compartment can be applied:

$$v * \frac{dC_F}{dt} = -k * \Delta C * A \quad (2)$$

where *v* is the volume of the feed solution and *A* the active surface of the SILM. The equation can be reorder and modified considering the gradient between the feed (F) and stripping (S) compartments ($\Delta C = C_F - C_S$) and the total mass balance with $C_0$ as initial feed concentration ($C_0 = C_F + C_S$):

$$\frac{dC_F}{\Delta C} = -\frac{k * A * dt}{v} \quad (3)$$

$$\frac{dC_F}{2C_F - C_0} = -\frac{k * A * dt}{v} \quad (4)$$

Integration can be applied:

$$\int_{C_0}^{C_F} \frac{dC_F}{C_F - \frac{C_0}{2}} = \int_0^t -\frac{2 * k * A * dt}{v} \quad (5)$$

$$ln\left[C_F - \frac{C_0}{2}\right]_{C_0}^{C_F} = -\frac{2 * k * A * t}{v} \quad (6)$$

$$ln\left(C_F - \frac{C_0}{2}\right) - ln\left(C_0 - \frac{C_0}{2}\right) = -\frac{2 * k * A * t}{v} \quad (7)$$

$$ln\left(\frac{C_F - \frac{C_0}{2}}{\frac{C_0}{2}}\right) = -\frac{2 * k * A * t}{v} \quad (8)$$

All the constant can be grouped into a unique constant K, called effective mass transfer constant:

$$ln\left(\frac{C_F - \frac{C_0}{2}}{\frac{C_0}{2}}\right) = -K * t \quad (9)$$

$$C_F = \frac{C_0}{2} * (1 + e^{-K*t}) \quad (10)$$

In a totally equivalent way, the evolution of the concentration in the stripping compartment $C_S$ can be obtained:

$$ln\left(\frac{\frac{C_0}{2} - C_S}{\frac{C_0}{2}}\right) = -K * t \quad (11)$$

$$C_S = \frac{C_0}{2} * (1 - e^{-K*t}) \quad (12)$$

## 4. Results

The evolution of the lignin concentration in the feed and stripping compartments of the cell with respect to time when the system worked without streams is shown in Figure 2. As it can be observed, the performance of the three tested ILs was quite similar and only minor differences could be identified.

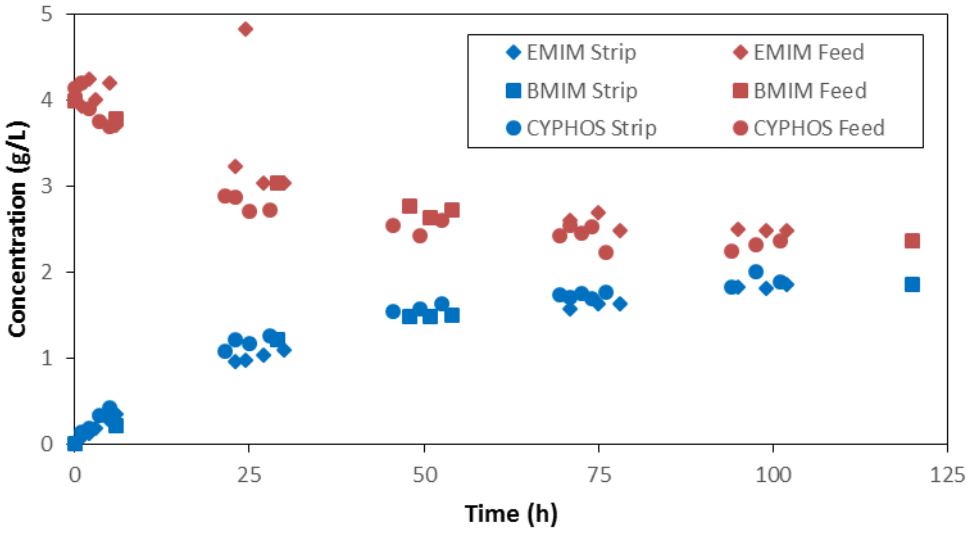


*Figure 2: Evolution of the lignin concentration in both compartments without streams*

The graphs show a higher permeation of lignin during the first hours of the experiments, when the concentration gradient was maximum. After that, the transference was reduced and the permeation slowed down as the concentrations get closer to the equilibrium. Moreover, the experimental results indicated that the nature of the IL was not a determining factor, as both imidazolium-based ILs (EMIM and BMIM), as well as the phosphonium-based CYPHOS, presented equivalent performance.

When the developed model was applied to calculate the effective mass transfer constants for lignin, very satisfactory fitting among the experimental and the modelled was found, as shown in Figure 3, where the representation of two examples of the logarithmic terms of the equation 11 versus time is depicted. The slopes of these graphs correspond to the effective mass transfer constant. All the effective mass transfer constant values fell in the range 0.0156-0.0254 $h^{-1}$, with $R^2$ values higher than 0.87.

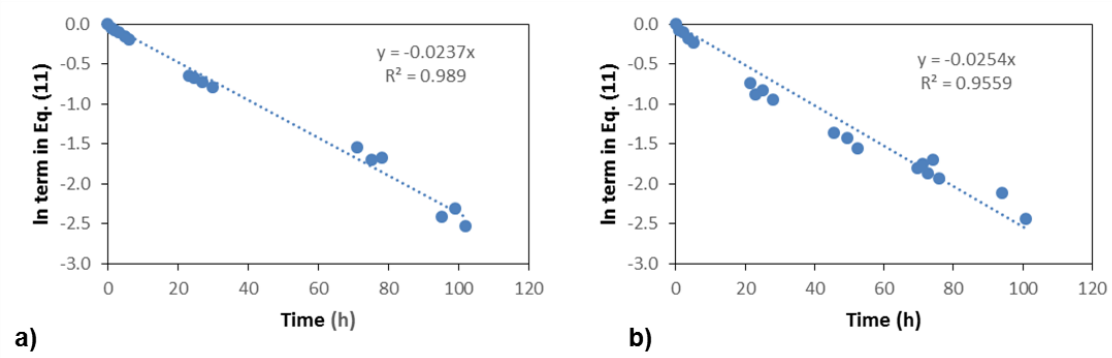


*Figure 3: Graphs of the logarithmic terms in Eq. (11) versus time for two ILs: a) EMIM and b) CYPHOS*

The experiments with glucose solutions were carried out under the configuration with streams using fresh prepared SILMs. The results obtained when EMIM and CYPHOS were selected as ILs are represented in Figure 4. As it can be observed, the mass transfer between both compartments in the cell is much faster: the concentrations resulted after 30 h were closer to the equilibrium situation than the ones obtained for lignin in the alternative configuration after 120 h. This difference can be more easily quantified when the corresponding effective mass transfer constants were calculated: the mean values fell in the range 0.0838-0.1076 $h^{-1}$, with $R^2$ values higher than 0.93. Consequently, the mass transfer has been increased at least four times when compared both series of experiments. This fact could be explained by the improvements in mass transfer due to higher agitation in the cell as a consequence of the inlet and outlet streams. Moreover, glucose could be considered as a more mobile solute because of its smaller size, especially when compared to lignin.

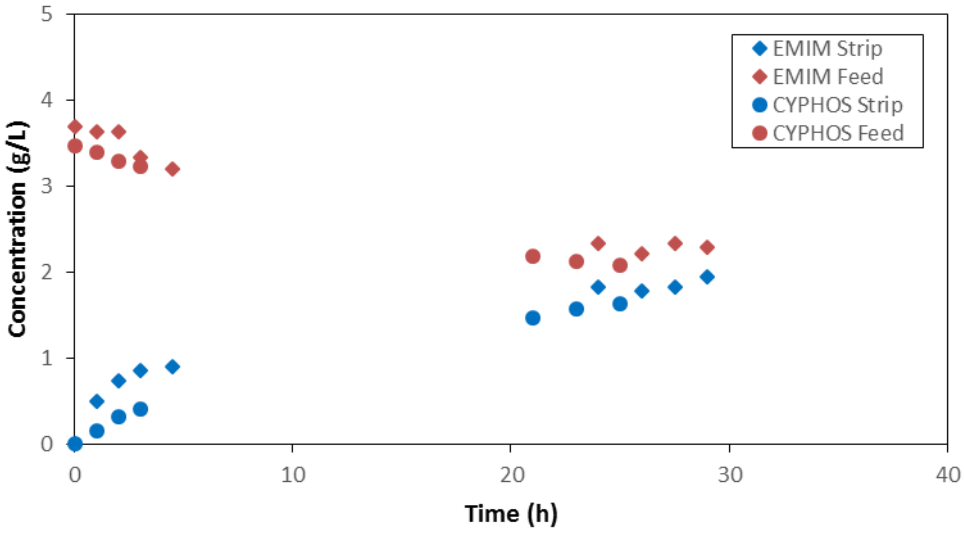


*Figure 4: Evolution of the glucose concentration in both compartments with streams*

However, when similar experiments (under the configuration with streams but for shorter times) were carried out using lignin instead of glucose as solute, the results were not too different. As shown in Figure 5, the comparison of both SILMs gave very similar results, independently of the selected solute. In view of these data, it can be concluded that the nature of the solute does not show any remarkable influence on the performance of the SILMs.

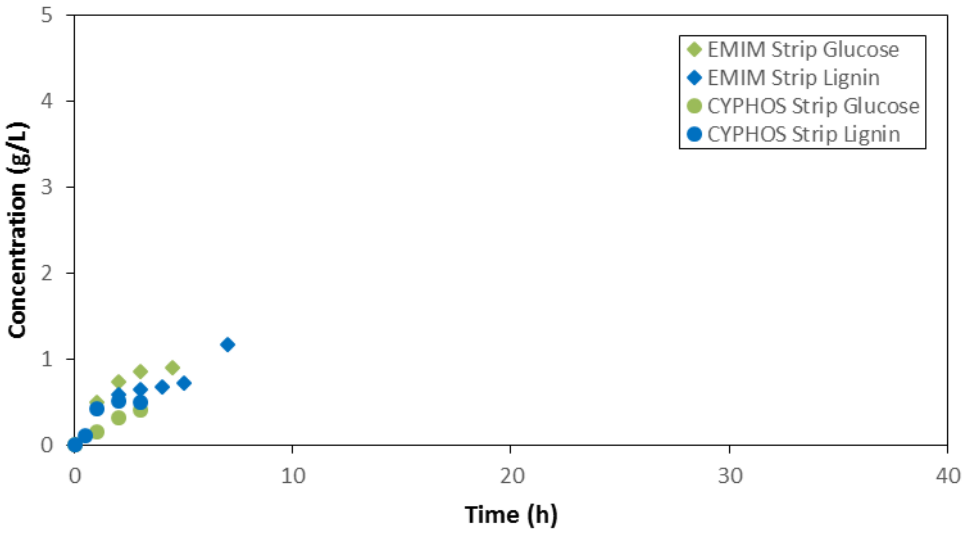


*Figure 5: Comparison of the evolution of the lignin and glucose concentration in the stripping compartment with streams*

Further tests were designed to get more information about the stability of the proposed SILMs (EMIM and CYPHOS). For this purpose, lignin solutions were employed in the configuration without streams. Once the tests with the fresh prepared SILMs were stopped, the SILMs were returned to the vacuum oven for at least 24 h and then weighted again to compared them with the virgin membranes and the fresh SILMs (the registered weights are included in Table 1). Later, the SILMs were employed for another test without new impregnation with the corresponding IL and the resulting effective mass transfer constants were calculated (Table 1).

*Table 1: Stability of the SILMs during repeated experiments without new impregnations*

| | EMIM | | | | | CYPHOS | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Membrane mass (g) | | K ($h^{-1}$) | | | Membrane mass (g) | | K ($h^{-1}$) | |
| Test | Before impregnation | After impregnation | Based on feed side | Based on strip side | Test | Before impregnation | After impregnation | Based on feed side | Based on strip side |
| 1 | 0.1282 | 0.4306 | 0.0156 | 0.0237 | 1 | 0.1274 | 0.4287 | 0.0237 | 0.0254 |
| | No impregnation | After vacuum oven | | | | No impregnation | After vacuum oven | | |
| 2 | | 0.1302 | 0.0193 | 0.0184 | 2 | | 0.1331 | 0.0128 | 0.0244 |
| 3 | | 0.1297 | 0.0138 | 0.0269 | 3 | | 0.1301 | 0.0264 | 0.0250 |

The stability tests resulted in unexpected outcomes. Despite the fact that the weights of the membranes after the tests were very close to the virgin weights before impregnation, the corresponding effective mass transfer constants were similar among all the tests. Therefore, while the mass transfer with the virgin membranes was not possible, there were minor differences between the fresh prepared SILMs and the used SILMs after several tests. Further work will be carried out in order to understand the mechanisms of transport through the membrane and the possible modifications they can suffer after the impregnation with the ILs.

## 5. Conclusions

This work has analysed the transport of lignin and glucose through SILMs based on [BMIM]$MeSO_4$, [EMIM]$EtSO_4$ and CYPHOS 108. Although the virgin hydrophobic PVDF membranes did not allow the permeation of lignin and glucose solutions, once these membranes were impregnated with the ILs, the solutes were able to pass from the feed compartment of the cell to the stripping one. Nevertheless, the prepared SILMs were not selective, as the influence of the selected IL or the tested solute on the solute transport was not important. Moreover, the stability of the SILMs has to be investigated more deeply, but consecutive tests gave results equivalent to the ones obtained with the fresh SILM.

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**References**

Abejón R., Garea A., Irabien A., 2012, Minimization of energy consumption for chemicals ultrapurification processes, Chemical Engineering Transactions, 29, 1549-1554.

Alén R., Hartus, T., 1988, UV spectrophotometric determination of lignin from alkaline pulping liquors, Cellulose Chemistry and Technology 22, 613-618.

Burns F.P., Themens P.A., Ghandi K., 2014, Assessment of phosphonium ionic liquid-dimethylformamide mixtures for dissolution of cellulose, Composite Interfaces, 21, 59-73.

Fu D., Mazza G., Tamki Y., 2010, Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues, Journal of Agricultural and Food Chemistry, 58, 2915-2922.

Glas D., Van Doorslaer C., Depuydt D., Liebner F., Rosenau T., Binnemans K., De Vos D.E., 2015, Lignin solubility in non-imidazolium ionic liquids, Journal of Chemical Technology and Biotechnology, 90, 1821-1826.

Keskar S.S., Edye L.A., Fellows C.M., Doherty W.O.S., 2012, ATR-FTIR measurement of biomass components in phosphonium ionic liquids, Journal of Wood Chemistry and Technology, 32, 175-186.

Liebmann B., Friedl A., Rodrigues J.F.C., 2012, Lignocellulosic biomass dissolution and fractioning using ionic liquids as a solvent, Chemical Engineering Technology, 29, 553-558.

Miller, G.L., 1959, Use of dinitrosalicylic acid reagent for determination of reducing sugar. Analytical Chemistry, 31, 426-428.

Prado R., Erdocia X., Labidi J., 2013, Lignin extraction and purification with ionic liquids, Journal of Chemical Technology and Biotechnology, 88, 1248-1257.

Pu Y., Jiang N., Ragauskas A.J., 2007, Ionic liquid as a green solvent for lignin, Journal of Wood Chemistry and Technology, 27, 23-33.