STUDY OF ACETONE, BUTANOL AND ETHANOL LIQUID EXTRACTION FROM PREPARED AQUEOUS SOLUTIONS USING MEMBRANE CONTACTOR TECHNIQUE

ESTUDIO DE LA EXTRACCIÓN LÍQUIDA DE ACETONA, BUTANOL Y ETANOL DE SOLUCIONES ACUOSAS PREPARADAS USANDO LA TÉCNICA DE CONTACTORES DE MEMBRANA

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ABSTRACT

Fermentative production of butanol using *Clostridium acetobutylicum* results in a mixture of acetone/butanol/ethanol (ABE), which reaches a maximum concentration between 26 and 32.6 kg/m^3, as a consequence of product inhibition. These low ABE concentrations demand an efficient separation system that allows the continuous ABE extraction. This study evaluated the extraction of ABE's prepared aqueous solutions with membrane contactors technique by using commercial extracting solvents (petroleum ether, hexane and toluene). The influence of temperature and initial concentration of butanol on the process was analyzed, in the range of 30 - 40°C and 4.8 - 20 kg/m^3 respectively, using a response surface experimental design (central composite 2^2+star), and finding the optimal values considering batch analysis (42°C and 1.65 kg of 1-butanol/m^3 as initial concentration). The experimental analysis was carried out by using Statgraphics Centurion XVI.I®. The approach of a mathematical model was performed, obtaining an error of 14.4% and 12.2% for acetone and butanol final concentrations in toluene solvent phase, respectively. It was concluded that extraction is achievable for recovery of acetone and butanol, by using toluene as solvent extractor, and obtaining partition coefficients of 0.761 for acetone and 0.998 for butanol.

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RESUMEN

La producción de butanol por vía fermentativa usando *Clostridium acetobutylicum* genera mezclas acetona/butanol/etanol (ABE), las cuales alcanzan una concentración promedio máxima entre 26 y 32.6 kg/m³, como resultado de la inhibición por producto. Estas bajas concentraciones demandan el uso de sistemas de separación eficientes que permitan la extracción de ABE de forma continua. Este estudio evaluó la extracción de ABE de soluciones acuosas preparadas con la técnica de contactores de membrana usando solventes comerciales (éter de petróleo, hexano y tolueno) como agente extractor. Se analizó la influencia de la temperatura y la concentración inicial de butanol sobre el proceso, en el rango de 30 - 40°C y 4.8 - 20 kg/m³ respectivamente, utilizando un diseño experimental de superficie de respuesta (central compuesto 2^2+estrella), y encontrando valores óptimos para estas variables basados en análisis en batch (42°C y 1.65 kg de 1-butanol/m³ como concentración inicial). El análisis experimental se llevó a cabo utilizando Statgraphics Centurion XVI.I.®. Se planteó un modelo matemático en estado transitorio, obteniendo % error de 14.4 y 12.2% para las concentraciones finales de acetona y butanol en el tolueno, respectivamente. Se concluye que esta técnica de extracción es posible para la recuperación de acetona y butanol usando tolueno como solvente extractor, obteniendo coeficientes de partición de 0.761 para la acetona y 0.998 para el butanol.

Palabras clave: ABE, Separación, Contactores, Membranas de PTFE.

RESUMO

A produção de butanol por via fermentativa usando *Clostridium acetobutylicum* gera misturas acetona/butanol/etanol (ABE), as quais atingem uma concentração média máxima entre 26 e 32.6 kg/m³, como resultado da inibição por produto. Estas baixas concentrações demandam o uso de sistemas de separação eficientes que permitam a extração de ABE de forma contínua. Este estudo avaliou a extração de ABE de soluções aquosas preparadas com a técnica de contatores de membrana usando solventes comerciais (éter de petróleo, hexano e tolueno) como agente extrator. Foi analisada a influência da temperatura e da concentração inicial de butanol sobre o processo, na faixa de 30 - 40°C e 4.8 - 20 kg/m³ respectivamente, utilizando um desenho experimental de superfície de resposta (central composto 2^2+estrela), e encontrando valores ótimos para estas variáveis baseados em análise em batch (42°C e 1.65 kg de 1-butanol/m³ como concentração inicial). A análise experimental foi realizada utilizando Statgraphics Centurion XVI.I.®. Foi proposto um modelo matemático em estado transitório, obtendo porcentagem de erro de 14.4 e 12.2% para as concentrações finais de acetona e butanol no tolueno, respectivamente. A conclusão foi que esta técnica de extração é possível para a recuperação de acetona e de butanol usando tolueno como solvente extrator, obtendo coeficientes de partição de 0.761 para a acetona e de 0.998 para o butanol.

Palavras-chave: ABE, Separação, Contatores, Membranas de PTFE.

1. INTRODUCTION

Currently, butanol is of interest because of its use as fuel. Unlike ethanol, it can be used directly (without modification) in conventional engines (Ni & Sun, 2009; Demain, 2009; Liu *et al.*, 2011). Additionally, butanol has an Energy Content (EC) of 0.036 kJ/kg close to the gasoline (EC: 0.0438 kJ/kg) and higher than the ethanol (EC: 0.027 kJ/kg) (Demain, 2009).

Butanol production may be achieved by chemical or biochemical routes. Produced by the latter route, an acetone/butanol/ethanol mixture is originated –ABE process–, which reaches an average maximum concentration from 26 to 32.6 kg/m^3 in the fermentation broth, as a result of product inhibition. From this concentration, approximately 20 kg/m^3 are butanol (Liu *et al.*, 2011). Whereas the ABE mixture is toxic to the microorganism (decreasing process performance), it is required to find a method of *in situ* recovery.

It has been found in various studies that membrane contactors (liquid-liquid extraction trough a membrane) are applied in the recovery of butanol. The membrane acts as a passive barrier separating two immiscible fluids. One of these fluids is immobilized by the pores of the membrane. Mass transfer occurs by diffusion due to a concentration gradient. Some of the advantages of this technique include: prevention of contamination by diffusion of the solvent in the fermentation broth, prevention of formation of emulsions and accumulation of microbial cells in the solvent/broth interface (Zheng *et al.*, 2009).

Some studies have been done on this subject, each using unconventional solvents. For example, Groot *et al.* (1990) studied the extraction of butanol *in situ* with membranes by using different solvents, especially high molecular weight esters. Furthermore, Grobben, Eggink, Cuperus and Huizing (1993) and Jeon and Lee (1987) studied the implementation of this technique using Oleyl alcohol as solvent and membranes of different materials (polypropylene and silicon, respectively). Tanaka *et al.* (2012) investigated butanol extraction using PTFE membranes (polytetrafluoroethylene) and 1-dodecanol as solvent extractor. Concerning membrane contactors, operating variables such as temperature and solute concentration were always considered to evaluate

process parameters such as partition coefficient (P) and membrane flux (Younas, Bocquet & Sánchez, 2011; Bocquet *et al.,* 2006; Kumar, Haddad, Alguacil & Sastre, 2005; Bothun *et al.*, 2003).

This study evaluated the extraction process using a membrane contactor as recovery method of acetone, butanol and ethanol from prepared aqueous solutions on laboratory scale, using commercial solvents (toluene, petroleum ether and hexane) as extracting agent. These solvents were chosen from a list of commercial ones taking into consideration: cost, resilience, security conditions (risks and hazards analysis) and partition coefficient. Improved operating conditions were found from batch analysis. Based on these results, a comparison was achieved with values obtained from a validated mathematical model describing the process. To our knowledge, it is the first time modeling considers transient state to evaluate this process extraction.

2. MATERIALS AND METHODS

Materials

Whatman PTFE membranes (Ø= 47 mm, pore diameter of 0.45 and 5 μm) were used. Also Acetone (99.7%) JJ Baker, 1-butanol (Butylalcohol, 99.8%) JJ Baker, ethanol (99.9%) Merck, hexane (90.3%) Mallinckrodt, petroleum ether (petroleum benzine) Merck, and toluene (99.5%) MS Science.

Methods

Determination of Partition Coefficients

6.5x10^{-5} m^3 of ABE mixtures were prepared and placed in flat bottom flasks with sockets, in direct contact with 6.5x10^{-5} m^3 of organic phase (solvent), to allow the diffusion of compounds between phases. The bottom flasks were hermetically sealed, and put under agitation of 200 rpm for 3 days at 298 K. After this time, phases were separated and ABE final concentrations were determined in each phase. For ABE mixtures, the maximum concentrations were established based on butanol inhibition condition during fermentation, 5.93 kg/m^3 of acetone, 2.48 kg/m^3 of ethanol (Bankar, Survase, Singhal & Granström, 2012) and 20 kg/m^3 of butanol (Volkov, Volkov & Khotimskii, 2009). The minimum concentrations used were ten times lower

(acetone: 0.593 kg/m³, ethanol: 0.248 kg/m³ and butanol: 2 kg/m³).

The coefficient was calculated using the following expression:

$$P = \frac{C^{Org}}{C^{Ac}} \qquad (1)$$

Where, c^{Org} is the concentration of the compound in the organic phase and c^{Ac} is the concentration of the compound in the aqueous phase.

Partition coefficients were calculated for each ABE compound in each commercial solvent evaluated (petroleum ether, toluene and hexane).

High Performance Liquid Chromatography (HPLC)

Individual quantification of each compound in the aqueous phase (acetone, butanol and ethanol) was performed by HPLC (Simoni, Chapeaux, Brennecke & Stadtherr, 2010; Li, Srivastava & Parnas, 2010; Ha, Mai & Koo, 2010), using a LC-20AD (Shimadzu) liquid chromatograph equipped with a refractive index detector RID-10A. The components were separated in a COR-10H column (Transgenomic Coregel) at 80°C using 8 mol/m³ H_2SO_4 as the mobile phase at a flow rate of 3.6x10⁻⁵ m³/s.

Gas Chromatography (GC)

Used to quantify the concentrations of the compounds in the organic phase (Areesirisuk, Laopaiboon, Khongsay & Laopaiboon, 2010; Liu *et al.*, 2011; Mariano, Qureshi, Filho & Ezeji, 2011). GC analysis was performed using a 7890A (Agilent Technologies) gas chromatograph in a Split mode. The separation took place in a 60 m long and 2.56x10⁻⁴ m inner diameter HP-88 capillary column. The injector and the FID were kept at 250°C. The column temperature was programmed from 50 to 96°C at a rate of 3°C/min.

Permeate Flux

Flux was calculated by dividing the mass of compound that permeates the membrane during the time passed between sampling and membrane surface, using the following equation:

$$N_{i(j)} = \frac{\left[C_{i(j)} - C_{i(j-1)}\right] \cdot V}{\left[t_{(j)} - t_{(j-1)}\right] . A} \qquad (2)$$

Where, C is the concentration of compound i, V is the volume of permeate compartment, t is the sampling time, j is the sampling number and A is the membrane surface.

System for the Study of Membrane Contactors

The stainless steel module shown in Figure 1 was used -2x10⁻⁴ m³ of capacity and 0.06 x 0.06 x 0.06 m-. This system consisted of two chambers separated by a membrane through which ABE aqueous solutions were in contact with the organic phase during 72 h. This system was used to analyze the influence of temperature and initial butanol concentration on the extraction process. Experimental was set up using a response surface design, central composite 2²+star. All experiments were carried out in batch, using prepared ABE aqueous solutions (i.e. prepared mixtures of acetone, butanol and ethanol in distilled water).

Figure 1. Stainless steel membrane contactor module.

Temperature was controlled from 303 to 313 K, using a temperature bath. This is typical range of temperature found in a butanol fermentation according to scientific articles (Qureshi & Maddox, 2005; Qureshi & Maddox, 1995). No transmembrane pressure was established between feed and solvent chambers (avoiding liquid leakage). Acetone and ethanol concentrations in the feed were established from butanol concentration. Butanol concentrations used were: inhibition concentration (20 kg/m³) (Volkov *et al.*, 2009) and a concentration that ensures a constant rate of butanol production (4.8 kg/m³) (Mariano *et al*, 2011). Acetone/butanol and ethanol/butanol ratios (w/w) were established from literature (acetone/butanol: 0.398 and ethanol/butanol: 0.109) (Qureshi & Maddox, 2005; Zheng *et al.*, 2009; Liu *et al.*, 2011). This system was also used to obtain results of the extraction at optimal conditions, adopted for modeling purposes. All experiments were twice performed.

General procedure was as follows: 1.) Assembled contactor module was placed in a temperature bath, 2.) Aqueous ABE solutions were prepared (feed), 3.) $2x10^{-4}$ m^3 of feed and solvent were introduced in its respectively chamber, 4.) Finally, samples were collected depending of the analysis (at 15 and 72 h, for butanol feed concentration and temperature analysis; and each 6 up to 72 h for modeling purposes).

3. RESULTS AND DISCUSSION

Selection of Solvent Extractor

Partition coefficient (P) was experimentally determined using three commercial solvents (petroleum ether, hexane and toluene) at room temperature and two concentration levels. Table 1 shows the partition coefficients obtained and equilibrium concentrations in solvent phase. From this table, it can be seen that using toluene as extracting solvent results in higher partition coefficients for each compound. In the case of hexane and toluene values, they correspond to those reported by Kim, Iannotti and Bajpai (1999). Concerning petroleum ether, it is the first

time partition coefficients are reported. Some deviation in values was found due to solvents and ethanol and acetone volatilities, causing some variations during sampling.

Partition coefficient depends on molecule to extract, its concentration and temperature of the system (Younas *et al.,* 2011). For example, using toluene as extracting solvent, it can be seen that low ABE concentrations made the partition coefficient decrease by 4.14, 18.82 and 89.80% for acetone, butanol and ethanol, respectively.

Table 2 resumes some P values reported by other authors. Only Kim *et al.* (1999) reported results using toluene as extracting solvent for liq-liq extraction. The results obtained in this work (at maximum ABE concentration) are similar of those obtained by Kim *et al.* (1999). Moreover, it can be seen in all cases that ethanol P values are in one order lower than those of butanol and acetone. Additionally, for butanol, there are other solvents with major P values, up to 2.9 (e.g. ionic liquids, oleic alcohol and 1-dodecanol), but it is also important to point out that all this solvents are less available, and thus expensive, when considering a a larger scale (in comparison with toluene).

Table 1. Equilibrium concentrations in solvent phase and partition coefficients (P) at 298 K, pH 5.5, for initial concentrations of acetone (A) of 0.593 and 5.93 kg/m^3, butanol (B) of 2 and 20 kg/m^3 and ethanol (E) of 0.248 and 2.48 kg/m^3.

Solvent	Compound	Equilibrium concentrations in solvent phase (kg/m^3)		P (dim)	
		at minimum initial concentration	at maximum initial concentration	at minimum initial concentration	at maximum initial concentration
Petroleum ether	A	0.0685 ± 0.0025	0.755 ± 0.038	0.380 ± 0.0359	0.191 ± 0.017
	B	0.1885 ± 0.0045	2.7535 ± 0.0235	0.136 ± 0.008	0.207 ± 0.009
	E	0	0.0124 ± 0.0026	0	0.005 ± 0.002
Hexane	A	0.0499 ± 0.0031	0.6770 ± 0.0420	0.109 ± 0.0004	0.128 ± 0.009
	B	0.1780 ± 0	2.8540 ± 0.1970	0.126 ± 0.0004	0.218 ± 0.024
	E	0	0.0112 ± 0.0064	0	0.004 ± 0.003
Toluene	A	0.2175 ± 0.0015	2.6465 ± 0.3115	0.717 ± 0.064	0.748 ± 0.057
	B	0.6435 ± 0.0645	8.0245 ± 0.0715	0.776 ± 0.086	0.956 ± 0.069
	E	0.0387 ± 0.0383	0.0986 ± 0.0215	0.005 ± 0.006	0.049 ± 0.0005

Table 2. Partition coefficients (P) reported for different extracting solvents.

Reference	Extracting solvent	P	Observations
Tanaka *et al.*, 2012	1-dodecanol	$P_B = 5.52$	ABE *in situ* extraction using PTFE membrane (5.02×10^{-3} m^2 of filtration area), at 303K and 1% w/w butanol
Simoni *et al.*, 2010	Ionic Liquids: [hmim] [Tf$_2$N], [HOhmim] [Tf$_2$N] and [hmim] [eFAP]	$P_B = 3.7$ for [hmim] [Tf$_2$N], $P_B = 3.8$ for [HOhmim] [Tf$_2$N] and $P_B = 3.5$ for [hmim] [eFAP]	Liq-liq extraction at 295K and 20% w/w butanol
Adhami, Griggs, Himebrook & Taconi, 2009	Biodiesel Derivates (BD), oleic alcohol	$P_B = 0.91$ and $P_E = 0.073$ for BD $P_B = 2.8$ and $P_E = 0.16$ for oleic alcohol	Liq-Liq extraction, from prepared butanol/etanol aqueous solutions at maximum product inhibition concentrations
Bothun *et al.*, 2003	Propane and CO$_2$	$P_A = 1.63$ and $P_E = 0.065$ for propane $P_A = 9.5$ and $P_E = 0.1$ for CO$_2$	Hollow fiber membrane contactor, acetone-ethanol aqueous solutions, at 298 K and 34 bar for propane and 69 bar for CO$_2$
Ishizaki *et al.*, 1999	Oleic alcohol, Methylated Crude Palm Oil (CPOE)	$P_A = 0.3$, $P_B = 3.3$ and $P_E = 0.2$ for oleic alcohol $P_A = 0.2$, $P_B = 0.9$ and $P_E = 0.05$ for CPOE	*In situ* liq-liq ABE extraction at 303 K
Kim *et al.*, 1999	Toluene	$P_B = 0.93$, $P_A = 0.63$ and $P_E = 0.034\text{-}0.085$	Liq-liq ABE extraction
Jeon & Lee, 1987	Oleic alcohol	$P_B = 3.56$	*In situ* ABE Silicone-membrane contactor extraction (2.27×10^{-1} m^2 of filtration area)

Influence of Initial Concentration of Butanol on the Process

Experimental tests at various temperatures and initial concentrations of butanol were performed, using toluene as extracting solvent. Partition coefficients, final concentrations in the aqueous phase and permeate flux for each compound were measured. Permeate flux was calculated from concentration in the organic phase at 15 h -time assuring constant extraction speed (experimentally determined)-. The data obtained are resumed in Table 3.

With the aid of Statgraphics Centurion XVI.I®, it was obtained the individual contribution for each variable studied.

Figure 2 resumes individual contribution for each output variable as regard to the initial concentration of butanol. This figure shows for the case of permeate flux of each compound (Figures 2a, 2b, 2c) that a 10% increase in the initial butanol concentration induces an increase of permeate flux of 22.6, 36.4 and 176.8%

Table 3. Permeate flux, final concentrations in aqueous phase and ABE partition coefficients, using toluene as extracting solvent, with different temperatures and initial butanol concentrations.

T (K)	[B] initial (kg/m^3)	Flux A permeate (kg/h·m^2)	Flux B permeate (kg/h·m^2)	Flux E permeate (kg/h·m^2)	[A] final aq. phase (kg/m^3)	[B] final aq. phase (kg/m^3)	[E] final aq. phase (kg/m^3)	P A (dim)	P B (dim)	P E (dim)
303	20	0.063±0.008	0.151±0.005	1.3x10^{-3}	5.8±0.09	11.54±1.64	2.47±0.06	0.32±0.07	0.59±0.11	0.01±0.02
303	4.8	0.013±0.005	0.025±0.003	0	1.49±0.29	2.97±0.09	0.56±0.24	0.43±0.1	0.62±0.01	0.12±0.03
308	23.1	0.084±0.001	0.203±0.002	1.6x10^{-3}	7.18±0.25	12.21±0.38	2.47±0.24	0.46±0.13	0.87±0.11	0.07±0.01
301	12.4	0.018±0.001	0.034±0.003	0	4.22±0.04	7.58±0.48	1.12±0.14	0.43±0.06	0.59±0.10	0.05±0.06
308	12.4	0.019±0.0005	0.039±0.003	3x10^{-4}	3.56±0.10	6.59±0.13	1.4±0.001	0.52±0.04	0.70±0.03	0.002±0.003
308	12.4	0.023±0.003	0.042±0.002	2x10^{-4}	3.83±0.23	6.7±0.18	1.29±0.32	0.50±0.08	0.71±0.04	0.02±0.02
308	1.65	0.002	0.003±0.001	0	0.47±0.01	1.01±0.01	0.23±0.003	0.49±0.06	0.57±0.09	0.06±0.02
313	20	0.041±0.003	0.088±0.004	3x10^{-4}	6.02±0.17	9.52±0.03	2.16±0.12	0.67±0.01	0.99±0.01	0.02±0.005
313	4.8	0.008±0.001	0.013±0.002	0	1.39±0.05	2.4±0.09	0.51±0.05	0.69±0.003	0.86±0.005	0.05±0.02
315	12.4	0.024±0.001	0.049±0.007	0	3.35±0.27	5.46±0.08	1.27±0.02	0.76±0.04	1.07±0.12	0

for acetone, butanol and ethanol, respectively. The differences between these percentages can be explained by differences in the concentration levels used (butanol concentrations are higher than acetone's and ethanol's), increasing the concentration gradient and thus the permeate flux.

In addition, it should be noted that, as obtained in the previous section (Table 1), partition coefficient for butanol increases with concentration; thus the butanol permeate flux. Furthermore, the high variation of values found for the ethanol could be explained because of the low flux obtained for this compound, making any increase more noticeable.

On the other hand, after analyzing the graphics of partition coefficients of each compound (Figures 2d, 2e, 2f), it can be concluded that for acetone and ethanol, the influence of the initial butanol concentration has no statistical significance. For these two compounds, p-values of 0.191 and 0.136 were obtained respectively (if p-values > 0.05 the influence is not statistically significant). However, in the case of butanol, it shows that increasing the initial concentration in 10%, the partition coefficient increments its value a 0.65% (p-value = 0.0046).

Final concentrations of ABE compounds (at equilibrium) in the aqueous phase (Figures 2g, 2h, 2i) increase

with butanol concentration in the feed. Therefore, when increasing the initial butanol concentration a 10%, the final concentrations of acetone, butanol and ethanol in the aqueous phase will increase 10.2, 9.6 and 8.7% respectively. This can be explained because increasing the initial concentration of butanol, forces the stabilization at higher concentration levels.

Influence of Temperature in the Process

To analyze the influence of temperature on the extraction process, the data summarized in Table 2 were used. As in the previous case, graphics that show the dependency of the output variables with respect to system temperature were obtained (Figure 3). From analyzing the flux of each compound (Figures 3a, 3b, 3c), it can be seen that temperature has no significant effect on the flux of acetone, ethanol and butanol, displaying p-values > 0.05. In the case of acetone and butanol partition coefficients (Figures 3d and 3e), an increase of 3.3% in temperature increments partition coefficients: 64.7% for acetone and 54.4% for butanol. This effect can be explained by changes in molecule solubility in each phase, due to changes of thermodynamics in each solution. A major increase of molecules solubility in the solvent can be inferred, with respect to the aqueous phase. Additionally, partition coefficient of ethanol is not significantly affected by temperature, obtaining a p-value equal to 0.0871.
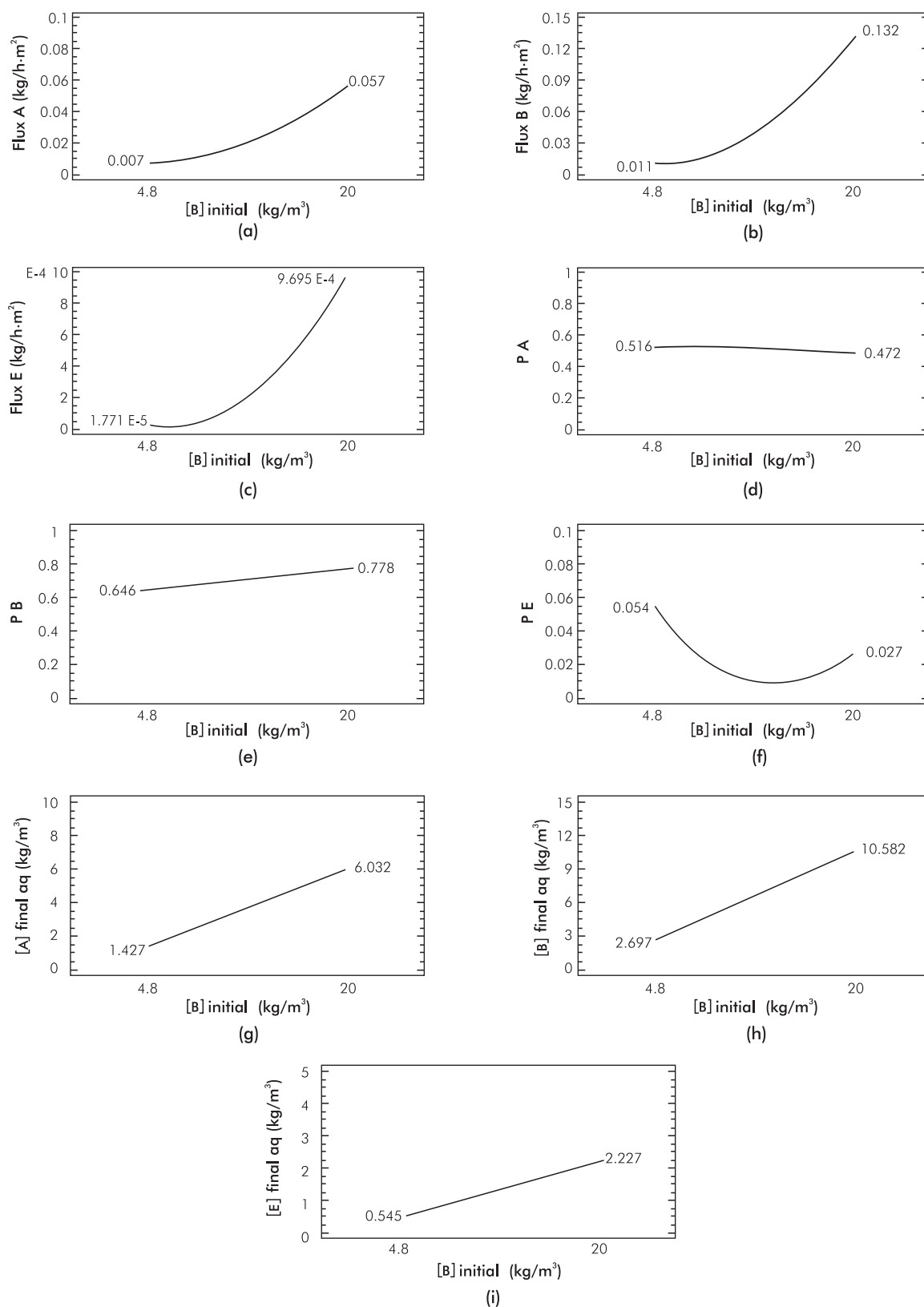
Figure 2. Individual influences of initial butanol concentration on the output variables using toluene as extracting solvent, statistically obtained using Statgraphics Centurion XVI.I.®. Output variables: a) Permeate flux of acetone; b) Permeate flux of butanol; c) Permeate flux of ethanol; d) Partition coefficient of acetone; e) Partition coefficient of butanol; f) Partition coefficient of ethanol; g) Final acetone concentration in aqueous phase; h) Final butanol concentration in aqueous phase. i) Final ethanol concentration in aqueous phase. respect to the aqueous phase.
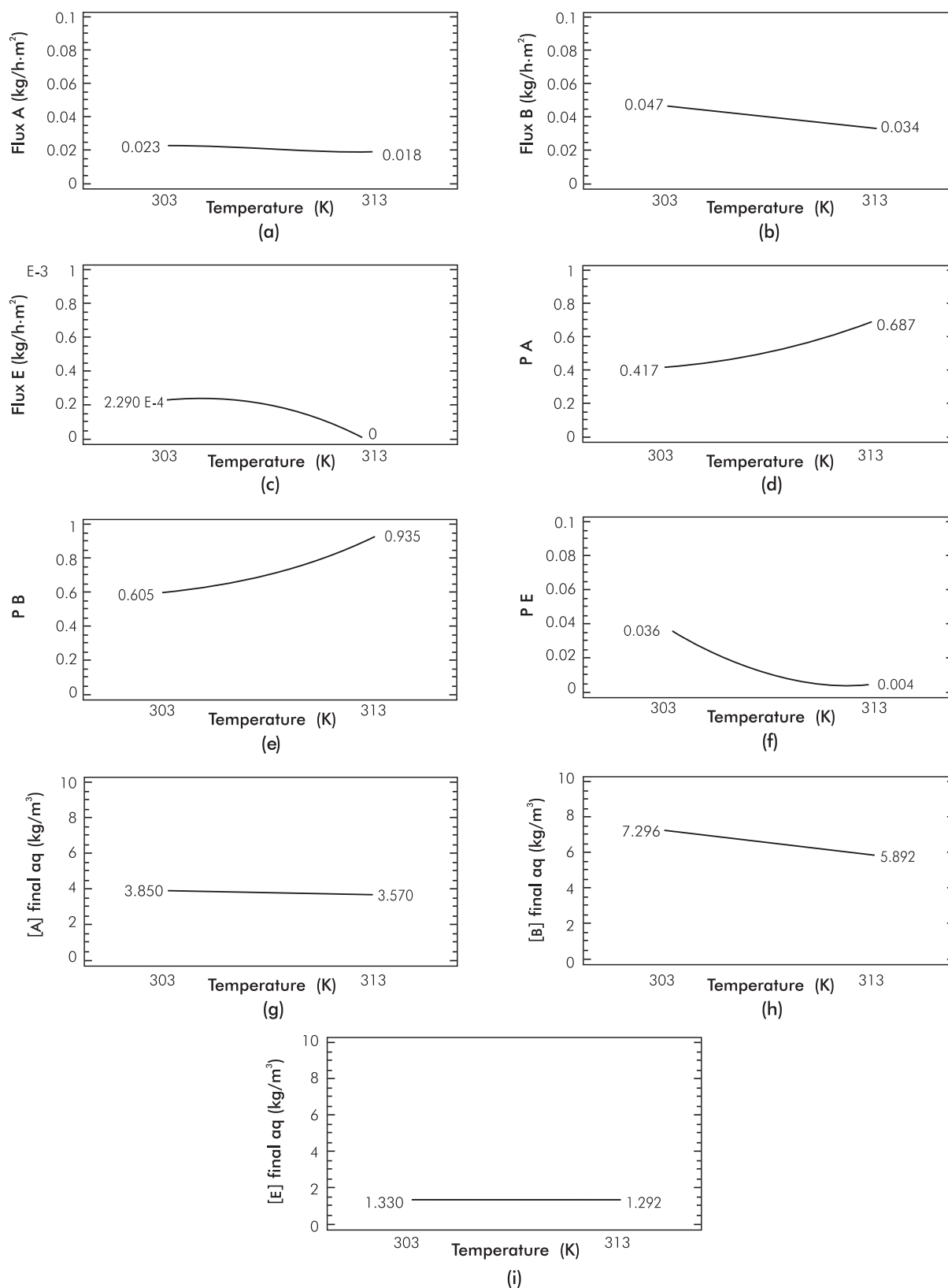
Figure 3. Individual influences of temperature on the output variables using toluene as extracting solvent, statistically obtained using Statgraphics Centurion XVI.I.®. Output variables: a) Permeate flux of acetone; b) Permeate flux of butanol; c) Permeate flux of ethanol; d) Partition coefficient of acetone; e) Partition coefficient of butanol; f) Partition coefficient of ethanol; g) Final acetone concentration in aqueous phase; h) Final butanol concentration in aqueous phase; i) Final ethanol concentration in aqueous phase.

In addition, temperature has a contrary effect on the final butanol concentration in the aqueous phase (Figures 3g, 3h, 3i). By increasing system temperature in 3.3%, the diffusion of this compound into the organic phase increments, thus decreasing the concentration remaining in the aqueous phase by 19.2%. Final concentrations in the aqueous phase of acetone and ethanol have not been significantly affected by temperature, showing p-values of 0.0664 to 0.7162 for acetone and ethanol, respectively.

As a result, an increase in separation efficiency by increasing the system temperature is evident. The differences in behavior found for acetone and ethanol can be explained due to the low concentration values used for these compounds (compared to butanol).

In summary, membrane contactors technique showed favorable results under the evaluated conditions for the extraction of acetone and butanol using toluene as solvent, with partition coefficients of 0.761 and 0.998, respectively. In the case of ethanol, partition coefficients were very low (< 0.1); suggesting the need to find another extraction technique for this compound.

Determination of Optimal Values

With the Statgraphics Centurion XVI.I® software and the experimental results presented in Table 3, it was possible to find the optimal operating conditions. Table 4 summarizes them with the predicted output variables. These optimal points correspond to the values of temperature and initial butanol concentration to which extraction rates and partition coefficients were maximized, and final ABE concentrations in the aqueous phase were minimized.

An experiment with the optimal values was performed and results were compared to the predicted values by Statgraphics Centurion XVI.I®. Figure 4 presents the comparison of these results for ABE compounds. Figures 4a, 4b and 4c show that the software provided a convenient prediction of optimal extraction conditions; mainly for partition coefficient and final butanol concentration in the aqueous phase (Figures 4a and 4b). In the case of butanol, results presented relative standard deviation of 5.9% for butanol partition coefficient (Figure 4a), 1.5% for final butanol

Table 4. Optimal variables estimated with Statgraphics Centurion XVI.I.®

Variable	Optimal value
Temperature (K)	315
$[\text{Butanol}]_{initial}$ (kg/m³)	1.65
Flux Acetone (kg/h·m²)	1.74×10^{-2}
Flux Butanol (kg/h·m²)	4.47×10^{-2}
Flux Ethanol (kg/h·m²)	2.63×10^{-4}
P Acetone (dim)	0.740
P Butanol (dim)	0.918
P Ethanol (dim)	0.047
$[\text{Acetona}]_{final}^{Aqueous}$ (kg/m³)	0.105
$[\text{Butanol}]_{final}^{Aqueous}$ (kg/m³)	0.788
$[\text{Etanol}]_{final}^{Aqueous}$ (kg/m³)	0.264

concentration in the aqueous phase (Figure 4b) and 70.5% for extraction rate of this compound (Figure 4c). It is important to take into account that extraction rate is a parameter determined when considering extraction at constant rate (at 15 h). However, this period could change between experiments. This fact could explain the high deviation found for extraction rate between predicted and experimental values.

Modeling of the Extraction Process

A semiempirical model in transient state that would describe the mass transfer phenomena during the extraction of the ABE compounds was developed. This model considered:

a) Completely stirred system (no concentration profiles on both sides of the membrane).

b) Membrane is symmetric and its pores are filled with solvent.

c) Equilibrium is reached in the liquid-liquid interface and is located on the side of the aqueous phase.

d) None mass transport occurs in nonporous parts of the membrane.

e) Aqueous phase and solvent are completely immiscible.
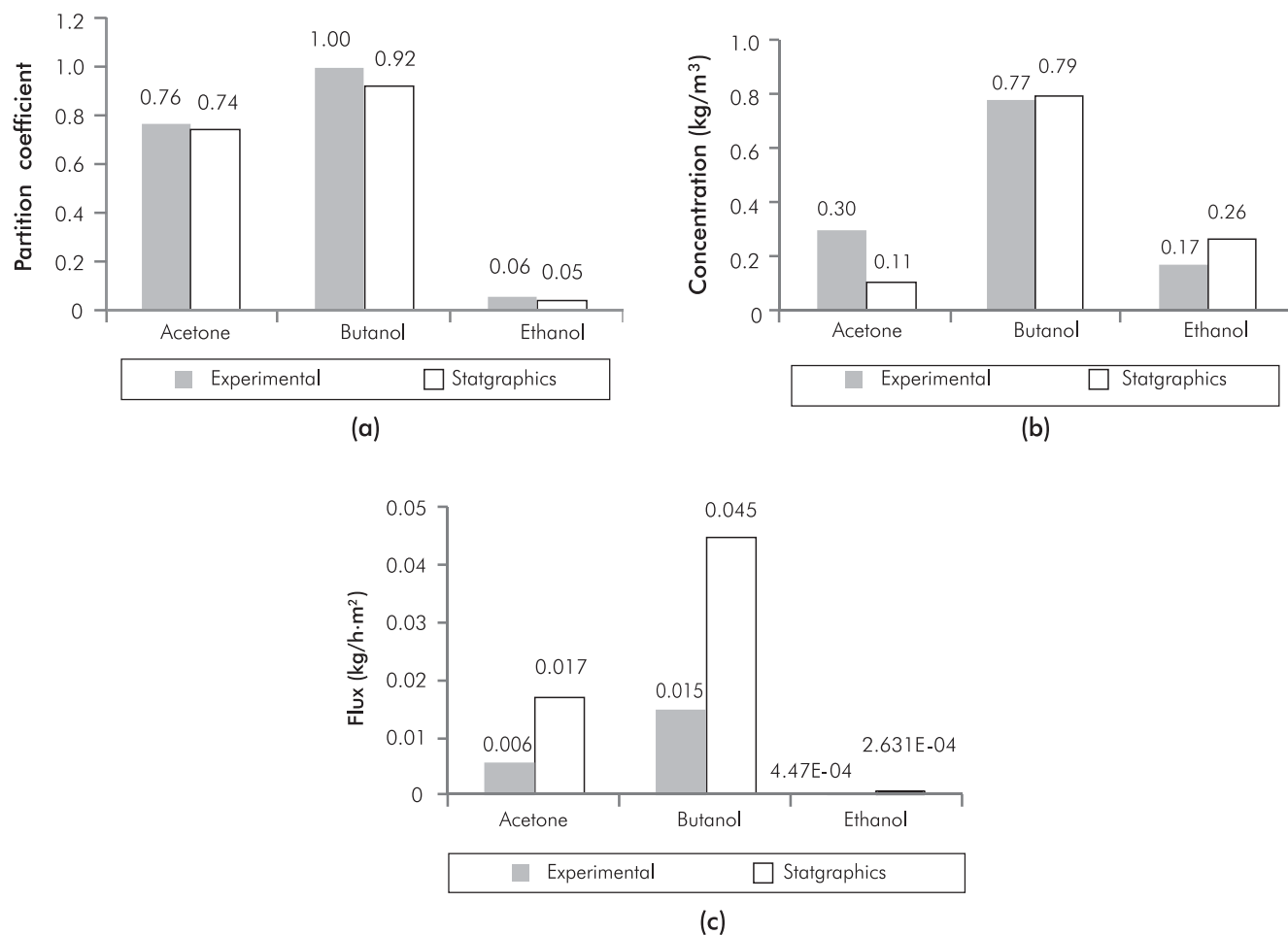
(a)

(b)

(c)

Figure 4. Predicted values and experimental data obtained at optimal operating conditions summarized in Table 4. a) Partition coefficient, b) Final concentration in the aqueous phase, and c) permeate flux.

A mass balance in transient state was performed for the system, with necessary equations being proposed. Concentration profiles in the system were considered as represented in Figure 5. This way, it was possible to obtain the variation of concentration in the two phases as a function of time. Expressions for viscosity, diffusivity and mass transfer rate through the membrane were included.

Equations:

• Mass balance in the organic phase

$$N_{(t)} \cdot A_M = \frac{d}{d_t} \left(V_S \cdot C_{A3(t)} \right) \qquad (3)$$

Where, A_M is the membrane area, V_S is the solvent volume in the system and $C_{A3(t)}$ is the concentration of the compound in the organic phase in time.
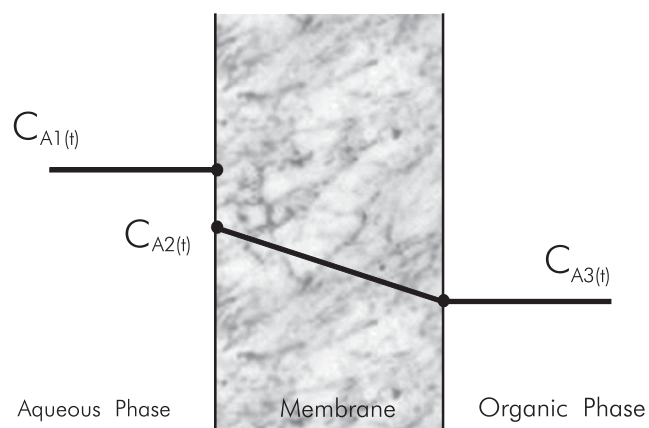

Figure 5. Representation of concentration profile considered at the interface of the system.

• Mass transfer through the membrane (Younas *et al.*, 2011; Bocquet *et al.*, 2005; Pierre, Souchon & Marín, 2001)

$$N_{(t)} = k_M \left(C_{A2(t)} - C_{A3(t)} \right) \qquad (4)$$

Where, k_M is the mass transfer coefficient through the membrane and $C_{A2(t)}$ is the concentration of the compound in the membrane pore in time.

- Partition coefficient (Younas *et al.*, 2011; Pierre *et al.*, 2001)

$$P_{(t)} = \frac{C_{A2(t)}}{C_{A1(t)}} \qquad (5)$$

Where, $C_{A1(t)}$ is the concentration of the compound in the aqueous phase in time.

- Mass transfer coefficient in the membrane (Bocquet *et al.*, 2006; Kumar *et al.*, 2005)

$$k_M = \frac{\varepsilon \cdot D_{mb}}{\tau \cdot E_m} \qquad (6)$$

Where, ε is the porosity, τ is the tortuosity, E_m is the thickness of the membrane and D_{mb} is the solvent diffusivity coefficient in the membrane.

- Solvent diffusivity coefficient in the membrane (Treybal, 1994)

$$D_{mb} = 1.173 \times 10^{-16} \left(\varphi . M_S \right)^{1/2} \frac{T}{\mu_S \cdot V_A^{0.6}} \qquad (7)$$

Where, φ is the solvent association factor, M_S is the solvent molecular weight, V_A is the molal volume of compound and μ_S is the solvent viscosity.

- Solvent Viscosity (Ec. de Eyring)

$$\mu_S = \frac{N \cdot h}{V} e^{\left(3.8 \frac{T_{eb}}{T} \right)} \qquad (8)$$

Where, N is the Avogadro number, h is the Planck constant, V is the molar volume, and T_{eb} is the normal boiling temperature of the solvent and T is the temperature of the system.

To complete the equations set, and taking into account the variation of partition coefficient in the

system with concentration (Table 2), it was determined an expression that related the partition coefficient of each compound with the final concentration in the aqueous phase and temperature of the system (*Equations 9, 10, and 11*). Statgraphics Centurion XVI.I® was used to calculate these expressions.

- Empirical expression for the partition coefficient of acetone, butanol and ethanol, respectively:

$$P_{A(t)} = -1.25486 + 0.05128T + 1.291 \times 10^{-3} T. C_{A1(t)}^2$$
$$- \frac{1.75494 \, C_{A1(t)}^2}{T} + \frac{21.5439 \, C_{A1(t)}}{T} - 0.597651 \, C_{A1(t)} \qquad (9)$$

$$P_{B(t)} = 0.49829 + 5.70525 \times 10^{-6} T^3 + 1.08082$$
$$\times 10^{-6} C_{B1(t)}^5 - \frac{2.95144 \times 10^{-6} T^3}{C_{B1(t)}^2} + 6.67508 \qquad (10)$$
$$\times 10^{-8} T^3 C_{B1(t)}^2 * \frac{0.0110183 \, C_{B1(t)}^3}{T}$$

$$P_{E(t)} = -0.302838 + \frac{14.8608}{T} - \frac{3476.7 \, C_{E1(t)}}{T^3}$$
$$+ 4.55959 \times 10^{-5} T \, C_{E1(t)}^5 - \frac{3.48585 \times 10^{-5}}{C_{E1(t)}^5} \qquad (11)$$

Where, $C_{A1(t)}$, $C_{B1(t)}$ and $C_{E1(t)}$ are the concentrations of acetone, butanol and ethanol in the solvent in time, respectively and T is the temperature of the system.

Equations 9, 10 and *11* where obtained from experimental data working with temperatures between $28 - 42°C$, and butanol concentrations between 1.65 - 23.1 kg/m³ (acetone/butanol: 0.398 w/w and ethanol/butanol: 0.109 w/w).

To solve the set of equations proposed, it was necessary to have information about the characteristics of the membrane and some parameters of the solvent used. These are summarized in Table 5.
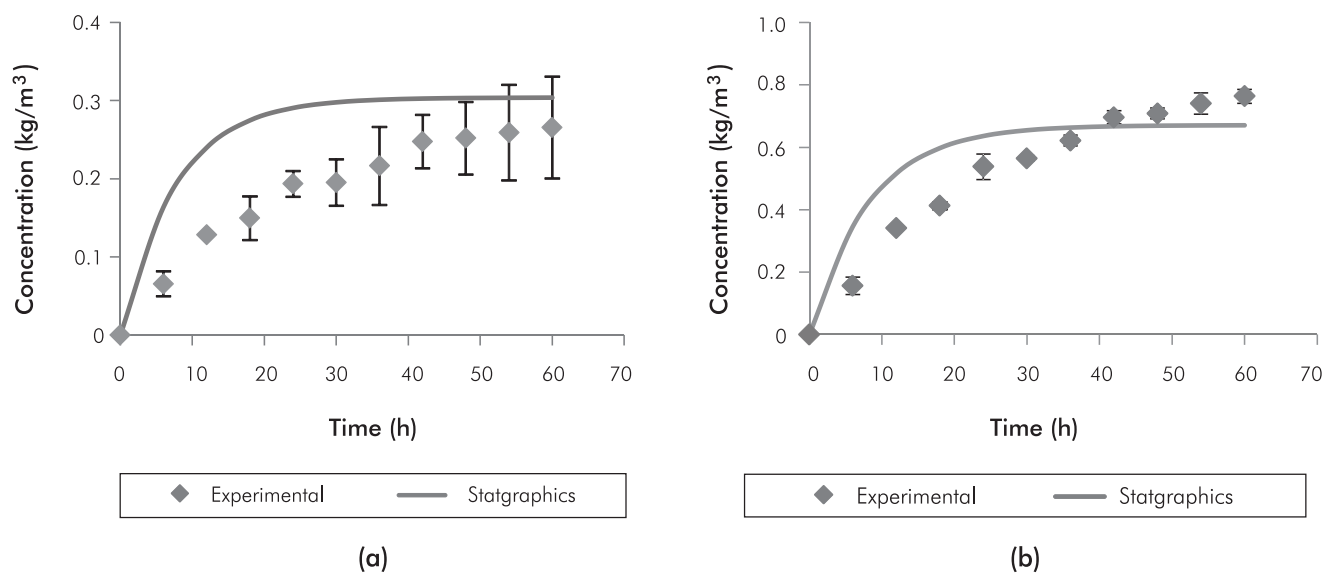
Finally, the model was used to simulate ABE extraction kinetics at optimal operating conditions (Table 4). The results were compared with those obtained experimentally (Figure 6a and 6b).

Table 5. Solvent characteristics and PTFE membrane parameters considered for modeling purpose.

Parameter	Value	Reference
Association factor of the solvent	1	Treybal, 1994
Molecular weight of toluene (kg/kmol)	92.13	
Normal boiling temperature of toluene (K)	383.8	MSDS Toluene (E.M. Science)
Toluene density (kg/m^3)	867	
Diameter of the membrane (m)	0.025	
Pore diameter of the membrane (m)	0.45×10^{-6}	Whatman™
Porosity ε	0.72	
Thickness (m)	2.20×10^{-4}	
Tortuosity $[\tau = 1/\varepsilon]$	1.388	Kumar et al., 2005

Figures 6a and 6b depict the model that describes the behavior shown by experimental data. Concentration values for acetone and butanol in time supplied by the model have a Mean Absolute Deviation (MAD) of 0.037 and 0.046 for acetone and butanol, respectively. An average error percentage of 53.7% for acetone and 29.1% for butanol concentrations in time were found. Related with final concentration at equilibrium in solvent phase, concentrations were predicted by the model: 0.30 kg/m^3 for acetone and 0.67 kg/m^3 for butanol with an error of 14.4% and 12.2% for acetone and butanol, respectively -experimental 0.266 kg/m^3 ± 0.065 for acetone and 0.764 kg/m^3 ± 0.022 for butanol-.

If stabilization time of the system is compared, it is observed that for acetone, experimental time is around 50 h, while model predicted 38 h (24% lower). For butanol, stabilization occurs at 45 h, and prediction results in 35 h (22% lower). These differences could be explained because an absence of concentration profiles in the phases was considered. This consideration was made in order to simplify the model, but results suggest there must be a concentration profile due to absence of agitation. Taking into consideration these profiles, the flux decreases across the membrane; thereby increasing stabilization times. Further studies should consider this to improve the mathematical model.

Figure 6. Experimental extraction and model values obtained at optimal operating conditions (see Table 4), using toluene as extracting solvent. a) Acetone and b) Butanol.

4. CONCLUSIONS

- Membrane contactors technique for the ABE extraction was studied using commercially available solvents. In this work, favorable results were found using toluene as solvent extractor in the recovery of acetone and butanol, with partition coefficients of 0.761 and 0.998, respectively. Although P coefficient values for toluene are inferior in some cases (2.9 times), this solvent has the advantage to be more commercially available in comparison with others already reported. The influence of operating variables (temperature and initial butanol concentration) during the extraction process was studied, and the optimal temperature (42°C) and initial butanol concentration (1.65 kg/m^3) were determined. The permeate flux obtained were 0.044 kg·m^{-2}·h^{-1} for butanol, 0.017 kg·m^{-2}·h^{-1} for acetone and negligible for ethanol. Furthermore, a mathematical model for the study of ABE compounds extraction in transient state is proposed for the first time. In the construction of this model, variation of P coefficient with ABE concentration and system temperature were taken into account, predicting the behavior of the extraction kinetics for acetone and butanol. Moreover, the model was compared with experimental data obtaining MAD of 0.037 for acetone and 0.046 for butanol. An average error percentage of 53.7% for acetone and 29.1% for butanol concentrations in time were found. However, in both cases, final concentrations in aqueous phase were predicted by the model. It is important to continue working on improving the mathematical model, specifically in the prediction of the stabilization time and considering fouling phenomena when using real ABE solutions (from fermentation broth).

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NOTATION

A	Acetone
B	Butanol
E	Ethanol
ABE	Acetone/Butanol/Ethanol
EC	Energy Content, kJ/kg
Dp_{mb}	Pore diameter of the membrane, m
P	Partition coefficient
A_M	membrane area, m^2
V_S	Solvent volume in the system, m^3
C_{A1}	Concentration of the compound in the aqueous phase, kg/m^3
C_{A2}	Concentration of the compound in the membrane pore, kg/m^3
C_{A3}	Concentration of the compound in the organic phase, kg/m^3
k_M	Mass transfer coefficient through the membrane, m/s
ε	Porosity
τ	Tortuosity
φ	Association factor of solvent
E_m	Thickness, m
D_{mb}	Diffusivity coefficient of the solvent in the membrane, m^2/s
μ_S	Solvent viscosity, Pa·s
M_S	Molecular weight of the solvent, kg/kmol
V_A	Molal volume of the compound, m^3
T_{eb}	Normal boiling temperature, K
N	Avogadro Number, molecules/mol
h	Planck constant, J·s/molecules
V	Molar volume of the solvent, m^3/mol