

Combining Ion Exchange and Water Adsorption Processes for High Grade Glycerol from Biodiesel

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Abstract- Two different ways to purify crude glycerol have been proposed depending on the catalyst used in the biodiesel production. When alkalis as NaOH or KOH are used ion exchange and adsorption could be advantageously employed to remove the salt and water content respectively. In this work, the water removal is accomplished by using three different molecular sieves zeolite 5A in Na⁺ and Ca²⁺-form, Zeolita A in Na⁺ and Ca²⁺-form and Zeolita A in K⁺-form commonly applied for water adsorption. The larger water sorption capacity of the zeolite 5A-Na, Ca at 303 K allowed selecting it as the best choice for the dehydration of glycerol. The adsorption experimental data were fitted with the adsorption model of Tóth and further experiments have been carried out at 318 and 333 K with the aim to obtain the thermodynamic properties ΔH° and ΔS° . The negative values of these both properties indicated that this adsorption process is exothermic and feasible. On the other hand, when sodium or potassium alkoxides are used in the biodiesel production water is not involved in glycerol purification. Thus, ion exchange studies for the systems H⁺/Na⁺ and H⁺/K⁺ using the resin Amberlite 252 for a solution containing a mixture 50/50 of glycerine in methanol and a methoxide content of 0.25 mol L⁻¹ at 298 K were carried out. Langmuir equation was used to fit the experimental equilibrium data and the shape of the isotherm confirms the irreversibility of the process leading to the methanol production. It was obtained that the Langmuir separation factor is independent on the system but the maximum ion uptake is higher for the K⁺ than Na⁺ attending to its low hydrated radii. These results confirm the feasibility to purify glycerol streams by applying the proper technology in a aqueous or non-aqueous media.

Keywords- Glycerol; Ion Exchange; Adsorption; Biodiesel

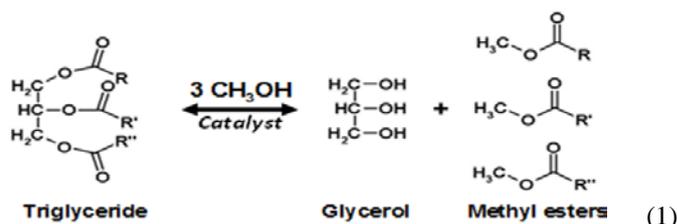
I INTRODUCTION

Nowadays, the environmental impact of fossil fuels is undergoing an important attention due to its combustion releases millions of tones of CO₂ into the atmosphere each year, which is widely believed to be contributing to global warming.¹ Additionally, the dependence of the human by this kind of energy attached with the continuous changes of the petroleum prices promotes the research in low cost alternative energy sources, which are environmental friendly. One of these alternative energies is obtained by the combustion of methyl esters of fatty acids which are known as biodiesel.

Biodiesel has better properties than petrodiesel fuel since it is biodegradable, non-toxic, has a high cetane number and provides engine lubricity to low-sulfur diesel fuel.^{2,3} Moreover, its combustion produces less smoke, diesel particulate matter, carbon monoxide, hydrocarbon emissions and carbon dioxide emissions a 78% lower than mineral diesel. On the other hand, the major drawbacks inhibiting commercial production of biodiesel include the high cost of raw materials, the presence of fatty acids, water in oils and the use of higher alcohol molar ratios.⁴ Government measures like The EU Directive 2009/28/EC on the promotion of the use of energy from

renewable sources requires biofuels to reach 10% of the total automotive fuel consumptions by the year 2020 and The US Energy Policy Act (EPAct) created in 2005 the Renewable Fuel Standard (RFS) program, establishing the amount of renewable fuel to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022. This amount of renewable fuel will correspond to a 9% of US consumed fuel in 2012.

Biodiesel is the product of transesterification of triglycerides with an alcohol to form esters and glycerol. Alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol are used in this process, being the methanol the most frequently used because of its low price. Besides, a molar ratio of alcohol to triglyceride 3:1 is required to complete stoichiometrically the transesterification reaction. In the practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Eq.1).

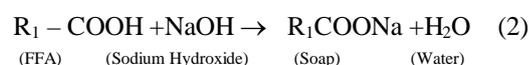


where R, R' and R'' hydrocarbon chains from 12 to 22 carbon atoms.

The reaction must be catalyzed either using homogeneous catalyst (acid or base) or heterogeneous catalyst (acid, base or enzyme). The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acid and hydrochloride acids are usually used as acid catalysts.⁵⁻⁷ On the other hand, metal oxides, acid and basic resins and enzymes are used as heterogeneous catalysts.

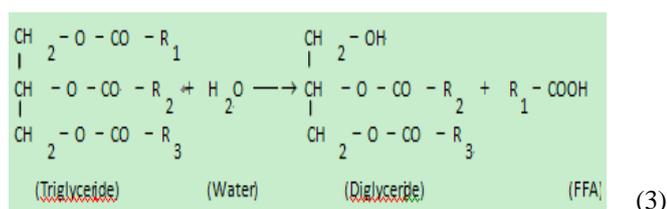
A Alkali-Catalyzed Transesterification

In *alkali-catalyzed transesterification*, anhydrous alcohols and vegetable oils with water and free fatty acid contents lower than 0.1 and 0.5 wt%, respectively, are required. In this way, the saponification reaction (Eq 2) is minimized, holding the activity of the alkali catalyst to achieve higher than 90% ester yield under the reaction conditions.^{4,5,8}



This reaction is undesirable because the increase in the biodiesel cost production, since the formed soap inhibits the separation of esters from the glycerol and an additional

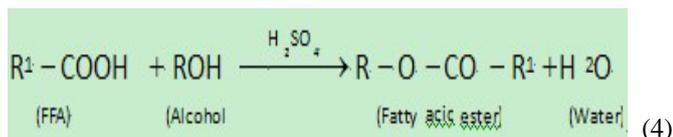
catalyst is spent.⁹ Besides, the original or formed water during the saponification reaction retards the transesterification reaction through the hydrolysis reaction (Eq 3).



Higher molar ratios of alcohol to oil (6:1) are recommended to solve the reversible problems encounter in stepwise reactions of reaction (Eq 1), driving the reaction to completion. Using NaOH as catalyst at concentration from 0.5 to 2 wt % respects to the oil fed and a reaction temperature ranged between 60 and 65 °C, a conversion higher than 95 % can be expected after 1 hour of reaction. Alkoxides are the most active catalysts, since they give very high yields (> 98%) in short reaction times even if they are applied at low molar concentrations (0.5 mol%).¹⁰

B Acid-catalysed Esterification

Acid-catalysed esterification has the advantage over alkali-catalyst because it has a low susceptibility to the presence of FFA in the starting feedstock. In this case, triglyceride mixtures with FFA contents higher than 4 wt % can be fed. However, acid-catalysed esterification is especially sensitive to water content, being inhibited at 5 wt% of water concentration.¹⁰ The esterification reaction is shown in Eq. 4.



The kinetic of this reaction is slower than those of alkaline catalysts and thus, larger catalyst load -molar ratios higher than 1.3 to 1 of sulphuric acid to oil-, higher temperatures - higher than 80 °C- and larger molar ratios of alcohol to oil of 50:1 are required to obtain a 97 % of conversion after 4 h of reaction.¹⁰

On the other hand, *heterogeneous transesterification* using materials such as Amberlyst-15, Nafion-NR50, vanadyl phosphate and sulphated zirconia between them can be used to produce biodiesel. Some of them can catalyze the esterification reaction being useful for feedstocks with high FFA content. Heterogeneous process has the advantage of its catalyst separation by filtration from the products but listing as disadvantages the low rate at which the reaction proceeds and the three phases involved in the process.⁹ In the case of the enzymatic process, catalyst is very expensive and has an unstable activity.⁷ Wang et al., (2008) working with the lipozyme TL IM at 35 °C have found that it is more stable when waste oil was used as feedstock than corn oil, indicating that a high fatty acid content improves its behaviour.

Currently, the most important factories around the world are working with homogeneous transesterification process obtaining two major products biodiesel and crude glycerine. Each has a substantial amount of the excess alcohol that was used in the reaction, and the glycerine phase that is much denser than the biodiesel phase is gravity separated and drawn off the bottom of the setting vessel.

Crude glycerol only can be used mixed with feed for animals.¹¹ Nevertheless, if it is refined, it can be transformed into high value products such as (mono- and di-fatty acids) by glycerolysis with methyl esters at temperatures between 200 to 210 °C or used as a source of renewable energy decreasing the water and salts contents by vacuum distillation and ion exchange, obtaining a product with a purity up to 99.5 to 99.7 %.^{12,13}

As aforementioned, the composition of the glycerol stream depends on the way how it was manufactured.

C Acid or Basic Catalyst-Neutralization

Glycerol stream leaving the separator contains a 50 wt % glycerine, methanol, catalyst and soaps. This stream is a low cost product, although its disposal is quite difficult.¹² Refining of glycerol started with an acid treatment to split the soaps into free fatty acid and salts. Fatty acids are not soluble in glycerol being separated from the top and recycled to the process. After that, methanol is recovered by vacuum distillation and obtained glycerol has a purity about 85 wt %, containing water and salts.^{12,14-16}

D Non-catalyst-neutralization

In this procedure sodium or potassium alkoxides are used in the transesterification process as catalysts instead of the alkalis NaOH or KOH. Glycerol stream leaving the separator is free of water and contains a 50 wt % of glycerine in methanol and alkoxides. In that case, a cationic resin can be used to remove the metallic ion releasing the protons and forming the alcohol from the alkoxide in an irreversible way (Eq.5). After that, methanol is recovered by vacuum distillation.



where M is the metallic ion, R is the resin and $-\text{SO}_3^+$ their corresponding actives sites.

Attending to the above comments, to research in technologies to improve the profit of biodiesel production is an important issue at the present time and the valorization of the secondary product *crude glycerol* avoiding the applications of expensive purification process will allow to produce this alternative energy at a competitive price that facilitate its implementation and to get government targets. Methods such as ion exchange,⁸ adsorption⁹ and membrane technologies^{10,17} have been applied for the elimination of salts from aqueous media. Regarding organic solutions, there is a lack of information in literature about the proper technology that should be applied. Ion exchange seems to be the most suitable method for small scale applications where liquids with a very low salt or metallic content because of its simplicity, effectiveness, selectivity, recovery and relatively low cost.^{10,11} Furthermore, when glycerol is contaminated by water, its purification could be accomplished by distillation but with a large energy consumption. In that case, the dehydration by adsorption on molecular sieves, such zeolites, is an interesting alternative due to its low energy cost and small capital investment. These materials have been widely used in the industry today as a drying medium due to their excellent properties as adsorbents and also, their polar nature makes them a reliable choice for separating water from organic compounds.^{18,19}

The aim of this work is to study the applicability of the strong-acid cation resin Amberlite 252 in H^+ form in non-

aqueous media to remove sodium and potassium from crude glycerol containing metallic peroxides. On the other hand, adsorption equilibrium studies of dehydration of crude glycerol by applying three molecular sieves at three different temperatures have been carried out.

II EXPERIMENTAL SECTION

A Chemicals

Glycerine ($C_3H_8O_3$) with a water content of 2 wt % was supplied by Sigma-Aldrich with a purity higher than 97 %. Sodium and potassium peroxide PA grade quality and dry methanol were supplied by Panreac. Demineralised water with conductivity lower than $5 \mu S$ was used to prepare the synthetic glycerol solutions simulating the conventional solutions obtained in biodiesel production processes.

B Adsorbents.

Experiments were carried out with three different synthetic zeolites. Total specific surface and average pore size were determined from nitrogen adsorption data acquired on a Micromeritics Asap 2010 apparatus using a BET method with an experimental error lower than 2 %. Zeolites compositions were also analyzed by using a X-ray fluorescence sequential spectrometer Philips MagixPRO. Their characteristics are shown in Table I. Pre-activation of the adsorbent was performed at a temperature of $300^\circ C$, for at least 24 hours.

TableI PROPERTIES OF ZEOLITES STUDIED FOR WATER ADSORPTION FROM GLYCEROL MIXTURES

Zeolite	Supplier by	BET SURF ACE (m^2/g)	POR E DIA MET ER (\AA)	Al_2O_3 (%)
Zeolite 5A in Na^+ and Ca^{2+} -forms (Z5A-Na,Ca)	Elf Atochem	22.1075	6.3902	25.191
Zeolite A in Na^+ and Ca^{2+} -forms (ZA-Na,Ca)	S.D.S	29.9788	6.555	22.404
Zeolite A K^+ -form (ZA-K)	Panreac	26.8069	4.672	26.272

C Ion exchange Resin.

Amberlite 252 (Rohm and Haas Co.), a macroreticular sulfonated polystyrene-divinylbenzene resin, was selected attending to its excellent behaviour in the uptake of alkali metals from glycerine/water mixtures and also from non-aqueous media.^{15,16} The main physical properties are given in Table II.

TableII PROPERTIES OF AMBERLITE 252.²¹

Active group	Particle size, D (m)	Resin capacity for sodium, D^∞ ($mol\ kg^{-1}$ dry resin)	Surface area, ($m^2\ kg^{-1}$)	Void fraction (%)	Apparent density, ρ_s ($kg\ m^{-3}$)
Sulfonic	$4.94 \cdot 10^{-4}$	4.83	2.487	7.2	1.323

The above resin were pre-treated and converted to the H^+ -form by repeated treatments in a column with $1.0\ mol\ L^{-1}$ NaOH and $1.0\ mol\ L^{-1}$ of HCl solutions.^{20, 21} Then it was thoroughly rinsed with dry methanol to remove adsorbed water.

D Analytical Methods

The sodium or potassium content of solutions was analyzed by atomic absorption spectrophotometry in a Varian 220 AS spectrophotometer. The amount of water in the organic phase was analyzed using a Karl Fischer titrator (Metrohm 870, KF Titrino). The standard uncertainty and reproducibility of measurements was found to be $\pm 0.1\ %$.

E Equilibrium Experiments

1) Adsorption:

The experimental set consisted of nine 100 ml Pyrex containers hermetically sealed and mechanically agitated, submerged in a temperature-controlled thermostatic bath. The fixed temperature (303, 318 and 333 K) was kept constant with maximum deviations of $\pm 0.1\ K$. Different known masses of dried adsorbents were put in contact with 25 g of synthetic mixture of water/glycerine (95/5 by weight).

2) Ion Exchange:

The experimental set consisted of seven 250 ml Pyrex containers hermetically sealed and mechanically agitated, submerged in a temperature-controlled thermostatic bath at a fixed temperature of 298 K with maximum deviations of $\pm 0.1\ K$. Different known masses the resin Amberlite 252, in the H^+ -form and washed and swelled in pure methanol, were put in contact with 100 ml of synthetic mixture of glycerine/methanol (50/50 by weight) and a methoxide content of $0.25\ mol\ L^{-1}$.

The accuracy of solids weighting was $\pm 0.0001\ g$. The suspension formed by solid and solution was vigorously agitated at 200 r.p.m by means of a multipoint magnetic stirrer. To ensure that the equilibrium was reached the experiments were left under stirring overnight. At the end of this period, the mixtures were filtered to remove either the zeolite in the adsorption or the resin in the ion exchange processes, respectively. Then, the filtrate was analyzed for water or sodium content as described above. The solid phase concentration in equilibrium with the liquid phase was obtained by means of the following mass balance Eq.6:

$$q_i^* = \frac{(C_{oi} - C_i^*)V}{W} \cdot 10^3 \quad (6)$$

where C_{oi} and C_i^* are the initial and equilibrium concentration in the liquid phase ($mol\ L^{-1}$), respectively; q_i^* denotes the solid phase equilibrium concentration ($mmol\ g^{-1}$ of dry resin), V is the initial volume of the synthetic solutions in litres, W is the weight of dry solid used in grams and i denotes the species water or sodium for the adsorption or ion exchange processes, respectively.

III RESULTS AND DISCUSSION

A Acid or Basic Catalyst-neutralization

Glycerol stream leaving the separator contains a 50 wt % glycerine, methanol, catalyst and soaps. This stream is a low cost product, although its disposal is quite difficult.¹² Refining of glycerol started with an acid treatment to split the soaps into free fatty acid and salts. Fatty acids are not soluble in glycerol

being separated from the top and recycled to the process. After that, methanol is recovered by vacuum distillation and obtained glycerol has a purity about 85 wt %, containing water and salts.^{12, 14-16}

The first step in the development of an integral process to produce a high grade glycerol would be of the removal of the metallic ions. The addition of water to enhance the dissociation of the salts makes easier the exchange but dilute the glycerol phase increasing the separation costs. So that initially the focus will be directed to the ion exchange in mixed glycerol-aqueous media.

B. Salt Removal

Studies of salt removal from this glycerine-water mixture were carried out by different authors and mainly using the ion exchange process. Carmona et al., (2009a, 2009b) have reported the equilibrium studies of ion exchange for the removal of NaCl or KCl from synthetic mixture of glycerine/water (90/10 by weight) containing a total salt concentration of 1 mol L⁻¹ at a temperature of 318 K. The sodium removal was studied using strongly acidic cation-exchange resins one of gel-form Amberlite IR-120 and other macroporous Amberlite 252. The best results were obtained using the resin Amberlite 252 and the equilibrium was extended at three different temperatures. In the same way, a strongly basic anion-exchange resin Amberlite IRA 420 was tested for the removal of Cl⁻ from the glycerine/water mixture.

For a binary system a reversible ion exchange process is defined by the Equation 7 where the ion exchange (r) is initially in the A-form and the counterion in the solution (s) is B. The counterions exchange occurs, and the ion A in the ion exchange is partially replaced by B,



where α and β are the valences of the ionic species A and B, respectively.

In equilibrium state, the solid and liquid phases contain both competing counter-ion species, A and B. Electroneutrality is necessarily maintained in this reaction whether the ion exchanger or in the aqueous solution. This indicates that counter-ion exchange occurs in equivalents or molar for monovalent ions and the ionic concentration for a binary system can be expressed as ionic fraction as follows:

$$x_A = \frac{C_A^*}{N}; \quad x_B = \frac{C_B^*}{N} \quad (8)$$

$$y_A = \frac{q_A^*}{q_0}; \quad y_B = \frac{q_B^*}{q_0} \quad (9)$$

where y_B and x_B represent the ionic fraction of the ion B in the solid and liquid phases, respectively. N is the total concentration of the co-ions in the solution phase (mol L⁻¹); and q_0 is the useful capacity of the resin in the studied system (mmol g⁻¹ of dry resin).

An important factor that should be considered in a comprehensive theory of ion exchange is the non-ideal behaviour of ions in solid and liquid phases. It can be a consequence of an ion-ion and ion-solid interactions, ionic charge, ionic radii and other molecular constants.²⁰ However, according to results reported by Carmona et al., (2009a, 2009b) the equilibria for the systems H⁺/Na⁺, H⁺/K⁺ and OH⁻/Cl⁻ using the cationic resins Amberlite IR-120 and Amberlite 252 and the anionic Amberlite IRA-420 in synthetic mixture of

glycerine/water (90/10) are ideals and the behavior for the both phases can be represented by the ideal mass action law (Eq.10). Thus, the ion-exchange equilibrium constant for the reversible Eq. 4 could be expressed by the following equation:

$$K_{AB}(T) = \frac{y_B}{(1-y_B)} \frac{(1-x_B)}{x_B} \quad (10)$$

A good agreement between the experimental data and the theoretical *ideal mass action law* model was found and the reported equilibrium parameters for the binary systems H⁺/Na⁺, H⁺/K⁺ and OH⁻/Cl⁻ are shown in Table III.

Table III EQUILIBRIUM AND THERMODYNAMICAL PROPERTIES OF THE SYSTEMS H⁺/NA⁺, H⁺/K⁺ AND OH⁻/CL⁻ BY IDEAL MASS ACTION LAW

System	T (K)	K _{AB}	q ₀ (mmol-dry g ⁻¹)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)
Amberlite IR-120						
H ⁺ /Na ⁺	318	1.939	5.0			
H ⁺ /K ⁺		3.603	5.0			
Amberlite 252						
	303	9.88				-5.77
H ⁺ /Na ⁺	318	6.80	4.34	-19.93	-46.71	-5.07
	333	4.85				-4.37
Amberlite IRA-420						
	303	20.604				-7.785
OH ⁻ /Cl ⁻	318	16.880	3.80	-13.618	-19.235	-7.200
	333	9.390				-6.907

According to these results, resin capacities are fully available for the exchange in this mixed media. Hydrated ionic radii for potassium and sodium are 1.65 and 2.2 Å, respectively, and this lower value for the K⁺ ion can be the cause that Amberlite IR-120 exhibits a higher selectivity for this ion.

Glycerol with a high dielectric constant allows the dissociation of salts and a certain mobility of the ions this fact makes that the ion exchange in this media works in a way quite similar to aqueous solution.

In the same way, these parameters confirm the higher preference of the studied resins by the entering ions but that selectivity decreases with temperature. The negative value of ΔG° indicates that this ion exchange process is feasible and spontaneous; the negative value of ΔH° confirms that the ion exchange processes are exothermic and whereas, the negative value of ΔS° suggests that the randomness decreased in the liquid/solid interface when the protons are eluted from the solid by the sodium ions initially present in the liquid phase.

On the other hand, cationic exchangers have a different selectivity for the sodium, being higher the value for Amberlite 252 respect to Amberlite IR-120. The ion exchange selectivity is depending on the solvation of counter ions and also on the solvation of ion exchange sites, which can be affected by the electrostatic field generated by both counter ions and the extent of ion-pair formation between an ion-exchange site and a counter ion.²³ Both resins Amberlite IR-120 and Amberlite 252 have the same kinds of ion exchange sites with a high charge density ($-SO_3^-$), which produce strong electrostatic fields without ion-pair formation. These

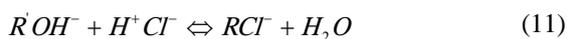
parameters indicate that the maximum capacity of the macroporous resin Amberlite 252 for sodium at a water content of 10 % is a little lower than the value exhibited by the Amberlite IR-120. Nevertheless, its equilibrium constant (6.802) is at least three times higher than that found above by the Amberlite IR-120 at 318 K. This result indicates that for sodium removal from glycerine-water mixtures the macroporous Amberlite 252 could be the best choice and also, taking into account the hydrated ionic radii on the ion exchange process, this resin should also be selected when potassium ions are the counter ions.

Table IV EQUILIBRIUM PARAMETERS OF THE SYSTEM H⁺/NA⁺ ON AMBERLITE 252 OBTAINED BY FITTING THE EXPERIMENTAL DATA TO THE IDEAL MASS ACTION LAW.

System	T (K)	Water content (%)	q ₀ (mmol·dry g ⁻¹)	K _{AB}
H ⁺ /Na ⁺	318	10.0	4.34	6.802
		30.0		3.848
		50.0		2.085
		100.0		1.560

C Water Removal

The presence of water in the media during ion exchange cannot be avoided because is part of the neutralization process involved in the exchange at least in the second stage of anion removal:



The water that always remains in the media together with that formed in the neutralization process has to be removed in any way. Although the possibility of do it by distillation exits adsorption with molecular sieves can be also an alternative for the elimination of moderate amounts of water in the glycerol phase. In such case the equilibrium isotherms for the water removal on different zeolites are necessary for an accurate design of the desiccation beds.

Langmuir and Tóth equations are some of the most widely used to describe adsorption isotherms for water removal in literature. Langmuir model describes monolayer solids and Tóth used to be employed to reproduce multilayer materials.

Equation 12 represents the Lagmuir model having two unknown parameters (K^{Lang}_{H₂O} and q₀).

$$q_{H_2O}^* = \frac{K_{H_2O}^{Lang} \cdot q_0 \cdot C_{H_2O}^*}{1 + K_{H_2O}^{Lang} \cdot C_{H_2O}^*} \quad (12)$$

where q₀ is the maximum amount of solute adsorbed by the solid per unit mass (mmol g⁻¹) and K^{Lang}_{H₂O} is the Langmuir equilibrium constant (l·mol⁻¹) which is related to the affinity of the binding sites and energy of adsorption.

Tóth model has been employed with excellent results in the modeling of water isotherms on 4A (NaA) zeolite. 25, 26 Tóth equation is thermodynamic and has three unknown parameters:

$$q_{H_2O}^* = q_m \frac{C_{H_2O}^*}{\left(1/K_1 + (C_{H_2O}^*)^m\right)^{1/m}} \quad (13)$$

where q_m represents the total adsorption capacity, m is the dissociation parameter and K₁ is the adsorption equilibrium constant. Tóth isotherm leads to Langmuir equation when m is equal to 1.

Figure 1 shows the experimental data and predicted isotherms by Tóth model for the water adsorption from glycerol/water mixtures onto studied zeolites.

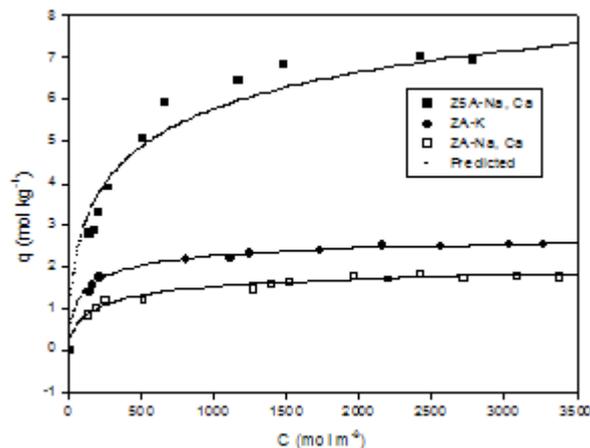


Fig.1 Isotherms of water adsorption from glycerol/water mixtures (95/5 by weight) at 303 K using three different zeolites, Tóth Treatment

The adsorption curves allows to select the material Z5A-Na,Ca-forms as the proper material from those studied to carried out the water uptake from glycerol/water mixtures. It is well known that the selectivity of zeolites to interact with water in the presence of other molecules increases with increasing concentration of aluminum per unit cell. 27-28 Nevertheless, Table I shows that this property is not the unique because ZA-K-form has the highest percentage of Al₂O₃ (26.272 % wt.) exhibiting a lower water uptake than Z5A-Na,Ca-forms with a lower percentage 25.191 % wt. In the same way, the surface area and the average pore diameter are similar indicating that metallic ions that compensate the negative charge of the zeolites, their size and their place in the lattice, their ionic potential and the hydration energy determine the zeolite properties for water adsorption (16).29

On the other hand, the surface characteristic of the adsorbents can be determined by using the different models. Experimental data were fitted by the three models being the fitting parameters and the respective coefficient of determination shown in Table V.

Table V EQUILIBRIUM PARAMETERS FOR WATER ADSORPTION OF ONTO ZEOLITES AT 303 K FROM GLYCEROL/WATER MIXTURES (95/5 BY WEIGHT)

Model	Parameters	Zeolites		
		Z5A-Na,Ca-forms	ZA-K-form	ZA-Na,Ca-forms
Langmuir	K ^{Lang} _{H₂O}	0.005	0.006	0.009
	q ₀	7.123	1.849	2.562
	r ²	0.907	0.983	0.967
Tóth	K ₁	0.339	0.125	0.187
	q _m	12.406	2.252	2.973
	m	0.335	0.517	0.514
	r ²	0.928	0.989	0.979

The highest coefficient of determination obtained using Tóth model as fitting equation indicates the heterogeneity of these materials although r^2 for ZA-K-form is close to 1 indicating that this material could be considered as homogeneous.

Attending to the highest adsorption capacity that Z5A-Na, Ca-forms exhibits for water uptake this material was selected to study the influence of temperature on the water adsorption.

The experimental data and modeling results achieved with Tóth model for three temperatures are shown in Figure 2 and the adsorption parameters and coefficients of determination (r^2) are listed in Table VI.

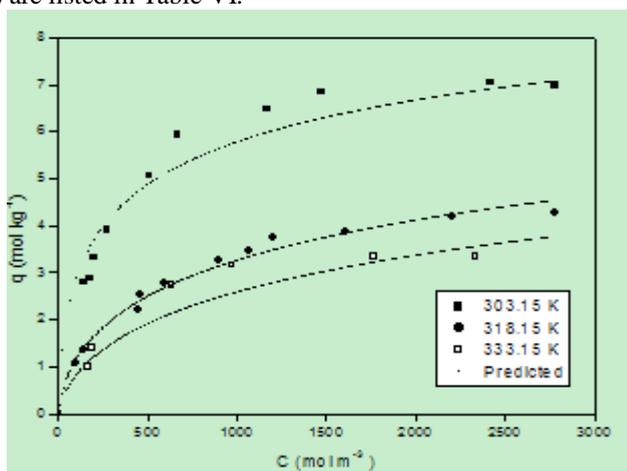


Fig.2 Isotherms of water adsorption from glycerol/water mixtures (95/5 by weight) at 303, 318 and 333 K using Z5A-Na⁺, Ca²⁺-forms. Tóth Treatment

Table VI EQUILIBRIUM PARAMETERS FOR WATER ADSORPTION OF ONTO THE ZEOLITE Z5A-NA,CA-FORMS AT 303, 318 AND 333 K FROM GLYCEROL/WATER MIXTURES (95/5 BY WEIGHT). TÓTH TREATMENT

Parameters	Temperature (K)		
	303	315	333
K_1	0.339	0.175	0.143
q_m	12.406	12.406	12.406
m	0.335	0.335	0.335
r^2	0.928	0.988	0.900

As can be seen, an increase in the temperature led to a decrease in adsorption capacity for the organic/water system. The decrease of adsorption capacity with increasing the temperature may be explained by the exothermic character of the adsorption process. The thermodynamic parameters enthalpy change (ΔH°) and entropy change (ΔS°) were estimated to evaluate the feasibility and exothermic nature of the adsorption process. These thermodynamic parameters have been calculated using the Tóth equilibrium constant, K_1 , in order to understand the adsorption type. The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_1$ versus ($1/T$) according to the following equation:

$$\ln K_1 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

where K_1 is Tóth equilibrium constant and T is temperature in Kelvin.

Negative values of ΔH° (-24.353 kJ/mol) and ΔS° -89.86 J/mol·K indicate the exothermic nature of this process and a

decrease in degree of freedom of the adsorbed species. The enthalpy value is lower than 40 kJ mol⁻¹ (this value is considered to be the upper limit of the enthalpy for physical adsorption in a general adsorption process). These small value indicate that the adsorption of water by Z5A-Na, Ca-forms is a physical adsorption process.^{30,31} According to the adsorption results it is possible to conclude that ion exchange and adsorption process applied in series could be used to purify the glycerol stream produced by acid neutralization.

D Non-catalyst-neutralization

In this procedure sodium or potassium alkoxides are used in the transesterification process as catalysts instead of the alkalis NaOH or KOH. Glycerol stream leaving the separator is free of water and contains a 50 wt % of glycerine in methanol and alkoxides. In that case, a cationic resin can be used to remove the metallic ion releasing the protons and forming the alcohol from the alkoxide in an irreversible way as it was shown in Equation 5.

Figure 3 shows the results obtained for the systems H⁺/Na⁺ and H⁺/K⁺ using the resin Amberlite 252, for a solution containing a mixture 50/50 of glycerine in methanol and a methoxide content of 0.25 mol L⁻¹ at 298 K.

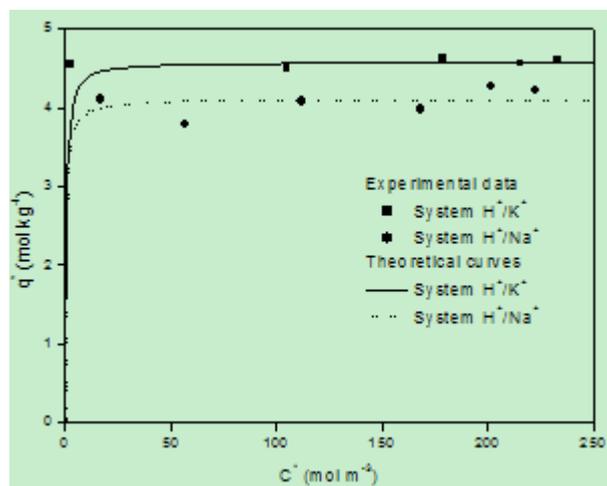


Fig.3 Isotherms for the binary systems H⁺/Na⁺ and H⁺/K⁺ using the resin Amberlite 252 in dry way.

As can be observed these ion exchange processes are irreversible and resin exhibits the maximum ion exchange capacity independently of the liquid concentration. For these non-ideal systems the equilibrium data were fitted by the Langmuir equation (Eq.11) with the aim to obtain the fitting parameters for each binary system, maximum capacity of the resin and the Langmuir constant.

Fitting procedure allows to conclude that Langmuir constant for this process was independent on the binary system studied and a value of 2170.68 L·mol⁻¹ was obtained whereas, the material presented two different values of q_0 depending on the loaded metallic ion, 4.58 and 4.11 mol·kg⁻¹ for potassium and sodium, respectively.

The high value of the Langmuir constant value indicates that this process is very favourable, irreversible in practice, for both ions. The values of q_0 inform about a higher exchange capacity of this resin for potassium, related with its low hydrated radii. On the other hand, the maximum capacity for sodium in this media 4.11 mmol·g⁻¹ is lower than that obtained in glycerine/water media (4.34 mmol·g⁻¹) confirming that the solvation of counter ions decreases when the methanol

is used instead of water attending to its lower dielectric constant at 298 K, 32.6 respects to 78.4.

These results indicate that ion exchange could be a suitable technique to remove the sodium and/or potassium ions from a non-aqueous phase with a subsequent single stage of methanol removal by distillation.

IV CONCLUSIONS

Equilibria for water uptake from solution of glycerine/water 95/5 by weight by using three different molecular sieves have been obtained at 303 K and zeolite 5A-Na,Ca seems to be the best choice to accomplish the water removal attending to its higher water uptake capacity. Experimental data were well fitted by two adsorption models Langmuir and Tóth, being the distribution coefficient higher when the Tóth model was used. Thus, these materials could be considered heterogeneous. According to the properties of these materials the water uptake was mainly depending on the metallic ions -size, ionic potential, hydration energy and how it is placed into the lattice- because the specific surface and the average pore diameter of studied materials are very similar and the zeolite Al₂O₃ percentage does not follow the literature expected trend. Thermodynamic properties H° and S° obtained from the equilibrium adsorption at 303, 318 and 333 K and applying the Tóth model demonstrates the exothermicity and feasibility of this adsorption process. Thus, ion exchange and adsorption could be used in series to purify glycerol stream neutralized with acid to recover the FFA.

Equilibrium studies of ion exchange for the systems H⁺/Na⁺ and H⁺/K⁺ using the resin Amberlite 252 for a solution containing a mixture 50/50 of glycerine in methanol and a methoxide content of 0.25 mol L⁻¹ at 298 K confirm the irreversibility of the process by the methanol production. Langmuir equation was used to fit the experimental equilibrium data indicating that Langmuir separation factor is independent on the system but the maximum ion uptake is higher for the K⁺ than Na⁺ attending to its low hydrated radii. These results confirm the feasibility to purify glycerol streams by applying the proper technology focused in a dry or wet way.

REFERENCES

- [1] J.V. Gerpen, "Biodiesel processing and production", Fuel Process Technol., vol. 86, pp. 1097-1107. 2005.
- [2] A.H. West, D. Posarac and N. Ellis, "Assessment of four biodiesel production processes using HYSYS Plant", Bioresource Technol., vol. 99, pp. 6587-6601. 2008.
- [3] A.L. Boehman, "Biodiesel production and processing", Fuel Processing Technol., vol. 86, pp. 1057-1058. 2005
- [4] I.Atadashi, M. Aroua, A. Aziz, "High quality biodiesel and its diesel engine application: A review", Renew. Sust. Energ. Rev., vol. 14, pp. 1999-2008. 2010.
- [5] M. Ma and Hanna, "Biodiesel production: a review", Bioresource Technol., vol. 70, pp.1-15. 1999.
- [6] R. Tresser, M. Di Serio, M. Guida, M. Nastasi and E. Santasesaria, "Kinetic of Oleic Acid esterification with methanol in the presence of triglycerides", Ind. Eng. Chem. Res., vol. 44, pp. 7978-7982. 2005.
- [7] N. Shibusaki-Kitakawa, H. Honda, H. Kuribayashi, T. Toda, T. Fukumura, T. Yonemoto, "Biodiesel production using ion-exchange resin as heterogeneous catalyst", Bioresource Technol., vol. 98, pp. 416-421. 2007.
- [8] F.Karaosmanoglu, B. Cigizoglu, M. Tüter, S. Ertekin, "Investigation of the refining step of biodiesel production". Energy & Fuel, vol. 10, pp. 890-895. 1996.
- [9] D.Leung, X. Wu, M. Leung., "A review on biodiesel production using catalyzed transesterification", Applied Energy, vol. 87, pp. 1083-1095. 2010.
- [10] Z. Helwani, M. Othman, N. Aziz, W. Fernando, J. Kim, "Technologies for production of biodiesel focusing on green catalytic techniques: A review", Fuel Process Technol., vol. 90, pp.1502-1514. 2009.
- [11] Y. Wang, H. Wu, M. Zong, "Improvement of biodiesel production by lipozyme TL IM-catalyzed methanolysis using response surface methodology and acyl migration enhancer", Bioresource Technol., vol. 99, pp. 7232-7237. 2008.
- [12] J.V. Gerpen, "Biodiesel processing and production", Fuel Process Technol., vol. 86, pp. 1097-1107. 2005.
- [13] H .Noureddini, V.Medikonduru, "Glycerolysis of Fats and Methyl Esters", J. Am. Oil Chem. Soc., vol. 74, pp. 419-425. 1997.
- [14] P. Meka, V. Tripathi, R.P. Singh, "Synthesis of biodiesel fuel from safflower oil using various reaction parameters". J. of Oleo Sci, vol. 56, pp. 9-12. 2007.
- [15] L.C. Meher, D. Vidya, S.N. Naik, "Technical aspects of biodiesel production by transesterification - a review". Renewable Sustainable Energy Rev., vol. 10, pp. 248-268. 2006.
- [16] L. Bournay, D. Casanave, B. Delfort, G. Hillion, J.A. Chodorge, "New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants". Catal. Today, vol. 106, pp. 190-192. 2005.
- [17] M. Mazzotti, B. Neri, D. Gelosa, Morbidelli, "Dynamics of a Chromatographic Reactor: Esterification Catalyzed by Acidic Resins", Ind. Eng. Chem. Res., vol. 36, pp. 3163-3172. 1997.
- [18] H.van Bekkum, E.M. Flanigen, J.C. Jansen, Editors, Introduction to Zeolite Science and Practice, Elsevier, Amsterdam 1991.
- [19] G. Rutkai, E. Csanyi, T. Kristof, " Prediction of adsorption and separation of water-alcohol mixtures with zeolite NaA". Microporous and Mesoporous Mat., vol. 114, pp. 455-464. 2008.
- [20] A.Velayudhan, C. Horvath, "Adsorption and ion exchange isotherms in preparative chromatography", J. Chromatogr. A, vol. 663, pp.1-10. 1994.
- [21] M. Carmona, J.L. Valverde, A. Pérez, J. Warchol, J.F. Rodríguez, "Purification of glycerol/water solutions from biodiesel synthesis by ion exchange: sodium removal Part I", J. Chem. Technol. Biotechnol., vol. 84, pp. 738-744. 2009a.
- [22] M. Carmona, J.L. Valverde, A. Pérez, J. Warchol, J.F. Rodríguez, "Purification of glycerol/water solutions from biodiesel synthesis by ion exchange: sodium and chloride removal. Part II", J. Chem. Technol. Biotechnol., vol. 84, pp.1130-1135, 2009b.
- [23] T. Okada, "Nonaqueous ion-exchange chromatography I. Role of salvation in anion-exchange resin", J. Chromatogr A, vol. 758, pp.19-28. 1997.
- [24] A.de Lucas, J.L. Valverde, M.C. Romero, J. Gómez, J.F. Rodríguez, "The ion exchange equilibrium of Na⁺/K⁺ in nonaqueous and mixed solvents on a strong acid cation exchanger", Chem. Eng. Sci, vol. 57, pp.1943-1954. 2002.
- [25] F.L Kevin, "Water isotherm models for 4A (NaA) zeolite", Adsorption, vol. 15, pp. 337-353. 2009.
- [26] A.Gorbach, M. Stegmaier, G. Eigenberger, "Measurement and Modelling of Water Vapor Adsorption on Zeolite 4A—Equilibria and Kinetics", Adsorption, vol. 10, pp. 29-46. 2004.
- [27] N.Y. Chen, "Hydrophobic properties of zeolites", J. Phys. Chem, vol. 80 (1), pp. 60-64. 1976.
- [28] J.Weitkamp, S. Ernst, B. Günzel, W.T. Deckwer, "Separation of gaseous water/ethanol mixtures by adsorption on hydrophobic zeolites", Zeolites, vol. 11(4), pp. 314-317. 1991.
- [29] E. Ivanova, M. Karsheva, B. Koumanova. "Adsorption of ammonium ions onto natural zeolite". J. Univ. Chem. Technol. Metal, vol. 45(3), pp. 295-302. 2010.
- [30] J. Chern, Y. Chien, "Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves", Water Res, vol. 36, pp.647-655. 2002.
- [31] J. Chern, C. Wu, "Desorption of dye from activated carbon beds: effects of temperature, pH, and alcohol", Water Res. vol. 35, pp. 4159-4165. 2001.