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Treball Final de Grau

Liquid-phase synthesis of butyl levulinate with simultaneous water removal.

Síntesi de butil levulinat en fase líquida amb eliminació d'aigua.

Maria del Mar Planas Mariano 15 (June 2017)



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"The important thing is to never stop questioning" Albert Einstein

En primer lloc, i sempre en primer lloc, vull agrair a la meva família el seu suport incondicional durant tots aquests anys. Sense el vostres consells i la vostra confiança amb mi no hagués estat possible.

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SUMMARY

Today, the world faces two major challenges, the energy crisis and environmental pollution. The world's energy comes from fossil fuels that are responsible for the largest air pollution. For this reason many countries have taken actions.

The EU directives on quality and composition of the fuels, that rule oxygen content of automotive fuels must be at least 15% in 2020. Consequently a reformulation of gasoline and diesel is needed in order to allow the contents stipulated in oxygenates.

The butyl levulinate is an ester with a boiling point coincides with the lighter fraction of the fuel. The addition of this in diesel, improves the commercial circulation of diesel cold and, in turn, reduces particulate emissions. The butyl levulinat is an alkyl levulinat that can be synthesized from levulinic acid, furfuryl alcohol or directly from cellulose or monosaccharides. Levulinic acid, is a platform molecule formed by means of lignocellulose hydrolysis in Biofine process. Then butyl levulinate will be considered as a biodiesel product.

Obtaining butyl levuliant by the esterification of levulinic acid with 1-butanol over several types of catalysts as zeolites, lipases, heteropoliacids (HPA) and ion exchange resins has been described. In the present work, the different behavior of different sulfonate polystyrenedivinylbenze resins is studied in the synthesis of butyl levulinat with simultaneous removal of water.

The results of experiments confirm that polymer catalysts can be used in order to obtain high conversions and selectivity in favor of butyl levulinat. The structure of the resin determines the results obtained. Swelling of the polymeric matrix is a determining factor in the behavior of the resins because resins that present a higher swell favor esterification. As a whole, resins with a lesser degree of crosslinking present good relation between yield, selectivity and reaction times. Dowex 50Wx2 is resin which the best relation between yield, selectivity and reaction times Dowex 50Wx2

Keywords: Esterification reaction, acidic catalysts, butyl levulinate, levulinic acid, butanol, removal water

RESUM

Actualment, el món s'enfronta a dos grans reptes, la crisis energètica i la contaminació ambiental. La major part de l'energia mundial prové de combustibles fòssil que son els majors responsables de la contaminació atmosfèrica. Per aquesta raó molts països han pres mesures.

Les directives de la UE, sobre la qualitat i composició dels combustibles, dictaminen que el contingut d'oxigen als combustibles d'automòbil han de ser, com a mínim, del 15% en el 2020. Conseqüentment es necessària una reformulació de gasolines i gasoils per tal de fer possible el contingut estipulat en compostos oxigenats.

El butil levulinat és un ester amb punt d'ebullició coincident amb la fracció més lleugera del gasoil, la introducció del qual al diesel comercial millora les propietats de circulació en fred del gasoil i, a la vegada, redueix la emissió de partícules. El butil levulinat es un alquil levulinat que es pot sintetitzar a partir de l'àcid levulinic, l'alcohol furfurílic o directament a partir de cel·lulosa o monosacàrids. L'àcid levulinic, es una molècula plataforma formada mitjançant la hidròlisi de la lignocel·lulosa per el procés Biofine. Llavors es un producte que tindrà consideració de biodièsel.

L'obtenció de butil levuliant per la reacció d'esterificació de l'àcid levulínic amb 1-butanol ha estat descrita mitjançant l'ús de catalitzadors con les zeolites, lipases, heteropoliàcids (HPA) i resines de bescanvi iònic. En el present treball estudia el diferent comportament de diferents resines de poliestirè-divinilbenzè sufonades en la síntesi de butil levulinat amb eliminació simultània d'aigua.

Els resultats indiquen que els catalitzadors polimèrics àcids poden ser emprats per tal d'obtenir conversions elevades y grans selectivitats a favor del butil levulinat. Els resultats obtinguts depenen de l'estructura de la resina, determinada pel procés de fabricació. Un dels factors determinants en el comportament de les resines es l'inflament de la matriu polimèrica ja que les resines que presenten un inflament més pronunciat afavoreixen l'esterificació. En

conjunt, les resines amb menor grau de reticulació presenten les millors relacions entre rendiment, selectivitat i temps de reacció. S'ha obtingut que la resina amb una millor relació entre rendiment, selectivitat i temps de reacció es la Dowex 50Wx2.

Paraules clau: Reacció d'esterificació, catalitzadors àcids, butil levulinat, àcid levulínic, butanol, eliminació d'aigua.

1. INTRODUCTION

1.1. FROM BIOMASS TO FUELS

The world population is continuously growing since the last 50 years, resulting in a large increase in primary energy consumption. Hence, the world is currently facing two major challenges, which are energy crisis and environmental pollution [1]. A great fraction of worldwide energy carriers and material products come from fossil fuel refinery. Therefore, fossil fuels currently serves the majority of our needs, both energetically and chemically. However, their combustion is believed to be responsible for approximately three-fourths of the anthropogenic emissions of CO₂ [2] a major greenhouse has that contributes to global warming. The possibility of reduced fossil fuel supplies in the future, either through geo-political conflicts, or through reaching a "Hubbert Peak" in their production, are also strong drivers for a search for alternatives [3]. Biofuels are likely to play a key role in the pursuit of these goals being one of the most advanced alternative energy sources.

The term biofuel is referred to biomass-to-liquid fuels (BLT). Based on the source and production technology, biofuels are classified into the first, second and third generation biofuels [4]. First generation biofuels usually refer to biofuels produced from raw materials as sugar, starch or oil crops. The most common 1st generation biofuels are bioethanol, biodiesel and starch-derived biogas, but also straight vegetable oils, biomethanol and bioethers may be included in this category [5]. Bioethanol is obtained from fermentation of edible biomass sources. The European union produces 3,44 billion liters of bioethanol [6]. Biodiesel is obtained by transesterification of triglycerides with methanol or ethanol to a lesser degree. World biodiesiel production surpassed 6 billion litres in 2006 [6]. In the last few years the consumption of these biofuels has increased exponentially. They are extensively produced and consumed mainly because their production is based on simple and well-known technologies, and are usually used blended with conventional fuels. Despite their chemical advantages, there are

drawbacks with first generation biofuels. Their costs can be high, particularly in Europe [7], and their net energy balance low. First generation biofuels production competes with food-requirements and feed industries. Because of this competition, these biofuels give rise to ethical, political and environmental concerns. Moreover, these biofuels possess other drawbacks, for instance, the low oxidation stability, the corrosive nature and poor cold flow properties.

In order to overcome 1st generation biofuels bottlenecks, second generation biofuels gained an increasing world-wide interest in the last few years. 2nd generation biofuels are produced form a variety of non-food crops [5]. These fuels are produced in biorefineries where could obtain a variety of end products according to the chemical components of the starting materials (lignocellulosic feedstocks). Examples of lignocellulosic biomass feedstocks include municipal/industrial wastes (household and green wastes, paper wastes), agricultural residues and dedicated energy crops (Miscanthus switchgrass) [8]. The main pitfall so far has been the technology concerns, which do not support cost-effective and competitive production of lignocellulosic bioethanol. The economical production is governed by three main factors: (1) The initial cost of raw materials, transportation, and processing. (2) The availability of suitable production and recovery procedures; and (3) the final product yield [9]. The key to exploiting the chemical value of lignocellulosic feedstocks is to depolymerize the lignocellulosic matrix in order to obtain smaller molecules. Economic analyses indicate that depolymerize stage could contribute 40-45% to the total biofuel cost [10]. Therefore, it is very important that pretreatments be carried out prior to hydrolysis.

Lignocellulose is composed of the biopolymers of cellulose, hemicellulose, and lignin. Cellulose (30-50% of total lignocellulose dry matter) has a strong molecular structure made by long chains of glucose molecules. The distinction with starch is given by the configuration of the bonds formed across the oxygen molecule that joins two hexoses units. Thus, enzymes or acid attack can readily hydrolyze starch to the single sugar monomers, while cellulose is much more difficult to hydrolyze and set free individual glucose monomers. Hemicellulose (20-40% of total feedstock dry matter) is amorphous heteropolysaccahride that is easier to break down than cellulose. Hemicellulose can contain among other pentoses, hexoses, glucose and mannose. Lignin (15-25% of total feedstock dry matter) is a complex three-dimensional polymer of phenyl

propane units. Lignin is essentially the glue that provides the overall rigidity to the structure of plants and trees.

Nowadays, the three main catalytic routes to transform biomass into fuels and chemicals are gasification, pyrolysis and hydrolysis. Gasification and pyrolysis deal with whole biomass leading to upgradeable platforms such as syngas and bio-oil. However, hydrolysis is the most complicated process that requires that lignocellulose is broken into its constituent parts [11]. As mentioned above, in order to converting lignocellulosic material into fuels and chemicals is needed to liberate cellulose from lignin structure. Once isolated, glucose monomers can be obtained through hydrolysis. Then these sugars can produce bio-based platform molecules as furfural, 5-hydroxymethyl-furfural (HMF) and levulinic acid through thermal dehydration in acid media.

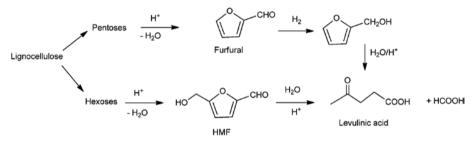


Figure 1. Production of levulinic acid from lignocellulose

Levulinic acid (LA), also known as 4-oxopentanoic acid, can be considered one of the most important compounds in the selected list of platform molecules derived from biomass [12]. LA possess a ketone carbonyl group (C=O) and an acidic carboxyl group (COOH) which imparts it an ability to react with different functional groups to form a wide range of derivatives, this reason making LA an ideal platform chemical.

LA can be synthesized from several different raw materials for instance, monosaccharides, precursors such as 5-hydroxymethylfurfural (HMF) and furfural, polysaccharides and renewable resources such as starch-rich waste and lignocellulosic biomass [13].

LA formed by dehydration in acidic media of hexoses to HMF, which upon subsequent hydration produces levulinic acid, equimolar amounts of formic acid along with large amounts of humic acid or humins, black insoluble materials that are produced by unwanted polymerization

reactions [14]. Fructose is most effective than glucose in the HMF synthesis, therefore the isomerization to fructose is required for HMF synthesis. Additionally, pentoses such as xylose, the main component of the hemicellulose fraction, can be converted to levulinic acid. Furfural (derived from hemicellulose pentoses) is reduced catalytically to furfuryl alcohol followed by its acid hydrolysis to yield LA.

LA production has been carried out since 1840s as reported by G.J.Mulder. Commercially, first LA synthesis took place in United States by A.E. Staley in 1940 using an autoclave [15]. At laboratory scale, LA has been produced successfully but commercialization of LA has met with limited success due to cost of raw, equipment cost, low yield of LA, difficulties in efficient product recovery, catalyst recovery cost, energy-inefficiency and the process economy [13]. Currently, overproduction of raw materials and developments in science and technology has opened doors to reevaluate industrial potential [16]. It was not until the Biofine Process became operational in 1996 that there was a reevaluation of LA's industrial potential. Biofine Process is one of the most advanced and commercially viable lignocellulosic-fractionating technologies currently available. The process involves the hydrolysis of polysaccharides to their monomeric constituents, and these are then in turn continuously converted to valuable platform chemicals [16]. The process involve a continuous two-stage reactor system operated at optimal conditions to produce LA with 70-80% theoretical yields, which corresponds to 50% mass yield on the basis of C6 sugars. In this process the lignocellulose is mixed with sulphuric acid (1.5-3 wt %) and supplied continuously to a first reactor at 488K and 25 bar. The completely mixed conditions of the second reactor favor the first order reaction sequence leading to LA rather than higher-order tar-forming condensation.

Currently LA costs between 5 to 8 USD per kilo but thanks to the Biofine Process will open up new opportunities for the cost-effective production of LA. Another key factor to an increased potential marketability for LA is the vast range of applications possible from LA and their derivatives. For example, diphenolic acid (LA derivate) has numerous uses including applications in lubricants, adhesives and paints [18]. Other example can be succinic acid, obtained from oxidation of levulinic acid, which most important uses are in food additives, soldering fluxes and pharmaceutical products. Sodium and calcium salts of LA have been found to have therapeutic as well as a potential application as a substitute of ethylene glycol in antifreeze [16].

Moreover, alkyl levuliantes have a wide range of applications. First of all, they are soluble in classical solvents as alcohols, ethers and chloroform so they are used as solvents. In 2011, Lomba [19-21] studied physicochemical characteristics (properties like surface tension, density, refractive index, viscosity, vapor pressure and static permittivity) of biobased liquids for green solvents application. Levulinates were shown to be more compressible due to internal organization of molecules and to possess much lower vapor pressures compared to usual solvents. Based on this, Bayarri Ferrer [22] patented the use of alkyl levulinates for metallic surface degreasing processes. Moreover, levulinic acid ester and their ketal adducts could find interest, for instance, in polymers, perfume, or flavouring preparations and latex coating compositions [23-25]. Finally, in the actual environmental concerned world, levulinic esters show a significant potential as blend components in diesel formulations.

Before use alkyl levulinates as biofuels or as additives to conventional fuels some minimum requirements are considered. All automotive fuels should comply with a minimum performance requirements set by countries. Therefore, a good biofuel candidate must meet the next minimum requirements:

- They should not deteriorate or contribute to the failure the emission control devices.
- They must produce low atmospheric emissions (SO₂ in exhaust gases and combustion fumes).
- They must provide an acceptable combustion rate inside the engine: neither too fast (which can cause overheating of the injector) nor too slow (to assure complete combustion of fuel).

EN 590 standard (Directive 2009/30/EC) specified the quality of European Union diesel fuels. Table 1 provides these specifications.

Cetane number is an indicator of the ignition speed of diesel fuel. The cetane number is an important factor in determining the quality of fuel. The higher the cetane number, the shorter the interval between the time the fuel is injected and the time it begins to burn. Increasing a cetane number can reduce or eliminate the NOx increase from oxygenates in some case. These is because of the reduced ignition delay, which reduces the degree of premixed autoignition zone,

thereby reducing the effect of changing stoichiometry during these phases of combustion [26]. Low cetane number usually causes an ignition delay in the engine, poor fuel economy, a loss of power and sometimes engine damage.

| Fuel property | Unit | Specification | | Test | |
|-----------------------------------|---------|---------------|-------------------|-----------------------|--|
| ruei property | Unit | Min | Max | - 1651 | |
| Cetane number | - | 51 | - | ISO 5165 | |
| Cetane Index | - | 46 | - | ISO 4264 | |
| Density (15°C) | kg/m³ | 820 | 860 | ISO 3675 / ASTM D4052 | |
| Sulfur | ppm | - | 50 | EN 24260 / ISO 8754 | |
| Flash Point | °C- | 55 | - | ISO 2719 | |
| Carbon residue (10%btms) | % (wt.) | - | 0.30 ^a | ISO 10370 | |
| Ash | % (wt.) | - | 0.01 | EN 26245 | |
| Water content | mg/kg | - | 200 | ASTM D1744 | |
| Copper strip corrosión, 3h (50°C) | - | - | Class 1 | ISO 2160 | |
| Oxidation stability | g/m³ | - | 25 | ASTM D2247 | |
| Viscosity (40°C) | mm²/s | 2.00 | 4.5 | ISO 3104 | |
| Distillation (vol. % recovered) | °C | | | ISO 3405 | |
| 10% point | °C | Report | - | | |
| 50% point | °C | Report | - | | |
| 65& point | °C | 250 | - | | |
| 85% point | °C | - | 350 | | |
| 95% point | °C | - | 370 | | |
| FAME content | % (wt.) | 7 | - | | |

Table 1 EN590: 2009 Diesel Fuel Specification

(a) limit does not apply if ignition improver additives are used

A minimum value for *density* guarantees that the engine will have sufficient power, while an excess might lead to smoke production. Density affects to heating value too. A moderate flow properties are needed to accept fuel and *viscosity* provides information about these properties. *Sulfur content* must be as low as possible because it can contribute to particle and SO₂ emissions.

Volatility characteristics are very specific because it must be adequate for high pressure injection and facilitate the atomization by spraying. The *flash point* is the lowest temperature at which fuel liberates vapors that ignite in contact with air or a flame.

If fuel is cooled, it will reach a temperature at which fuel will lose transparency. This is the *cloud point*. When fuel no longer flows or turns solid is known as the *pour point*. Another key property of diesel fuel is the cold filter plug point (CFPP), which is the temperature where fuel can no longer flow freely through a fuel filter.

There are many contaminants in fuels. *Carbone residue* gives a measure of the carbon depositing tendencies of a diesel fuel after evaporation and pyrolysis. Ash particles can damage a fuel injection system and cause combustion chamber deposits. Water is one of the more common contaminants in fuel and this can affect fuel filters and injector by corrosion [27].

However, a compromise between above properties and requirements is necessary. Various esters of levulinic acid have been studied recently such as methyl levulinate (ML), ethyl levulinate (EL), n-butyl levulinate (BL). Meanwhile, ML and EL have been studied as possible candidates as fuel additive, BL has been left untapped. Among possible candidates, long alkyl chain levulinates (4-10 carbons) are currently mainly studied due to lower water solubility and water-soluble fuels are more difficult to handle. For example ML is fully miscible with water and can separate from gasoline at cold temperatures. For all of that, EL and BL are the best candidates as both neat oxygenates and blends with diesel fuel.

The advantage of introducing alkyl levulinates in transportation fuel mixtures can be, for example, the substitution of conventional additives (ethanol, methyl-tert-butylether) by biomassderived products [28, 29]. Besides, the presence of these oxygenated compounds leads to cleaner combustion processes with fewer smoke or NOx emissions [30]. Another reported advantage is that butyl levulinates cause lower degradations to some elastomeric constituents of the engine than other additives [31].

In 2011, Christensen [26] assessed and compared both EL and BL as diesel blend components. They were relatively free of *impurities*, although EL contained some acidic compounds (due to residual levulinic acid) and both contained parts-per-million levels of calcium from the manufacturing process. Both esters exhibited a very low *cetane number* which can be addressed with cetane improver additives. BL exhibits lower cetane number than EL. Both

reduce vapor pressure in diesel blends [32]. The *melting points* of both esters were less than - 60°C and their *boiling point* and *flash point* are in the acceptable range for diesel fuel. The water solubility of EL was 15,2wt% while that of BL was only 1,3wt%. The water-saturated EL was found to contain 8,5 wt% water, and the water-saturated BL contained 2,6wt%.

BL remained in solution and raised the diesel cloud point unlike EL which separates from diesel fuel as a separate liquid phase at low temperatures. Because of the poor *solubility* of EL in diesel fuel at low temperatures, its use as a diesel blend component will be technically challenging. The formation of a separate liquid phase is unacceptable from a fuel performance standpoint because of the potential for EL to accumulate in the bottom of storage and vehicle fuel thanks, leading to engine stalling or poor operation. Additionally, it is not clear how diesel engine fuel pumps and injectors will perform with a two-phase mixture. Both esters were found to significantly increase diesel *lubricity* and *conductivity*. In terms of the *volumetric energy content* of the esters is roughly 30% lower than that of a conventional diesel fuel but this is already an improvement on bioethanol.

So meanwhile EL has been recommended as gasoline additive, BL appears to be more adequate for diesel blending.

1.2. SYNTHESIS OF ALKYL LEVULINATES

First reports concerning alkyl levulinates date from 19th century. As mentioned above, alkyl levulinates are biobased chemicals having a strong potential to be used in various applications and substituting current chemicals produced from petro-chemical routes is one of the most important. The wide range of applications is due to their specific physicochemical properties.

Alkyl levulinates are obtained in high yields and selectivities from simple biomass-derived products like levulinic acid (LA) or furfuryl alcohol. They are also obtained directly from lignocellulosic resources with generally limited yields [33]. In figure 2 different routes for manufacturing of alkyl levulinates are represented.

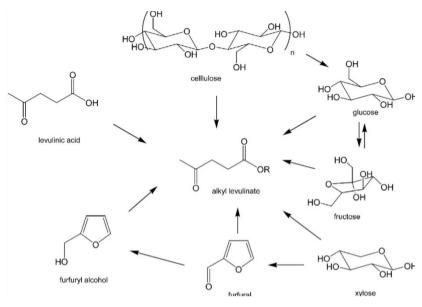


Figure 2. Synthesis routes for alkyl levulinate

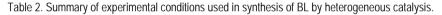
Sah [34] and then Schuette [35] studied the formation of several alkyl levulinates from LA in the corresponding alcohol (in excess) in the presence of HCI (acid catalyst). By this method yields were reportedly low (35-65%) and relatively high temperatures (110-162°C). The very different experimental conditions are the reason of difficult comparison but some general trends can be outlined. For example, alcohol always acts as a solvent and for this reason is always in excess. Furthermore, esterification is a reversible reaction so excessive alcohol is favourable to ester formation. Nevertheless, the molar ratio of alcohol to LA falls in the range from 5 to 10. Concentrated solutions are justified by the fact that a too diluted system could imply mass transfer limitations of the reactant and favor intermolecular alcohol dehydration [33].

The homogeneous catalytic process uses, as acid catalysts inorganic liquid acids as HCl, H_3PO_4 and H_2SO_4 . These liquid acids cause environmental problems due to their toxic and corrosive nature. Consequently, heterogeneous catalysts are now the preferred.

The heterogeneous catalysed esterification of LA often uses as catalysts solids with Brønsted acids. In this case, for the formation of alkyl levulinates is necessary the adsorption through the protonated carbonyl group of the carboxylic function thus enabling a nucleophilic attack of the alcohol assisted by an oxygen atom from the oxide network [36-38]. Among acid

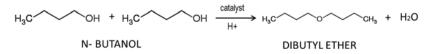
catalysts, zeolites [39] and heteropoly acids (HPAs) [40] are the preferred choices. It has also been synthesized using PS-DVB acidic sulfonic resins as baseline reference catalysts, usually Amberlyst 15. There are other catalysts options as hybrid catalysts, sulfated carbon nanotubes and functionalised Starbon[®] mesoporous materials functionalised. [39-42].

However, despite being a potential diesel-blending component, a quiet little attention has been paid to the BL synthesis. Butanol like ethanol can be synthetized from renewable crop resources. As previously stated, alkyl levulinates first attempts at synthesis were undertaken with homogeneous catalysis [34, 35]. Then, estefication of LA with butanol was studied over several types of solids catalysts such as zeolites, heteropolyacid (HPA) [43] supported on acid-treated clay montmorillonite (K10). In addition, the production of BL by esterification of LA has been attempted via immobilized lipase catalysis [44]. In 2015, the catalysis with different acidic ion-exchange resins was studied [45].



| $H_{3}C$ OH $H_{2}C$ OH H^{+} LEVULINIC ACID n-BUTANOL | | | | | | | + н ₂ о |
|---|------------------------|-------------------------|---------------|------|--------|------------------|---------------------|
| Ref. | Catalyst | Solvent | Catalyst load | t(h) | T (°C) | R BuOH/LA | X _{LA} (%) |
| [39] | Zeolite | None (BuOH) | 7-14 wt% | 4-12 | 120 | 6-8 | 82 |
| [43] | HPA on K10 | None (BuOH) | 7-30 wt% | 1-6 | 120 | 4-10 | 97 |
| [44] | Immobilized lipase | t-butyl methyl ether | 10-50 mg | 2 | 30-60 | 1-4 | 88 |
| [45] | lon exchange resins | None (BuOH) | 0.8-1.5 wt% | 8 | 80-120 | 3-9 | 80-99 |

In these studies, dibutyl ether is formed as a by-product which is obtained by dehydration of butanol.



1.3. ACIDIC ION-EXCHANGE RESINS OF POLYSTYRENE-DIVINYLBENZENE (PS-DVB) AS CATALYSTS

Nowadays, 90% of the chemical processes are catalytic and at least 80% of these processes use heterogeneous catalysis. Between 15 and 20 percent of the economic activities in industrialized countries depend directly on catalysis, as well as, the commercial value of the catalysts produced annually amounts to 14billion US\$ approximately. These numbers reflect the economic importance of catalysis [46].

The heterogeneous catalysis by solids prosperity is because this has many advantages and benefits such as easy handling, low cost, high reactivity, easy recovery and reuse. Moreover, in the case of acid catalysts, one other advantage is that the use of solid acids limits corrosion and disposal issues present when using liquid mineral acids.

Nevertheless, catalysis with solids present some limitations related with available surface of catalyst. Because of one reagent must be adsorbed a large and extensive surface is needed. Consequently, while the surface is saturated completely the reaction cannot advance.

As having a large and extensive surface is essential most heterogeneous catalysts are porous solids, which feature a large surface area in a small volume. The structure of solid catalyst particles (number, size and pore volume) is fundamental in catalyst performance. Moreover, their chemical composition is also important because determine the interaction between the reactants and surface. In order to, the reagents will be able to react in heterogeneous catalysts three steps are necessary. These essential steps are Adsorption, Surface Reaction and Desorption and all of them take place in the specific place on the catalyst surface called active sites. Solid catalysts can be metals, oxides, metallic salts, sulphides and organic materials such as organic hydroperoxides, ion exchangers, and enzymes [47, 48].

Ion exchange resins (IERs) are solid polymers which are functionalized. IERs are capable of exchanging ions with the medium in which they are immersed and this exchange capacity can be expressed as milliequivalents (meq) per g IER. The resins consist of an insoluble matrix in which active sites are supported and can be acid, basic or salt.

IERs have been exploited since a long time for many industrial chemical uses and the annual consumption of ion-exchange resins for water treatment alone is in hundreds and thousand tons worldwide. These have been used in water softening, removal of toxic metals from water in the environment, wastewater treatment, hydrometallurgy, sensors, chromatography, and biomolecular separations. Between all applications, acid catalysis is apparently the most important catalytic application of IERs but their use will probably grow significantly in the fields of biocatalysis and of supported metal catalysis [49, 50].

The wide use of the ion-exchange resins as solid catalyst is due to their have many advantages. First, there is the ease of handling, storage, and separation. Secondly, they have many other interesting properties like non-volatile, nontoxic and often recyclable. Moreover, in case acid solid catalyst is used, corrosion problems can be avoided because most protons are on the inside of catalyst particles and waste treatment is much simplified. Finally, IERs are very useful because of the insolubility of the matrix allows, after contact with the ion-containing solution, the resin can be separated by filtration which leads to higher purity products and yields

The structure of resin, their mechanical and chemical resistance depend on degree of crosslinking and manufacturing process. Our attention is focused upon S/DVB, which are by far the most important catalysts precursors. The degree of cross-linking is based on total volume or weight of reticulating agent (DVB). Most commercial ion-exchange resins produced have cross-linker concentrations in the range of 2-20% DVB [51]. As mentioned above, the amount of crosslinking defines the physical and chemical properties of the resin and these properties define the performance of resins in terms of kinetics and sorption equilibrium. In addition, this variable that controls resin porosity.

A low cross-linked product increases moisture retention and does not withstand oxidation conditions. All of these reasons leading to physical degradation and thus they need for frequent resin replacement. Furthermore, low cross-linking resins are soft, gelatinous, elastic and mechanically unstable. On the other hand, the resins of a higher cross-linking degree had a longer working life because a high DVB% provides greater strength and stiffness to resins. Moreover, these resins are more likely to withstand oxidation conditions but often are more brittle. As a rule of thumb, the higher is the cross-linking degree, the slower is the diffusion of the molecules of the reactants inside the polymer mass [49].

The S/DVB resins are usually obtained by polymerization of styrene and the subsequent addition of a specific amount of divinylbenzene in water, under strictly controlled conditions (figure 3). At the beginning of the reaction, droplets of the monomers are dispersed in water. Each droplet behaves as a batch reactor. If a macroreticular (macroporous) material is desired a porogenic agent must be added. In the absence of a porogen, gel-type resins are obtained. On cue, these resins are sulfonated by means of concentrated sulfuric acid bath in order for them to acquire their acid properties. So, depending on their structure could be classified IERs in two main classes: gel-type resins (microporous) and macroporous resins (macroreticular).

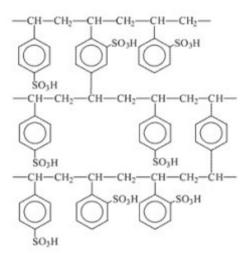


Figure 3. Structure of a sulfonated resin of PS-DVB

Most catalysts resins contain one or more groups of pores, whose size, distribution and specific areas can vary over a wide range according to the polymerization conditions [49].

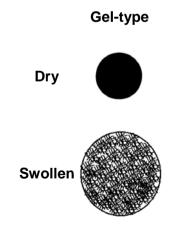
The pores are classified into different classes [52, 53]:

- Micropores (size <2nm) are located in between the nodules, there is a family of very small pores.
- Mesopores (2nm<size<50nm) are located in between the microspheres.
- Macropores (size>50nm) are located between the agglomerates. This type pores are permanent.

As mentioned above, a numerous charged functional groups are attached to the polymer matrix. The four functional groups commonly found in the four categories of resins are strongly acidic groups, sulfonated group (-SO3-); weakly acidic groups, carboxylate group (-COO-); strongly basis groups, quaternary amine group [-N+(CH3)4]; and weakly basic groups, tertiary amine group [-N+(CH3)3].

Thus, depending on the structure IERs can classified in gel-type resins or macroreticular resins. The gel type resins have a low cross-linking degree and have a reduced surface area in the dry state (<1m2/g). This resin type is resins without an appreciable porosity in the dry state, whose interior is accessible only after swelling in the reaction environment. In contrast, macroreticular (macroporous) resins with a high cross-linking degree have two phase structure: microspheres and macrospheres. This type of resin has a permanent pore structure. It is worth noting that, macroporous resins have far larger BET surface areas than gel-type ones.

Accessibility of the active centres in these materials is dramatically affected by the extent of swelling of the polymer mass in contact with the reaction medium. The swelling behaviour of ion exchange resins depends on the cross-linker concentration [51], so the more cross-linked the resin is, the smaller is the degree of the swelling. In figure 4 the different behaviour of different type resins, in regards to swelling, is shown.



Macroreticular

Figure 4. Morphological changes during swelling of a gel-type and macroporous catalyst

There are two types of resin densities: dry resin density and water-swollen resin density. Resin density is the mass of the dry resin per unit volume and depends on resin type, the degree of cross-linking and the functional groups.

Because ion-exchange resins must operate for long periods of time they must be chemically, thermally and mechanically stable. Mechanical strength is referred to resistance to compression and breaking. The resistance of resins increases with the degree of cross-linking, and reduces after regeneration. Thermal stability allows a resin to withstand higher temperatures. This property varies in relation depending on the degree of cross-linking between 120-150°C and gel-type resins are more thermally stable than macroreticular resins. For improve, thermal stability could add electron donating groups to the sulfonated benzene ring.

So in order to describe the catalytic activity of a resin it is necessary to consider the following factors: the functional group, the active surface and the accessibility due to porous.

Description of resin morphology is totally necessary to interpret resin effects observed in reactions in liquid media because the structure and catalytic activity of resin are very related. Resin morphology changes on swelling and nonpermanent pores appear so, a description of their characteristics and morphology can't be obtained by techniques such as N2 absorption (BET) or Hg intrusion porosimetry. This is because these instrumental techniques do have the potentially severe limitation in that they refer to the dry state resin. Thus, in order to study the morphology of IERs other characterization techniques are needed.

Among the currently available methods, inverse steric exclusion chromatography (ISEC) yields the best quantitative assessment of the morphology of swollen resins. ISEC is a chromatographic technique based on measurements of elution volumes of solutes whose molecular size is known. The description of the morphological features is based on the following assumptions: (1) the pore system can be described using simple geometric models; (2) it can be modeled as a discrete set of fractions, each consisting of simple pores of a single size only [49]. In 1985 Jerábek proposed an approach based on modeling of the porous structure as a set of discrete fractions, each composed of pores having a simple geometry and uniform sizes [54]. Nevertheless, this model is not applicable in all cases and sometimes the values of parameters may be unrealistic. A geometrical model developed by Ogston, in which micropores are described by spaces between randomly oriented rigid rods is for the three-dimensional polymer

network a better approximation. The parameter characteristic of this model is the specific volume of the swollen polymer (volume of the free space plus that occupied by the skeleton), Vsp. The Ogston model also allows distinguishing zones of swollen gel phase of different density or polymer chain concentration (total rod length per unit of volume of swollen polymer, nm-2). The final output of the ISEC of the swollen-state resin morphology is the information on both the distribution pattern of the macropores and the volume distribution of the differently dense gel fractions in the swollen polymer mass. [49,54]. The morphological information given by ISEC technique has been employed successfully with the catalytic activity of ion-exchangers in polar environments [53,55-57] in which, the accessibility of the reactant to acid centers was described as a key factor.

2. OBJECTIVES

Environmental pollution is one of the global concerns that has led to the need to propose the conversion of biomass into biofuels. Butyl levulinate, which can be obtained from the esterification of levulinic acid with butanol, has properties that allow it to be a good choice for use as additives in conventional diesel and gasoline.

This work is a part of a larger project that deals with synthesis of biomass-derived products as additives for diesel. The aim of this current study is to investigate the performance of ionexchange resins of PS-DVB for the esterification of LA with BuOH with simultaneous water removal due to the lack of information about the performance of that type of catalysts in this reaction. This investigation will include the following objectives:

- Selection of suitable acidic ion-exchange resins for this reaction in terms of LA conversion, selectivity and yield.
- Assessment of effect of removal water on the behavior resins at the reaction conditions.

3. EXPERIMENTAL SECTION

3.1. MATERIALS: REACTANTS, AUXILIARTS AND CATALYSTS

Experiments for the catalytic synthesis of butyl levulinate were carried out using ionexchange polystyrene-divinylbenzene (PS-DVB) sulfonated resins were used as catalysts throughout the experiments. The acidic resins used were Amberlyst 15 (A15), Amberlyst 16 (A16), Amberlyst 35 (A35), Amberlyst (A36), Amberlyst (A39), Amberlyst 46 (A46), Amberlyst 121 (A121) and Dowex 50Wx2, Dowex50Wx4, Dowex50Wx8 (Dow chemicals).

The resins used in this study have two types of morphology: macroreticular (all Amberlyst except Amberlyst 121) and gel-type (Amberlyst 121 and all Dowex resins). The ion-exchange resins were selected with wide range of %DVB, i.e. from 2% up to 20%. This property, the percentage of cross-linking agent (%DVB), is related to a greater or lesser stiffness of the polymeric

There are three types of sulfonation present: conventionally sulfonated (CS), oversulfonated (OS) and surface-sulfonated (SS). The sulfonation type influences acid capacity, and as a rule oversulfonated resins have a greater number of active sites, when surface sulfonated ones with sulfonic groups only in the outermost layer have very low acid capacity. Important resin properties are specified in the Table 4.

The reaction was carried out over a set of reagents. Levulinic acid (LA) (ACROS ORGANICS, China, Code: 125140010) with purity of 98% and 2% water content and 1-butanol (BuOH) (ACROS ORGANICS, Spain, Code: 232080025) with minimum purity 99.5% and water content under 0.5%.

In the chromatographic calibration the reagents used were 1-butanol and levulinic acid, as specified above. In addition to that, we also used butyl levulinate (SIGMA ALDRICH, Germany, Code:101495705) with purity of 98% and 2% of acid levulinic content. Water (Mili-Q, Millipore)

and dibutyl ether (DBE) (ACROS ORGANICS, Germany, Code:149690010) with 99% purity and 1% of butanol content were also used for said calibration purposes.

The chromatographic carrier gas was helium of 99.998% purity which were supplied by Abelló Linde (Barcelona, Spain).

| Properties | 1-Butanol | Levulinic acid | Butyl levulinate | |
|--|-----------|---------------------------------------|-----------------------------------|--|
| CAS number | 71-36-3 | 123-76-2 | 2052-15-5 | |
| Molecular mass (g/mol) | 74,12 | 116,12 | 172,22 | |
| Density (kg/m ³) | 810 | 1114.7 | 974 | |
| Melting point (°C) | -90 | 33-35 | Not available | |
| Boiling point (ºC, at 760mmHg) | 118 | 245,5 | 237,8 | |
| Flash point (°C) | 35 | 137 | 92 | |
| Flammable limits | 1,4%(v) | Not available | Not available | |
| Hazzard information Hazzard information Flammable Corrosive Irritant/Tox | | 2 2 Corrosive Irritant/Toxic | WHMIS:B3 Combustible liquid | |

Table 3. Compendium of reagent relevant properties

| Catalyst | Туре | Sulfonati on type ^a | Acid capacity (mmol H+/g) ^b | %DV B | d _p c (mm) | Water retentio n (%) ^c | T _{ma} x (°C) c | d _{pore} (nm) d | ∑V _{pore} (cm³/g) ^d | ∑ S _{pore} (m²/g) ^d | ∑V _{sp} e (cm³/g) |
|----------------|-------|-----------------------------------|---|----------|--------------------------|---|-----------------------------------|--------------------------------|--|---|-------------------------------|
| A15 | Macro | CS | 4,81 | 20 | 0,74 | 52-57 | 120 | 12,4 | 0,616 | 192,00 | 0,622 |
| A16 | Macro | CS | 4,80 | 12 | 0,70 | 52-58 | 130 | 15,5 | 0,188 | 46,00 | 1,136 |
| A35 | Macro | OS | 5,32 | 20 | 0,51 | 51-57 | 150 | 12,6 | 0,720 | 199,00 | 0,504 |
| A36 | Macro | OS | 5,40 | 12 | 0,63 | 51-57 | 150 | 14,8 | 0,259 | 68,00 | 1,261 |
| A39 | Macro | CS | 4,82 | 8 | 0,71 | 60-66 | 130 | 15 | 0,155 | 56,00 | 1,643 |
| A46 | Macro | SS | 0,87 | 25 | 0,73 | 26-36 | 120 | 10,3 | 0,470 | 186,00 | 0,190 |
| A121 | Gel | CS | 4,8 | 1 | 0,77 | 74 | 130 | - | - | - | 3,154 |
| Dowex50W x2 | Gel | CS | 4,83 | 2 | 0,499 | 74-82 | 150 | - | - | - | 2,677 |
| Dowex50W x4 | Gel | CS | 4,95 | 4 | 0,499 | 64-72 | 150 | - | - | - | 1,920 |
| Dowex50W x8 | Gel | CS | 4,83 | 8 | 0,499 | 50-58 | 150 | - | - | - | 1,404 |

Table 4. Properties of the acidic resin catalysts used in this study

(a) Conventionally sulfonated (CS), oversulfonated (OS) and surface sulfonated (SS).

(b) Titration against standard base.

(c) Manufacturer data.

(d) Swollen data (in water).

(e) Specific volumen of swollen polymer in water, measured by ISEC technique.

3.2. EXPERIMENTAL SET UP

The experimental set-up consists mainly in a Pyrex round-bottom distilling flask (AFORA reference 66); a Dean-Stark apparatus (VIDRAFOC 6969) and a Dimroth reflux condenser (AFORA 1630) (See figure 6). This experimental set-up allows to operate at atmospheric pressure. The distilling flask has a capacity of one litre (an outer diameter of 132mm and a height of 197mm) with three ground-necked (see figure 5) and one of them it is a neck angle type (the angle-neck type for loading reagents; the central one for an electric temperature probe (CRISON reference 8656); and the vertical neck type is equipped with a Dean-Stark apparatus).

The Dean-Stark apparatus typically consists of vertical cylindrical glass tube, often with a volumetric graduation along its full length and a precision stopcock at its lower end, very much like a burette and allows operation at atmospheric pressure. The burette, which a capacity of 25mL, collects the condensate vapors. Here, the immiscible liquids separate into layers (water below and solvent above it). When their combined volume reaches the level of the side-arm, the upper, less-dense layer will begin to flow back to the reactor while the water layer will remain in the trap. The trap will eventually reach capacity when the level of the water in it reaches the level of the side-arm. At this point, the trap must be drained into the receiving flask. In addition, all ground-glass joints have a 29/32 size.



Figure 5. Distilling flask in oil bath

The flask heat in an oil bath with a magnetic mixing heating set under stirring. The magnetic stirring device (STURAR heat-stir model SB162) that has a metallic resistance and may heat up to 300°C and stir until 1500rpm.

System composition is determined by means of a gas chromatograph (Hewlett Packard HP 6890 GC Series, Germany, Serial #DE00020827) equipped with a thermal conductivity detector (TCD). Samples are collected manually when the experiment ends and are injected in the gas chromatograph (GC).

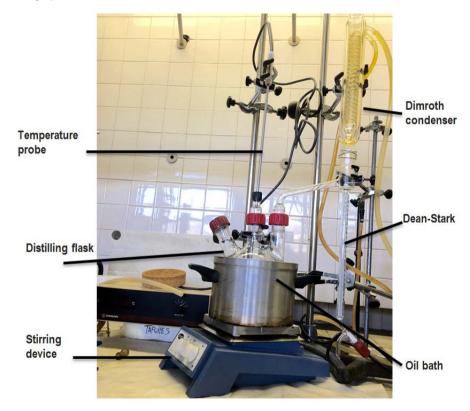


Figure 6. Disassembled experimental set-up

In GC the sample injected is carried through the capillary column by He gas. The column measurements are $20\mu m$ internal diameter, 0.5 μm stationary thickness and 50m length with

He carrier gas and methyl siloxane as stationary phase (HP 190915-001, HP-Pona Methyl Siloxane).

GC runs analysis method BULEVVAL.M. Initially the oven temperature is of 50°C and it will rise 10°C/min reaching 250°C and finally remains at 250°C for 7min. Run time is of 27 min, with an additional 15 min cool-down. System response is calibrated manually.

3.3. EXPERIMENTAL PROCEDURE

3.3.1. Resin pre-treatment

Before being used, all acidic resins have been washed with deionized water, and dried at ambient temperature. Due to the highly hygroscopic nature of the PS-DVB resins a specified procedure was used to eliminate all water content. First, the resins were dried for a minimum of 2 hours in an atmospheric oven at 110°C, followed by drying in a vacuum oven at 110°C and 10mbar overnight. All type resins are used with their commercial size (see table 5).

| Catalyst | d _p (mm) |
|------------|------------------------|
| A15 | 0,74 |
| A16 | 0,70 |
| A35 | 0,51 |
| A36 | 0,63 |
| A39 | 0,71 |
| A46 | 0,73 |
| A121 | 0,77 |
| Dowex50Wx2 | 0,499 |
| Dowex50Wx4 | 0,499 |

Table 5. Manufacture diameter.

3.3.2. Reactor loading

The feed mixture is prepared with the corresponding proportion of LA and BuOH. Reactants are weighed separately and introduced in the reactor through angle neck. The volume of liquid

inside the flask is 400 mL. Following this, the mass of dry catalyst is introduce through angle neck.

3.3.3. Experiment launching

Before startup a several actions have must be done. First, all ground-glass must be checked (joints are well connected) and plug valve of Dean-Stark trap is closed. Secondly, the flask is put in the oil bath in such a way that feed is immersed in oil. Then, the magnetic stirring device is switch on and temperature probe is placed into feed mixture. Temperature and agitation are set 225°C and 200rpm respectively. Finally, the refrigeration of the system is turned on.

The system begins to warm up for about 30-40 min approximately, and then the first drop falls to the burette. At the same time the timer is started (t=0).

3.3.4. Sampling

After the first drop falls, temperature, time, and millilitres of accumulated water are registred first every 5 min, then every 10 min and finally every 20 min until 18mL of water is collected (this volume correspond to water stoichiometric). At that moment, the experiment is stopped, the magnetic stirring device is switched off so, the heating system is shut down too. Samples are collected and weigthed. Initially, a sample is collected before starting the experiment. Then, samples collected are from the aqueous phase of the burette, from the organic phase and from inside the flask. In order to, sample from inside the flask is collected, all ground-glass joints are disconnected. The content of flask is weighted and filtered for the recovery of the catalyst.

3.3.5. Sample analysis

The sample collected is analysed in gas chromatograph. The corresponding method loaded (BULEVVAL.M) in chromatograph and examine the samples. In GC 0.1µL of the sample is needed. The results obtained will be recorded and mole composition was calculated by the calibration curves obtained in previous study [45]. It should be said that all samples are analized three times.

3.3.6. Clean-up

After the completion of the last GC sample analysis, the program Instrument Online is closed on the computer, and the GC is put on low-consumption mode. For this on the GC panel button OVEN the set point temperature is manually changed to 100°C (then press ENTER). Next in the FRONT INLET button, press ON in the Gas Saver option. In the FRONT DET, press OFF in the Temp and Filament options.

As has already been said after collect all samples, all ground-glass joints are disconnected. The flask and Dean-Stark trap are washed with deionized water, ethanol and air dried with synthetic air. Then, all parts of set up are connect again for the next experiment.

3.4. EXPERIMENTAL CONDITIONS

Experiments of 3-5h duration were carried out in atmospheric pressure and in the range of ambient temperature up to 128-129 °C approximately. The screening of catalysts was done working with an excess of BuOH to avoid undesirable humin by-product formation. The molar ratio can be defined as:

$$R_{BuOH}_{/LA} = \frac{n^{\circ}_{BuOH}}{n^{\circ}_{LA}} \left[\frac{mol}{mol}\right] (1)$$

Based on previous work [45], the ratio will be set to $R_{BuOH}_{/LA} = 3$. In this study it was observed that at higher $R_{BuOH}_{/LA}$ the selectivities are better but the conversions worse. Furthermore, in experiments with lower molar ratios, miscibility problems have been detected.

The nominal capacity of the reactor is 1L but because of safety concerns the loading volume of reagents will be 400ml, as previously mentioned.

In order to screen for different catalysts it is decided to always use the same catalyst mass. The mass of dry catalyst used was 2,8g (0,8 wt%) approximately in all screening experiments.

As has already been said, stirring speed and temperature was fixed at 200rpm and 225°C respectively.

During the experiment and thanks to the use of Dean-Stark the water that was formed is eliminated from the reaction mixture. This prevents the formation of two phases (in the case of having enough water) that is undesired fact due to several reasons. First of all aggregate formation severely affects conversion. Secondly, the presence of two separate liquid phases can cause large deviations from an ideal reactor. Besides, the capacity of determining the composition of the system, at different points and at any time, decreases. Finally, another benefit of water removal is the displacement of the equilibrium reaction, thus achieving an almost total conversion of levulinic acid.

4. RESULTS AND DISCUSSION

4.1. CALCULATIONS

The synthesis of butyl levulinate from levulinic acid and BuOH by esterification not involves major by-products. The only relevant by-product that was detected is dibutyl ether (DBE) which obtained by dehydration of BuOH.

In order to infer differences of catalytic activity, parameters as conversion and selectivity are needed. Conversion of reactants (Equation 2) also can be calculated from reaction invariants (Equations 3 and 4) in order to avoid sensibilities in the GC analysis at high acid conversions.

$$X_{j}(t) = \frac{n_{j}^{o} - n_{j}(t)}{n_{j}^{o}(t)} \left[\frac{mol}{mol}\right] (2)$$
$$X_{LA} = \frac{n_{BL}}{n_{BL} + n_{LA}} (3)$$
$$X_{BuOH} = \frac{n_{BL} + 2 \cdot n_{DBE}}{n_{BL} + n_{BuOH} + 2 \cdot n_{DBE}} (4)$$

Because of LA is the limiting reagent, throughout this study the conversion is referred to it.

The number of moles was calculated with the aid of the set of calibration equations obtained from a previous study [45] (See table 6).

On the other hand selectivity of a reagent towards a product is defined as the quotient of the moles of product formed and the total moles of reagent consumed in a given reaction time.

$$S_j^k = \frac{\text{moles of j forming } k}{\text{moles of j consumed}} = \frac{n_k(t)}{n_j^o - n_j(t)} (5)$$

Considering the reaction stoichiometry selectivity can be written as:

$$S_{LA}^{BL} = \frac{n_{BL}}{n_{BL}} (6)$$
$$S_{LA}^{H_2 O} = \frac{n_{H_2 O}}{n_{H_2 O}} (7)$$
$$S_{BuOH}^{BL} = \frac{n_{BL}}{n_{BL+2} \cdot n_{DBE}} (8)$$

$$S_{BuOH}^{DBE} = \frac{2 \cdot n_{DBE}}{n_{BL} + 2 \cdot n_{DBE}} (9)$$

Moreover, yield as the quotient between the moles of product formed and the moles of reagent consumed.

$$Y_j^k = X_j \times S_j^k = \frac{n_k(t)}{n_j^o} \left[\frac{mol}{mol}\right] (10)$$

As the reactions were performed in a discontinuous reactor and the catalyst mass may not be exactly equal, standardized time variable is used:

Standardised time, $\frac{w_{cat} \cdot t}{n_{LA}^o} = \frac{catalyst mass (g) \cdot t(min)}{initial molts of levulinic acid (mol)}$ (11)

Table 6. Calibration equations for all the components of the LA esterification reaction system

| Component | %MASS=f(%AREA) | R ² |
|------------------|--|----------------|
| H ₂ O | %MASS = (0.114 ± 0.110) + (0.877 ± 0.016)·%AREA | 0.9983 |
| BuOH | %MASS = (0.818 ± 0.021) · %AREA + (0.0014 ± 0.0001) · %AREA ² | 0.9999 |
| DBE | %MASS = (1.169 ± 0.036)·%AREA – (0.048 ± 0.013)·%AREA ² | 0.9996 |
| LA | %MASS = (1.700 ± 0.038)·%AREA – (0.017 ± 0.002)·%AREA ² | 0.9997 |
| BL | %MASS = (1.288 ± 0.024)·%AREA − (0.003 ± 0.001)·%AREA ² | 0.9998 |

4.2. DESCRIPTION OF AN EXPERIMENT

As an example of experiment, figure 7 shows the reactor temperature evolution and the amount of water collected in the Dean Star trap throughout experiment 8 with the A15 catalyst. In order to withdraw the water formed the reaction runs at the mixture boiling point. As the pressure is set at that of the lab, the reactor temperature has to increase as the experiment proceeds because it corresponds to the mixture boiling point, which increases with the reaction progresses on increasing BL concentration at the fixed pressure. Experimentally, it was observed that the temperature increased from about 118-120 °C (boiling point of butanol-LA mixture) to a maximum, as can be seen in figure 7 which corresponds to the highest BL

concentration as full conversion for LA is reached. Throughout LA consumtion, the rate of water withdrawal rate could be considered as a rough measured of the BL formation rate. As shown in the figure 7, the temperature first increases and then decreases to a minimum. It is due to the removal of water from the reaction mixture causing a decrease in the boiling point. As regards the evolution of water collected, at the beginning is faster than the end.

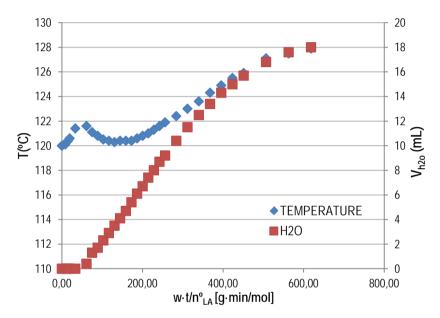


Figure 7. Evolution of reactor temperature and volume of removed water for experiment 8 with A15

Before analyzing the activity of the catalysts, it is important to study the experimental error. In order to do it, experiments were replicated. Three replicates of each type of resin used were made. Amberlyst 35 (A35) as the macro-type catalyst and Dowex 50Wx8 as the gel-type one.

The replicated experiments shows almost perfect overlap in curves of evolution of temperature and volume of water collected vs. normalized time (see figure 8). The calculated conversions, selectivity and yield have an experimental error less than 3-5%.

Moreover, the mass balance must be checked to verify the validity of experiments.

 $m_{t=0} = m_{distilling \ flask}(t) + m_{organic \ phase}(t) + m_{aqueous \ phase}(t)$ (11) In all the experiments, at the end the material balance mass losses between 0-1.5%. This range is accepted as a manipulation error and does not significantly disturb the results.

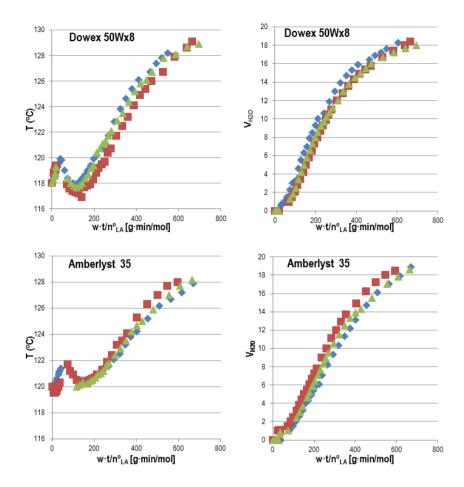


Figure 8. Study of experimental error in the evolution of reaction temperature and volume of removed water in the three replicas of A35 and Dowex 50Wx8

4.3. A SCREENING STUDY OVER ION-EXCHANGE RESINS

This study has attempted to ascertain which catalyst properties have a greater effect on catalyst efficiency for the specific reaction of the esterification of LA with BuOH. To this effect the different relevant properties of PS-DVB acidic resins have been related to selectivity of butyl levulinate.

Through a blank, without catalyst, the reaction achieved a conversion of 51% after 4hours (approximately the same time as with heterogeneous catalysis). In these conditions, the time required for the formation of water to start is twice as long. This indicates that reaction takes place homogeneously without catalyst, although with rater low conversion

Thus, experiments were carried out with several catalysts to later choose the best. First, the evolution of reaction temperature and volume of removed water is presented for different type of catalysts, according to their structure: gel-type (see figure 9) and macroreticular (see figure 10). In general terms, a similar behavior of the evolution of the temperature and the speed of formation of water can be observed between resins of the same type.

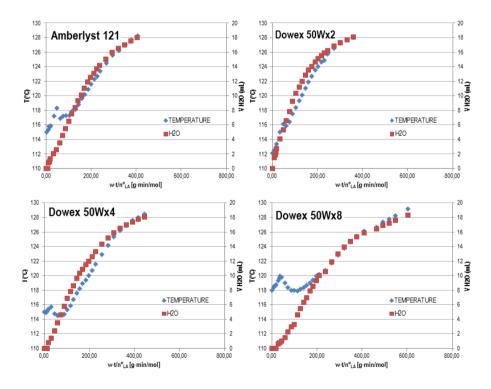


Figure 9. Evolution of reaction temperature and volume of removed water for gel-type resins.

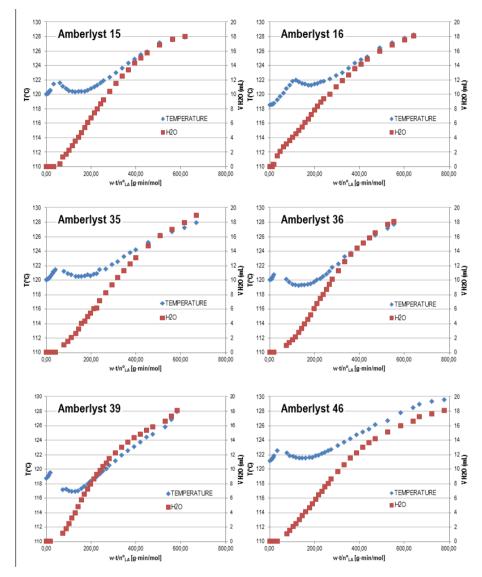


Figure 10. Evolution of reaction temperature and volume of removed water for macroreticular resins.

Then table 7 presents the results (conversion, selective, yield) obtained in the end of experiment from different catalysts. In this table it can be seen how the conversions of LA obtained are 100% or very close. It is the result of shifting the equilibrium point to BL formation through the removal of the formed water during the chemical reaction by distillation and reflux of

the organic phase. Also it is observed that gel type resins obtain total conversion of levulinic acid with lower reaction times than macroporous resins.

| Catalyst | Reaction time (w∙t/n⁰LA) | X _{LA} (%) | $S^{BL}_{BuOH}(\%)$ | $S^{DBE}_{BuOH}(\%)$ | $Y^{BL}_{BuOH}(\%)$ | $Y^{DBE}_{BuOH}(\%)$ |
|----------------------------|--------------------------------|---------------------|---------------------|----------------------|---------------------|----------------------|
| Amberlyst 15 | 618.00 | 99.80 | 96.84 | 3.16 | 35.23 | 1.15 |
| Amberlyst 16 | 642.80 | 100.00 | 97.64 | 5.98 | 35.45 | 2.26 |
| Amberlyst 35 ^a | 642.92 | 99.78 | 94.77 | 5.23 | 36.57 | 2.01 |
| Amberlyst 36 | 554.32 | 99.54 | 94.76 | 5.24 | 36.25 | 2.00 |
| Amberlyst 39 | 585.59 | 100.00 | 96.56 | 3.44 | 36.82 | 1.31 |
| Amberlyst 46 | 779.95 | 100.00 | 99.03 | 0.97 | 35.23 | 0.35 |
| Amberlyst 121 | 405.05 | 100.00 | 97.74 | 2.26 | 36.29 | 0.84 |
| Dowex 50W x 2 | 359.39 | 100.00 | 97.64 | 2.36 | 36.16 | 0.87 |
| Dowex 50W x 4 | 446.22 | 100.00 | 96.96 | 3.04 | 35.57 | 1.11 |
| Dowex 50W x 8 ^a | 654.52 | 100.00 | 94.14 | 5.86 | 33.10 | 2.06 |

Table 7. Conversion, selectivity and yields final values and reaction time for each catalyst

(a) Average value of the three replicas

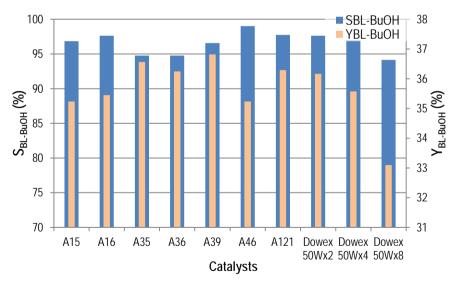


Figure 11. Selectivity and yield of butanol to butyl levulinate

The first criterion for the selection of the best catalyst will be to select the one with the highest yield ($Y_{BL-BuOH}$) because yield value takes account of both the catalyst activity (conversion) and the reaction rate (selectivity).

As the values of $Y_{BL-BuOH}$ are very similar and the associated experimental error is between 3-5%, other criteria for the selection of the best catalyst should be considered. For instance, a high selectivity or a low reaction time.

The results obtained indicate that A39 is the catalyst with which a higher $Y_{BL-BuOH}$ (see figure 11) value is achieved but in terms of selectivity A39 is one of the resins that gives lower values.

On the other hand, regarding selectivity A46 gives a higher selectivity value of butyl levulinate with values of $S_{BuOH}^{BL} = 99.03$ y $S_{BuOH}^{DBE} = 0.97$. This high value is due to the fact that this resin only has active centres on the surface and for this reason does not present steric hindrance to the reaction of levulinic acid. Although A46 has good selectivity and a high yield will not be the best option because the reaction time to obtain these results is very high. From an engineering point of view, a longer reaction time means a higher reactor.

The catalysts with a good yield, selectivity and reaction time ratio are A121 and Dowex 50Wx2. Both are gel type, with a low % DVB and a similar acid capacity. As a rule, gel-type resins have a greater swelling capacity than macroporous ones, which have a rigid permanent structure and higher degree of cross-linking. Thus, this suggests that a good swelling capacity is desirable for a catalyst of the LA esterification reaction.

In order to understand the behavior of the macroporous resins several comparisons are made. A15 and A35, both macroreticular type, have the same % DVB but different acid capacity, being higher for A35 (5.32 mmol H+/g) than for A15 (4.18 mmol H+/g). Thus, it would be expected that for A35 the water formation velocity would be higher. Instead, as can be seen in figure 12, the rate of water formation for A15 is higher (steeper slope) than for A35. This is because A35 is an oversulfonated resin, and hence, has a more rigid polymer structure causing greater difficulties in the access of the reagents in the active centers.

If the selectivity values are analyzed (table 8), A35 has a lower selectivity than A15. This is also due to the greater rigidity of A35.

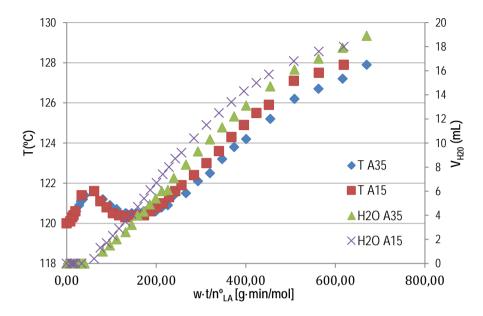


Figure 12. Comparison of behavior between A15 and A35

| Catalyst | A15 | A35 |
|-----------------|-------|-------|
| XLA | 99.80 | 99.78 |
| S_{BuOH}^{BL} | 96.84 | 94.77 |
| Y_{BuOH}^{BL} | 35.23 | 36.57 |

Table 8. Conversion, selectivity and yield for A15 and A35

On the other hand, A16 and A36 are macroporous resins with the same %DVB but with different acidic capacity (4.8 mmol H+/g for A16 and 5.4 mmol H+/g for A36) and different type of sulfonation (A36 is an oversulfonated resin). By analogy with the case of A15 and A35 one would expect a similar behavior but instead it is seen that A16 presents a behavior different than expected (see figure 13). The evolution of the temperature for A16 presents an anomaly in comparison to all the other realized experiments (see figure 10). The peak temperature and the subsequent decrease temperature occur much later than in the other cases. This is because the dry A16 resin has a small pore volume (0.013nm) compared to A36 (0.143nm) or other resins. Therefore, the resin is practically collapsed and will also take longer to reach the specific

volume swollen in an aqueous medium (1.136 cm³/g). For all this, the reaction time for A16 is greater than for A36, and the selectivity is higher for A16 (table 9).

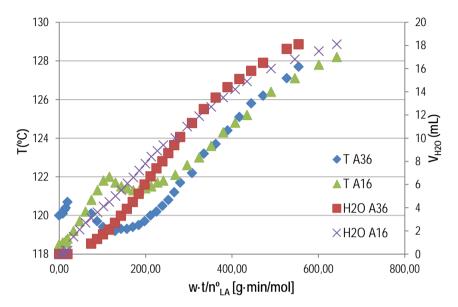


Figure 13. Comparison of behavior between A15 and A35

| Table 9. Conversion, selectivity | and yie | ld for A15 | and A35 |
|----------------------------------|---------|------------|---------|
|----------------------------------|---------|------------|---------|

| Catalyst | A16 | A36 |
|-----------------|--------|-------|
| X_{LA} | 100.00 | 99.54 |
| S_{BuOH}^{BL} | 97.64 | 94.76 |
| Y_{BuOH}^{BL} | 35.45 | 36.25 |

Hence, in the case of having resins with high degrees of cross-linking (DVB> 12%), with a rigid structure, a greater number of active centres (acidic capacity) can not counteract this stiffness effect provided by the degree of Cross-linking. The previous comparisons also help to conclude that the structure of the resins influences much their behaviour. Because only conversion, selectivity, and final-time yield values are available and these are very similar (see figure 14) no conclusions can be drawn about how the structure of the resin affects the reaction. Only a global trend can be drawn.

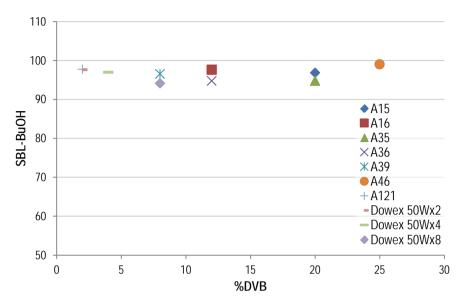


Figure 14. Selectivity of different resins vs. %DVB

Regarding to microporous resins, it is possible to determine a relation between % DVB or accessible active centers in the swollen resin (H^+/V_{sp}) and selectivity or yield. As seen in the table 10 at lower% DVB the selectivity and yield are higher even though the active centers accessible in the swollen resin are less.

This suggests that to a lesser degree of cross-linking the structure is less rigid and consequently the swelling is easier. These results indicate that an important factor for good catalytic efficiency is the molecular access to the active centers. The polar molecules show affinity for the sulfonic groups and their network of hydrogen bonds. When immersed in a polar solvent the polymer catalysts swell due to the interaction of the medium with the catalytic structure. In the swelling state new pores appear, thus creating a large number of accessible active centers. Therefore, a good swellability in solvent (since the water is removed) is desired for the catalysis of the reaction.

| Catalyst | %DVB | H+/V _{sp} | S ^{BL} BuOH | Y^{BL}_{BuOH} |
|-------------|------|--------------------|-------------------------|-----------------|
| A121 | 1 | 1,52 | 97,74 | 36,29 |
| Dowex 50Wx2 | 2 | 1,80 | 97,64 | 36,16 |
| Dowex 50Wx4 | 4 | 2,58 | 96,96 | 35,57 |
| Dowex 50Wx8 | 8 | 3,44 | 94,14 | 33,10 |

Table 10. Comparison between %DVB, H+/V_{sp}, selectivity and yield for gel-type resins.

In the 15 and 16 figures the differences between the evolution of the temperature and the evolution of the volume of collected water can be observed. What would be expected is that at lower% DVB and higher Vsp the temperature at which the first drop is formed was lower and increased more rapidly (due to the faster formation of BL). In addition, at lower% DVB the speed of water production is also expected higher. Finally, the reaction time (to form the 18mL corresponding to the stoichiometric water) is also predicted to be lower. All of the aforementioned about the rigidity offered by the degree of cross-linking agent and the accessibility to the active centers explain all these predictions.

The first observation to be made on the 15 and 16 graphs is the contradictory behavior of the A121 resin evolution. It would expect an initial temperature of A121 lower than that of Dowex 50Wx2, as well as higher temperatures and a higher water collection rate, and this is not obtained. The particle diameter of the Dowex 50Wx2 which is smaller than for the A121, 0.499 mm and 0.77 mm respectively, could explain this contradictory behavior. Then, the surface area of the Dowex 50Wx2 is higher (at the initial time before swelling) than that of the A121 and consequently the contact between solid and solvent is higher in the Dowex 50Wx2.

In addition, the large swelling capacity of A121 causes the centers in the reaction environment on the surface to be far apart, hence the small value of H + / Vsp. As far as the other gel type resins are concerned, they comply with the expected behavior.

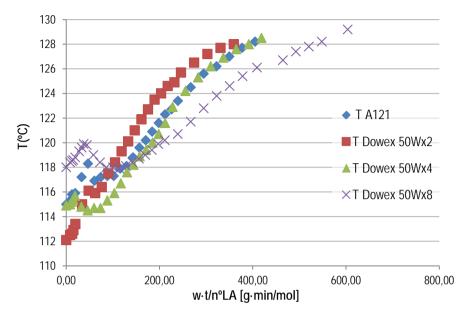


Figure 15. Evolution of reactor temperature for gel-type resins

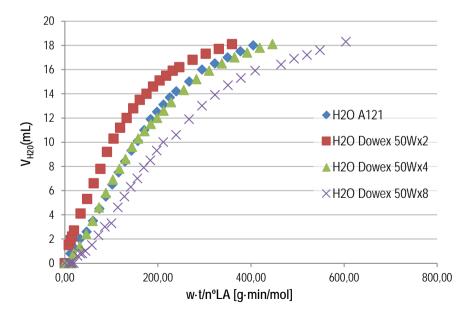


Figure 16. Evolution of volume of removed water for gel-type resin

5. CONCLUSIONS

This study has shown that the esterification of levulinic acid with butanol can take place at atmospheric pressure and in the range of ambient temperature up to 128-129°C, and with simultaneous water removal. This reaction has a total conversion of levulinic acid and high selectivity (around 96%).

The property that has the most control over catalyst efficiency is the resin swelling capacity. Higher swelling capacity leads to better final reaction rates. At low degrees of cross-linking agent (%DVB), the structure is less rigid, the swelling capacity is better and consequently the reaction rates increase. However, the large swelling capacity of resin can cause that the centers in the reaction environment on the surface to be far apart. Therefore, accessible active centers in the swollen resin (H_{+}/V_{sp}), is a parameter which must be analyzed.

Another thing that affects stiffness (and consequently to swelling behavior) is the type of sulfonation. The oversulfonated resins have more rigid structure causing difficulties in the access of the reagents in the active centers.

Gel-type resins (with low degree of cross-linking) show a good selectivity and yield with less reaction time. Of the catalyst employed in this study, Dowex 50Wx2 was found to be the best thanks to has the best relation between selectivity, yiend and reaction time.

In previous study [45], ion-exchange resins have been found to be better option than zeolites [39], lipases [44] and heteropolyacid supported on acid-treated clay montmorillonite [43]. In this study it has been observed that if the water produced by the reaction is eliminated, total conversions can be obtained with a shorter reaction time in comparison with previous work [45]. In contrast, the selectivity is lower and the operational temperature is higher. It can be concluded that ion-exchange resins are quite efficient for the esterification of levulinic acid with butanol for produce butyl levulinate. Moreover, they are cheaper and more readily available commercially.

Nevertheless, futher studies can be applied to acidic ion.exchange resins in order to ascertain whether or not they are suitable for use in an industrial setting. As recommendation, a

possible study on how molar ratio $R_{BuOH/LA}$ decrease affects. As well, studies of the lifespan and reausability of these catalysts would be necessary.

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ACRONYMS

| BL | Butyl levulinate |
|----------------------|--|
| BuOH | 1-butanol |
| CS | Conventionally sulfonated |
| dp | Particle diameter, mm |
| dpore | (macro)pore diameter, mm |
| DBE | Dibutyl ether |
| DVB | Divinylbenzene |
| HMF | Hydroxymethyl-furfural |
| ISEC | Inverse size exclusion chromatography |
| LA | Levulinic acid |
| m _{cat} | Catalyst mass |
| nj | Mol of species j |
| OS | Oversulfonated |
| PS | Polystyrene |
| R _{BuOH/LA} | Molar ratio of butanol versus levulinic acid |
| S ^k j | Selectivity of reagent j towards product k |
| SS | Surface sulfonated |
| t | Time |
| Т | Temperature, °C |
| Vsp | Specific volume of swollen polymer, cm ³ /g |
| Xj | Conversion of reagent j |
| ∑ S pore | Global (macro)pore surface, m ² /g |
| ∑ V pore | Global (macro)pore volume, cm ³ /g |

APPENDICES

APPENDIX 1: EXPERIMENTAL DATA

The data obtained from the monitoring of every experiment undertaken and deemed relevant to

this study have been included in this section.

Table 11. Data corresponding to Experiment 1

| N° Experiment | 1 | m H20 | 3,60 | g | n H20 | 0,20 | mol | Maqueous phase | 3,85 | g |
|---------------|-------|--------|---------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | Blank | m BUOH | 229,51 | g | n BUOH | 3,10 | mol | Morganic phase | 17,05 | g |
| | | m LA | 120,001 | g | n LA | 1,03 | mol | Mdistilling flask | 328.83 | 0 |
| m cat | - | | | | | | | mulsuning nask | 520,05 | 9 |

| AQUEOUS PHASE | | | | ORGANIC PHASE | | | | | REACTOR | | | |
|---------------|----------|-------|----------|---------------|----------|-------|----------|--|---------|---------|---------|----------|
| j | AREA (%) | MASS% | nj (mol) | j | AREA (%) | MASS% | nj (mol) | | j | AREA (% |) MASS% | nj (mol) |
| H2O | 89,67 | 90,82 | 0,19 | H2O | 23,94 | 29,68 | 0,28 | | H2O | 1,56 | 1,48 | 0,27 |
| BuOH | 9,06 | 7,55 | 0,00 | BuOH | 76,06 | 70,32 | 0,16 | | BuOH | 66,51 | 60,60 | 2,69 |
| DBE | 0,03 | 0,03 | 0,00 | DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,00 | 0,00 | 0,00 |
| LA | 0,00 | 0,00 | 0,00 | LA | 0,00 | 0,00 | 0,00 | | LA | 11,14 | 16,81 | 0,48 |
| BL | 1,24 | 1,60 | 0,00 | BL | 0,00 | 0,00 | 0,00 | | BL | 20,79 | 26,78 | 0,51 |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO |
|------------|----------------|--------|----------|-----------|
| XLA (%) | A (%) SBL-BuOH | | YBL-BuOH | YDBE-BuOH |
| 51,78 | 100,00 | 0,00 | 15,98 | 0,00 |

Table 12. Data corresponding to Experiment 2

| N° Experiment | 2 | m H20 | 3,62 | g | n H20 | 0,20 | mol | Maqueous phase | 18,11 | g |
|---------------|--------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | A35 | m BUOH | 229,42 | g | n BUOH | 3,10 | mol | Morganic phase | 9,78 | g |
| | 0.0040 | m LA | 120,99 | g | n LA | 1,04 | mol | mdistilling flask | 322.96 | a |
| mcat | 2.8046 | | | | | | | Thus anny hask | 022,00 | 9 |

| | AQUEOUS | S PHASE | | | | ORGAN | IC PHASE | | REACTOR | | | | |
|------|----------|---------|----------|---|-------------|----------|----------|----------|---------|---------|---------|----------|--|
| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) | j | AREA (% |) MASS% | nj (mol) | |
| H2O | 94,21 | 82,74 | 16,27 | | H2O | 31,26 | 36,96 | 7,27 | H2O | 0,93 | 0,93 | 0,18 | |
| BuOH | 5,76 | 4,76 | 0,46 | B | 3uOH | 67,71 | 61,81 | 2,95 | BuOH | 48,15 | 42,63 | 2,04 | |
| DBE | 0,00 | 0,00 | 0,00 | 1 | DBE | 0,83 | 0,97 | 0,03 | DBE | 1,03 | 1,20 | 0,03 | |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | LA | 0,00 | 0,00 | 0,00 | |
| BL | 0,03 | 0,04 | 0,00 | | BL | 0,20 | 0,26 | 0,01 | BL | 49,90 | 64,27 | 1,32 | |

| CONVERSION | SELEC | TIVITY | RENDIMIENTO | | | | |
|------------|-----------|------------|-------------|------------|--|--|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH | | | |
| 100 | 95,29 | 4,71 | 38,60 | 1,91 | | | |

| Nº Expe | eriment | 3 | | m H | H20 | 3,62 | g | n | H20 | 0,2 | 20 m | ol | | aqueous phase | 18,16 | g |
|---------|--------------|---------|----------|------|------|----------|--------|-----|----------|-----|------|-----|------|------------------|----------|---|
| Cata | Catalyst A35 | | 5 | m Bl | UOH | 230,18 | g | n E | BUOH | 3, | 11 m | | | organic phase | 10,52 | g |
| m | cat | 2.48 | 35 | ml | LA | 120,85 | g | n | LA | 1,(| 04 m | ol | | tilling flask | 323,41 | g |
| | _, | | | | | | | | | | | | | | 020,11 | - |
| | AQUEOU | S PHASE | | 1 L | | ORGAN | IC PHA | ASE | | L | | - 1 | REAC | TOR | | |
| j | AREA (%) | MASS% | nj (mol) | | j. | AREA (%) | MASS | S% | nj (mol) |] [| j | ARE | A (% | MASS% | nj (mol) | |
| H2O | 92,38 | 81,13 | 0,82 | | H2O | 22,78 | 28,2 | 8 | 0,17 |] [| H2O | 2 | ,21 | 2,05 | 0,37 | |
| BuOH | 7,59 | 6,29 | 0,02 | E | BuOH | 75,94 | 70,2 | 0 | 0,10 | | BuOH | 5 | 0,48 | 44,87 | 1,96 | |

1,18

0,00

0,34

SELECTIVITY

0,00

0,00

0,00

SDBE- BuOH

5,00

DBE

LA

BL

YBL- BuOH

35,65

1,01

0,11

46,18

YDBE- BuOH

1,88

RENDIMIENTO

1,18

0,19

59,48

0,03

0,01

1,12

Table 13. Data corresponding to Experiment 3

Table 14. Data corresponding to Experiment 4

| N° Experiment | 4 | m H20 | 3,61 | g | n H20 | 0,20 | mol | Maqueous phase | 18,26 | g |
|---------------|--------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | A35 | m BUOH | 231,06 | g | n BUOH | 3,12 | mol | Morganic phase | 8,71 | g |
| mcat | 2,7185 | m LA | 120,22 | g | n LA | 1,04 | mol | Mdistilling flask | 323,45 | g |

| | AQUEOUS | PHASE | | | ORGAN | IIC PHASE | | REACTOR | | | | |
|------|----------|-------|----------|----|-----------------|-----------|----------|---------|---------|---------|----------|--|
| j | AREA (%) | MASS% | nj (mol) | | AREA (%) | MASS% | nj (mol) | j | AREA (% |) MASS% | nj (mol) | |
| H2O | 88,59 | 77,81 | 0,80 | H2 | 0 22,05 | 27,54 | 0,13 | H2O | 1,27 | 1,23 | 0,22 | |
| BuOH | 7,81 | 6,48 | 0,01 | Bu | DH 76,81 | 71,09 | 0,08 | BuOH | 50,94 | 45,30 | 1,98 | |
| DBE | 0,03 | 0,04 | 0,00 | DE | E 0,85 | 0,99 | 0,00 | DBE | 1,24 | 1,44 | 0,04 | |
| LA | 0,00 | 0,00 | 0,00 | L | A 0,00 | 0,00 | 0,00 | LA | 0,05 | 0,08 | 0,00 | |
| BL | 3,56 | 4,59 | 0,00 | В | L 0,30 | 0,38 | 0,00 | BL | 46,51 | 59,90 | 1,13 | |

| CONVERSION | SELEC | TIVITY | RENDIMIENTO | | | | |
|------------|-----------|------------|-------------------|------------|--|--|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | Y BL- BuOH | YDBE- BuOH | | | |
| 99,80 | 94,02 | 5,98 | 35,45 | 2,26 | | | |

DBE

LA

BL

0,00

0,00

0,03

0,00

0,00

0,04

0,00

0,00

0,00

DBE

LA

BL

CONVERSION

XLA (%)

99,54

1,01

0,00

0,26

SBL- BuOH

95,00

| N° Exp | eriment | 5 | | m | H20 | 3,59 | g | r | n H20 | 0, | 20 n | nol | | iqueous bhase | 17,90 | g |
|--------|-------------------------|---------|------|---------------|------|----------|-----|-------|----------|----|----------|------|----------|------------------|----------|---|
| Cata | alyst | Dowex 5 | 0Wx8 | m l | BUOH | 229,71 | g | n | BUOH | 3, | 10 n | nol | | organic bhase | 10,56 | g |
| m | cat | 2,86 | 30 | n | n LA | 119,44 | g | | n LA | 1, | 03 n | nol | <u> </u> | tilling flask | 321,59 | g |
| | AQUEOUS PHASE | | | ORGANIC PHASE | | | | | | | REAC | | | | | |
| j | j AREA (%) MASS% nj (mo | | | | j | AREA (%) | MAS | SS% | nj (mol) | | j | AR | EA (%) | MASS% | nj (mol) | |
| H2O | 91,31 | 80,19 | 0,80 | 1 | H20 | 30,01 | 35 | .60 | 0,21 | 1 | H2O | 4 | .40 | 3,97 | 0,71 | |
| BuOH | 6,20 | 5,13 | 0,01 | | BuOH | 68,83 | 62 | ,97 | 0,09 | | BuOH | 5 | 1,60 | 45,97 | 1,99 | |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,59 | 0, | 69 | 0,00 | | DBE | | ,90 | 1,06 | 0,03 | |
| LA | 1,78 | 2,93 | 0,00 | | LA | 0,01 | 0, | 02 | 0,00 | | LA | | 00,0 | 0,00 | 0,00 | |
| BL | 0,71 | 0,91 | 0,00 | | BL | 0,55 | 0, | 71 | 0,00 | | BL | 4 | 3,09 | 55,51 | 1,04 | |
| | | | | VER | SION | SE | LEC | rivit | ΓY | | REND | IMIE | NTO | | | |
| | > | | x | LA (9 | 6) | SBL- BuC | н | SDB | E- BuOH | Y | BL- BuOH | YD | BE- BuC | н | | |
| | | | | 100 | | 95,21 | | 4 | 1,79 | : | 33,62 | | 1,69 | | | |

Table 15. Data corresponding to Experiment 5

Table 16. Data corresponding to Experiment 6

| N° Experiment | 6 | m H20 | 3,60 | g | n H20 | 0,20 | mol | Maqueous phase | 17,95 | g |
|------------------|-------------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | Dowex 50Wx8 | m BUOH | 230,08 | g | n BUOH | 3,10 | mol | Morganic phase | 10,69 | g |
| m _{cat} | 2.8485 | m LA | 119,50 | g | n LA | 1,03 | mol | | 321.60 | g |

| | AQUEOUS | PHASE | | | ORGA | NIC PHASE | | | REAC | TOR | |
|------|----------|--------------|----------|----|----------|-----------|----------|------|---------|---------|----------|
| j | AREA (%) | MASS% | nj (mol) | | AREA (%) | MASS% | nj (mol) | j | AREA (% |) MASS% | nj (mol) |
| H2O | 89,51 | 78,61 | 0,78 | H | 27,60 | 32,72 | 0,19 | H2O | 2,61 | 2,40 | 0,43 |
| BuOH | 6,65 | 5,50 | 0,01 | Bu | OH 69,75 | 63,91 | 0,09 | BuOH | 56,53 | 50,72 | 2,20 |
| DBE | 0,00 | 0,00 | 0,00 | DI | BE 0,71 | 0,83 | 0,00 | DBE | 1,11 | 1,30 | 0,03 |
| LA | 1,90 | 3,08 | 0,00 | L | A 0,12 | 0,21 | 0,00 | LA | 0,00 | 0,00 | 0,00 |
| BL | 1,94 | 2,50 | 0,00 | B | L 1,81 | 2,33 | 0,00 | BL | 39,75 | 51,20 | 0,96 |

| CONVERSION | SELEC | TIVITY | REND | DIMIENTO | | |
|------------|-----------|------------|-----------|------------|--|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH | | |
| 100 | 93,72 | 6,28 | 29,68 | 1,99 | | |

| Nº Experiment | 7 | m H20 3,58 g | | n H20 | 0,20 | mol | Maqueous phase | 17,50 | g | |
|---------------|-------------|---------------------|--------|-------|--------|------|-------------------|-------------------|--------|---|
| Catalyst | Dowex 50Wx8 | m BUOH | 229,47 | g | n BUOH | 3,10 | mol | Morganic phase | 11,24 | g |
| mcat | 2,8219 | m LA | 118,77 | g | n LA | 1,02 | mol | | 319,81 | g |

| | AQUEOUS | S PHASE | | | ORGANIC PHASE | | | | REAC | FOR | |
|------|----------|---------|----------|--------|---------------|---------|----------|------|----------|-------|----------|
| j | AREA (%) | MASS% | nj (mol) | j | AREA (%) | MASS% | nj (mol) | j | AREA (%) | MASS% | nj (mol) |
| H2O | 93,79 | 94,82 | 0,92 | H2O | 27,38 | 33,32 | 0,21 | H2O | 2,70 | 2,48 | 0,44 |
| BuOH | 6,11 | 5,05 | 0,01 | BuOH | 71,16 | 65,34 | 0,10 | BuOH | 49,55 | 43,97 | 1,90 |
| DBE | 0,00 | 0,00 | 0,00 | DBE | 0,90 | 1,04 | 0,00 | DBE | 1,35 | 1,57 | 0,04 |
| LA | 0,00 | 0,00 | 0,00 | LA | 0,00 | 0,00 | 0,00 | LA | 0,00 | 0,00 | 0,00 |
| BL | 0,11 | 0,14 | 0,00 | BL | 0,23 | 0,30 | 0,00 | BL | 46,40 | 59,77 | 1,11 |
| | | | | EDSION | SE | ECTIVIT | v | DEND | | | |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO |
|------------|-----------|------------|-----------|------------|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH |
| 100 | 93,49 | 6,51 | 35,98 | 2,50 |

Table 18. Data corresponding data to Experiment 8

| Nº Experiment | 8 | m H20 | 3,58 | g | n H20 | 0,20 | mol | Maqueous phase | 17,55 | g |
|---------------|--------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | A15 | m BUOH | 229,85 | g | n BUOH | 3,10 | mol | Morganic phase | 12,30 | g |
| | | m LA | 118,68 | g | n LA | 1,02 | mol | | 240.44 | a |
| m cat | 2,8488 | | | | | | | Thusaning nusic | 319,41 | 9 |

| | AQUEOUS | PHASE | | [| | ORGAN | IC PHASE | | | REAC | TOR | |
|------|----------|-------|----------|---|------|----------|----------|----------|------|----------|-------|----------|
| j | AREA (%) | MASS% | nj (mol) | [| j | AREA (%) | MASS% | nj (mol) | j | AREA (%) | MASS% | nj (mol) |
| H2O | 88,86 | 78,04 | 0,76 | [| H2O | 24,60 | 30,23 | 0,21 | H2O | 2,35 | 2,17 | 0,39 |
| BuOH | 9,22 | 7,67 | 0,02 | | BuOH | 74,60 | 68,82 | 0,11 | BuOH | I 51,32 | 45,66 | 1,97 |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,61 | 0,72 | 0,00 | DBE | 0,62 | 0,72 | 0,02 |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | LA | 0,05 | 0,08 | 0,00 |
| BL | 1,92 | 2,47 | 0,00 | | BL | 0,18 | 0,23 | 0,00 | BL | 45,62 | 58,76 | 1,09 |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO |
|------------|-----------|------------|-----------|------------|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH |
| 99,80 | 96,84 | 3,16 | 35,23 | 1,15 |

Γ

| N° Exp | eriment | 9 | | m | H20 | 3,60 | g | r | n H20 | 0, | ,20 | mol | | queous hase | 17,62 | g |
|---------------|---------------------------|-------|------|---------------------|-------|-----------------------|------|-----|----------|-------------------|------------------------|--------------|---------|-----------------|-------|---|
| Cata | atalyst A16 | | 6 | m E | BUOH | 230,94 | g | n | BUOH | 3 | ,12 | mol | | organic hase | 11 | g |
| m | cat | 2.85 | 37 | m | LA | LA 119,60 g n LA 1,02 | | ,03 | mol | mdistilling flask | | 321.82 | g | | | |
| AQUEOUS PHASE | | | 1 | | ORGAN | | IASE | : | | | | REAC | IOR | | | |
| i | j AREA (%) MASS% nj (mol) | | | 1 | i | AREA (%) | | SS% | nj (mol) |) | j AREA (%) MASS% nj (n | | | | | |
| H2O | 92,12 | 80,90 | 0,79 | 1 | H2O | 27,07 | 32 | 66 | 0,20 | 1 | H20 |) | 0,95 | 1,23 | 0,22 | |
| BuOH | 6,95 | 5,75 | 0,01 | | BuOH | 71,62 | 65 | 79 | 0,10 | | BuO | н е | 51,94 | 45,30 | 1,98 | |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 1,11 | 1, | 29 | 0,00 | | DBI | : | 0,90 | 1,44 | 0,04 | |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0, | 00 | 0,00 | | LA | | 0,00 | 0,08 | 0,00 | |
| BL | 0,93 | 1,20 | 0,00 | | BL | 0,20 | 0, | 26 | 0,00 | | BL | 4 | 6,20 | 59,90 | 1,13 | |
| | | | CON | VERSION SELECTIVITY | | | | REN | DIMIE | NTO | | | | | | |
| | | | x | LA (9 | 6) | SBL- BuO | н | SDB | E- BuOH | Y | BL- BuO | H Y D | BE- BuO | н | | |

| Table 10 | Data corresp | onding data | to Experiment 9 |
|-----------|--------------|--------------|-----------------|
| Table 17. | Data corresp | ionunny uala | to Experiment 9 |

| Table 20. Data corresponding data to | Experiment 10 |
|--------------------------------------|---------------|
|--------------------------------------|---------------|

94,02

99,80

| N° Experiment | 10 | m H20 | 3,60 | g | n H20 | 0,20 | mol | Maqueous phase | 17,80 | g |
|---------------|--------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | A36 | m BUOH | 229,51 | g | n BUOH | 3,10 | mol | Morganic phase | 10,83 | g |
| mcat | 2,8359 | m LA | 120,00 | g | n LA | 1,03 | mol | Mdistilling flask | 321,19 | g |

5,98

35,45

2,26

| | AQUEOUS PHASE | | | | | ORGAN | IC PHASE | | | REAC | TOR | |
|------|---------------|-------|----------|---|------|----------|----------|----------|------|----------|-------|----------|
| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) | j | AREA (%) | MASS% | nj (mol) |
| H2O | 94,73 | 83,19 | 0,82 | | H2O | 23,39 | 28,95 | 0,17 | H2O | 2,40 | 2,22 | 0,40 |
| BuOH | 5,27 | 4,35 | 0,01 | E | 3uOH | 75,61 | 69,86 | 0,10 | BuOH | 49,70 | 44,11 | 1,91 |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,83 | 0,97 | 0,00 | DBE | 1,08 | 1,26 | 0,03 |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | LA | 0,11 | 0,19 | 0,01 |
| BL | 0,00 | 0,00 | 0,00 | | BL | 0,17 | 0,21 | 0,00 | BL | 46,72 | 60,17 | 1,12 |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO |
|------------|-----------|------------|-------------------|------------|
| XLA (%) | SBL- BuOH | SDBE- BuOH | Y BL- BuOH | YDBE- BuOH |
| 99,54 | 94,76 | 5,24 | 36,25 | 2,00 |

REACTOR

0,85

50,38

0,71

0.00

48,05

YDBE- BuOH

1,31

RENDIMIENTO

H2O

BuOH

DBE

LA

BL

YBL- BuOH

36,82

AREA (%) MASS% nj (mol)

0,86

44,76

0,83

0.00

61,89

0,15

1,94

0,02

0.00

1,15

| N° Experiment | 11 | m H20 | 3,59 | g | n H20 | 0,20 | mol | Maqueous phase | 17,80 | g |
|---------------|--------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | A39 | m BUOH | 229,34 | g | n BUOH | 3,09 | mol | Morganic phase | 10,81 | g |
| Mcat | 2,8445 | m LA | 119,58 | g | n LA | 1,03 | mol | Mdistilling flask | 321,27 | g |

ORGANIC PHASE

24,69

74,50

0,55

0.00

0,26

SBL- BuOH

96,56

i

H2O

BuOH

DBE

LA

BL

CONVERSION

XLA (%) 100 AREA (%) MASS% nj (mol)

30,26

68,76

0,64

0,00

0,34

SELECTIVITY

0,18

0,10

0,00

0,00

0,00

SDBE- BuOH

3,44

Table 21. Data corresponding data to Experiment 11

Table 22. Data corresponding data to Experiment 12

| Catalyst A46 m BUOH 230,27 g n BUOH 3,11 mol | | | |
|--|-------------------|--------|---|
| | Morganic phase | 10,93 | g |
| mcat 2,8643 mLA 118,55 g nLA 1,02 mol | | 320.93 | q |

| | AQUEOUS PHASE | | | | | ORGANIC PHASE | | | | | REACTOR | | | | |
|------|---------------|-------|----------|---|------|---------------|-------|----------|---|-----|----------|---------|----------|--|--|
| j | AREA (%) | MASS% | nj (mol) | [| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) |) MASS% | nj (mol) | | |
| H2O | 90,49 | 79,47 | 0,77 | | H2O | 26,68 | 32,39 | 0,20 | H | 120 | 3,53 | 3,21 | 0,57 | | |
| BuOH | 8,54 | 7,09 | 0,02 | | BuOH | 72,85 | 67,03 | 0,10 | B | uOH | 52,56 | 46,86 | 2,03 | | |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,20 | 0,23 | 0,00 | |)BE | 0,19 | 0,22 | 0,01 | | |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | 1 | LA | 0,00 | 0,00 | 0,00 | | |
| BL | 0,97 | 1,25 | 0,00 | | BL | 0,28 | 0,35 | 0,00 | | BL | 46,23 | 59,54 | 1,11 | | |
| | | | | | | | | | | | | | | | |

| CONVERSION | ONVERSION SELECTIVITY | | | IMIENTO | |
|------------|-----------------------|------------|-------------------|------------|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | Y BL- BuOH | YDBE- BuOH | |
| 100 | 99,03 | 0,97 | 35,23 | 0,35 | |

AQUEOUS PHASE

94,84

5,16

0,00

0.00

0,00

i

H2O

BuOH

DBE

LA

BL

AREA (%) MASS% nj (mol)

83,29

4,26

0,00

0.00

0,00

0,82

0,01

0,00

0.00

0,00

| N° Experiment | 13 | m H20 | 3,60 | g | n H20 | 0,20 | mol | Maqueous phase | 17,66 | g |
|---------------|--------|-------------------|--------------|---|--------|------|---------------------------|-------------------|--------|---|
| Catalyst | A121 | m BUOH | 230,09 | g | n BUOH | 3,10 | mol | Morganic phase | 10,97 | g |
| mcat | 2.8450 | m LA | 119,89 | g | n LA | 1,03 | mol | | 322.51 | g |
| | | | | | | | | | | |
| j AREA (%) |) | ORGAN AREA (%) | IC PH MAS | | | | REACTOR EA (%) MASS% I | nj (mol) | | |

| Table 23. Data corre | esponding data to | Experiment 13 |
|----------------------|-------------------|---------------|
|----------------------|-------------------|---------------|

| | AQUEOUS | S PHASE | | ORGANIC PHASE | | | | | | | REAC | TOR | |
|------|----------|---------|----------|---------------|------|----------|---------|----------|---|------|----------|-------|----------|
| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) |
| H2O | 92,55 | 92,55 | 0,80 | | H2O | 24,72 | 30,37 | 0,19 | Γ | H2O | 2,90 | 2,66 | 0,48 |
| BuOH | 7,13 | 7,13 | 0,01 | | BuOH | 74,72 | 68,95 | 0,10 | | BuOH | 50,21 | 44,60 | 1,94 |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,41 | 0,48 | 0,00 | | DBE | 0,45 | 0,52 | 0,01 |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 |
| BL | 0,32 | 0,32 | 0,00 | | BL | 0,16 | 0,20 | 0,00 | | BL | 46,44 | 59,82 | 1,12 |
| | | | CONV | | SION | 95 | ECTIVIT | v | | | MIENTO | | |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO | |
|------------|-----------|------------|-----------|------------|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH | |
| 100,00 | 97,74 | 2,26 | 36,29 | 0,84 | |

Table 24. Data corresponding data to Experiment 14

| N° Experiment | 14 | m H20 | 3,60 | g | n H20 | 0,20 | mol | Maqueous phase | 17,80 | g |
|---------------|-------------|--------|--------|---|--------|------|-----|-------------------|--------|---|
| Catalyst | Dowex 50Wx2 | m BUOH | 230,02 | g | n BUOH | 3,10 | mol | Morganic phase | 11,07 | g |
| mcat | 2,9208 | m LA | 119,85 | g | n LA | 1,03 | mol | Mdistilling flask | 321,19 | g |

| | AQUEOUS PHASE | | | | | ORGAN | IC PHASE | | REACTOR | | | | |
|------|---------------|-------|----------|--|------|----------|----------|----------|---------|---------|---------|----------|--|
| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) | j | AREA (% |) MASS% | nj (mol) | |
| H2O | 90,47 | 79,46 | 0,79 | | H2O | 24,23 | 25,18 | 0,15 | H2O | 0,70 | 0,72 | 0,13 | |
| BuOH | 8,07 | 6,70 | 0,02 | | BuOH | 74,10 | 72,02 | 0,11 | BuOH | I 51,41 | 45,76 | 1,98 | |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,38 | 2,53 | 0,00 | DBE | 0,48 | 0,56 | 0,01 | |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | LA | 0,00 | 0,00 | 0,00 | |
| BL | 1,46 | 1,88 | 0,00 | | BL | 0,21 | 0,27 | 0,00 | BL | 47,41 | 61,07 | 1,14 | |

| CONVERSION | SELEC | TIVITY | REND | IMIENTO |
|------------|-----------|------------|-----------|------------|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH |
| 100,00 | 97,64 | 2,36 | 36,16 | 0,87 |

| N° Experiment | 15 | m H20 | 3,63 | g | n H20 | 0,20 | mol | Maqueous phase | 17,80 | g |
|---------------|-------------|--------|--------|-----|--------|------|---------|---------------------------|--------|---|
| Catalyst | Dowex 50Wx4 | m BUOH | 229,76 | g | n BUOH | | mol | Morganic phase | 10,96 | g |
| m cat | 2,8368 | m LA | 121,07 | g | n LA | 1,04 | mol | M distilling flask | 323,29 | g |
| | | ORGAN | C PH | ASE | | | REACTOR | | | |

| Table 25. Data corresponding to Experiment 15 | |
|---|--|
| | |

| AQUEOUS PHASE | | | | [| ORGANIC PHASE | | | | REACTOR | | | | |
|---------------|----------|-------|----------|---|---------------|----------|-------|----------|---------|------|----------|-------|----------|
| j | AREA (%) | MASS% | nj (mol) | [| j | AREA (%) | MASS% | nj (mol) | | j | AREA (%) | MASS% | nj (mol) |
| H2O | 94,03 | 82,58 | 0,82 | [| H2O | 26,40 | 32,08 | 0,20 | F | H2O | 1,04 | 1,02 | 0,18 |
| BuOH | 5,76 | 4,76 | 0,01 | | BuOH | 72,93 | 67,12 | 0,10 | B | BuOH | 51,70 | 46,03 | 2,01 |
| DBE | 0,00 | 0,00 | 0,00 | | DBE | 0,39 | 0,45 | 0,00 | | DBE | 0,61 | 0,71 | 0,02 |
| LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 | | LA | 0,00 | 0,00 | 0,00 |
| BL | 0,21 | 0,27 | 0,00 | | BL | 0,28 | 0,36 | 0,00 | | BL | 46,65 | 60,09 | 1,13 |
| | | | | | | | | | | | | | |

| CONVERSION | SELEC | TIVITY | RENDIMIENTO | | | |
|------------|-----------|------------|-------------|------------|--|--|
| XLA (%) | SBL- BuOH | SDBE- BuOH | YBL- BuOH | YDBE- BuOH | | |
| 100,00 | 96,96 | 3,04 | 35,57 | 1,11 | | |