



Treball Final de Grau

Etherification of furfuryl alcohol to butyl levulinate, an oxygenate of second generation

Eterificació de l'alcohol furfurílic a butil levulinat, un oxigenat de segona generació

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La nostra recompensa es troba en l'esforç i no en el resultat. Un resultat total és una victòria completa.

Mahatma Gandhi

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REPORT

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1. SUMMARY

Governments have established ambitious targets to replace an important fraction of fossil fuels with renewable sources within next 20 years. The EU directives of the Quality & Composition of the fuels expect that the oxygen content of automobile fuels has to be at least 15% at 2020. Consequently, the reformulation of gasoline and diesel oil is needed. Recently, alkyl levulinates, which are bio-based chemicals, have been proposed as gasoline and diesel additives. Butyl levulinate (BL) is an oxygenate of second generation that can be used as diesel additive because it improves the lubricity, conductivity and cold flow properties of the diesel fuel into which it is blended and leads to cleaner combustion processes with fewer smoke or NO_x emissions. It can be synthesized from furfuryl alcohol (FA) through acid-catalyzed alcoholysis. Several authors presented efficient catalytic strategies of the reaction using solid acid catalysts. However, the catalysis by means of acid ion exchange resins has been barely investigated.

The experiments performed in this work prove that ion exchange resins can be used in the etherification of FA with butanol to obtain BL at 100°C. The reaction has two steps: conversion of FA to an intermediate which was always complete within 4h and the conversion of the intermediate to butyl levulinate which was more complex. The most relevant byproducts were oligomeric substances indicating that polymerization of FA also took place. The catalyst with the best performance regarding selectivity and mole production was Amberlyst 39 with 67% of selectivity. Besides, it has been found that there is an optimal between accessibility of the active sites of the resin and their acid capacity. The influence of temperature was studied and the selectivity to BL decreased with temperatures lower than 100°C. Finally, the initial molar ratio effect was also investigated and it was found that selectivity to BL dropped with the increase in initial FA concentration implying that the reaction of polymerization was promoted.

Keywords: Butyl levulinate, etherification reaction, ion-exchange resins, furfuryl alcohol, butanol.

2. RESUM

Els governs han establert objectius ambiciosos per a substituir una fracció important de combustibles fòssils per fonts renovables en menys de 20 anys. Les directives de la UE sobre la qualitat i composició dels combustibles preveuen que el contingut d'oxigen als combustibles d'automòbil ha de ser, com a mínim, del 15% al 2020. S'imposa, en conseqüència, la reformulació de gasolines i gasoils per tal de fer possible el contingut estipulat. Recentment, els alquil levulinats, els quals provenen de la biomassa, han estat proposats com a additius per la gasolina i el dièsel. El butil levulinat (BL) és un oxigenat de segona generació que pot ser usat com a additiu pel dièsel perquè millora la lubricitat, conductivitat i les propietats en fred del dièsel en el qual està barrejat. A més, redueix la emissió de partícules com el NO_x. El BL pot ser sintetitzat a partir de l'alcohol furfúric (FA) mitjançant la alcohol·lisis per catàlisi àcida. Varis autors han presentat estratègies per la reacció mitjançant catalitzadors sòlids. Tot i així, la reacció no ha sigut quasi investigada mitjançant resines àcides de bescanvi iònic.

Els experiments realitzats en aquest treball demostren que les resines de bescanvi iònic poden ser utilitzades en la eterificació del FA amb butanol per obtenir BL a 100°C. La reacció té dos passos: la conversió del FA a l'intermediari, la qual sempre és completa en menys de 4h, i la conversió del intermediari al BL, pas molt més lent. Els subproductes més rellevants són substàncies oligomèriques, indicant que la polimerització del FA hi té lloc. El catalitzador amb millor rendiment va ser el Amberlyst 39 en quan a selectivitat i mols de producte produïts, amb una selectivitat del 67%. A més, s'ha trobat que hi ha un òptim en quan a accessibilitat dels centres actius de la resina i la capacitat àcida. La influència de la temperatura va ser estudiada i s'ha trobat que la selectivitat decreix amb la temperatura. Finalment, la raó molar inicial també ha sigut estudiada i s'ha trobat que la selectivitat empitjora amb l'increment de la concentració inicial del FA, implicant que la reacció de polimerització és afavorida.

Paraules clau: butil levulinat, reacció d'eterificació, resines de bescanvi iònic, furfúric alcohol, butanol.

3. INTRODUCTION

3.1. BIOMASS AS A SUBSTITUTE FOR PETROLEUM IN THE PRODUCTION OF FUELS

Nowadays fossil fuels are the primary source of energy, chemicals and materials for our modern society. Petroleum, natural gas and coal supply most of the energy consumed worldwide and their massive utilization has allowed our society to reach high levels of development in the past century. Transportation sector worldwide is responsible for 60% of the world oil consumption (1). However, these natural resources are highly contaminant, unevenly distributed around the world and they are in diminishing supply. These important concerns have stimulated the search for new well-distributed and non-contaminant renewable sources of energy such as solar, wind, hydroelectric power, geothermal activity and biomass. This shift toward a renewable-based economy is currently spurred by governments which have established ambitious targets to replace an important fraction of fossil fuels with renewable sources within next 20 years (2). The improvement of energy efficiency is a key objective of the European Community and the aim is to achieve a 20% improvement in energy efficiency by 2020 by the development of energy from renewable sources (3).

In this sense, biomass is considered the only sustainable source of organic carbon currently available on earth and, consequently, it is the ideal substitute for petroleum in the production of fuels, chemicals and carbon-based materials (4). Biomass-based fuels are known as biofuels and offer many advantages over petroleum-based fuels: biofuels are easily available from common biomass sources, they have a considerable environmentally friendly potential as a sustainable energy source, can contribute to increase the agricultural income for rural poor in developing countries, they are biodegradable and contribute to sustainability (5). Large-scale production of biofuels offers an opportunity for certain developing countries to reduce their dependence on oil imports and they are becoming cost-wise competitive with fossil fuels (6).

The biofuels most widely used today are bioethanol and biodiesel which are obtained from edible biomass sources. Bioethanol is produced by fermenting plant-derived sugars to ethanol such as sugar cane, corn, wheat and sugar beet. Biodiesel is produced by transesterification

from vegetable oils as rapeseed oil and palm oil. The simple and well-known technologies for their production and the partial compatibility of these biofuels with existing transportation infrastructure of diesel and gasoline have contributed to the rapid expansion of biofuels (7). However, biofuels possess important drawbacks: bioethanol has to be used in form of dilute mixtures with gasoline, it contains less energy density than gasoline, its corrosiveness, lower vapor pressure and it induces water absorption in the fuel when added to gasoline (8), (9). Besides, first generation biofuels are obtained from edible biomass, thereby impacting the supply of food for humans and animals and food prices could rise if too much biofuel is made from these crops. Furthermore, their availability is not sufficient to satisfy the demands presently met by petroleum (10). These important limitations of conventional biofuels, together with new trends in legislation, have stimulated the research for new technologies that allow high energy-density, infrastructure-compatible fuels which could be easily implemented in the existing hydrocarbon-based transportation infrastructure and more importantly, not using edible-biomass for their production. This new fuels are called second generation biofuels (2GBs) or advanced biofuels and its goal is to extend the amount of biofuel that can be produced sustainably by using biomass consisting of the residual non-food parts of current crops, such as stems, leaves and husks that are left behind once the food crop has been extracted, as well as other crops that are not used for food purposes.

The best source for advanced biofuels is lignocellulose, since it is the most abundant form of biomass in the planet and it is widely and easily available as waste biomass, as conventional wood and as fast rotation crops. However, lignocellulose is a complex biomass resource that must be first processed into simpler compounds (so-called platform molecules) which can be subsequently transformed into a number of valuable products. The selection of these platform molecules was initially performed by the US Department of Energy (DOE) and include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethylfurfural) and acids (succinic, levulinic, lactic acids). Second generation biofuels are not yet produced commercially but a considerable number of pilot and demonstration plants have been announced or set up in recent years (11). The reason they are taking so long is that 2GBs are not currently cost competitive with 1GBs and fossil fuels, even given the extra financial incentives (12). That's because the process of releasing the sugars economically and in high yields is difficult and it has been estimated that this stage can contribute 40-45% of the total biofuel cost (13). The most reactive sugar polymers in the plant are protected by the highly

unreactive lignin fraction. For that reason, an effective pretreatment step is necessary to break down the refractory lignin seal, disrupt the crystalline structure of the cellulose, and increase the surface area of the biomass.

Once fermentable sugars can be isolated from lignocellulosic material at cost of approximately 0,22\$/kg then biorefineries could be commercially viable(14). Furthermore, platform molecules are highly oxygenated compounds and their conversion into liquid hydrocarbon fuels requires oxygen removal reactions (i.e. dehydration, hydrogenolysis, hydrogenation, decarbonylation/decarboxylation, etc.). However, research in biorefining is advancing rapidly and commercial facilities are expected in the near-term.

Another interesting use of platform molecules in the field of renewable biofuels is their transformation into fuel additives. In general, a fuel additive is a chemical compound that is added to fuels in order to accomplish a variety of functions such as helping to maintain the cleanliness of engine parts, temper fuel gelling and nozzle choking, prevent corrosion and incomplete combustion of the fuel, improve fuel economy and reduce greenhouse gas and particulate emissions (15). Since the introduction of reformulated and oxygenated gasoline in 1990, an important research on fuel additives has been developed in order to meet the ever more severe emission specifications of vapor pressure, sulfur, olefins, soot and smog reduction.

Thus, the transformation of platform molecules into hydrocarbon biofuels or fuel additives is cost competitive with petrochemical technologies and for that is required the development of new approaches that simplify processing by reducing the number of reactions, purification and isolation processes.

3.2. CHEMICAL ROUTES FOR THE TRANSFORMATION OF BIOMASS INTO BIOFUELS

A variety of chemistries and processes can be applied to convert lignocellulosic materials to valuable fuels and chemicals. For instance, thermal reactions are exploited in the pyrolysis of biomass to charcoal, oil and/or gases and its gasification to synthesis gas and/or hydrogen. All these products can be used without further processing to provide heat or power. Moreover, the synthesis gas and the pyrolysis oil can also be converted to high quality liquid fuels. Alternatively, lignocellulose can also be hydrolyzed to liberate the lignin and depolymerize the polysaccharides to sugars. Then the sugars, xylose, glucose and fructose, can subsequently be converted to a variety of fuel and chemical components via chemical or biological routes.

Furfural (FUR) and 5-hydroxymethylfurfural (HMF) are considered excellent platform molecules which can be converted into fuel additives (16). They are produced from the dehydration of pentoses (xylose) and hexoses (glucose), respectively using homogeneous and heterogeneous acid catalysts (17), (18). Furfural is identified as one of the top 30 high-value bio-based chemicals (19). The first commercial process for FUR production was achieved in 1921 by Aquarker Oats (20) by using aqueous sulfuric acid in a batch mode. Ionic liquids have also been tested for the production of furfurals (21). Commercial furfural production is currently carried out by acid catalysts in a batch or continuous reactor.

Furfural and HMF are not attractive fuel components because of their melting point and stability; however, they can be used as starting materials to produce a variety of high value added furan derivatives as well as to produce liquid alkanes and fuel additives. Furfuryl alcohol (FA) is the most important furfural derivative that is used in the production of furan resins and alkyl levulinates. Levulinic acid (LA) and furan are the other important furan derivatives that can be produced from furfural.

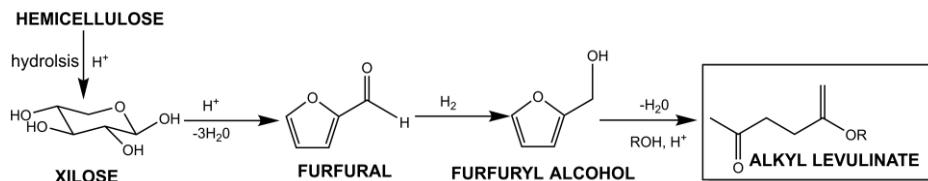


Figure 1. Reaction pathway for the conversion of hemicellulose into levulinate ester.

Alkyl levulinates were identified already in 2004 as one of the top 10 biorefinery candidates (19) due to their specific physicochemical properties. Indeed, they could find applications as specialty chemicals and in the chemical and petrochemical industries (22). First reports concerning alkyl levulinates date from the 19th century. However, the recent interest for biomass transformation and the discovery of new applications for bio-based products have considerably increased this literature. Consequently, the majority of the publications have appeared during the last five years. Levulinate esters, like methyl levulinate (ML), ethyl levulinate (EL) and butyl levulinate (BL) are a kind of short chain fatty esters with their properties similar to the biodiesel fatty acid methyl esters (FAME). These esters are suitable to be used as additives for gasoline and diesel of transportation fuels, which have manifold excellent performances, such as non-

toxic, high lubricity, flashpoint stability and better flow properties under cold condition (23). On the other hand, levulinate esters also can either be used in the flavoring and fragrance industries or as substrates for various kinds of condensation and addition reactions at the ester and keto groups in organic chemistry for the synthesis of different chemicals and drugs (24), (25), (26).

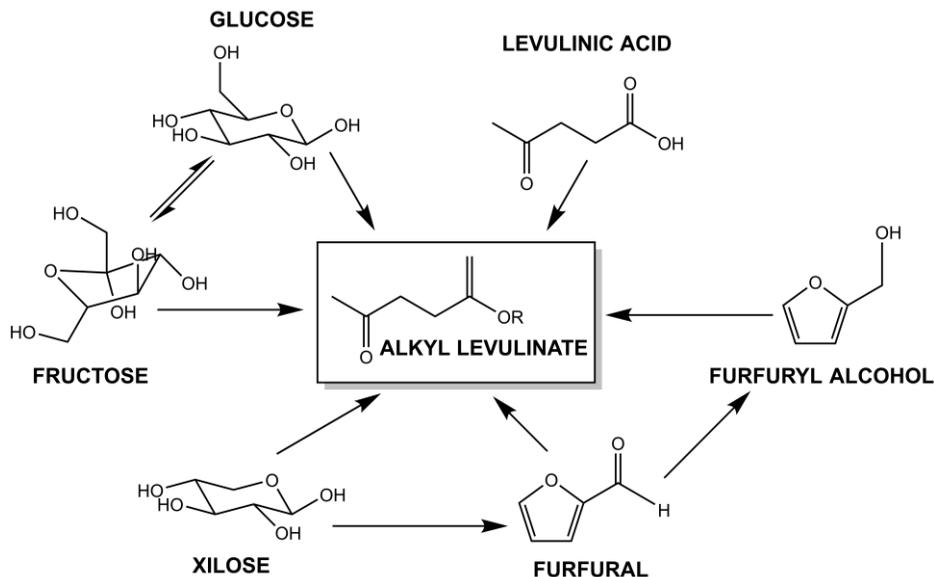


Figure 2. Different routes from the synthesis of alkyl levulinates.

Alkyl levulinates can be synthesized from acid levulinic and furfuryl alcohol. They are also obtained directly from lignocellulosic resources with limited yields (27). Industrially, levulinate esters were mainly obtained through esterification of levulinic acid with alkyl alcohols in the presence of sulfuric acid that leads to a high yield of products (28). However, LA as raw material for this purpose is of high cost. Direct production of levulinate esters from biomass is also possible by the acid-catalyzed reaction with alcohols, which is more attractive, has yet to be developed. One-pot system for the direct conversion was developed (29) but it was using sulfuric acid, that causes equipment corrosion and it is not a green catalyst. It is extremely important and necessary to develop an environmentally benign catalyst with high activity for the production of levulinate esters.

Levulinic acid esters can be also synthesized from furfuryl alcohol (FA) through acid-catalyzed alcoholysis (30), (31), (32). To develop an economically feasible process for future industrial applications, the identification of a proper acid catalyst for the conversion of FA to alkyl levulinates is of great importance. Traditionally, dilute mineral acids such as H₂SO₄ and HCl have been employed as effective catalysts in this reaction. However, it was found that FA readily polymerizes to form oligomeric products in the presence of dilute mineral acids, thus giving only to a moderate yield of alkyl levulinates. Besides, the use of dilute mineral acids usually leads to objectionable corrosion of the equipment and environmental pollution (33), (34).

Recently, solid acid catalysts have attracted considerable interests as heterogeneous catalysts, which can overcome the above mentioned disadvantages of the inorganic acid in acid catalysis. Presently, commercially available heterogeneous acid catalysts mainly include ion-exchange resin, zeolite, sulfated metal oxide, and inorganic metal salt. Table 1 shows the state of art of the BL synthesis with different catalysts. It was found that in the production of EL, macroporous resins are more active in the producing than acidic zeolites (35). Later, several authors presented efficient catalytic strategies of the conversion of FA with butanol (BuOH) into alkyl levulinates using acid catalysts such as organic-inorganic hybrid material (36), sulfonic acid functionalized ionic liquids (37), (38) and propylsulfonic acid-functionalized mesoporous silica (39). It should be pointed out that these catalysts are costly due to their complex synthetic technique. For this reason, the production of BL through alcoholysis of FA should be studied on catalysts whose production is cheaper.

Table 1. State of art of the BL synthesis from the alcoholysis of FA.

Ref	year	System	Catalyst	t(h)	Yield (%)	R _{BuOH/FA} (mol/mol)
(39)	2014	Heterogeneous	SBA15	4	96%	>30
(36)	2011	Heterogeneous	organic-inorganic hybrid	12	93%	48
(40)	2013	Heterogeneous	A15 and AL-TUD-1(21)	24	72% and 60%	-
(41)	2014	Homogeneous	sulfuric acid(<0,01M)	8	97	-

3.3. APPLICATIONS OF BUTIL LEVULINATE

Butyl levulinate is an FDA-approved (Food and Drug Administration) flavor and fragrance that also finds application in the solvent and plasticizer sectors (39). Only very recently more focused studies have appeared on their properties of new applications as an oxygenate of second generation. Oxygenate is a term commonly referred to a group of chemical compounds that raise the oxygen content of gasoline to help it burn more completely, reducing harmful tailpipe emissions from motor vehicles.

As FUR, LA, ML and EL, butyl levulinate has been proposed as a **green solvent** (42) due to its physicochemical characteristics (43). Properties like surface tension, density, refractive index, viscosity, vapor pressure and static permittivity were evaluated at temperatures from 5 to 65°C. Levulinates were shown to be more compressible due to internal organization of molecules and to possess much lower vapor pressures compared to usual solvents (1,56 kPa for BL), which makes it easier to meet the required minimum temperatures for combustion. On the basis of this, BL has been patented for metallic surface degreasing processes (43).

Other possible application of alkyl levulinates concern the use as additives to conventional diesel (44) or gasoline (45) fuels, gas oil-based fuels (46) and even biodiesels (44) due to greater solubility in the hydrocarbonated fraction concomitant to lower water solubility (47). However, a compromise between above properties and other requirements like density, viscosity, boiling flash and cloud points of the final mixture has to be found (45).

The addition ratio (alkyl levulinate/fuel) falls in the range of 0,5-20 vol. %. The advantage of introducing alkyl levulinates in transportation fuel mixtures can be, for example, the substitution of conventional additives (ethanol, methyl-tert-butylether) by biomass-derived products (45). Besides, BL improves the lubricity and conductivity of the diesel fuel into which it is blend (47) and it has been shown that the presence of these oxygenated compound leads to cleaner combustion processes with fewer smoke or NO_x (nitrogen oxides) emissions (48).

Another reported advantage is that BL cause lower degradations to some elastomeric constituents of the engine (swelling) than other additives (46). A computer based study (53) confirmed that BL possesses characteristics like density (1.091), viscosity (4,5 cSt), and cetane number, which is 48, close to those of diesel and can be acceptable for such application. However, although this compound improved the lubricity and conductivity of fuel, their relative low cetane number and poor diesel solubility would limit their use for this application.

3.4. ACIDIC ION-EXCHANGE RESINS

The use of ion exchange resins (IER) in such applications as solvent purification and catalysis of organic reactions has attracted increasing attention in the past few years (49). Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930.s. Few years later resins consisting of polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed.

An ion-exchange resin is a kind of synthetic resin that is manufactured by introducing functional groups such as sulfonic acid and quaternary ammonium into three-dimensionally crosslinked polymer matrix. The typical polymer matrix is a co-polymer made from two kinds of monomers, one is styrene and the other is divinylbenzene (DVB) and the standard industrial products are spherical shaped, the diameters of which are 300-1180 μm . These crosslinked polymers are synthesized from styrene and DVB that has two vinyl groups at the same benzene ring through suspension polymerization in water.



Figure 3. Image of an ion exchange resin.

The density of crosslink varies in accordance with the ratio of DVB versus styrene. That is, when we increase the amount of DVB the chain branching increases in the polymer matrix of the IER and thus it has a dense network which enhance the stiffness and chemical stability of resins. When we decrease the amount of DVB, on the other hand, the network becomes sparse. In this way, DVB play the connecting knots of the styrene polymer chains and so they are called “crosslinking agent”. Then exist “micropores” in the wet IERs and ion exchanges do occur within such micropores where ions could diffuse. The micropores become smaller in accordance with

the higher crosslinkage, and it becomes more difficult for ions to diffuse in the micropores. Although ion diffusion becomes easy in the low crosslinkage, micropores of which are large, it comes hard to handle them because of their softness and weakness as resin-materials when their crosslinkage is too low. The standard crosslinkage might be around 8%.

Based on their structure, S-DVB resins can be divided into two main classes:

- **Microporous** or gel-type resins: generally low crosslinked (1-8% DVB), they are solids with low surface areas in dry state ($< 1 \text{ m}^2/\text{g}$), which do not have permanent porosity, but swell to some extent in polar solvents. Their pores, referred to as micropores, are very small (0,7 to 2 nm), and only appear in the swollen state. Just like the surface area, the porosity decreases on increasing % DVB, so that in microporous resins with more than 8% DVB only the external surface is accessible.
- **Macroreticular** resins: they are obtained when the polymerization of styrene is carried out with 5-60% DVB and in the presence of porogens. During the polymerization, phase separation occurs and, after the extraction of the diluent and drying, permanent pores or holes of various sizes are created. When the amount of DVB is increased, the surface area increases unlike microporous resins. Macroreticular resins have far larger surface areas than gel-type ones. Furthermore, a very high DVB is related to having very few styrene monomers that can be sulphonated and thus a small number of active sites.

The catalytic behavior of ion-exchange resins depends on their structure and on the number of accessible active sites. Therefore, the pore structure and the ability to swell of the catalyst have a great importance because they affect directly the diffusion of reactants and products, and consequently, they affect the activity and the selectivity of the resin. Moreover, the catalytic behavior is also influenced by the acidic strength of the resin.

The swelling properties of gel-type resins are also dependent on the crosslinking degree. The swelling ratio increases as the amount of DVB decreases. The situation is more complex for the macroreticular resins, which involve a polymer phase and the free space of the pores. In the presence of a polar medium, the pores are filled by the liquid and the polymer phase may be swollen to a varying extent.

Acid capacity shows the number of functional groups that are accessible in given conditions. It is usually expressed as equivalents per mass or volume of resin and it is commonly determined by titration against standard base.

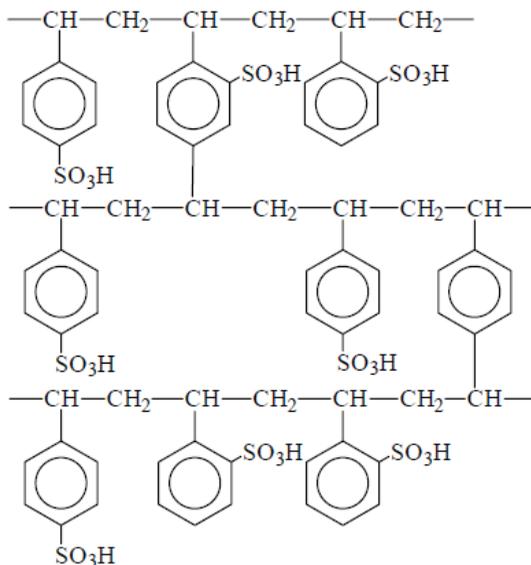


Figure 4. A strongly acid sulfonated polystyrene cation exchange resin.

The stability of resins is a key-factor since they are thought to be operative during long time. The chemical stability is referred to the capacity for a resin to work in highly oxidizing conditions that may change the polymer matrix, causing a loss of exchange capacity and partial dissolution of the resin. Thermal stability of sulfonic PS-DVB resin matrix depends on the crosslinking degree. Macroreticular resins are less stable than microporous. On the other hand, oversulfonated resins are more stable than conventionally sulfonated. Mechanical stability is defined in the basis of its resistance to attrition and osmotic shock. In general, macroreticular resins are more stable than gel type.

The advantages of ion exchange processes are the very low running costs. Very little energy is required, the regenerating chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be taken into account very carefully during the design stages. When itemized these limitations appear to represent a formidable list and the impression can be given that ion

exchange methods might have too many short comings to useful in practice. However, this is not the case as the advantages mentioned above are very great and compensation can readily be made for most restrictions.

4. OBJECTIVES

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 conversion of FA into BL catalyzed by acidic ion-exchange resins due to the lack of information about the performance of that type of catalysts in this reaction. This investigation will include the following objectives:

- 1- Perform a screening of different types of ion-exchange resins in order to determinate which resin is the most suitable for the etherification of FA at 100° C in terms of FA conversion, selectivity and yield to BL .
- 2- Check the influence of temperature on product distribution in the range 70-100°C.
- 3- Evaluate the effect of the initial concentration of the reactants to determinate which molar relation suits the best the reaction.

5. EXPERIMENTAL

5.1. MATERIALS

5.1.1. Reactants

Experiments for the etherification of FA were carried out with 1-butanol (BuOH) (*Acros Organics*, code: 232080025) with a purity of 99,5% and with furfuryl alcohol (*Aldrich Chemistry*) with a purity of 98%.

Additionally, butyl levulinate (*Aldrich Chemistry*, Code: 101495705) with a purity of 98% and water (Mili-Q, Millipore) were used for the chromatographic calibration.

The table X shows some properties of the chemicals.

Table 2. Relevant properties of the reagents and the product.

PROPERTIES	1-BUTANOL	FURFURYL ALCOHOL	BUTYL LEVULINATE
Molecular mass (g/mol)	74,122	98,100	172,22
Density (kg/m ³)	809,8	1128,5	974
Melting point (°C)	-89,8	-29	Unknown
Boiling point (°C)	117,7	170	238
Flash point (°C)	35	65	92

5.1.2. Auxiliary gas

Besides, nitrogen was used as inert gas for pressurizing the reactor with a purity of 99,9995% and helium was the carrier gas (mobile phase) in gas chromatography with a purity of 99,998%. Both gases are supplied by Abello Linde.

5.1.3. Catalysts

All the experiments in this work were performed by using commercial acidic PS-DVB resins. The resins were selected based on those that have been most successful in other experiments, such as Amberlyst 35 (39) and Amberlyst 15 (40), two acidic resins that have a high percentage of divinylbenzene (20%).

The percentage of cross-linking agent (%DVB) provides the ability to be more or less rigid to the resin. Therefore, in order to compare the effect of the crosslinking degree two more resins

with different % DVB were added: Amberlyst 39 (low %) and Amberlyst 46 (even higher % than A35 and A15). A high percentage of DVB gives stiffness to the resin.

All the aforementioned resins are macroreticular so it was added a gel type Amberlyst 121. Gel type resins have a very low % of DVB.

The following tables shows the main properties of the different selected resins:

Table 3. Properties of the acidic resin used in this study.

Catalyst	Structure	Sulfonation type ^a	DVB (%)	Acid capacity (meq H+/g)
A15	macro	CS	20	4,81
A35	macro	OS	20	5,32
A39	macro	CS	8	4,81
A46	macro	SS	high	0,87
A121	gel	CS	2	4,80

(a) CS=conventionally sulfonated; OS=oversulfonated; SS=surface sulfonated or low sulfonated.

(b) Dry measures.

Table 4. Properties of resins measured by BET and ISEC techniques.

Catalyst	Dry measures (BET)			ISEC measures		
	d _{pore} (nm)	S _{BET} (m ² /g)	V _g (cm ³ /g)	V _{sp} (cm ³ /g)	V _g (cm ³ /g)	S _g (m ² /g)
A15	31,8	42,01	0,21	0,82	0,63	157
A35	23,6	28,9	0,21	0,74	0,62	166
A39	17,6	0,09	0	1,45	0,36	181
A46	19,2	57,4	0,26	0,16	0,48	186
A121	32,9	0,02	3E-04	3,26	0	0

All of them despite A46 and A121 have values of acid capacity over 4,8 meq H+/g which means a sulphonation of all styrenics groups of the matrix. A35 is oversulphonated whereas A46 presents the lowest value of acid capacity because it only has the sulfonic groups on the surface of microspheres.

5.2. EXPERIMENTAL SETUP

A scheme with the main elements of the experimental set up is represented in figure 5. The system consists in a 100 mL nominal stainless steel (316 SS *Autoclave Engineers*) batch reactor with 150 bar as maximum operating pressure and 232°C as maximum operating temperature. At the head of the reactor are found both the inlet and outlet of the fluid into the chromatograph, the rupture disc and relief valve. The reactor also has a stirring, a thermocouple and a pressure gauge.

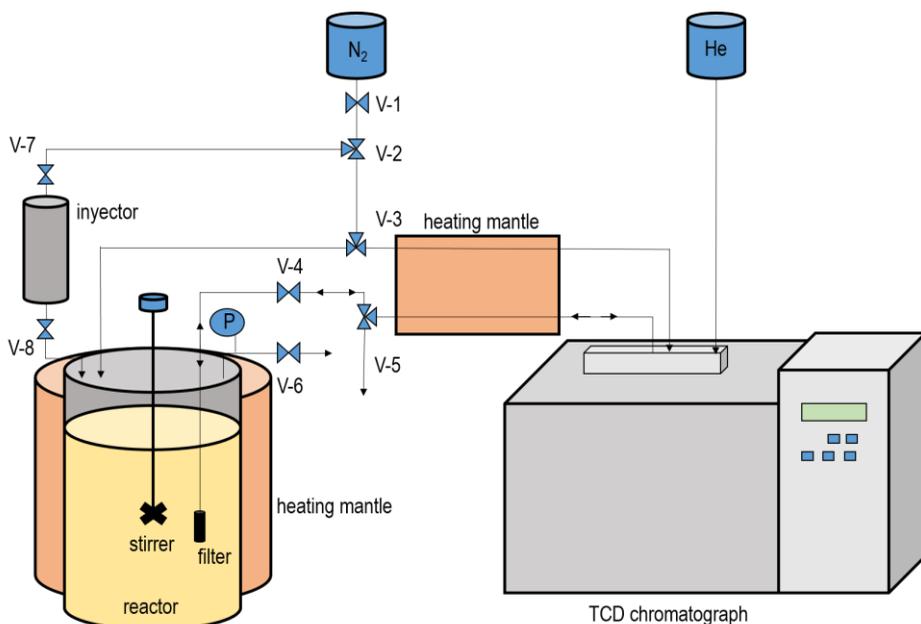


Figure 5. Scheme of the experimental setup.

The stirrer is a turbine with four paddles which stirring speed is controlled by an external tachometer. The heating system consists of an electric oven with two controllers and two temperature sensors type K (chromel – alumel) that measure the internal temperature of the outer wall. Both measuring temperatures can regulate the power supplied by the resistance of the furnace by the United Nations System Control proportional integral derivative or PID and performs as an alarm in the reactor wall to protect it in case of overheating. The thermocouple also performs as an internal baffle and it is situated parallel to the stirrer.

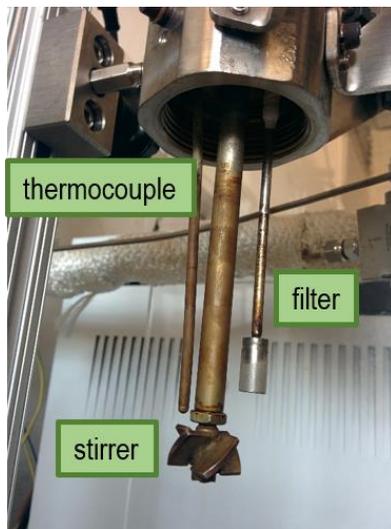


Figure 6. Head of the reactor with internal accessories.

This setup also has safeties as a safety valve and a rupture disc, which breaks when pressure increases over 200 bar.

The composition of liquid mixtures was analyzed by using gas chromatography. The sampling system of the reactor into the chromatograph is through an 1/8" conduction that has a 0,5 μm mesh filter to prevent particles from damaging the chromatograph valves. The sample is returned to not lose mass so the mass balance can be accomplished. An electrical resistance keeps the sampling circuit at 40°C.

The gas chromatograph Hewlett Packard GC 7820A (GC-TCD) is equipped with a thermal conductivity detector (TCD) that can detect the presence of water. It also has a capillary column of 50 m length, 0,200 mm internal diameter and 0,5 μm of thickness of the stationary phase which is methyl siloxane and the carrier gas is helium.

The process takes place at constant flow, increasing the pressure on the head of the column throughout the analysis. The speed which many species migrate depends on its tendency to dissolve in the methyl siloxane. Moreover, sample injection is performed automatically by a mechanical valve which is operated by compressed air.

The process of sampling takes 7 minutes to ensure that the sampling line is completely filled. Then, the analysis starts and it is over in 21 minutes for the program *BUL_VALV_PONA*.

The oven starts with 45°C and holds it for 5,5 min. Next, the temperature is gradually increased at a rate of 50°C/min to 300°C. After that, the maximum temperature remains constant for 10 minutes. Helium was used as carrier gas at a total flow rate of 20 mL/min.

The retention times of the substances are characteristic of each substance in the reaction system. To identify each substance a mass spectrometer was used. Table 8 in appendix shows the retention times with the identified substances.

Figure 7 shows the experimental system with all the located valves and accessories.

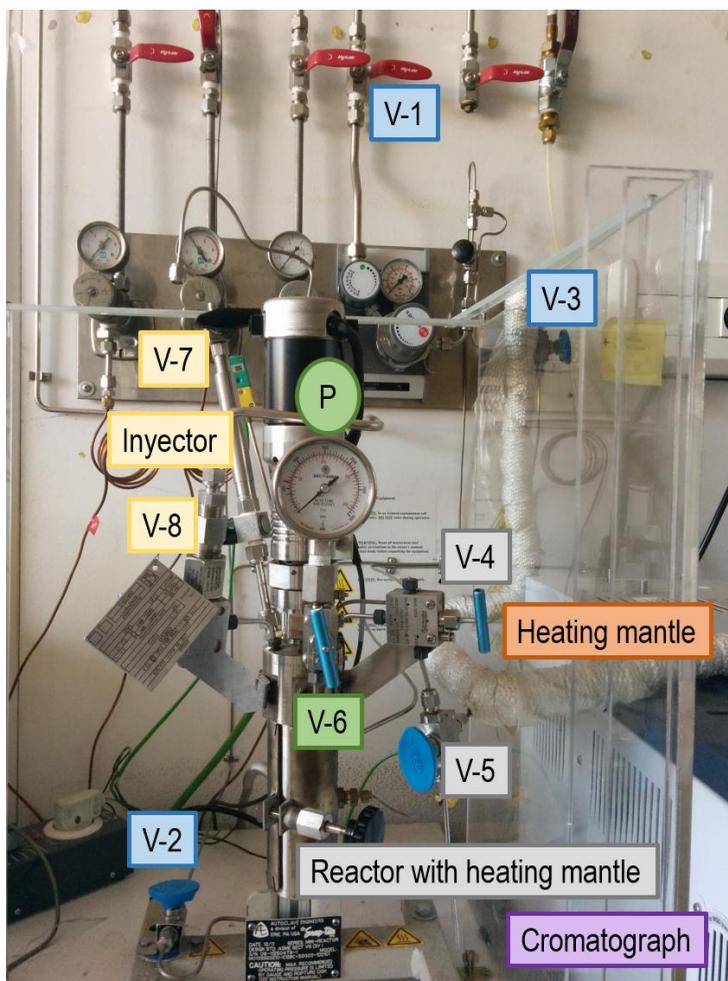


Figure 7. Experimental setup with specified accessories and valves.

5.3. EXPERIMENTAL PROCEDURE

5.3.1. Pretreatment of the catalyst

First of all, ion-exchange resins should be pretreated in order to remove its high moisture content as they are delivered with a content of water between 40% and 60%. Excess water decreases catalytic activity of the resin and furthermore, it can produce error in the determination of the amount of water as reaction product. Therefore, resins shall undergo a first drying in an oven at 100°C for 2 hours. Then, the catalyst will remain in a vacuum oven for a day. Once dry, the resins should be used immediately due to its hygroscopic properties.

5.3.2. Startup

Once the catalyst is ready, the following steps are followed:

1. Connect the heating of the sampling line and the *GC 7820 (online)* program and then load method analysis *BUL_VALV_PONA.M* which is programmed to automatic injection by valve.
2. Weigh and load the chemicals, corresponding to 70 mL of liquid mixture and the catalyst.
3. Close the reactor and pressurize to 40 bar. Valve V-4 and V-6 closed and V-2 and V-3 in the right direction for nitrogen flow into the reactor. Then open valve V-1 (nitrogen inlet valve). To verify the absence of leaks, close V-1 and check by the gauge pressure if the pressure inside the reactor does not decrease.
4. Connect the stirring at 500 rpm.
5. Connect the oven and put the set-point of the reactor to the operating temperature and the set-point of the heating mantle to the maximum operating temperature.
6. Wait for the temperature. The time the mixture reaches the working temperature is considered as zero time of experiment.
7. Pressurize the reactor up to 40 bar, corresponding to the working pressure.
8. Sampling at time zero:
 - a. The V-3 valve on the reactor pressurization position.
 - b. Close the valve V-5.

- c. Open the valve V-4.
 - d. Wait 7 minutes to ensure that the sample flows and fills the chromatograph valve.
 - e. Press *Run-Method* in the program.
 - f. Wait 30 seconds and change the direction of the valve V-3 to retrieve the sample.
 - g. Release pressure by valve V-6 to 30-20 bar to favor the return of the sample to the reactor. Repeat this step until pressure returns to 40 bar quickly.
 - h. Close valve V-4.
 - i. Purge the recirculation line by changing the direction of the valve V-5.
 - j. Repeat point 8 every hour until the end of the experiment, therefore until 6 hours.
9. Once the experiment ended, close the valve V-1, disconnect heating of the sampling line, put the set-point temperature of the reactor at 0°C in order to decrease gradually the mantle temperature and stop stirring.

5.4. EXPERIMENTAL CONDITIONS

The etherification reaction was carried out under the following conditions:

- Molar ratio and initial mass

Molar ratio is defined as the initial moles of 1-butanol divided by the initial moles of furfuryl alcohol that are introduced into the reactor.

$$R_{\frac{BuOH}{FA}} = \frac{n^0_{BuOH}}{n^0_{FA}} \quad (1)$$

In literature, it is found that molar ratios for this reaction usually are two high (over 30, as it can be seen in Table 1). However, for industrial applications higher concentrations of the reagent are desired. Therefore, in this study, lower molar ratios are chosen in order to determine the effect of the initial concentration of FA: R=4 and R=6.

The initial mass of alcohols is calculated with the molar ratio and the reactor volume that although the volume is 100 mL, this is only filled with 70 ml due to the internal elements that it has, such as the stirrer and the filter. Therefore, the following table shows the initial mass of the alcohols for the two molar ratios:

Table 5. Different molar ratio used in this study.

$\frac{R_{BuOH}}{FA}$	m ⁰ BuOH	m ⁰ FA
4	45,819	15,160
6	48,950	10,798

- Temperature and working pressure

The working pressure is hold at 40 bar to maintain all substances in liquid phase. In most experiments the temperature is 100°C. Besides, three experiments were also performed at 90, 80 and 70°C to study the possibility of obtaining good yields under 100°C.

- Particle diameter

Since commercial catalyst were used, they presented a distribution of particle diameters, which were between 0,4 and 0,63 mm in most resins but Amberlyst 46 which particle diameter is between 0,63 and 0,80 mm.

The particle size may influence the internal resistance of mass transfer but in this work this effect was not studied. However, in other studies that used the same resins, size variation proved not to influence the reaction rate (50). Therefore, it is assumed that resistance to internal mass diffusion stage is negligible compared to the reaction stage.

- Stirring speed

The stirring speed is fixed at 500 rpm. Based on previous studies mentioned above, the influence of external mass transfer in the reaction rate is assumed to be negligible at this agitation rate (50).

6. RESULTS AND DISCUSSION

6.1. DESCRIPTION OF AN EXPERIMENT

Blank experiments showed that products were not formed in measurable amounts when catalyst was not added to the reacting media, confirming the necessity of H^+ for the reaction under study.

The reaction catalyzed by acidic ion-exchange resins between furfuryl alcohol and butanol yields to several products, since many reactions are involved. The liquid phase composition that was produced by the reaction was analyzed using GC-TCD and GC-MS, and a typical example of a GC-TCD chromatogram is given in Figure 8. Several distinct substances were detected in the liquid-phase and, among them, many were identified, namely BuOH, FA, 2-(butoxymethyl)furan (BmF), H_2O , 5-5-dibutoxy-2-pentanone (DBPent) and BL. Other peaks were detected in the chromatographic analyses but their peak areas were always lower than 1%. BmF and DBPent are reported to be intermediates (40). Among all the identified substances, BmF and BL were the two major products from the etherification of FA.

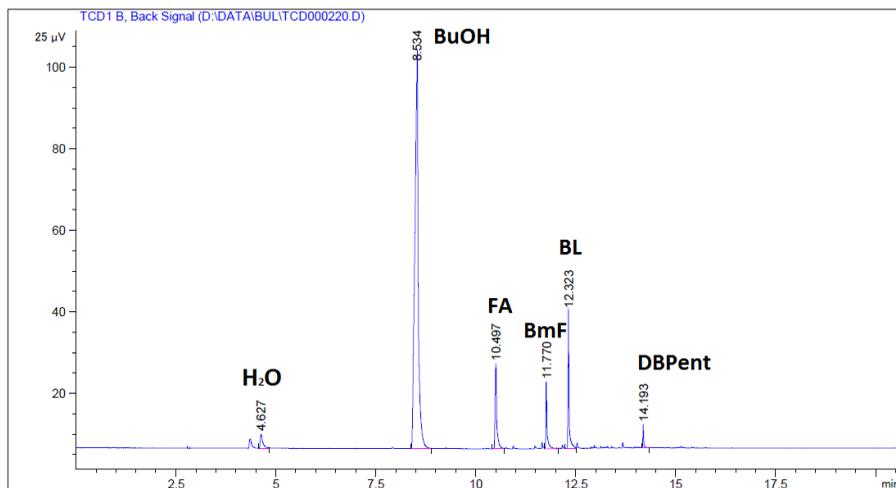


Figure 8. Typical gas chromatogram for the conducted experiments.

During the experiments, dark-brown insoluble substances known as oligomeric products, which result from the side-reactions of the acid-catalyzed alcoholysis of FA, are observed. These substances are known to be produced due to the polymerization of FA (51) and they cannot be analyzed by the GC because of insolubility. For this reason, FA oligomerization was

not followed directly, but their products were considered from mass balances for the calculation of selectivity.

Figure 9 shows a typical mole profile of reactants and products as a function of the reaction time. One can observe that the concentration of FA dropped swiftly and it was fully consumed within the relatively short time of 4 h. The amount of BmF was slightly higher during the initial stage of the reaction, but later decreased, indicating that it is an intermediate and with the prolonging of reaction time, the moles of BL gradually increased.

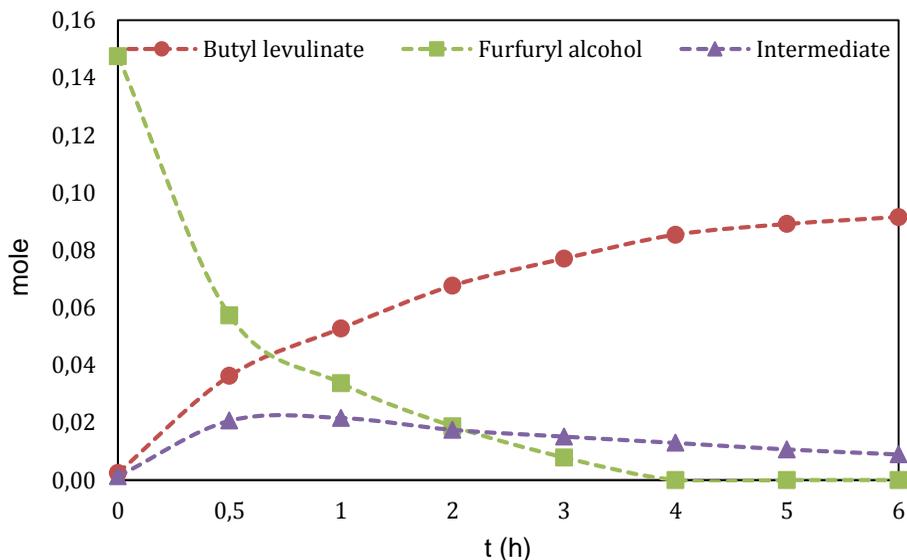


Figure 9. Mole of BL, FA and BmF over reaction time (Reaction conditions: R=4, T=100°C, A-39).

Thus, the reaction can be described by the following equations:



As shown in Figure 9, the conversion of the intermediate into BL is much slower than the conversion of FA. Hence, the reaction rate was controlled by Eq. (3).

There have been several reports on the mechanism of furfuryl alcohol alcoholysis. One possible mechanism is the dehydration of FA to α -angelica lactone, which is in turn readily attacked by alcohols to form BL (52). Another mechanism, is that the primary pathway involves solvent-assisted transfer of a water molecule from the partially detached protonated hydroxyl group of FA to a ring carbon, followed by intra-molecular hydrogen shift (53). And more recently, the reaction is described in multiple steps: In the initial step, FA reacts with BuOH by means of intermolecular dehydration to form the key intermediate BmF. Then, the intermediate 1 is generated via a 1,4-addition. Subsequently, the discharge of *n*-butanol results in the next intermediate 2, which can be further dehydrated to BL under the reaction conditions (Figure 10).

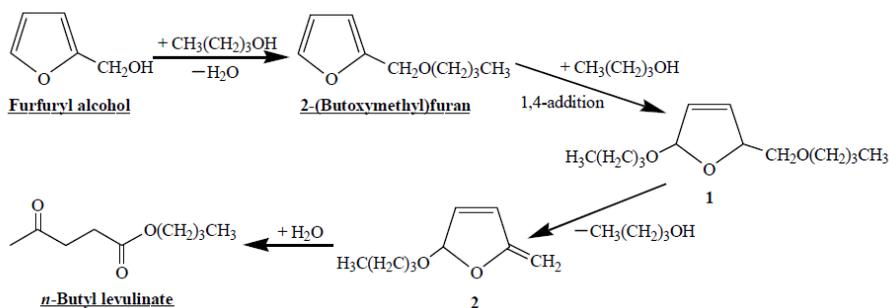


Figure 10. Possible reaction pathway of the reaction.

(extracted image from Peng, L., Li, H., Xi, L., Chen, K., & Chen, H. (2014). Facile and efficient conversion of furfuryl alcohol into *n*-butyl levulinate catalyzed by extremely low acid concentration. *BioResources*, 9(3), 3825-3834.)

Regarding this pathway, the conversion of the intermediate to BL is more arduous and complex than the conversion of FA to the intermediate and it adjusts to the results in this study, although neither the intermediates 1 nor 2 were detected in the analysis.

For analysis and comparison between different conditions, the calculation of a series of variables versus time is required: conversion of FA, selectivity towards the relevant products and yield. For almost all the resins, full conversion was achieved early (within 4h), so the most relevant variable is selectivity.

The reagent conversion in a discontinuous system is defined as:

$$X_j(t) = \frac{n_j^0 - n_j(t)}{n_j^0} = \frac{n_{FA}^0 - n_{FA}(t)}{n_{FA}^0} \frac{\text{mol}}{\text{mol}} \quad (5)$$

Conversion of BuOH is not calculated in this study as the limiting reactant of the reaction is FA. Besides, GC analysis is more sensitive to mole changes in FA than BuOH because it is in excess.

Selectivity of the reagents towards the products is defined as:

$$S_j^k = \frac{\text{mole of } A \text{ that converts in } k}{\text{total mole of } j \text{ that reacts}} \quad (6)$$

As we do not know the stoichiometry of the secondary reactions of FA, selectivity of the reagent is calculated from the initial mole of FA and the mole products. Total selectivity of FA is calculated as S_{FA}^{BL} and S_{FA}^{BmF} because BmF reacts only to the product.

$$S_{FA}^{BL} = \frac{n_{BL}(t)}{n_{FA}^0 - n_{FA}(t)} \quad (7)$$

$$S_{FA}^{BmF} = S_{BmF}^{BL} = \frac{n_{BmF}(t)}{n_{FA}^0 - n_{FA}(t)} \quad (8)$$

$$S_{FA}^{BL} + S_{FA}^{BmF} = S^{BL} \quad (9)$$

Finally, the yield is calculated as:

$$Y_{FA}^{BL} = X_{FA} \cdot S^{BL} \quad (10)$$

The experiments with A-35 at 100°C and A-35 at 80°C were replicated twice in order to study the experimental error and it has been found that experimental error is less than 1,8%.

6.2. EFFECTS OF THE CATALYST AMOUNT

The effect of the catalyst amount on the reaction was investigated by means of two different catalyst loading: 1 and 2 g. The experiments were carried out at 100°C, R=4 and using the catalyst A-35. It can be seen in Figure 11 that the yield of BL increased with an increasing reaction time for both experiments. Besides, the more the catalyst dosage was, the higher the BL yield. For 1 and 2 g of catalyst amount, the yield at 6 h was 0,37 and 0,50 respectively.

Furthermore, when the catalyst loading was 1g, the BL yield grew continually, indicating that an incomplete conversion of FA happened: X_{FA} at 6h was only 0,76. Nonetheless, X_{FA} was complete just in an hour for 2 g of catalyst dosage. This effect should be attributable to an increase in the availability and number of catalytically active sites. Hence, the rest of the experiments were carried out with 2 g of catalyst.

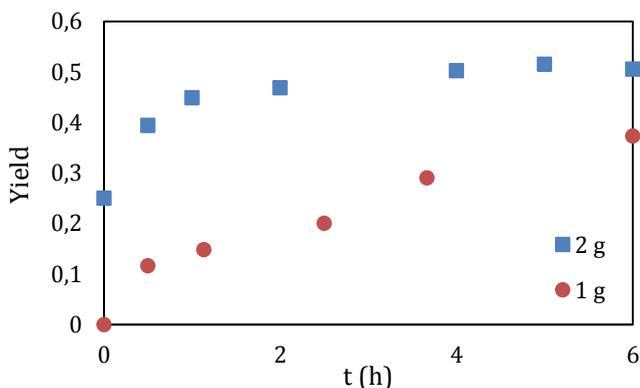


Figure 11. Influence of the catalyst amount on the reaction.

6.3. EFFECTS OF REACTION TEMPERATURE

The reaction under study was studied at different temperatures in order to check the influence of it on the product distribution. The experiments were carried out at 100, 90, 80 and 70°C and the reaction conditions were R=4 and 2 g of loading catalyst which was A-35.

Figures 12 and 13 show that temperature played an important role in the reaction process, as expected. As the FA conversion was complete for all of the experiments at similar times (an hour for 100°C and half an hour for 70°), the effect of temperature is more important for the second reaction step of the mechanism (see eq. 3).

High temperature was able to accelerate the rate of chemical reaction as well as enhance the selectivity to BL (Table 6). This may be because at a higher temperature the activation energy barriers to BL are favorably overcome in relation to those associated with the formation of by-products (31). At lower temperatures, such as 70 and 80 °C, there is barely difference on the BL production with reaction time and selectivity.

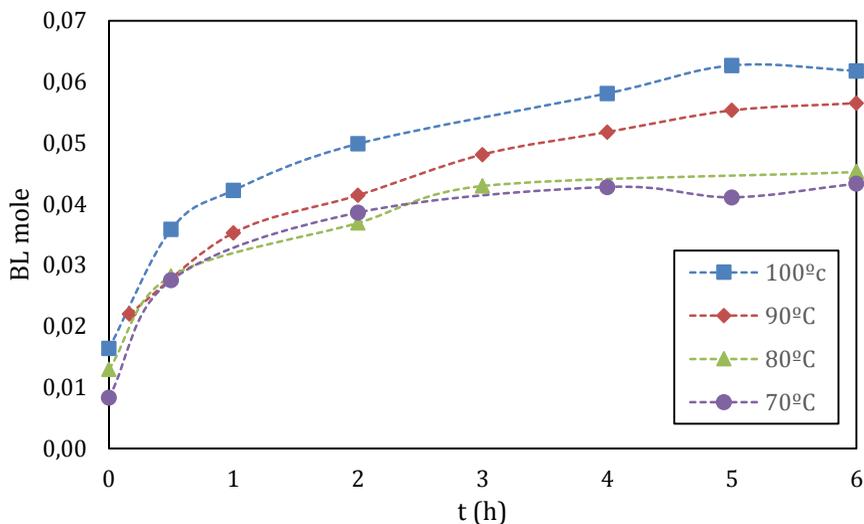


Figure 12. Influence of the reaction temperature on FA alcoholysis.

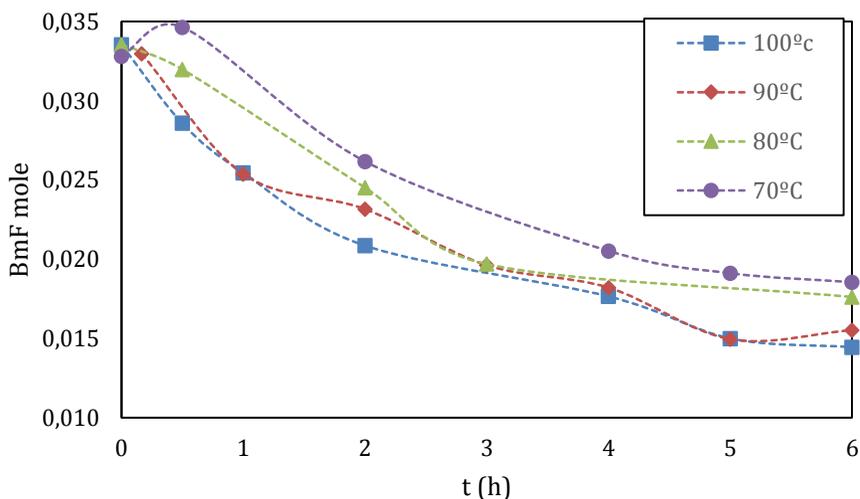


Figure 13. Influence of the reaction temperature on intermediate mole.

When the temperature was increased from 80 to 90°C the production rate of BL and selectivity grew significantly (table 6). Then, when the temperature was further increased from 90 to 100°C the production took place at even faster rate.

Table 6. Selectivity of BmF and of FA towards BL and the total for different temperatures.

T (°C)	S _{FA} (6h)	S _{BmF} (6h)	S ^{BL} (6h)
70	0,29	0,12	0,41
80	0,29	0,11	0,41
90	0,37	0,10	0,47
100	0,41	0,10	0,51

6.4. CATALYST SCREENING

The etherification of furfuryl alcohol was carried out using various ion exchange resins in order to compare their performance. All the experiments produced a considerable amount of BL.

This experiments were carried out at 100°C, with R=4 and with a catalyst loading of 2 g. The time of the reaction was fixed to 6 h, enough time for a complete conversion of FA. It should be pointed out that during pre-heating process (usually 10-15 minutes) an amount of BL was already formed and the conversion of reagent during this stage depends on which catalyst was used (see Table 7).

Table 7. Variables for diferent resins.

Catalyst	X _{FA} (t=0)	BmF mole (t=6h)	S ^{BL} (6h)	BL mole (6h)
A-15	0,45	0,005	0,58	0,082
A-35	0,55	0,014	0,51	0,062
A-39	0,02	0,009	0,67	0,092
A-46	0,78	0,023	0,59	0,065
A-121	0,13	0,001	0,46	0,068

Amberlyst 39 was the catalyst that gave the most quantity of BL (Table 7), followed by Amberlyst 15. Then, A-121, A-46 and A-35 produced similar quantities of product mole.

Regarding the selectivity, A-39 is also the best resin followed by the rest of macroreticular resins. On the other hand, the gel-type resin was the worst resin in terms of selectivity despite of being the only one that almost finished the intermediate. One explanation of this is that A-121 may enhance all the reactions in the system, including the polymerization of FA, thus giving the worst selectivity.

The production of oligomeric products is proved by the fact that $S_{FA}^{BL} + S_{FA}^{BmF}$ is below 1 and there were no other products detected by the GC in appreciable amounts so it means that there is a production of insoluble substances which may be the mentioned above.

As the main reaction takes place in two steps, conversion of FA to BmF, and conversion of BmF to BL, the performance of the catalysts will be analyzed for each step and considering that FA also reacts to other byproducts.

To analyze the first step of the reaction, conversion of FA is represented in Figure 14. It can be appreciated that A-15, A-35 and A-46 are the resins that accelerate the most the conversion of FA. This three resins are the ones that have high % DVB (macroreticular resins). However, as FA can react also to form oligomeric products, it is important to see the production of BmF.

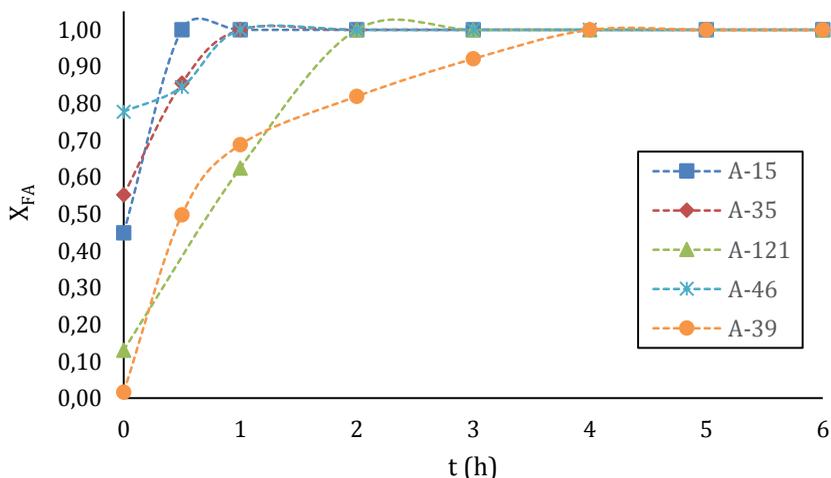


Figure 14. Comparison of FA conversion over time for 5 different catalysts.

Even though A-39 gave the best performance regarding BL mole produced, it was the catalyst that took more time to complete conversion (4 h). Hence, it seems that the other catalyst produced more byproducts consuming FA rapidly.

In Figure 15 it can be observed how BmF mole curve increases and decreases for A-121 and A-39 (low % DVB), showing the intermediate character of BmF. However, for A-15, A-35 and A-46 BmF mole curve only decreases. This is because the maximum production of BmF was already reached in the pre-heating time for this resins, reinforcing the idea that high % DVB increases the velocity of the reaction at the beginning. The explication of this may be that A-15, A-35 and A-46 have permanent macroporous (see Table 4) that make the accessibility of FA to the active centers less hindered. On the contrary, A-121 and A-39 do not have permanent pores and they need the presence of a polar compound to swell. 1-BuOH is able to swell a little these catalysts, permitting the access of FA to some active centers, react to form BmF and water, which in turn swells more the inner structure of these resins.

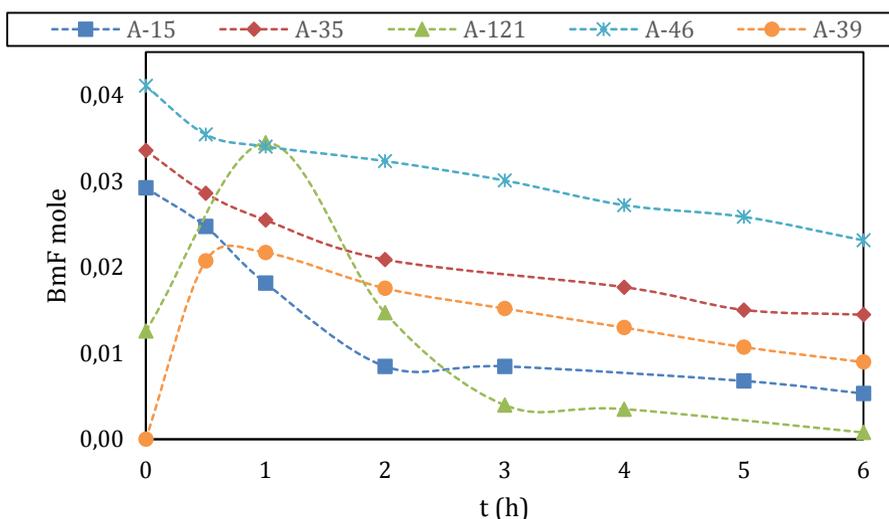


Figure 15. Comparison of moles of BmF over time for 5 different catalysts.

Figure 16 shows the amount of BL mole produced over reaction time. For most of the catalysts, the curves of the product reached a plateau after a certain reaction time, which could possibly indicate catalyst deactivation. One important reason may be that some insoluble substances, such as oligomeric products from the FA polymerization, were absorbed on the solid catalyst (36), (40).

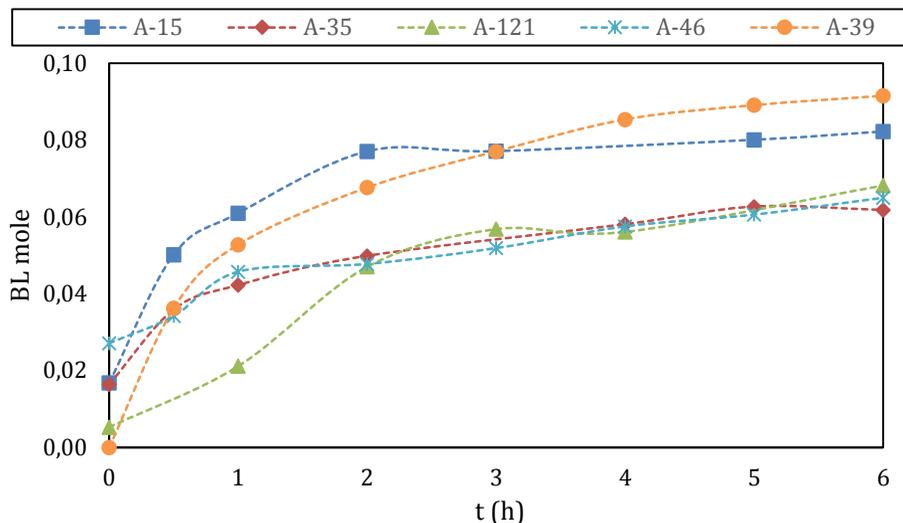


Figure 16. Comparison of BL mole over time for 6 different catalysts.

It seems interesting to relate ion exchange properties to their catalytic behavior. Since conversion of FA was complete for all catalysts, this part is focused on the selectivity of the reaction.

The acid capacity, since it is a quantification of the number of active centers that each catalyst has, seems to be an important parameter to be taken into account. However, as Figure 17 shows, the acid capacity has not any influence on the selectivity at $t=6$ h. There are 3 resins with similar acid capacity that gave different results. Furthermore, A-46, which is a surface-sulfonated resin has very low acid capacity and gave a relative high selectivity.

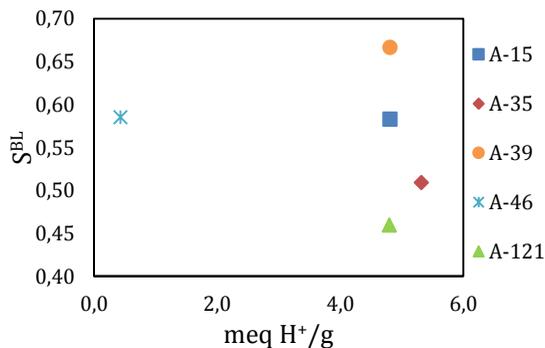


Figure 17. Selectivity to BL vs acid capacity.

Thus, it seems that the accessibility to the active sites is more important than having a higher number of it. This property is related to V_{sp} (volume of the swollen phase) and % DVB.

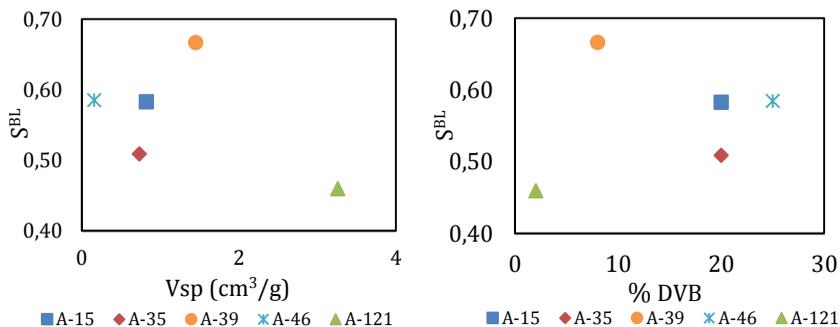


Figure 18. Selectivity to BL vs V_{sp} and %DVB.

V_{sp} is a measure of the capacity of a resin to swell in water. The higher the value is, the higher the capacity of swelling and thus, the accessibility of reagents to the active sites is less hindered. Besides, it is related to the amount of crosslinking agent (%DVB) because when % DVB decreases, the structure of the catalyst is less rigid and hence, it can swell more easily. So, comparing these two catalyst properties, it can be seen in Figure 18 that there is an optimal value of V_{sp} and %DVB (1,451 m²/g and 8 %DVB) for the selectivity, which corresponds to A-39.

It can be appreciated that resins with high %DVB (A-15 and A-35) gave similar selectivity to A-46 (only surface-sulphonated) suggesting that the reaction is somehow hindered and/or not all the acid sites are accessible.

When V_{sp} increases, the selectivity increases until the optimal, which is A-39. This can be explained as the swelling of the resin increases the accessibility of the reagents to the active sites. Then, selectivity decreases for an even higher value of V_{sp} which is the gel-type resin A-121. As mentioned before, A-121 gave the worst selectivity because it possible enhances the polymerization of FA.

However, A-15 and A-35 have the same %DVB but A-15 gave a higher quantity of BL. This may be because A-35 is over-sulphonated by 10-20% and this fact can give to the resin an extra stiffness, reducing even more swelling.

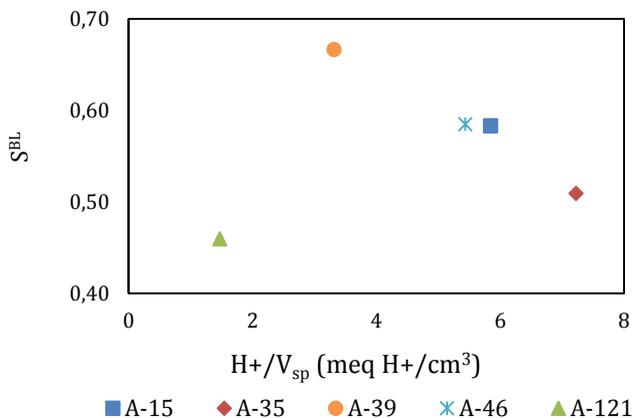


Figure 19. Selectivity to BL vs H^+/V_{sp} .

The parameter H^+/V_{sp} (defined as the number of sulphonic groups per volume of swollen gel-phase) takes into account both effects: high values mean a high acid capacity but a low V_{sp} (typically oversulphonated macroreticular resins such as A-35), while low values correspond to conventionally sulfonated microporous resins such as A-121. Figure 19 plots selectivity to BL against the parameter H^+/V_{sp} (meq H^+/cm^3). It is observed, as in previous figures, that there is an optimal value that combines number of active sites and accessibility to them.

6.5. EFFECTS OF INITIAL MOLAR RATE

It is reported in literature that FA readily polymerizes at a high concentration to form oligomeric products (51). To study the effect of FA concentration, two experiments were carried out at two different molar ratio ($R=6$ and $R=4$).

Figure 20 shows that for both experiments, the number of BL moles was almost the same with reaction time indicating that is more efficient with less moles of FA ($R=6$). It can be appreciated also in the figure that a higher intermediate mole is reached when the concentration of FA is lower. Moreover, the selectivity at 6 h is 0,6 and 0,5 with $R=6$ and $R=4$, respectively. Hence, the reaction of polymerization was promoted with a higher FA concentration, reducing the production rate of BL as a result.

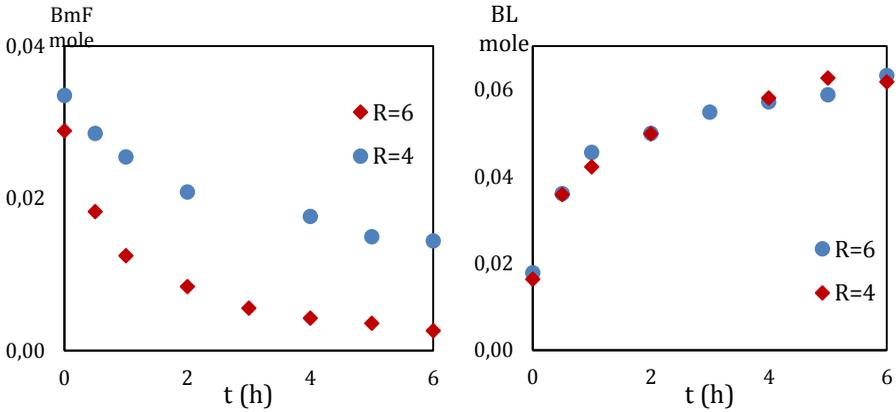


Figure 20. BL moles and BL mole vs time reaction.

However, in practical applications a higher concentration of FA is desired not only because it can enhance the production efficiency of BL, but also because it can cut down on the energy consumption that occurs during the purification of the product. Therefore compromises have to be made with regards to the concentration and selectivity of BL for practical usage to reduce production cost (41).

7. CONCLUSIONS

The experiments performed in this work proves that ion exchange resins can be used in the etherification of FA with butanol to obtain BL at 100°C. The reaction has two steps: conversion of FA to an intermediate which was always complete within 4h and the conversion of the intermediate to butyl levulinate which was more complex and slower step. The most relevant byproducts were oligomeric substances indicating that polymerization of FA also took place.

The catalyst with the best performance regarding selectivity and mole production was Amberlyst 39 which gave 67% selectivity to BL. The accessibility to the acid sites of the resins seemed to be the property with higher influence of the resins performance. Reaction rate for macroreticular resins improved with the increase of the volume of swollen pores (V_{sp}) and with the reduction of %DVB. However, A-121 which is a gel-type resin and can swell more than macroreticular resins has the worst selectivity indicating that also enhances non desired reactions. Hence, it has been found that there is an optimal between accessibility of the active sites of the resin and their acid capacity.

The influence of temperature was studied and the selectivity to BL decreased with temperatures lower than 100°C. Finally, the initial molar ratio effect was also investigated and it was found that selectivity to BL dropped with the increase in initial FA concentration implying that the reaction of polymerization was promoted.

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9. ACRONYMS

%DVB divinylbenzene percentage

1GBs first generation biofuels

2GBs second generation biofuels

A % area percentage

BL butyl levulinate

BmF 2-(butoxymethyl)furan

BuOH butanol

CS conventionally sulfonated

DBPent 5-5-dibutoxy-2-pentanone

d_{pore} catalyst pore diameter (nm)

EL ethyl levulinate

FA furfuryl alcohol

FUR furfural

HMF 5-hydroxymethylfurfural

IER ion exchange resin

ISEC Inverse Steric Exclusion Chromatography

j reactant

k product

LA acid levulinic

ML methyl levulinate

OS oversulfonated

PS-DVB polystyrene-divinylbenzene

S_{BET} surface area in dry state obtained by BET method (m^2/g)

S_{g} mesoporus surface area (m^2/g)

S_j^k selectivity of reactant j toward product k

SS Surface sulfonated

T temperature ($^{\circ}\text{C}$)

V_{g} pore volume (cm^3/g)

V_{sp} specific volume of the swollen phase (cm^3/g)

X_j conversion of reactant j

Y_j^k yield of reactant j

APPENDICES

APPENDIX 1: CHROMATOGRAPHIC ANALYSIS

Table 8. Retention times for the substances detected by GC-MS

Substances	Retention time (min)
H ₂ O	4,627
BuOH	8,534
FA	10,497
BmF	11,77
BL	13,323
DBPent	14,193

Table 9. Vials prepared for the calibration.

Substances	Mass %			
	FA	BUTANOL	BL	H ₂ O
VIAL 1	24,929	75,071	0,000	0,000
VIAL FINAL	0,000	56,402	43,598	0,000
VIAL 2	20,122	78,394	1,484	0,000
VIAL 3	8,094	82,201	8,579	1,126
VIAL 4	4,602	81,248	12,814	1,335
VIAL 5	3,077	79,428	16,247	1,248
VIAL 6	1,622	78,254	19,010	1,114
VIAL 7	6,970	71,252	21,035	0,743
VIAL 8	3,580	73,952	21,087	1,381
VIAL 9	5,486	78,606	13,746	2,162
VIAL 10	15,933	71,532	10,849	1,686
VIAL 11	20,101	74,895	4,193	0,811

Table 10. Average area % obtained for BL after making replicas of the vials.

BL calibration						
Name	% masa	% area 1	% area 2	% area 3	average area %	
VIAL 1	0,000	0,000	0,000	0,000	0,000	± 0,000
VIAL 2	1,467	1,367	1,347	1,325	1,346	± 0,021
VIAL 3	8,471	6,898	6,962	6,902	6,921	± 0,036
VIAL 4	12,654	10,428	10,546	10,544	10,506	± 0,068
VIAL 5	16,047	13,547	13,350	13,308	13,402	± 0,128
VIAL 6	18,781	15,592	15,501	15,646	15,580	± 0,073
VIAL 7	20,805	17,098	17,664	17,713	17,492	± 0,342
VIAL 8	20,845	17,486	17,613	17,433	17,511	± 0,093
VIAL 9	13,577	11,583	11,536	11,497	11,539	± 0,043
VIAL 10	10,728	8,989	9,185	9,022	9,065	± 0,105
VIAL 11	4,145	3,490	3,537	3,798	3,608	± 0,166

Figure 21. Example of a linear regression for the calibration of BL.

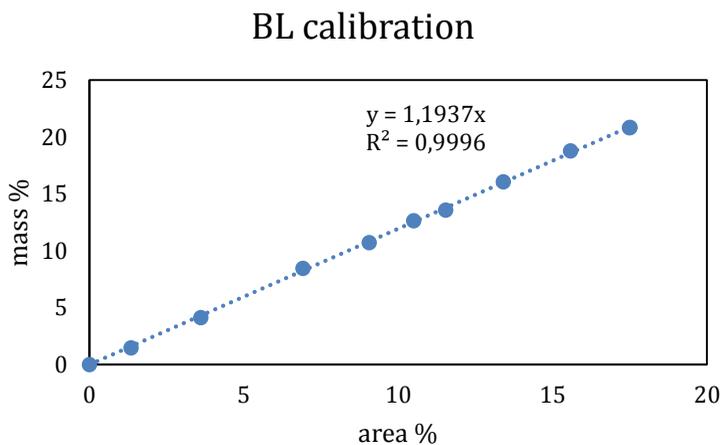


Table 11. Calibration straight lines obtained, where y is mass% and x is area %

Substance	Equation	R ²
FA	$y = 1,194x \pm 0,009$	0,9997
BuOH	$y = (1,100 \pm 0,063)x - (10,831 \pm 4,976)$	0,9934
BL	$y = (1,194 \pm 0,008)x$	0,9996
H2O	$y = (1,107 \pm 0,115)x - (0,931 \pm 0,240)$	0,9945
BmF	$y = (1,194 \pm 0,008)x$	-

APPENDIX 2: SAFETY DATA SHEETS

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CDC - 1-BUTANOL - International Chemical Safety Cards - NIOSH



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NIOSH Home International Chemical Safety Cards (ICSC)

ICSC: 0111

1-BUTANOL

n-Butanol n-Butyl alcohol Propyl carbinol Butan-1-ol Butyl alcohol $C_4H_{10}O / CH_3(CH_2)_3OH$ Molecular mass: 74.1 ICSC # 0111	CAS # 71-36-3 RTECS # EO1400000 UN # 1120 EC # 603-004-00-6 April 19, 2005 Validated
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TYPES OF HAZARD/ EXPOSURE	ACUTE HAZARDS/ SYMPTOMS	PREVENTION	FIRST AID/ FIRE FIGHTING
FIRE	Flammable.	NO open flames, NO sparks, and NO smoking.	Powder, water spray, foam, carbon dioxide.
EXPLOSION	Above 29°C explosive vapour/air mixtures may be formed.	Above 29°C use a closed system, ventilation, and explosion-proof electrical equipment.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE			
•INHALATION	Cough. Sore throat. Headache. Dizziness. Drowsiness.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest.
•SKIN	Redness. Pain. Dry skin.	Protective gloves.	Remove contaminated clothes. Rinse skin with plenty of water or shower.
•EYES	Redness. Pain.	Safety goggles.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
	Abdominal pain.	Do not eat, drink, or	Rinse mouth. Give

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• INGESTION	Drowsiness. Dizziness. Nausea. Diarrhoea. Vomiting	smoke during work.	plenty of water to drink. Do NOT induce vomiting. Refer for medical attention.
SPILLAGE DISPOSAL	STORAGE		PACKAGING & LABELLING
Personal protection: filter respirator for organic gases and vapours. Collect leaking liquid in sealable containers. Absorb remaining liquid in sand or inert absorbent and remove to safe place. Wash away remainder with plenty of water.	Fireproof. Separated from strong oxidants, aluminium.		Xn symbol R: 10-22-37/38-41-67 S: 2-7/9-13-26-37/39-46 UN Hazard Class: 3 UN Packing Group: III
ICSC: 0111	Prepared in the context of cooperation between the International Programme on Chemical Safety & the Commission of the European Communities (C) IPCS CEC 1994. No modifications to the International version have been made except to add the OSHA PELs, NIOSH RELs and NIOSH IDLH values.		

1-BUTANOL**ICSC: 0111**

I M P O R T A N T D	<p>PHYSICAL STATE; APPEARANCE: COLOURLESS LIQUID , WITH CHARACTERISTIC ODOUR.</p> <p>PHYSICAL DANGERS:</p> <p>CHEMICAL DANGERS: Reacts with aluminium when heated to 100°C, strong oxidants , such as chromium trioxide forming flammable/explosive gas (hydrogen - see ICSC0001). Attacks some forms of plastic, rubber and coatings.</p> <p>OCCUPATIONAL EXPOSURE LIMITS: TLV: 20 ppm as TWA; (ACGIH 2005). MAK: 100 ppm, 310 mg/m³; Peak limitation category: I(1); Pregnancy risk group: C;</p>	<p>ROUTES OF EXPOSURE: The substance can be absorbed into the body by inhalation of its vapour and by ingestion.</p> <p>INHALATION RISK: A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C.</p> <p>EFFECTS OF SHORT-TERM EXPOSURE: The substance is irritating to the skin , and is severely irritating to the eyes . The vapour is irritating to the eyes and the respiratory tract. Exposure far above the OEL could cause lowering of consciousness. If this liquid is swallowed, aspiration into the lungs may result in chemical pneumonitis.</p>
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A T A	(DFG 2004). OSHA PEL _T : TWA 100 ppm (300 mg/m ³) NIOSH REL: C 50 ppm (150 mg/m ³) skin NIOSH IDLH: 1400 ppm 10%LEL See: 71363	EFFECTS OF LONG-TERM OR REPEATED EXPOSURE: The liquid defats the skin.
PHYSICAL PROPERTIES	Boiling point: 117°C Melting point: -90°C Relative density (water = 1): 0.81 Solubility in water, g/100 ml at 20°C: 7.7 Vapour pressure, kPa at 20°C: 0.58 Relative vapour density (air = 1): 2.6	Relative density of the vapour/air-mixture at 20°C (air = 1): 1.01 Flash point: 29°C c.c. Auto-ignition temperature: 345°C Explosive limits, vol% in air: 1.4-11.3 Octanol/water partition coefficient as log Pow: 0.9
ENVIRONMENTAL DATA		
NOTES		
Transport Emergency Card: TEC (R)-30S1120-III NFPA Code: H1; F3; R0;		
ADDITIONAL INFORMATION		
ICSC: 0111		1-BUTANOL
(C) IPCS, CEC, 1994		
IMPORTANT LEGAL NOTICE:	Neither NIOSH, the CEC or the IPCS nor any person acting on behalf of NIOSH, the CEC or the IPCS is responsible for the use which might be made of this information. This card contains the collective views of the IPCS Peer Review Committee and may not reflect in all cases all the detailed requirements included in national legislation on the subject. The user should verify compliance of the cards with the relevant legislation in the country of use. The only modifications made to produce the U.S. version is inclusion of the OSHA PELs, NIOSH RELs and NIOSH IDLH values.	

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CDC - NIOSH Pocket Guide to Chemical Hazards - Furfuryl alcohol



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Enter search terms separated by spaces.

Furfuryl alcohol					
Synonyms & Trade Names 2-Furylmethanol, 2-Hydroxymethylfuran					
CAS No. 98-00-0	RTECS No. LU9100000 (/niosh- rtecs/LU8ADAEo.html)		DOT ID & Guide 2874 153 (http://www.wapps.tc.gc.ca/saf-sec-sur/3/erg-gmu/erg/guidepage.aspx/guide153/) (http://www.cdc.gov/Other/disclaimer.html)		
Formula C ₅ H ₆ O ₂	Conversion 1 ppm = 4.01 mg/m ³	IDLH 75 ppm See: 98000 (/niosh/idlh/98000.html)			
Exposure Limits NIOSH REL : TWA 10 ppm (40 mg/m ³) ST 15 ppm (60 mg/m ³) [skin] OSHA PEL † (nengapdxg.html): TWA 50 ppm (200 mg/m ³)			Measurement Methods NIOSH 2505 (/niosh/docs/2003- 154/pdfs/2505.pdf) See: NMAM (/niosh/docs/2003-154/) or OSHA Methods (http://www.osha.gov/dts/sltc/methods/index.html) (http://www.cdc.gov/Other/disclaimer.html)		
Physical Description Colorless to amber liquid with a faint, burning odor. [Note: Darkens on exposure to light.]					
MW: 98.1	BP: 338°F	FRZ: 6°F	Sol: Miscible	VP(77°F): 0.6 mmHg	IP: ?
Sp.Gr: 1.13	FL.P: 149°F	UEL: 16.3%	LEL: 1.8%		
Class IIIA Combustible Liquid; FL.P. at or above 140°F and below 200°F.					
Incompatibilities & Reactivities Strong oxidizers & acids [Note: Contact with organic acids may lead to polymerization.]					
Exposure Routes inhalation, skin absorption, ingestion, skin and/or eye contact					
Symptoms irritation eyes, mucous membrane; dizziness; nausea, diarrhea; diuresis; resp, body temperature depression; vomiting; dermatitis					
Target Organs Eyes, skin, respiratory system, central nervous system					
Personal Protection/Sanitation (See protection codes (protect.html)) Skin: Prevent skin contact			First Aid (See procedures (firstaid.html)) Eye: Irrigate immediately Skin: Water flush immediately		

<http://www.cdc.gov/niosh/npg/npgd0298.html>

1/2

18/6/2015

CDC - NIOSH Pocket Guide to Chemical Hazards - Furfuryl alcohol

Eyes: Prevent eye contact

Wash skin: When contaminated

Remove: When wet or contaminated

Change: No recommendation

Provide: Quick drench

Breathing: Respiratory support

Swallow: Medical attention immediately

Respirator Recommendations

NIOSH

Up to 75 ppm:

(APF = 10) Any chemical cartridge respirator with organic vapor cartridge(s)*

(APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister

(APF = 25) Any powered, air-purifying respirator with organic vapor cartridge(s)*

(APF = 10) Any supplied-air respirator*

(APF = 50) Any self-contained breathing apparatus with a full facepiece

Emergency or planned entry into unknown concentrations or IDLH conditions:

(APF = 10,000) Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode

(APF = 10,000) Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus

Escape:

(APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister

Any appropriate escape-type, self-contained breathing apparatus

[Important additional information about respirator selection \(pgintrod.html#mustread\)](#)

See also: [INTRODUCTION \(/niosh/npg/pgintrod.html\)](#) See ICSC CARD: [0794 \(/niosh/ipcsneng/nengo794.html\)](#) See MEDICAL TESTS: [0111 \(/niosh/docs/2005-110/nmedo111.html\)](#)

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