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***sec*-Butyl levulinate production by esterification of levulinic acid with 1-butene over acidic ion-exchange resins: a screening study**

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El 20% de los esfuerzos generan el 80% de los resultados.

Vilfredo Pareto

A mis padres por su apoyo. A la Dr. Eliana Ramirez por su ayuda y dedicación. Al Dr. Jordi Hug Badia, por su incondicional ayuda y actitud constructiva en muchos momentos difíciles durante la realización de este trabajo

Gracias.

CONTENTS

SUMMARY

The need to reduce petroleum dependence and its emissions, a tough environmental legislation and the obligation to achieve the 10% in volume use of additives from renewable resources by 2020 in Europe forces the industry to focus on obtaining green-fuels to reduce pollution. Acid hydrolysis of cellulosic materials produce carbohydrates C_5 and C_6 whose transformation results in a series of compounds called platform chemicals, which are the first step to the synthesis of numerous compounds of potential interest in the chemical industry.

One of them is levulinic acid (LA). This acid can be obtained with semi-commercial processes such as Biofine, and the literature proposes it as a starting point for obtaining fine chemicals and additives compounds suitable in fuels reformulation with bio-compounds. Moreover, the raw material proceeds from inedible biomass which means that a possible ethic issue is avoided.

Butyl levulinates, a levulinic acid derivative, have excellent properties as fuel additives because has good cetane index close to commercial fuels, improves good circulation at low temperatures and reduces the exhaust emissions. In particularly, *sec*-butyl levulinate is a good octane improver

This work is focused on the liquid phase esterification reaction of levulinic acid with 1-butene (1B) to obtain *sec*-butyl levulinate (SBL) by acid catalysis. SBL can also be synthesize by reacting LA with 2-butanol instead of 1B, but the use of the olefin is desirable since it avoids the formation of unwanted products, such as polymerization compounds, ethers and water, which are produce when the alcohol is used. Also, is a refinery stream currently without commercial value, so ester production would allow its upgrading. To carry out the reaction, it is proposed to work with acidic ion-exchange resins as catalysts, which are economic catalysts able to work at low temperatures, with a flexible morphology and with a high adaptability to the reaction medium. The main goal of the work is to find an active resin in terms of conversion and selectivity towards ester, which minimizes the oligomers formation as by-products at temperatures below 140 ºC.

Experiments conducted show that the use of acid resins in levulinic acid esterification with 1-butene to obtain *sec*-butyl levulinate can result in with high conversions and selectivity. Macroreticulated resins have shown the highest catalytic activity, Amberlyst 15 (A15) showing a higher rate of sec-butyl levulinate generation. Therefore, it can be concluded that resins with more DVB, higher acid capacity and lower gel phase are favoured in this reaction medium.

Keywords: biofuels, *sec*-butyl levulinates, biomass, levulinic acid, acidic ion-exchange resins.

RESUMEN

La necesidad de reducir la dependencia del petróleo y sus emisiones, el endurecimiento de la legislación medioambiental y la obligación de cumplir con un uso de al menos un 10% en volumen de aditivos provenientes de fuentes renovables antes del 2020 en Europa obliga a la industria a dirigir su atención a la obtención de combustibles exentos de contaminación. La hidrólisis ácida de material celulósico origina carbohidratos C5 y C6 cuya transformación da lugar a una serie de compuestos llamados “platform chemicals”, los cuales son el primer paso a la síntesis de numerosos compuestos de potencial interés en la industria química.

Uno de ellos es el ácido levulínico. Este ácido puede obtenerse mediante procesos semicomerciales como el Biofine, y la literatura lo propone como punto de partida a la obtención de compuestos de química fina, aditivos y componentes aptos para ser utilizados en reformulación de gasolinas y gasóleos con biocompuestos. Además, al proceder de biomasa no comestible no implicaría un problema ético en cuanto a su uso.

Los butil levulinatos, derivados del ácido levulínico, tienen excelentes propiedades como gasóleos. Cuentan con un buen índice de cetano próximo a los combustibles comerciales, buenas propiedades de circulación en frío y reducen la emisión de humos.

El objetivo del este trabajo es estudiar la reacción de esterificación en fase líquida mediante catálisis ácida del ácido levulínico con 1-buteno para obtener *sec*-butil levulinato. La misma reacción podría llevarse a cabo usando un alcohol en lugar de una olefina, pero el uso del 1-buteno evita la obtención de subproductos no deseados como compuestos de polimerización, éteres o agua que vendrían asociados al uso del alcohol. Además, el 1-buteno es un compuesto actualmente sin salida comercial, por lo que la producción del éster va a permitir la revalorización de esta corriente de refinería. Para llevar a cabo la catálisis, se propone trabajar con resinas ácidas de intercambio iónico, catalizadores baratos aptos para trabajar a bajas temperaturas, con una morfología flexible y capaz de adaptarse al medio de reacción. El objetivo es encontrar una resina activa desde el punto de vista de la conversión y la selectividad hacia el éster, que minimice la formación de oligómeros como subproducto a temperaturas inferiores a 140ºC.

Los experimentos llevados a cabo demuestran que con el uso de resinas acidas en la esterificación del ácido levulínico con 1-buteno para obtener *sec*-butil levulinato pueden obtenerse conversiones y selectividades relativamente altas. Las resinas macroreticuladas han mostrado una mayor actividad catalítica, siendo Amberlyst 15 (A15) la que mostrado una mayor velocidad de generación de *sec*-butyl levulinato. Por tanto, se puede concluir que resinas con mayor cantidad de DVB, mayor capacidad ácida y menor fase gel se ven favorecidas en este medio de reacción.

Palabras clave: biocombustibles, *sec*-butil levulinato, biomasa, ácido levulínico, resinas ácidas de intercambio iónico.

1. INTRODUCTION

1.1. A BRIEF HISTORY IN GASOLINE AND OCTANE IMPROVERS

Gasoline is a petroleum derivative which consists of a mixture of hydrocarbons with 4 to 12 Carbon atoms. It is a mixture of paraffins (16%), olefins (16%), naphthenes (8%), isoparaffins (30%) and aromatics (30%) (*Shrivastav et al. 2017*). Different types of gasoline can be catalogued according to their octane number, which quantifies the anti-knock capability of a fuel. Knock occurs when fuel is prematurely ignited into the engine, which degrades and can be damaging to itself. The higher the octane number of a fuel, the more resistant against knocking. One of the main strategies to increase the octane number of a given fuel, is to add octane-enhancing additives to it, to a maximum of 10 percent in volume. Such additives have changed over the years in accordance with environmental requirements posed by organizations like the Environmental Protection Agency (EPA) in the United States.

1.1.1. Lead

In 1921, General Motors discovered that tetraethyl lead (TEL) increases octane rating of gasoline. TEL is obtained by reacting chloroethane with sodium-lead alloy (only reacts the 25% of it) according to the reaction in (1).

$$4\ NaPb + 4\ CH_3CH_2Cl \rightarrow (CH_3CH_2)_4Pb + 4\ NaCl + 3\ Pb \qquad (1)$$

The final product is recoated by steam distillation, remaining sodium chloride and a mud of lead. TEL is a viscous soluble liquid in petrol due to its alkyl groups and was preferred before aromatic hydrocarbons or alcohols also used at the time due to its lower production cost[1-5].

However, shortly after introducing TEL to fuel formulation, that is in 1924, the firsts cases of lead poisoning appeared and the Surgeon General, the operational head of U.S Public Health Service Commissioned Corps (PHSCC), temporally cancelled the leaded gasoline production to investigate this potential damage against public health. This first investigation did not find enough remarkable poisoning evidences over a short period of time and it would not be until 1960 that the health impacts of lead exposure were defined. This investigation established that children were particularly sensitive to lead poisoning, revealing anaemia, behavioural disorders, nerve damage and reading or learning disabilities. In adults, lead causes hypertension and cardiovascular diseases. Finally, in 1976 lead-based additives were banned for on-road vehicles fuel formulations. Nowadays, leaded fuel is still used in aviation fuels [1-5].

1.1.2. MTBE

Methyl tertiary-butyl ether (MTBE) was used at low levels of concentration in the United States during the 80s as a lead substitutive. In 1990, the Clean Air Act Amendments (CAA), required the use of oxygenate gasolines in areas that had a high level of air pollution. This kind of fuel has an increased oxygenate content, which enables a more complete combustion and decreases the ozone precursors and other toxic components. As a result, in 1992, MTBE was introduced in gasoline formulations at higher concentrations and, by the end of 90s, around the 87 % of reformulated gasolines included it, because of MTBE's low cost, easy transport and blend characteristics [1-5].

Despite of reducing ozone precursors in smog-affected areas, MTBE was phased out because of its high solubility in water. It could contaminate public water systems if gasoline was spilled out on the ground or inside storage tanks. Also, it is known that MTBE is not easily biodegradable, so if the contamination occurs, it would be difficult to eliminate.

As a consequence, in 2005, the Energy Policy Act banned the use of MTBE to accomplish the oxygen requirement for reformulated gasolines in the United States, and companies decided to use ethanol instead, due to state laws and tax subsidies. However, MTBE is still being used as a gasoline additive in some places of the world.

1.1.3. BTEX Complex

BTEX complex is a mixture of benzene, toluene, xylene and ethyl-benzene. These compounds are refined from low-octane petroleum products into a high-octane additive. This compound are already present in gasoline when it is refined, but their concentration is increased to boost the fuel octane rating. Its use increased from 20 percent to a third of gasoline pool due to is use as lead substitute. Due to some investigations in the charge of health professionals that questioned the safety for the public health using this compound, EPA decided to reduce the aromatics concentration to 25-28 percent in volume. Nowadays, it is known that even a low exposure against BTEX contribute against reproductive immunological response and cardio-pulmonary running. Also, BTEX form ultra-fine particulates (UFP) and polycyclic aromatic hydrocarbons (PAHs) when it has an incomplete burned that are mutagenic, carcinogenic and neurodegenerative [1-5].

1.1.4. Ethanol

In 1973, during the oil embargo caused by the participation of USA supporting Israel in the *Yom Kipur* war, gasoline prices were increased at around a 57 percent. This event and the current air pollution regulation motivated an interest for renewable fuels and vehicles powered by electricity. One of these renewable fuels was ethanol, due to its excellent capacity as octane improver, low economic cost and toxicity. Moreover, in health aspects, an increase from 10 to 15 vol.% in ethanol provides a 6.6 percent reduction in cancer risk [5,6].

Today, the majority of ethanol is used to produce E10. It is necessary to detail that the ethanol content in front of the gasoline content is marked by the number that goes with the E letter. As an example, E15 fuel has 15 percent of ethanol and 85 percent of gasoline.

1.2. BIOMASS AND BIOFUELS

Despite the high energy production of gasoline and, in general, all fossil fuels, it is necessary to reduce its consume due to the polluting nature of its emissions. Nowadays, new renewable and sustainable alternatives are being studied as a future substitute of fossil fuels.

Biomass is organic material originated by plants and animals. It can be grown in crops, waste from food or sewage plants, animal farming, food processing, etc. Those materials are precursors of clean energy without the polluting emissions difficulties against environment. To prepare the biomass for being used, it is necessary to a conversion process. The conversion processes usually used are the following ones [7].

- **Combustion**. Flammable materials burned in oxygen presence. It is use to heat steam for electricity generation or domestic uses, like space heating.
- **Gasification**. Biomass conversion into a combustible gas mixture of producer gas ($CO+H_2+CH_4$) and Syngas ($CO+H_2$).
- **Pyrolysis**. Thermal decomposition in oxygen absence. This process is the gasification precursor.
- **Bio digestion**. It is based in anaerobic bacteria use for breaking down the organic material producing methane and a solid residue. Methane and this solid residue can be captured and burned respectively to produce energy.
- **Fermentation**. Consists in the conversion of glucose or a carbohydrate into an alcohol or acid. Yeast or bacteria are added to the material for exhaust sugars to produce ethanol and a carbon dioxide. Ethanol can be distilled and dehydrated to increase alcohol concentration in an automotive fuel to achieve the required purity. The solid residue and sugar of the fermentation can be used as cattle feed and as fuel for boilers or gasification, respectively.

Based on these processes, it is possible to convert biomass into a solid, liquid or gas green-fuel. Biofuels are what is known as a carbon-neutral fuels. This definition is based on the fact that the carbon dioxide emissions associated to the use of biofuels are equal to the carbon dioxide absorbed by the plants from where the biofuel was obtained due to photosynthesis. It is possible to identify four different types of biofuels depending on the land that was used to grow it: 1st, 2nd, 3rd and 4th biofuel generation [7,8].

1st biofuels generation are biofuels made from food crops grown on arable land. Particularly, the biomass used is only seeded for fuel production. Sugar or vegetable obtained from crops are converted into biodiesel or ethanol by transesterification or yeast fermentation respectively.

2nd generation biofuels are made from lignocellulosic biomass, grasses, jatropha and other seed crops, waste vegetable oil, municipal solid waste, waste plant material and other agricultural residues. This kind of biomass is not fit for human consume. The main advantage of 2nd generation biofuels is that crops are grown into non-arable lands, fully used for biofuels synthesis due to its non-human consume characteristic. In contrast, the fuel synthesis is difficult due to the high-energy requirement for breaking the lignin strands. In particularly, 2nd generation biofuels are interesting in terms of streams revalue. It is possible to use waste streams with a low or almost negative value for biofuels production. In addition, the fact that non-human biomass is consume for the synthesis of this kind of biofuels avoid the possible ethical problem of using biomass with alimentary possibilities.

3rd generation biofuels are still under investigation and they are based in algae as biofuels source. For instance, from 1978 to 1996, the National Renewable Energy Laboratory (NREL) conducted an experiment in the Aquatic Species Program to obtain biofuels by means of algae. Also, the UNH Biofuels Group studied the replacement of all fuels currently being used by those produced by algae. According to this study, algae can be grown in ponds at wastewater treatment plants, and the oil obtained as a product can be converted into ethanol.

4th generation biofuels are almost equal to 3rd generation biofuels in terms of it being associated with algae as well. However, 4th generation biofuels are based on the genetic modification of some algae species to allow higher CO_2 capture [9].

1.3. LEVULINIC ACID

Levulinic acid (LA), or 4-oxopentanoic acid, is an organic compound obtained from the acid hydrothermal conversion of cellulosic biomass. It is used in nylon, fragrance products, synthetic rubber, plasticizers and pharmaceutical products production. Also, it is used at tobacco industry for increase nicotine and neuronal cells union. In particularly, LA is known as a platform chemical due to its versatility as intermediate chemical that can be converted into a high range of bio-based compounds and it has been identified as one of the chemicals used from renewable cellulosic resources to replace chemicals from crude oil or coal by US Department of Energy[10].

The Biofine process is proposed for its synthesis due to the high yield obtained from cellulose (composed by S-glucose units) and hemicellulose (composed by D-galactose, D-glucose and D-mannose) Biofine process *(Christensen et al. 2011)*. This method is a high temperature acid-catalysed hydrolysis using lignocellulosic biomass. The main goal is to refine biomass into products that are easy to separate and purify. These products are levulinic acid, formic acid, furfural acid and biochar, a carbonaceous compound that can be gasified or burned to produce steam and electric power. LA derivates, levulinic esters, traditionally used as additives for polymers, latex, fragrances and flavour preparations show potential to be also used as liquid fuel extenders [11]. In Figure 1 are detailed the main obtention routes of those products.

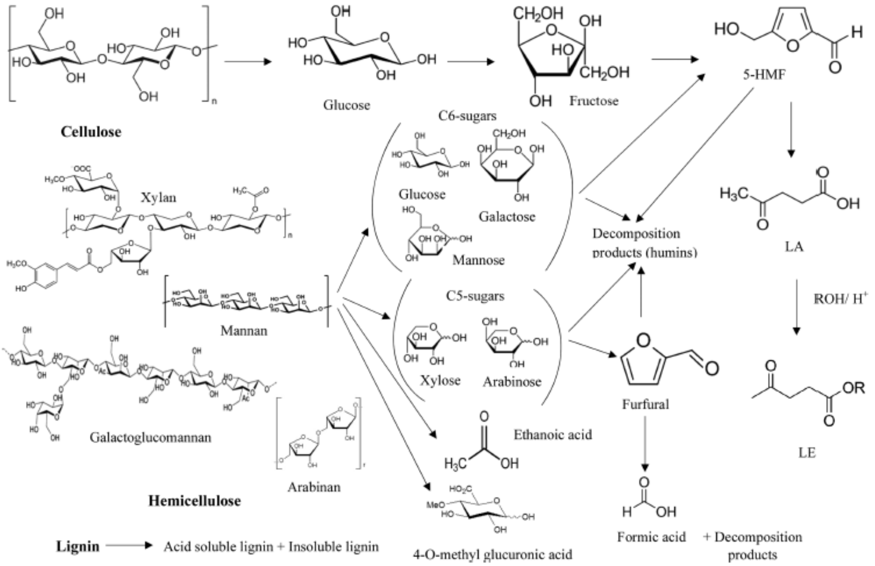


Figure 1. Conversion of lignocellulosic biomass components (Wei Tong et al. 2018).

This process is carried out in a two-stage thermocatalytic reactor system and allows a high LA yield (>70%). Firstly, the ray feedstock is pre-treated to remove hemicellulose and then, the high-cellulose residue is slurred using an acid (2-7 vol.%) and introduced into tubular reactor at 210-250ºC with a 7-30 seconds reaction to make possible the cellulose breakdown and converted into a mixture of hydroxymethylfurfural (HMF) and sugars. Then the resulting mixture is introduced into a second acid degradation stage (3-10 vol. %) at 150-200ºC with a reaction time between 1-30 minutes where sugars are converted into LA, formic acid and furfural acid. The insoluble char produced because of the reaction is separated and then LA is purified with a clarified hydrolysate. Formic acid is extracted from flash vapours and the pentose fraction of the previously preextracted hemicellulose is submitted to an acid-catalysed dehydration to be converted in furfural acid [12]. In Figure 2 is presented the flowsheet of the Biofine process.

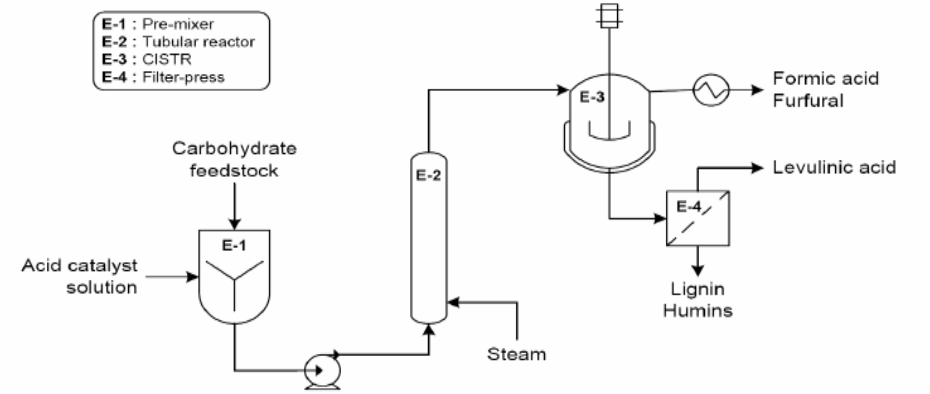


Figure 2. Biofine process [14]

1.3.1. Alkyl Levulinates

Alky levulinates are biomass-based compounds used in mineral oil refining with the potential to replace some petrochemicals additives used in diesel and gasoline formulations due to its properties. These compounds can be prepared by esterification of levulinic acid with butanol by acidic homogeneous or heterogeneous catalysis. Also, can be prepared directly from cellulose, sugars and furfuryl alcohol producing by-products such as *din*-butyl ether and water due to the alcohol dehydration or polymeric products (humins) because of furanic structures breakdown. (*Démolis et al. 2017*). In Figure 3 are described the alkyl levulinates synthesis routes.

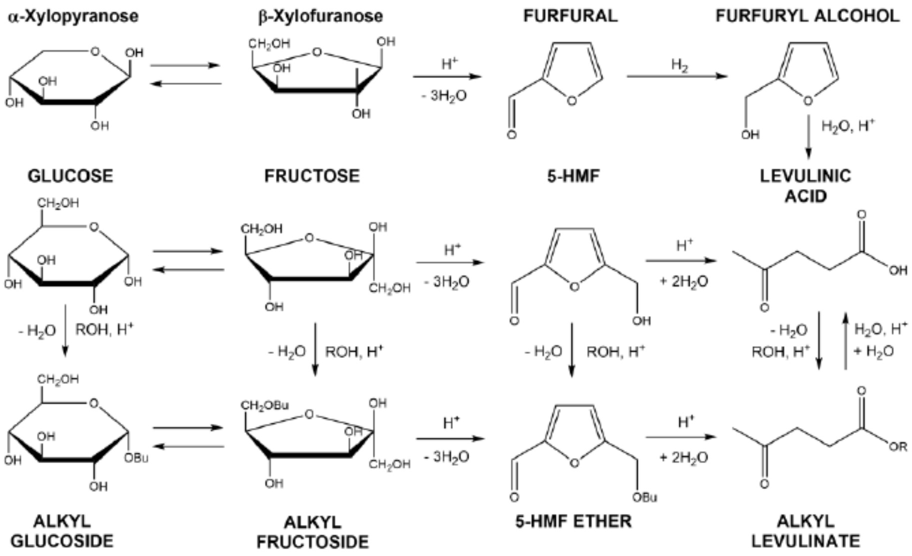


Figure 3. Alkyl Levulinate synthesis routes [24]

The most studied alkyl levulinate for use as biofuel is EL (ethyl levulinate). Its synthesis is based in a homogeneous acid catalysis using HCl, H_2SO_4 and H_3PO_4. Nowadays, due to the high polluting level of this products there are used eco-friendly solid acid catalysts including HPA (hypophosphorous acid), zeolites, sulphated carbon nanotubes, sulphated metal oxides, PS-DVB acidic sulfonic resins (usually Amberlyst 15) and others *(M.A. Tejero et al. 2016)*.

On the other hand, *n*-butyl levulinate (BL), which is another alkyl levulinate, has been mostly unexplored so far. This compound could also be a promising diesel or gasoline additive. Both levulinates, EL and BL, reduce vapor pressure and its freezing, boiling and flash point are acceptable for use in diesel. In addition, in mixtures formed by a 20% levulinate blends, EL form a separate liquid phase in diesel fuels at temperatures above the cloud point (10ºC), whereas BL still remains soluble below the cloud point (-25.8ºC approximately). As well as, a high content BL diesel mixture (20 wt. %) improve the out-smoke engine reducing it in a 55% and cause a free-soot combustion. Nevertheless, EL and BL show off a low cetane number and need to be enhanced using additives. Cetane number is an important combustible parameter that measures the fuels delay ignition. If it is had a high cetane number, implies a shorter period between the fuel injection and its burn. However, a low number implies a longer time between the injection and burned, that can be damaging for the engine and a power loss *(Yang et al. 2018)*.

Apart from BL and EL use as additives, exists another none-studied levulinate alternative for the same use, *sec*-butyl levulinate. The literature described sec-butyl levulinate obtention with 1-butene in excess of H_2SO_4, reaching a yield of 85% at 100ºC for 2h of reaction *(Gürbüz et al. 2018)*. It is a promising compound due to its properties as octane improver and its reactant's provenance, that come from an untapped refinery stream.

1.4. ACIDIC ION-EXCHANGE RESINS

Ion exchange resins are spherical or granules solids insoluble materials based in a cross-linked copolymer matrix with functional groups anchored through its structure. Two main commercial types of resins exist: macroreticular and microreticular [24].

. Macroreticular resins have a rigid external shell that shows the active's centres regardless of environment, unlike microreticular, that only presents its microporous structure, called gel-phase, that only shows if is in contact with a polar solvent. Depending on the pore diameter that copolymer matrix gives, resins present different type of porosimetry: ultramicropores (<0.7nm), micropores (<2nm), mesopores (2nm to 50nm) and macrospores (>50nm) [23].

The specific properties of each resin are given by the concentration of functional groups they present and by the characteristics of their polymeric matrix, which depends on the polymerization method. Its use as catalysts implies many advantages like easy handling and stockpiling, low corrosion problems, waste treatment much easier due to the reduced pH of final streams and a higher purity product because of its easy distinction by filtering. Also, due to their low density, resins are often in suspension even at low stirring speeds in most organics' solvents, allowing high yields. All these advantages cause an operational reduction cost [23,24].

One of the main resin types used in the industry are formed by styrene and with divinylbenzene as the cross-linking agent (PS-DVB). Their obtention process is based in the styrene polymerization and the divinylbenzene addition once the polymerization occurs. In addition, these resins are sulfonated, which means that a concentrated sulfuric bath is given to them in order to add acid properties to the catalysts. Three types of sulfonation are usually distinguished according to the number of sulfonic groups presents: over-sulfonation (OS), conventional sulfonation (CS) and surface sulfonation (SS) in descending order of high to less sulfonation[23,24]. In Figure 4 is outlined the structure of a sulfonated resin.

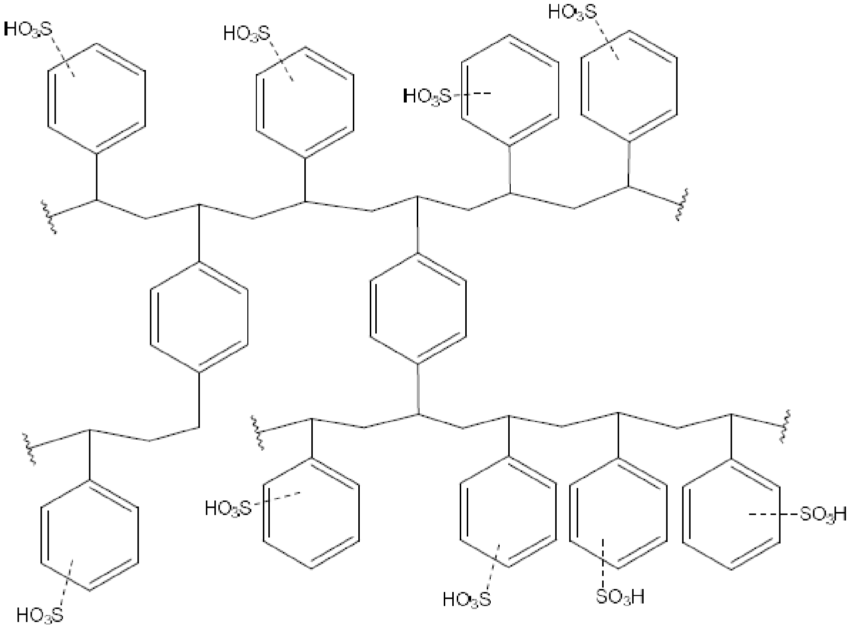


Figure 4. Representation of PS-DVB sulfonated ionic-exchange resin [23]

The parameters that affect to each of catalyst and determinate its optimal use for one particularly process are DVB%, swelling, stability, particle diameter, density, water affinity and acid capacity [23,24].

DVB% establishes the type of polymeric structure. Low cross-linked agent implies a soft, elastic and mechanically unstable gel-type resin with a reduced surface contact area and a high number of actives sites that can be sulfonated due to the high percent of styrene in front of the DVB percent. Whereas, with high DVB% are obtained macroreticular resins that has a larger surface contact than gel-type, but with less % of styrene so less actives sites for the catalysis. Also, a high percent of DVB causes problems of internal mass transference due to the high density of the structure [24].

Swelling capacity is the volume variation of a resin owing to its interaction with a polar substance and difference osmotic pressure outside and inside of the particle. In Figure 5 can be observed the swelling effect to the resin depending on if is macroreticular or gel-type in the presence of a polar solvent [23,24].

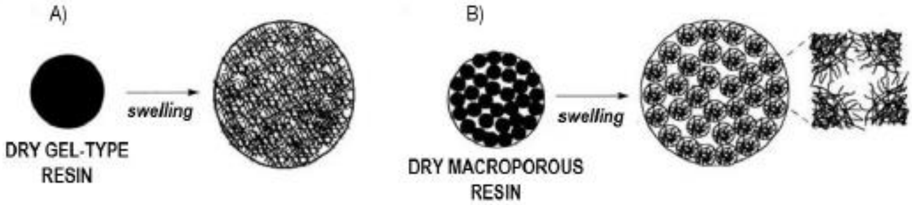


Figure 5. Swelling effect at gel-type resin (A) and macroreticular resin (B) [24]

For evaluate resins morphology in a swollen state it is used the ISEC (Inverse Exclusion Chromatography) technique. It is a chromatographic technique based in the elution volume of standard solvents with known molecular sizes using a chromatographic column fill with a mixture of the solute and resin to treat [23,24].

Density is a relation between as the dry mass of resin per unit of volume. %DVB, matrix structure and functional groups determine this parameter.

Stability is by three points: mechanical, chemical and thermal. Mechanical stability is defined as resin tolerance against compression or breaking. This resistance is given by the matrix structure. Thus, macroreticular resins are stiffer than gel-type regarding mechanical forces. Chemical stability is the capacity of working in an oxidizing medium of the resin's polymeric structure without suffering any change. High DVB% resins are more resistant against an oxidizing medium than the low DVB% resins. Thermal stability is the capacity of the resin of bear high temperatures. Macroreticular resins, that have a high percent of DVB, has less thermal stability (120-150ºC) than gel-type ones (150ºC) [23,24].

Water content is defined as the relation between water in the mixture and the mass of resin hydrated.

Acid capacity is marked by the accessible sulfonic groups number in a swollen state. It Is determined by acid-base titration. This method consists in a quantitative analysis of acid or base concentration in a substance neutralizing it with an acid or base standard solution with known concentration. It is measured in terms of mmols per unit of mass or volume. If it is had a resin with a high percent of sulfonation it will has a high acid capacity [23,24].

In this study it has been tried to correlate the morphological catalysts properties with the SBL formation rate at initial times. To that end, a screening study of different catalysts has done. Also, a swelling determination has been made to check its behaviour in the reaction media.

2. OBJECTIVES

This study is part of a larger project which goal is to produce additives to improve fuel characteristics from biomass. In particular, the objectives of this study are:

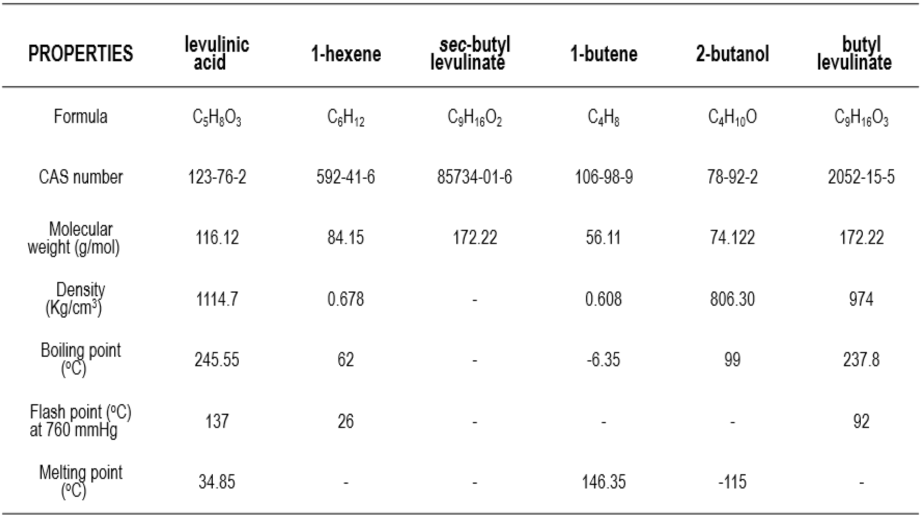
1. To perform a screening study of the different chosen acidic ion-exchange resins to produce sec-butyl levulinate from esterification of levulinic acid and 1-butene.
2. To determine which types of acidic ion-exchange resins are better for the reaction comparing reaction rates and yield to the ester expressed as the product of selectivity and conversion.
3. To explain catalytic behaviour based on the structural and morphological resins properties.

3. EXPERIMENTAL SECTION

3.1. REACTANTS AND CATALYSTS

The experiments for the synthesis of sec-butyl levulinate were carried out with levulinic acid (ACROSS ORGANICS, Code: 125140010, purity 98% and 2% water) and 1-butene (AIR LIQUIDE, purity 99.9%). In the calibration process, analytic standards were also used: 2-butanol (PANREAC, Code: 163851.1611, purity 99% and 1% water) and butyl levulinate (SIGMA ALDRICH, Code: 101495705, purity 98% and 2% water). In the swelling experiments, besides levulinic acid, 1-hexene was used (ACROSS ORGANICS, Code: 213210025, purity 97% and 3% water). Main properties of the used reagents are listed in Table 1.

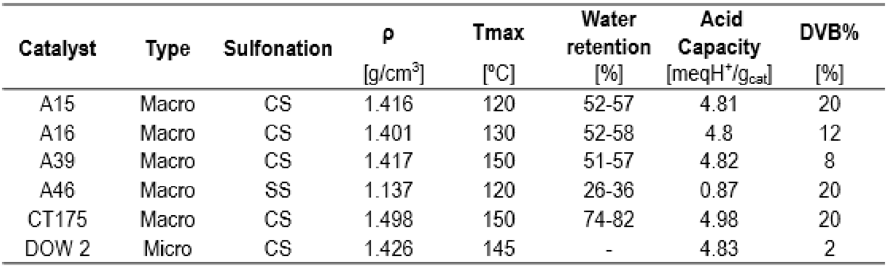
Table 1. Reactants and products used in screening study and swelling determination



PROPERTIES	**levulinic acid**	**1-hexene**	***sec*-butyl levulinate**	**1-butene**	**2-butanol**	**butyl levulinate**
Formula	$C_5H_8O_3$	C_6H_{12}	$C_9H_{16}O_2$	C_4H_8	$C_4H_{10}O$	$C_9H_{16}O_3$
CAS number	123-76-2	592-41-6	85734-01-6	106-98-9	78-92-2	2052-15-5
Molecular weight (g/mol)	116.12	84.15	172.22	56.11	74.122	172.22
Density (Kg/cm^3)	1114.7	0.678	-	0.608	806.30	974
Boiling point (ºC)	245.55	62	-	-6.35	99	237.8
Flash point (ºC) at 760 mmHg	137	26	-	-	-	92
Melting point (ºC)	34.85	-	-	146.35	-115	-

Ion-exchange polystyrene-divinylbenzene sulfonated resins were used. The resins used as catalysts were Amberlyst 15 (A15), Amberlyst 16 (A16), Amberlyst 39 (A39), Amberlyst 46 (A46), Dowex 50Wx2 (Dow2) and Purolite CT-175 (CT175). All resins are conventionally sulphonated (CS) except for A46, a surface sulphonated (SS) one. Regarding the structure, all resins are macroreticular except for Dow2, a microreticular one. In Table 2 are specified the catalysts used and its morphological properties.

Table 2. Catalysts properties



Catalyst	**Type**	**Sulfonation**	**ρ** [g/cm^3]	**Tmax** [ºC]	**Water retention** [%]	**Acid Capacity** [meqH$^+$/g$_{cat}$]	**DVB%** [%]
A15	Macro	CS	1.416	120	52-57	4.81	20
A16	Macro	CS	1.401	130	52-58	4.8	12
A39	Macro	CS	1.417	150	51-57	4.82	8
A46	Macro	SS	1.137	120	26-36	0.87	20
CT175	Macro	CS	1.498	150	74-82	4.98	20
DOW 2	Micro	CS	1.426	145	-	4.83	2

3.2. EXPERIMENTAL SETUP

The experimental setup consists of a 250 mL batch reactor with 200 mL of useful volume (Autoclave Engineers, INC. SERIAL Nº. E89-10735-1) equipped with a six-blade stirrer. The reactor's temperature is controlled by a 1,2-propanediol-water thermostatic mixture.

The analysis was made by a gas chromatograph (Agilent 6890 GC Series System) in a capillary column (Santa Clara, US; 100% dimethylpolysiloxane, 50 m x 0.2 mm x 0.50 µm) connected to a mass selective detector (Agilent 5973 Network Mass Selective Detector). Main parts of the setup are specified in Figure 5.

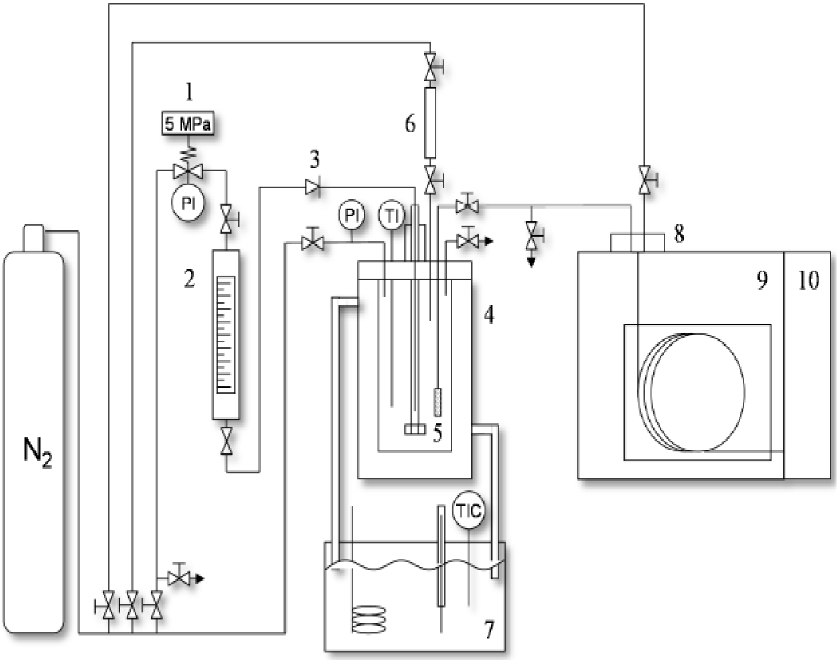


Figure 5. Setup. 1: safety valve, 2: pressure burette, 3: one-way valve, 4: batch reactor, 5: 2µm filter, 6: catalyst injector, 7: thermostatic bath,8: sampling valve, 9: gas chromatograph, 10: mass selective detector [23].

3.2.1. Resins pre-treatment

Before carrying out every experimental, all resins were dried at room temperature first, and heated up later in order to reduce their water content, which are listed in Table 2. After room temperature drying, resins are introduced into an atmospheric oven at 110 ºC for 2 hours and 30 minutes. This first step allows reducing the contain of non-tied water that the particle has. Afterwards, resins are introduced into a vacuum oven at 100 ºC overnight (at least 12 hours). This final stage allows reducing a certain amount of water that is still tied to the resin.

3.2.2. Experimental procedure

Reactants are weighed separately and then introduced into the reactor. Firstly, it is necessary to heat levulinic acid above its melting point at atmospheric pressure (34.85 ºC) in order to handle it properly. Once LA is in the liquid state, the necessary mass is weighed and introduced in the reactor vessel, which is then closed. Previously, the heating system of the reactor is switched on to increase its temperature to the desired value for the experiment. Then, 1-butene is introduced by charging it before into a pressure burette, previously weighed empty, and then weighed with the reactant for knowing the mass entered. It is necessary to introduce it with the minimum pressure increase to have an increase of pressure as high as possible between the cartridge where the resin is placed (at 25 bars) and the reactor to ease the injection of all the solid resin into the reactor vessel.

Once reactants are into the reactor, the agitation system is set to 750-800 rpm. Finally, when the reactor temperature reaches approximately 100ºC, the catalyst, previously charged into the cartridge and then pressurized to 25 bars, is introduced into the reactor. This is the zero time of the reaction. Then, a sample is extracted using the sample valve and sent to the chromatograph for the analysis which takes 20 minutes.

It is necessary to return the sample to the reactor to keep approximately the same mixture's mass as the beginning. Sample valve is closed, and recirculation valve is opened to make possible the nitrogen flow. Secondly, vent valve is opened to reduce the overpressure to 20 bars and then once it is arrived at pressure required it is closed. Finally, sample valve is opened to introduce the mixture into the reactor using nitrogen to drag the sample and it is closed when the manometer marked 25 bars approximately. For purge the pipe line for avoiding sample contamination it is used nitrogen expelled out throw the purge valve.

3.2.3. Reactor and setup cleaning

After the final analysis, the heating system is turned off. Once the temperature has enough decreased, the reactor is opened, cleaned and prepared for the next run. To remove the mixture inside the reactor, it is necessary to use a vacuum extractor equipment. Then, acetone is used to drag the acidic resins particles that still remains into the reactor. The resultant mixture is extract using the same equipment before. These mixtures are deposited into a special drum, filtering the acidic resins that there are present.

3.2.4. Sampling method

To make an analysis is necessary to extract a mixture sample from the reactor. Sample valve of the reactor is opened, and chromatograph pipes are filled with mixture. Once this happens, the chromatographic method is turned on and a 2 µL sample is analysed. Firstly, the sample is heated up to 40 ºC for 6 minutes and then it is heated to 200 ºC using a rate of 35 ºC/minute. Once is heated to 200 ºC, this process will be standing for 9 minutes. Figure 6 is an example of a chromatogram obtained at the end of one analysis with the temperature variation previously explained.

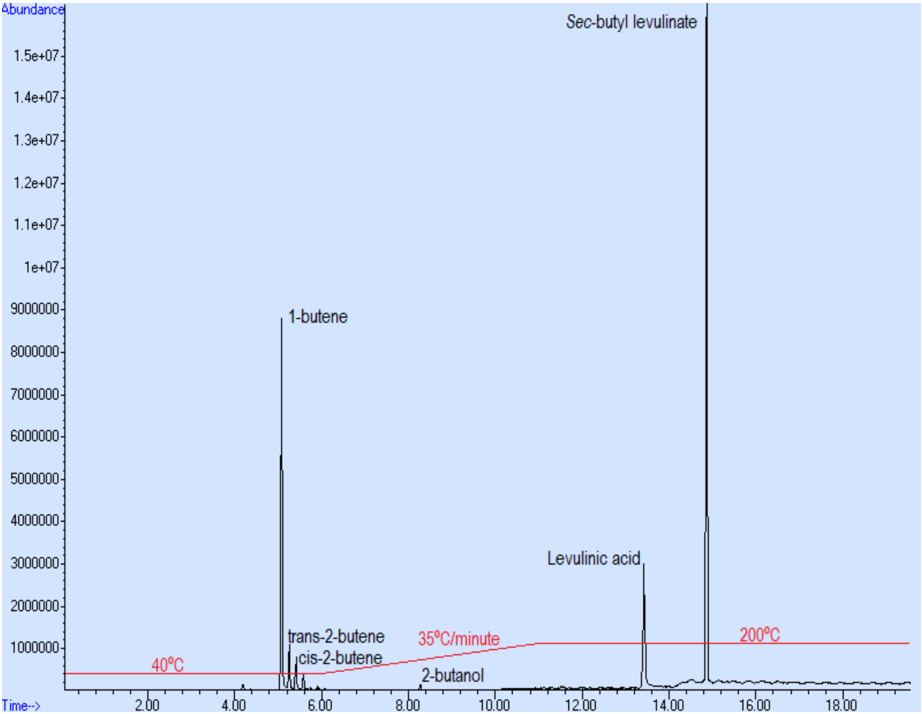


Figure 6. Analysis of reaction sample (T=100ºC, $R_{LA/1B}$ = 0.5, 2g of CT175)

3.3. OPERATION CONDITIONS

Experiments of approximately 5 hours were carried out at 100 ºC and 25 bars of pressure to keep 1-butene in the liquid state and to allow the sample flow. Initial molar ratio of levulinic acid to 1-butene was set at 0.5 and commercial particle diameter for the resins. The LA/1B molar ratio is defined as:

$$R^0_{LA/1B} = \frac{n^0{}_{Levulinic\ acid}}{n^0{}_{1-butene}} \left[\frac{mol\ LA}{mol\ 1B}\right]$$

These experimental conditions had been found in a previous work, in which A15 was used as the catalyst and several temperatures and initial molar ratios were explored in order to find the best experimental conditions; that is those maximizing yield towards *sec*-butyl levulinate. Main results for that study are summarized in Table 3.

Table 3. Results for the screening with different experimental conditions.

TABLE III

SUMMARY OF EXPERIMENTAL RESULTS OVER A-15 CATALYST

Experimental conditions	T (°C)	χ°_{1B} (mol/mol)	X_{1B}	X_{LA}	S^{SBL}_{1B}	S^{SBL}_{LA}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
1	110	0.50	0.99	0.42	0.14	1	0.14	0.42
2	100	0.67	0.97	0.78	0.62	1	0.60	0.78
3	100	0.33	0.98	0.32	0.80	1	0.79	0.32
4	75	0.50	0.78±0.01	0.23±0.02	0.29±0.11	1	0.22±0.09	0.23±0.02
5	75	0.25	0.85	0.11	0.42	1	0.36	0.11
6	75	0.72	0.88	0.78	0.52	1	0.46	0.78
7	50	0.67	0.11±0.02	0.19±0.08	0.32±0.18	1	0.04±0.02	0.19±0.08
8	50	0.34	0.21±0.04	0.002±0.001	0.07±0.03	1	0.017±0.010	0.002±0.001

3.4. SWELLING DETERMINATION

To know the effect of the nature of the reaction media on resin morphology, several swelling experiments have been performed. The protocol to carry out those experiments is as follows: firstly, a certain amount of each resin is introduced into a graduated test tube, and both its weight and volume are recorded. Then, the solute is added until it overpasses the resins volume. Then, the solute volume and mass are recorded. Finally, each tube is covered with parafilm and put to rest for about two days. Once this period passes, resin and solute volumes are recorded again.

The solvents of choice have been levulinic acid and 1-hexene. Note that 1-hexene was used instead of 1-butene because it is liquid at room pressure and temperature. These two solvents are opposed in terms of polarity, with levulinic acid being a polar solvent and 1-hexene an apolar one.

Resin swelling is calculated with equation 2, where V is the particle volume in the solvent and V_0 is the particle volume when air-dried. From swelling values, it is possible to calculate the solvent moles absorbed by the polymer mass by means of equation 3, where ρ_j and M_j are the density and molecular weight of compound j, and ρ_s the skeletal density of the resin [25].

$$\text{Swelling} = \frac{V-V_0}{V_0} \times 100\ [\%]\ (2)$$

$$\text{Mole of solvent per gram of catalyst} = \frac{V-V_0}{V_0} \times \frac{\rho_j}{\rho_s} \times \frac{1}{M_j}\ \left[\frac{\text{mole solvent}}{\text{g catalyst}}\right]\ (3)$$

3.5. CALIBRATION

To follow the reaction progress and to quantify reactants and products, a calibration of the reaction system needed. To do it samples of known compositions have been analysed in the GC. Calibration data and the process followed to find the various parameters are presented in the corresponding appendix 1. The expressions found for each component are described in Table 4.

Table 4. Expressions for calibration

Compound	Expression	Parameters		
		a	b	c
levulinic acid	$y = ax$	1.1310±0.0793	-	-
sec-butyl levulinate	$y = ax^b$	0.9586±0.0802	1.7997±0.2481	-
2-butanol	$y = ax + b$	3.0424±0.4737	-	-
1-butene	$y = ax < 0.4$	2.5696±0.3434	-	-
	$y = a * \left(b - e^{(-cx)}\right) \geq 0.4$	0.7553±0.0000	1.3361±0.0000	3.5562±0.0000

3.6. GENERAL CALCULATIONS

Mass fraction from each compound is found using the calibration equations. Molar fraction is calculated with 4, where x_j and MW_j is mass fraction and molecular weight from compound j.

$$\mathrm{x_{mj}} = \frac{\mathrm{x_j} / \mathrm{MW_j}}{\sum_{\mathrm{j=1}}^{\mathrm{n}} \mathrm{x_j} / \mathrm{MW_j}} \ [-] \ (4)$$

1B and LA conversions are calculated with 5 and 6 respectively. Each term corresponds to the molar fraction of the compound specified.

$$\mathrm{X_{1B}} = \frac{\mathrm{x_{m_{SBL}} + x_{m_{t2B}} + x_{m_{c2B}} + x_{m_{2B}}}}{\mathrm{x_{m_{1B}} + x_{m_{SBL}} + x_{m_{t2B}} + x_{m_{c2B}} + x_{m_{2ButOH}}}} \ [-] \ (5)$$

$$\mathrm{X_{LA}} = \frac{\mathrm{x_{m_{SBL}}}}{\mathrm{x_{m_{SBL}} + x_{m_{LA}}}} \ [-] \ (6)$$

1B selectivity is calculated with 8, where each term corresponds to the molar fraction. LA selectivity value is 1 due to all of LA consumed is for SBL formation.

$$\mathrm{S_{LA}^{SBL}} = 1 \ [-] \ (7)$$

$$\mathrm{S_{1B}^{SBL}} = \frac{\mathrm{x_{m_{SBL}}}}{\mathrm{x_{m_{t2B}} + x_{m_{c2B}} + x_{m_{2ButOH}}}} \ [-] \ (8)$$

1B yield is calculated with 9, where X_{1B} is 1B conversion and S_{1B}^{SBL} its selectivity regards SBL. LA yield is calculated with 10, where X_{LA} is LA conversion and S_{LA}^{SBL} its selectivity regards SBL.

$$\mathrm{Y}_{\mathrm{1B}}^{\mathrm{SBL}} = \mathrm{X}_{\mathrm{1B}} \times S_{1B}^{SBL} \; [-] \quad (9)$$

$$\mathrm{Y}_{\mathrm{LA}}^{\mathrm{SBL}} = \mathrm{X}_{\mathrm{LA}} \times S_{LA}^{SBL} = \mathrm{X}_{\mathrm{LA}} \; [-] \quad (10)$$

Contact time is defined in 11, where *w* is mass of catalysts use, *t* reaction time and *n_j* is the number of moles.

$$\tau_{\mathrm{cat}} = \frac{\mathrm{w} \times \mathrm{t}}{n_j} \; (\mathrm{g\,min\,mol^{-1}}) \quad (11)$$

4. RESULTS AND DISCUSSION

4.1. CATALYSTS MASS EFFECT

To carry out the screening study it has been necessary to choose in the first place the amount of catalysts to be used. Therefore, different experiments have been made varying the catalyst weight (w_{cat}). These experiments were done to verify that different amounts of catalyst do not affect the reaction progress. In Figure 7 are illustrated LA and 1B conversion in front of the contact time between resin and each LA and 1B mol. Contact time (τ) is defined in 11, where *w* is mass of catalysts use, *t* reaction time and n_j is the number of moles at that time.

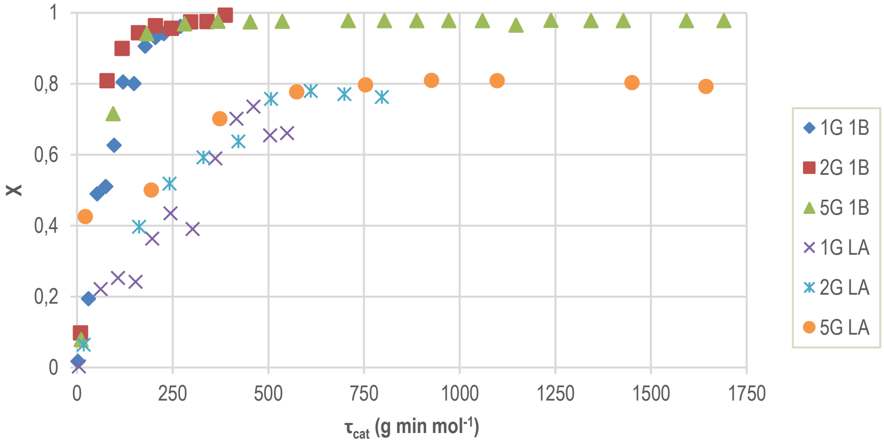


Figure 7. Conversion of LA and 1B with contact time using 1g, 2g and 5g of catalyst

It is observed that a variation between 1 g, 2 g and 5 g of catalyst has not an effect in the final conversion degree, around 80% regarding to LA and almost complete conversion regarding to 1B for all the experiments carried out. These means that material transference has not relevance using this catalysts rank, which means that it is possible to use for a screening study a charge between 1 g and 5 g without any effect of material transference.

According to these experiments, it was decided to use 2 g of catalysts due to a clearly reaction monitoring in a determinate time which, on the contrary a use of 5 g or 1 g it would imply a too fast or too slow reaction respectively, hindering the later analysis.

4.2. REACTION SYSTEM EVOLUTION

During the course of the reaction, the moles number of products and reactants are monitored. In Figure 8 it can be observed an example of each compound evolution through the reaction according to mass fraction during the reaction time. Mass fraction is calculated as detailed in the general calculations section.

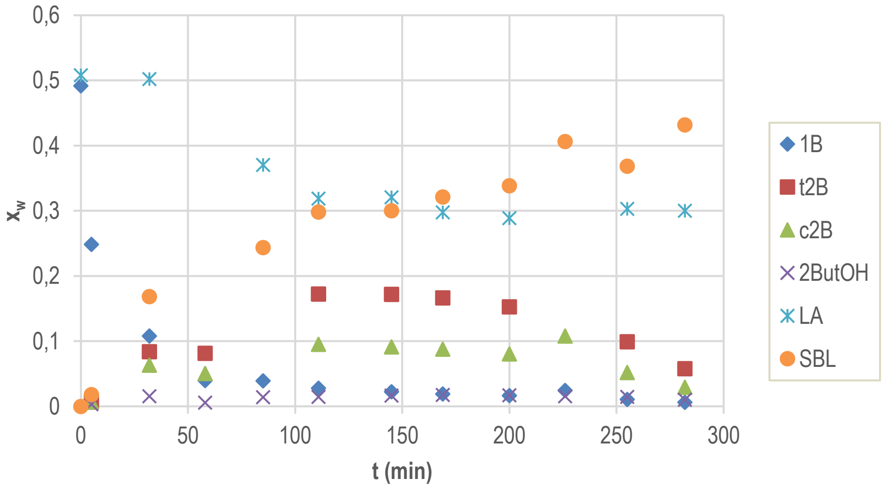


Figure 8. Mass fraction of products and reagents over the reaction time (T=102.6ºC, $R^0_{LA/1B}$=0.50, 2.0735g of CT175)

Levulinic acid reacts with 1-butene to produce *sec*-butyl levulinate. For all the performed experiments no by-products formed from levulinic acid have been observed, so its selectivity towards *sec*-butyl levulinate has been considered as equal to unity. However, it is noticed a formation of side-products like 2-butanol and oligomeric compounds. 2-butanol production can be caused by hydration of 1-butene due to water content in catalysts and reactants used. Also, isomeric compounds from 1-butene as *trans*-2-butene and *cis*-2-butene are observed that react between them forming dimers. The appearance of all these products explains the lower selectivity values obtained from 1-butene in comparison with levulinic acid selectivity.

4.3. CATALYST SCREENING

For every screening experiment, initial SBL formation rates have been determined. Rates at the initial reaction time are considered as suitable to establish activity comparisons between catalysts since the experimental conditions are the same for all the resins. Experimental reaction rate values are calculated as indicated in equation 12, where w_{cat} is the amount of catalyst used and dn_{SBL}/dt, the moles variation of SBL over the reaction time, in this case, at t=0.

$$r_{SBL}^{0} = \frac{1}{w_{cat}} \times \left(\frac{dn_{SBL}}{dt}\right)_{t=0} \left[\frac{\mathrm{mol}}{\mathrm{h\ g_{cat}}}\right] \quad (12)$$

To determine the rate values, an empirical equation to describe SBL moles evolution in time has been fit to experimental data. To do it, expression 13 was used, where y is n_{SBL}/w_{cat}, a, b and c constants and x is time

$$\mathrm{y = a \times (b - exp(-cx))} \quad (13)$$

In Figure 9 it is represented the CT175 calculus, an example of a typical fit. Also, are detailed the parameters found. To fit the predicted values to experimental ones, it has been done least squares method. From this method, is possible to calculate SBL production rate for each reaction time.

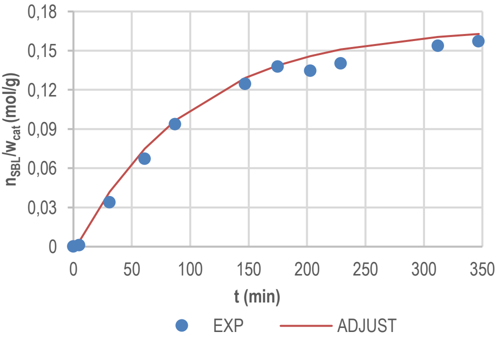
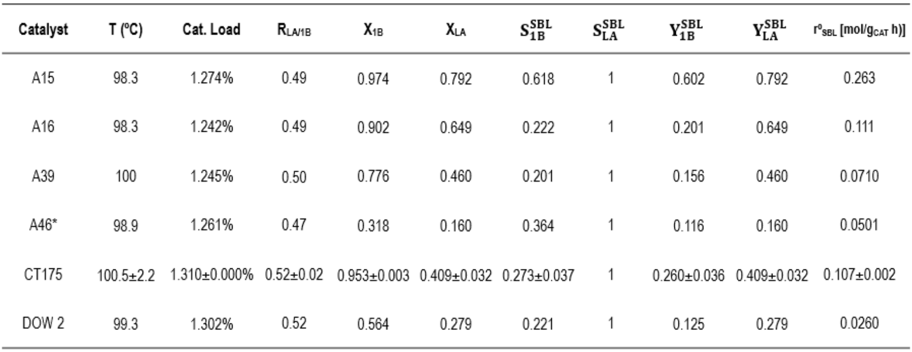


Figure 9. T=98.3 ºC, $R^0_{LA/1B}$=0.53, 2.0488g of CT175

Based on this method, SBL formation rate is calculated for all the catalysts used. In Table 5 are detailed the results for each catalyst. Notice that CT175 is expressed with error values, due to the realization of three valid replies.

Table 5. Screening results at approximately 200 minutes of reaction time



Catalyst	T (ºC)	Cat. Load	$R_{LA/1B}$	X_{1B}	X_{LA}	S_{1B}^{SBL}	S_{LA}^{SBL}	Y_{1B}^{SBL}	Y_{LA}^{SBL}	r^0_{SBL} [mol/g_{CAT} h)]
A15	98.3	1.274%	0.49	0.974	0.792	0.618	1	0.602	0.792	0.263
A16	98.3	1.242%	0.49	0.902	0.649	0.222	1	0.201	0.649	0.111
A39	100	1.245%	0.50	0.776	0.460	0.201	1	0.156	0.460	0.0710
A46*	98.9	1.261%	0.47	0.318	0.160	0.364	1	0.116	0.160	0.0501
CT175	100.5±2.2	1.310±0.000%	0.52±0.02	0.953±0.003	0.409±0.032	0.273±0.037	1	0.260±0.036	0.409±0.032	0.107±0.002
DOW 2	99.3	1.302%	0.52	0.564	0.279	0.221	1	0.125	0.279	0.0260

**values obtained at 96 minutes.*

According to Table 5, the best catalysts for this reaction are macroreticular ones. In particularly A15, obtaining the highest conversion, yields and 1B selectivity values regarding SBL. Its best result is due to its particularly morphological properties Notice that A46 has the lowest yield, conversion and selectivity values, due to its lower sulfonation than the others catalysts. These properties are determining for understanding its catalytic behaviour. In Table 6 are detailed the properties used for the catalytic activity analysis.

Table 6. Morphological properties of the screening catalysts

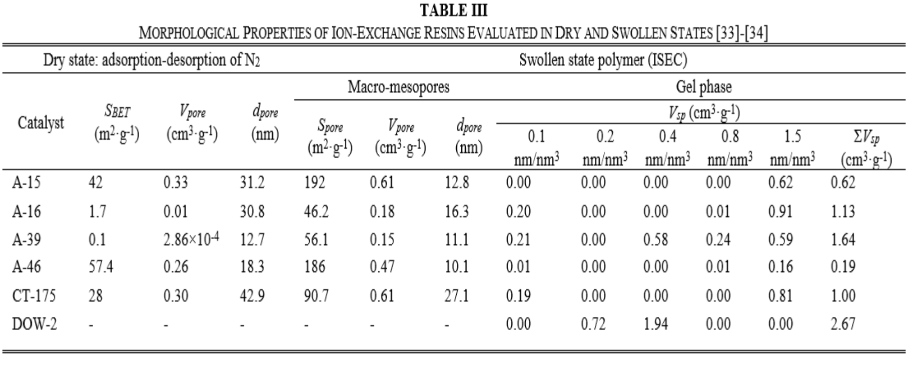


TABLE III

MORPHOLOGICAL PROPERTIES OF ION-EXCHANGE RESINS EVALUATED IN DRY AND SWOLLEN STATES [33]-[34]

Dry state: adsorption-desorption of N_2				Swollen state polymer (ISEC)								
				Macro-mesopores			Gel phase					
Catalyst	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	d_{pore} (nm)	S_{pore} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	d_{pore} (nm)	V_{sp} ($cm^3 \cdot g^{-1}$)					
							0.1 nm/nm^3	0.2 nm/nm^3	0.4 nm/nm^3	0.8 nm/nm^3	1.5 nm/nm^3	ΣV_{sp} ($cm^3 \cdot g^{-1}$)
A-15	42	0.33	31.2	192	0.61	12.8	0.00	0.00	0.00	0.00	0.62	0.62
A-16	1.7	0.01	30.8	46.2	0.18	16.3	0.20	0.00	0.00	0.01	0.91	1.13
A-39	0.1	2.86×10^{-4}	12.7	56.1	0.15	11.1	0.21	0.00	0.58	0.24	0.59	1.64
A-46	57.4	0.26	18.3	186	0.47	10.1	0.01	0.00	0.00	0.01	0.16	0.19
CT-175	28	0.30	42.9	90.7	0.61	27.1	0.19	0.00	0.00	0.00	0.81	1.00
DOW-2	-	-	-	-	-	-	0.00	0.72	1.94	0.00	0.00	2.67

Firstly, an attempt to correlated macroporous catalysts with its dry-state properties has done. In Figure 10 are represented the different r_{SBL}^{0} obtained for each macroreticular catalyst related to its d_{pore}, S_{pore} and V_{pore}.

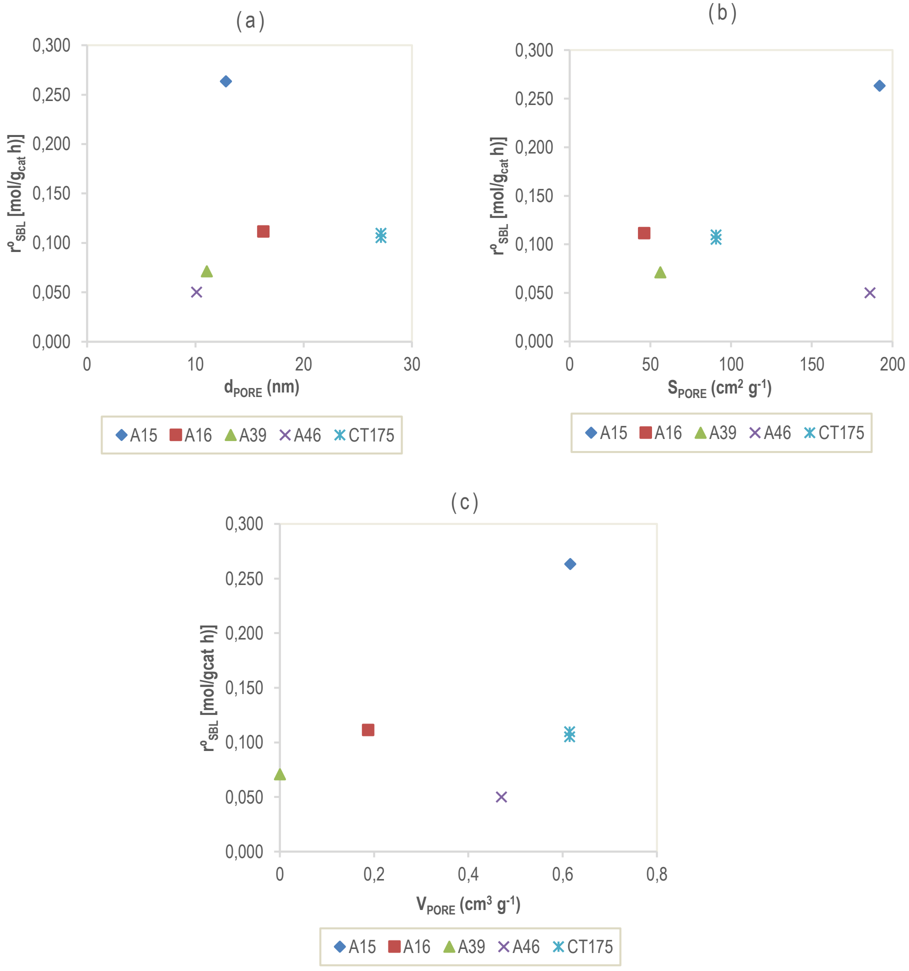


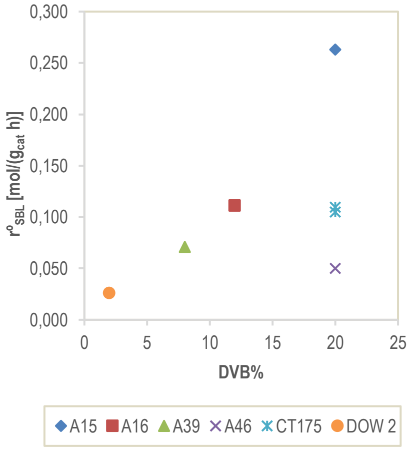
Figure 10. Sec-butyl levulinate formation rate at t=0 min, related to (a) d_{pore}, (b) S_{pore} and (c) V_{pore}.

In general, resins with larger pores, in terms of pore diameter, area and volume are expected to present higher rates, due to the easier access of the molecules to the active centres. In the present reaction medium, these factors play an important role because the size, relatively large, of the molecules involved, such as levulinic acid and SBL. Also, in general terms, a higher sulfonation degree would imply a higher concentration of actives sites, what would entail higher r_{SBL}^{0} values.

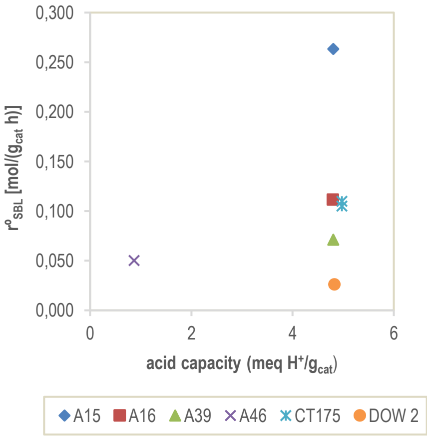
In (a) it is not observed a correlation between the pore diameter of the used catalysts and r_{SBL}^{0}. With a higher pore catalyst diameter, higher r_{SBL}^{0} would be achieved, but, according to Table 6, the catalyst that has highest r_{SBL}^{0} is A15, staying behind of A16 and CT175 in terms of pore diameter. In (b) it is observed a correlation between the surface pore and r_{SBL}^{0}. With higher pore area, higher velocity is achieved, being A46 as an exception, which is clearly related to its poor sulfonation degree. Also, A16, that would be expected to present a lower r_{SBL}^{0} according to its surface, is above of A39. In (c) it is observed that larger pore volumes are related to higher r_{SBL}^{0} values. As before, A46 is an exception due to its poor sulfonation.

Apart from compared its morphological pore structure, can be compared, between macroreticular and microreticular, its amount of crosslinking agent (DVB%), acid capacity (meq H^{+}/g) and gel-phase volume (V_{sp}), a microporous volume that appears when catalysts are in swelling state. In Figure 11 are represented the different r_{SBL}^{0} obtained for each catalyst related to its DVB%, acid capacity (meq H^{+}/g_{cat}) and ΣV_{sp} ($cm^{3}\ g^{-1}$).

(a)



(b)



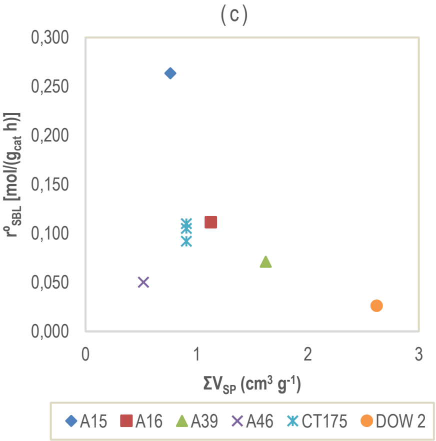


Figure 11. Sec-butyl levulinate generation velocity at t=0 min, related to (a) DVB%, (b) acid capacity and (c) ΣV$_{sp}$.

It is observed in Figure 11 (a) a correlation between amount of crosslinking agent and r_{SBL}^{0}. An increasing in DVB% implies a higher reaction rate. This could be due to the limited need of macroreticular resins to swell in the present reaction medium. Catalysts in swollen state have its actives centres more dispersed inside, which means that molecules that enter into the resin will take longer to interact with an active centre, which would mean a slower catalytic activity. High percentage of DVB implies a high rigidity, which means that swollen state is lesser in comparison with resins with lesser DVB%, thus affecting as it is said before, the concentration of actives centres inside the catalyst. This would explain the observed higher r_{SBL}^{0} values with resins that present larger amounts of DVB.

As can be expected, in Figure 11 (b) is observed that catalysts with higher sulfonation have a higher r_{SBL}^{0} due to the higher concentration of actives centres. On its own, this property would not explain the different r_{SBL}^{0} achieved with the different resins with similar sulfonation. It should be explained with morphological properties, as it is previously said.

In Figure 11 (c) is observed a correlation between the gel-phase volume (ΣV$_{sp}$) and r_{SBL}^{0}, being the catalysts with lower ΣV$_{sp}$ the ones presenting higher catalytic activity. This could be due to the presence of a microporous phase inside the resin during the catalysis. Levulinic acid, in particularly, is the biggest molecule of this reaction system and it consume or not has a direct influence on the course of the reaction due to olefins excess (1-butene). DOW 2 has the highest ΣV_{sp} value, around 1.62 cm^3/g, and it is the catalyst with the lowest r^0_{SBL} value. This could be explained by assuming that resins with larger ΣV_{sp} present a denser microporous structure and, as a consequence, levulinic acid would experience some transport hindrances to access an active centre, which would slow down the reaction. Thus, resins with thinner gel-phase would be expected to present higher r^0_{SBL} values, because their active centres would be more accessible Even the r^0_{SBL} is related to morphological properties, it does not explain the difference between A15 and CT175 *sec*-butyl formation rates. It is supposed, according to its morphological properties, that both are identical, but, as it is observed, its results are considerably different. Since the assessment of the observed results based on morphological characteristics of the resins cannot provide a satisfactory explanation to the differences observed between A15 and CT175, which are considered as similar catalysts an alternative approach has been adopted.

Swelling phenomena constitutes an important factor related to the molecular permeation through the polymer backbone of a resin and the adsorption on an active site. With regard to the gel phase morphology in swollen state, ISEC provides experimental data of the expanded volume in polymer domains of different densities swollen in water [23]. In Figure 12 are detailed the mass polymer densities of the catalysts, measured in nm/nm^3, related to ΣV_{sp} and its X_{LA} at 200 minutes of the reactions time, according to Table 5.

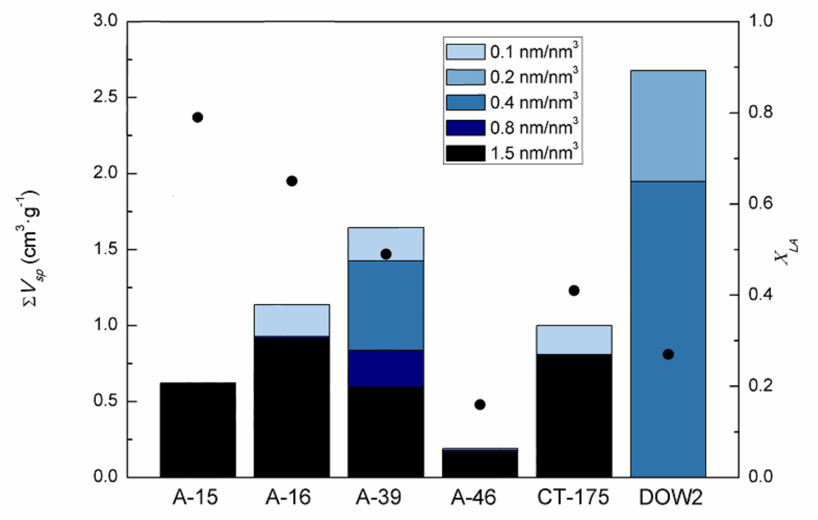


Figure 12. Conversion achieved at 200 minutes related to ΣV_{sp} and density polymeric fractions according to ISEC.

It can be considered that the number of actives centres inside a catalyst is proportional to its polymer chain length. On the other hand, it could be expected that a catalyst with a high polymer density would present a lower catalytic activity, since its acid centres are less accessible than the catalysts that have a less dense polymeric matrix. As observed in Figure 12, among the different possible gel-phase fractions, according to their density, A15 presents only that with 1.5 nm/nm^3, the heaviest one, whereas the gel-phase of CT175 is also formed by a fraction of 0.1 nm/nm^3 one, the lightest one. This difference between polymeric densities, being A15 denser than CT175, and having a higher pore surface (192 m^2/g) than CT175 (90.7m^2/g), could explain that A15 has a higher r_{SBL}^{0} than CT175 because it has a higher concentration of actives centres due to its high polymeric density and a largest surface, which means a higher area to react with levulinic acid. It is true that A15 has lower d_{pore} than CT175, 12.8 nm and 27.1 nm respectively, which would imply a lesser geometrical space to levulinic acid entrance, but it seems that this is not a relevant factor to take account in this case.

4.4. SWELLING RESULTS

Several experiments have been done to check the volume increase of the catalysts in the reaction media. It is observed that resins with high DVB% have a higher swollen state in apolar solvent than polar solvent. Considering the extremes of the catalysts in the screening study, A15 and Dow 2, according to its morphological properties, A15 has a higher swollen state in 1-hexene (apolar) than Dow 2. On the other hand, Dow 2 manifest a swollen state in levulinic acid (polar) than A15.

5. CONCLUSIONS

This study has proven that levulinic acid esterification with 1-butene to produce *sec*-butyl levulinate can be done at temperatures below 140ºC with the appropriate catalyst.

Morphology properties of catalyst can be related to sec-butyl levulinate formation rates. ΣV_{sp} and DVB% are the mainly factors that affect to the catalytic efficiency, having the best SBL formation rate catalysts with the lowest values of Vsp and the highest of DVB%. Also, resin swelling is a decisive factor related to the earlier mentioned. A higher DVB% implies a lesser swollen resin, showing also a lesser gel-phase (V_{sp}).

In conclusion, macroreticular resins with lower percent of swelling, the highest DVB% and the lowest gel-phase shows better catalytic activity at this reaction media in the screening conditions of molar ratio, temperature and amount of catalyst. In particularly, A15 has shown the highest activity in the screening conditions.

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ACRONYMS

LA	levulinic acid
1B	1-butene
t2B	*trans*-2-butene
c2B	*cis*-2-butene
SBL	*sec*-butyl levulinate
BL	butyl levulinate
EL	ethyl levulinate
2ButOH	2-butanol
DVB	divinylbenzene
OS	Over sulfonated
SS	Surface sulfonated
CS	Conventionally sulfonated
d_{pore}	(macro)pore diameter, mm
ISEC	Inverse size exclusion chromatography
r^0_{SBL}	*sec*-butyl levulinate formation rate
n_j	Mol of species j
PS	Polystyrene
$R^0_{LA/1B}$	Initial molar ratio of levulinic acid versus 1-butene
Y^E_j	Yield of reagent j towards product E.
S^E_j	Selectivity of reagent j towards product E.
t	Time, min

T	Temperature, ºC
Tmax	Maximum work temperature, ºC
V_{sp}	Specific volume of swollen polymer, cm^3/g
X_j	Conversion of reagent j
x_j	Mass fraction of compound j
$x_{m(j)}$	Molar fraction of compound j
S_{pore}	Global (macro)pore surface, m2/g
V_{pore}	Global (macro)pore volume, cm3/g

APPENDICES

APPENDIX 1: CALIBRATION

Table 7. Calibration values.

levulinic acid		
x_w	Area	
X	**Y**	**Y***
0.7629	0.8062	0.8629
0.0873	0.1462	0.0987
0.0087	0.0771	0.0098
0.0392	0.0114	0.0443
0.4809	0.5979	0.5438
0.1774	0.2376	0.2006
0.0905	0.0973	0.1023
0.0534	0.0507	0.0604
0.0084	0.0117	0.0095
0.0196	0.0150	0.0222
0.1773	0.1880	0.2005
0.0455	0.0408	0.0515
0.3830	0.4619	0.4331

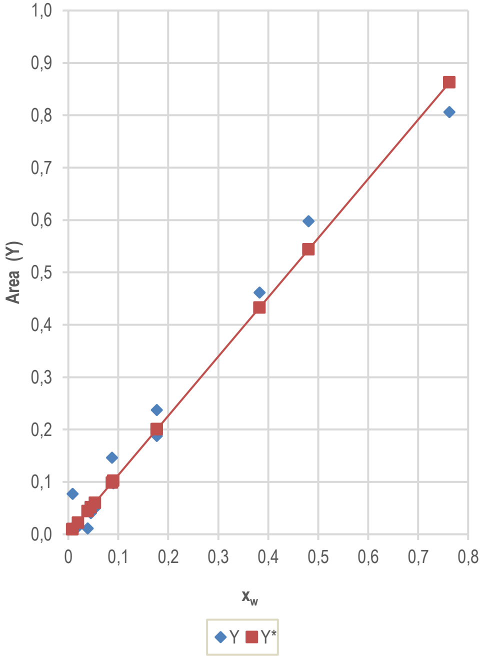

Figure 13. Calibration adjusts.

*Table 8. Error calculus. *Error calculated as the difference between estimated and Lower 95%*

	Coefficients	Error	t estadistic	Probability	Lower 95%	Superior 95.0%
X	**1.1310**	0.03642	31.0570	7.81E-13	**1.05165**	1.2103

1.1310 ± 0.0793*

Table 9. Calibration values.

***sec*-butyl levulinate**		
x_w	**Area**	
X	**Y**	**Y***
0.2002	0.0923	0.0530
0.9461	0.8703	0.8676
0.0496	0.0046	0.0043
0.6068	0.4207	0.3902
0.4805	0.2506	0.2563
0.7705	0.6072	0.5997
0.6124	0.3482	0.3966
0.5495	0.3259	0.3263

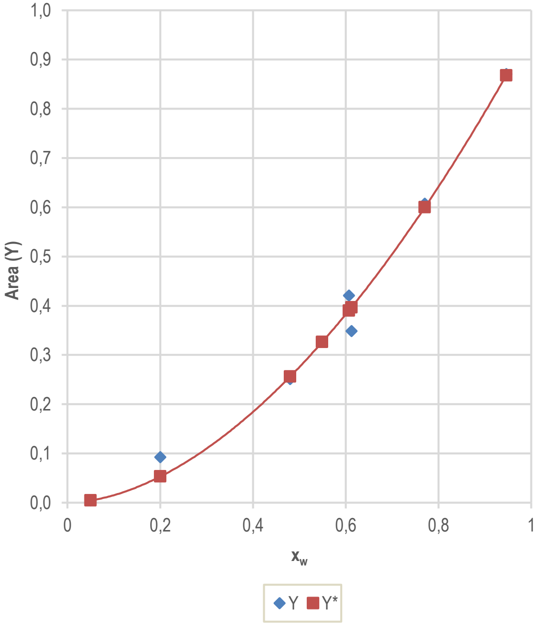

Figure 14. Calibration adjusts.

Table 10. Error calculus.

Parameters	Estimated	Lower IC (95%)	Superior IC (95%)
a	**0.9586**	**0.8784**	1.03879
b	**1.7997**	**1.5515**	2.04766

a	0.9586 ± 0.08022*
b	1.7997 ± 0.2481*

*Error calculated as the difference between estimated and Lower IC (95%)

Table 11. Calibration values.

2-butanol		
x_w	Area	
X	**Y**	**Y***
0.001145	0.003368	0.003483
0.001084	0.002554	0.003299
0.001915	0.006002	0.005826
0.001571	0.004229	0.004779
0.001972	0.006744	0.005999

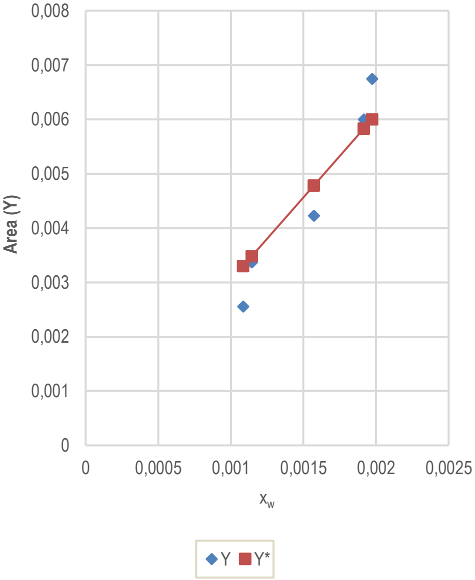

Figure 15. Calibration adjusts.

Table 12. Error calculus

	Coefficients	Error	t estadistic	Probability	Lower 95%	Superior 95.0%
X	**3.04239**	0.1706	17.8337	5.81E-05	**2.5687**	3.5161

3.04239 ± 0.4737*

**Error calculated as the difference between estimated and Lower 95%*

Table 13. Calibration values.

1-butene		
	$x_w < 0.4$	
X	**Y**	**Y***
0.0308	0.0924	0.0791
0.0125	0.0455	0.0321
0.0369	0.1465	0.0948
0.0492	0.1450	0.1264
0.2415	0.6425	0.6205
0.0765	0.3301	0.1965
0.3330	0.7916	0.8557
0.0654	0.2054	0.1680
	$x_w > 0.4$	
X	**Y**	**Y***
0.9014	0.9789	0.9786
0.4890	0.8771	0.8765
0.6092	0.9216	0.9227

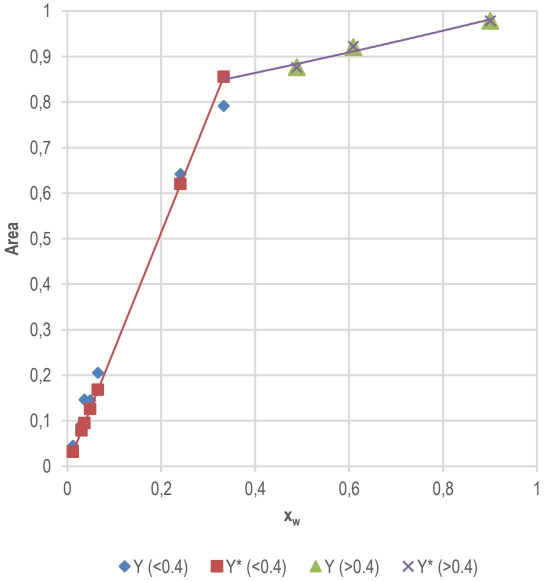

Figure 16. Calibration adjusts.

Table 14. Error calculus for $x_w < 0.4$

$x_w < 0.4$	Coefficients	Error	t estadistic	Probability	Lower 95%	Superior 95%
	2.5696	0.1452	17.6933	4.54E-07	2.2261	2.9128

1-BT w<0.4

2.5696	±	0.3434

Table 15. Error calculus for xw > 0.4

$x_w > 0.4$	Parameters	Estimated	Lower IC (95%)	Superior IC (95%)
	a	**0.755329**	0.755329	0.755329
	b	**1.3361**	1.3361	1.3361
	c	**3.55617**	3.55617	3.55617

1-BT w>0.4

0.7553	±	0.0000
1.3361	±	0.0000
3.5562	±	0.0000

APPENDIX 2: EXPERIMENTAL SCREENING DATA

Table 16. Initial conditions for A15.

A15_R05_T100_2G					
$R^0_{LA/1B}$		0.49		**T_0 (ºC)**	98.3
LA (g)	81.28	**1B (g)**	80.79	**Catalyst**	A15
LA (mol)	0.50	**1B (mol)**	1.44	**Catalyst mass (g)**	2.0645
		t_0	12:59		

Table 17. Area results for A15.

t_{EXP} (min)	1B	t2b	c2B	2ButOH	Minority	LA	SBL	Σ%minority
0								
6	0.7025	0.0206	0.0182	0.0019	0.0000	0.1528	0.1007	0.5112%
55	0.0242	0.0295	0.0189	0.0016	0.0019	0.3397	0.5833	0.4308%
82	0.0136	0.0343	0.0194	0.0018	0.0027	0.2590	0.6682	0.5414%
112	0.0079	0.0365	0.0192	0.0019	0.0057	0.2136	0.7153	0.7527%
143	0.0049	0.0329	0.0176	0.0018	0.0067	0.1883	0.7469	0.9399%
172	0.0080	0.0596	0.0299	0.0021	0.0087	0.1098	0.7807	1.2052%
207	0.0040	0.0367	0.0187	0.0021	0.0086	0.1053	0.8237	1.1709%
237	0.0036	0.0332	0.0172	0.0020	0.0079	0.1117	0.8230	1.1118%
270	0.0006	0.0041	0.0018	0.0008	0.0036	0.1276	0.8614	0.4416%

Table 18. Results for A15.

t_{EXP} (min)	x_{mj}						X_j		S^E_j	Y^E_j	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6729	0	0	0	0.3271	0					
6	0.8354	0.0433	0.0383	0.0039	0.0745	0.0045	0.0973	0.0574	0.0504	0.0049	0.0574
55	0.1192	0.1455	0.0929	0.0075	0.3882	0.2468	0.8052	0.3887	0.5010	0.4034	0.3887
82	0.0705	0.1776	0.1007	0.0090	0.3113	0.3310	0.8977	0.5154	0.5354	0.4807	0.5154
112	0.0421	0.1950	0.1026	0.0097	0.2648	0.3858	0.9428	0.5930	0.5567	0.5248	0.5930
143	0.0274	0.1838	0.0984	0.0097	0.2444	0.4363	0.9637	0.6409	0.5991	0.5774	0.6409
172	0.0383	0.2843	0.1427	0.0100	0.1216	0.4032	0.9564	0.7683	0.4799	0.4590	0.7683
207	0.0223	0.2052	0.1045	0.0112	0.1367	0.5200	0.9742	0.7919	0.6183	0.6024	0.7919
237	0.0209	0.1901	0.0985	0.0111	0.1484	0.5310	0.9755	0.7816	0.6392	0.6236	0.7816
270	0.0046	0.0297	0.0131	0.0060	0.2151	0.7315	0.9941	0.7728	0.9374	0.9319	0.7728

Table 19. Initial conditions for A16.

A16_R05_T100_2G					
$R^0_{LA/1B}$		0.49		**T_0 (ºC)**	98.3
LA (g)	81.4	**1B (g)**	80.57	**Catalyst**	A16
LA (mol)	0.70103	**1B (mol)**	1.4360	**Catalyst mass (g)**	2.0117
		t_0	12:48		

Table 20. Area results for A16.

t_{EXP} (min)	**1B**	**t2b**	**c2B**	**2ButOH**	**Minority**	**LA**	**SBL**	**Σ%minority**
0							0	
132	0.0668	0.1188	0.0714	0.0067	0.0129	0.1787	0.5439	2.0394%
166	0.0617	0.1761	0.0971	0.0059	0.0159	0.0820	0.5605	2.2526%
197	0.0277	0.1240	0.0673	0.0071	0.0166	0.1319	0.6247	2.4475%
236	0.0198	0.1251	0.0657	0.0073	0.0072	0.1248	0.6492	1.5432%
263	0.0159	0.1201	0.0622	0.0073	0.0076	0.1203	0.6657	1.5726%
296	0.0121	0.1031	0.0532	0.0077	0.0196	0.1232	0.6803	2.8073%
324	0.0110	0.1027	0.0527	0.0074	0.0209	0.1216	0.6828	2.9140%
353	0.0104	0.1018	0.0516	0.0073	0.0219	0.1231	0.6831	2.9980%
396	0.0099	0.0963	0.0494	0.0077	0.0242	0.1260	0.6857	3.2635%

Table 21. Results for A16.

t_{EXP} (min)	**x_{mj}**						**X_j**		**S^E_j**	**Y^E_j**	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6720	0.0000	0.0000	0.0000	0.3280	0.0000					
132	0.1913	0.3402	0.2044	0.0187	0.1188	0.1266	0.7829	0.5160	0.1835	0.1437	0.5160
166	0.1518	0.4334	0.2390	0.0142	0.0468	0.1148	0.8408	0.7103	0.1433	0.1205	0.7103
197	0.0884	0.3960	0.2149	0.0221	0.0977	0.1809	0.9020	0.6493	0.2223	0.2005	0.6493
236	0.0643	0.4069	0.2138	0.0234	0.0942	0.1974	0.9290	0.6769	0.2346	0.2180	0.6769
263	0.0535	0.4047	0.2097	0.0240	0.0941	0.2140	0.9409	0.6945	0.2510	0.2362	0.6945
296	0.0449	0.3812	0.1965	0.0277	0.1057	0.2440	0.9498	0.6978	0.2873	0.2729	0.6978
324	0.0411	0.3828	0.1963	0.0269	0.1052	0.2476	0.9540	0.7018	0.2901	0.2768	0.7018
353	0.0390	0.3827	0.1941	0.0268	0.1074	0.2500	0.9563	0.6995	0.2929	0.2801	0.6995
396	0.0380	0.3714	0.1906	0.0290	0.1128	0.2582	0.9572	0.6960	0.3041	0.2910	0.6960

Table 22. Initial conditions for A39.

A39_R05_T100_2G					
$R^0_{LA/1B}$		0.50		**T_0 (ºC)**	100
LA (g)	82.32	**1B (g)**	79.24	**Catalyst**	A39
LA (mol)	0.72	**1B (mol)**	1.41	**Catalyst mass (g)**	2.0114
		t_0	13:25		

Table 23. Area results for A39.

t_{EXP} (min)	**1B**	**t2b**	**c2B**	**2ButOH**	**Minority**	**LA**	**SBL**	**Σ%minority**
0							0	
6	0.8847	0.0000	0.0114	0.0000	0.0000	0.0448	0.0166	4.2561%
35	0.4821	0.0306	0.0265	0.0040	0.0108	0.1027	0.3406	1.7518%
61	0.4033	0.0768	0.0012	0.0063	0.0025	0.2346	0.2714	1.2719%
147	0.0853	0.0939	0.0625	0.0083	0.0083	0.2371	0.5012	1.6601%
175	0.0618	0.1001	0.0627	0.0086	0.0086	0.2185	0.5365	2.0308%
206	0.0367	0.0852	0.0513	0.0092	0.0112	0.2240	0.5793	2.3503%

Table 24. Results of A39.

t_{EXP} (min)	**x_{mj}**						**X_j**		**S^E_j**	**Y^E_j**	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6658	0.0000	0.0000	0.0000	0.3342	0.0000					
6	0.9495	0.0000	0.0263	0.0000	0.0240	0.0002	0.0271	0.0082	0.0075	0.0002	0.0082
35	0.7790	0.0651	0.0562	0.0084	0.0507	0.0407	0.1794	0.4452	0.2388	0.0428	0.4452
61	0.6968	0.1539	0.0024	0.0123	0.1091	0.0255	0.2179	0.1897	0.1315	0.0287	0.1897
147	0.2487	0.2737	0.1822	0.0236	0.1604	0.1113	0.7038	0.4098	0.1884	0.1326	0.4098
175	0.1891	0.3062	0.1918	0.0257	0.1551	0.1320	0.7762	0.4597	0.2013	0.1562	0.4597
206	0.1294	0.3002	0.1809	0.0319	0.1832	0.1745	0.8416	0.4878	0.2538	0.2136	0.4878

Table 25. Initial conditions of A46.

A46_R05_T100_2G					
$R^0_{LA/1B}$	0.47			**T_0 (ºC)**	98.9
LA (g)	81.37	**1B (g)**	83.6	**Catalyst**	A46
LA (mol)	0.70	**1B (mol)**	1.49	**Catalyst mass (g)**	2.0803
		t_0	13:09		

Table 26. Area results for A46.

t_{EXP} (min)	**1B**	**t2b**	**c2B**	**2ButOH**	**Minority**	**LA**	**SBL**	**Σ%minority**
0							0	
4	0.1138	0.0031	0.0000	0.0000	0.0070	0.8527	0.0221	0.8264%
29	0.0880	0.0024	0.0031	0.0000	0.0026	0.7925	0.1104	0.3556%
70	0.1328	0.0123	0.0143	0.0015	0.0031	0.5252	0.3092	0.6273%
97	0.1240	0.0170	0.0183	0.0015	0.0014	0.4766	0.3597	0.4277%

Table 27. Results for A46.

t_{EXP} (min)	**x_{mj}**						**X_j**		**S^E_j**	**Y^E_j**	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6801	0.0000	0.0000	0.0000	0.3199	0.0000					
4	0.3612	0.0100	0.0000	0.0000	0.6284	0.0005	0.0281	0.0007	0.0437	0.0012	0.0007
29	0.3142	0.0085	0.0112	0.0000	0.6569	0.0091	0.0842	0.0137	0.3151	0.0265	0.0137
70	0.4443	0.0411	0.0478	0.0049	0.4079	0.0539	0.2495	0.1166	0.3645	0.0910	0.1166
97	0.4239	0.0581	0.0627	0.0050	0.3781	0.0721	0.3184	0.1602	0.3644	0.1160	0.1602

Table 28. Initial conditions for CT175 (1).

CT175_R05_T100_2G					
$R^0_{LA/1B}$		0,49		**T_0 (ºC)**	96.3
LA (g)	81.47	**1B (g)**	82.24	**Catalyst**	CT175
LA (mol)	0.70	**1B (mol)**	1.47	**Catalyst mass (g)**	2.0541
		t_0	13:56		

Table 29. Area results for CT175 (1)..

t_{EXP} (min)	**1B**	**t2b**	**c2B**	**2ButOH**	**Minority**	**LA**	**SBL**	**Σ%minority**
0								
67	0.1137	0.0417	0.0351	0.0050	0.0059	0.4644	0.3329	1.2122%
95	0.0832	0.0903	0.0609	0.0051	0.0025	0.3126	0.4438	0.9137%
123	0.0143	0.0314	0.0197	0.0044	0.0026	0.2928	0.6331	0.8758%

Table 30. Results for CT175 (1).

t_{EXP} (min)	**x_{mj}**						**X_j**		**S^E_j**	**Y^E_j**	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6763	0.0000	0.0000	0.0000	0.3237	0.0000					
67	0.3535	0.1298	0.1091	0.0153	0.3352	0.0571	0.4683	0.1456	0.1835	0.0859	0.1456
95	0.2429	0.2636	0.1776	0.0145	0.2117	0.0897	0.6919	0.2976	0.1644	0.1138	0.2976
123	0.0731	0.1604	0.1009	0.0218	0.3473	0.2966	0.8881	0.4607	0.5117	0.4544	0.4607

Table 31. Initial conditions for CT175 (2).

CT-175_R05_T100_2G r2					
$R^0_{LA/1B}$		0.53		**T_0 (ºC)**	98.8
LA (g)	80.66	**1B (g)**	73.6	**Catalyst**	CT-175
LA (mol)	0.70	**1B (mol)**	1.32	**Catalyst mass (g)**	2.0488
		t_0	12:13		

Table 32. Area results for CT175 (2).

t_{EXP} (min)	1B	t2b	c2B	2ButOH	Minority	LA	SBL	Σ%minority
0							0	
5	0.2692	0.0474	0.0160	0.0006	0.0075	0.6121	0.0370	1.8355%
31	0.0807	0.0188	0.0165	0.0047	0.0033	0.6288	0.2468	0.8456%
61	0.0491	0.0491	0.0356	0.0063	0.0047	0.4927	0.3620	1.1504%
87	0.0459	0.0899	0.0572	0.0062	0.0060	0.3586	0.4362	1.2168%
147	0.0178	0.1098	0.0574	0.0066	0.0100	0.2869	0.5112	1.6910%
175	0.0112	0.0889	0.0472	0.0072	0.0120	0.2920	0.5411	1.9544%
203	0.0096	0.0866	0.0456	0.0070	0.0127	0.3043	0.5339	2.0015%
229	0.0084	0.0818	0.0429	0.0070	0.0146	0.2989	0.5460	2.1928%
312	0.0063	0.0653	0.0343	0.0065	0.0144	0.2979	0.5751	2.1153%
347	0.0058	0.0609	0.0325	0.0062	0.0145	0.2977	0.5821	2.1004%

Table 33. Results for CT175 (2)

t_{EXP} (min)	x_{mj}						X_j		S^E_j	Y^E_j	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S^{SBL}_{1B}	Y^{SBL}_{1B}	Y^{SBL}_{LA}
0	0.6518	0.0000	0.0000	0.0000	0.3482	0.0000					
5	0.5661	0.0996	0.0336	0.0013	0.2987	0.0008	0.1928	0.0025	0.0056	0.0011	0.0025
31	0.2909	0.0677	0.0595	0.0167	0.5264	0.0388	0.3857	0.0686	0.2123	0.0819	0.0686
61	0.1782	0.1779	0.1293	0.0225	0.4147	0.0774	0.6956	0.1573	0.1901	0.1322	0.1573
87	0.1471	0.2881	0.1832	0.0194	0.2667	0.0955	0.7994	0.2636	0.1629	0.1302	0.2636
147	0.0598	0.3689	0.1929	0.0216	0.2238	0.1330	0.9229	0.3728	0.1857	0.1714	0.3728
175	0.0421	0.3343	0.1776	0.0266	0.2548	0.1647	0.9435	0.3927	0.2343	0.2210	0.3927
203	0.0366	0.3304	0.1741	0.0260	0.2695	0.1633	0.9498	0.3773	0.2353	0.2235	0.3773
229	0.0332	0.3221	0.1690	0.0270	0.2732	0.1754	0.9543	0.3910	0.2529	0.2414	0.3910
312	0.0273	0.2837	0.1488	0.0276	0.3003	0.2123	0.9610	0.4142	0.3157	0.3034	0.4142
347	0.0260	0.2714	0.1448	0.0272	0.3081	0.2226	0.9625	0.4195	0.3343	0.3217	0.4195

Table 34. Initial conditions for DOW 2.

DOW 2_R05_T100_2G					
$R^0_{LA/1B}$		0.52		**T_0 (ºC)**	99.3
LA (g)	81.38	**1B (g)**	76.25	**Catalyst**	DOW 2
LA (mol)	0.70	**1B (mol)**	1.36	**Catalyst mass (g)**	2.053
		t_0	12:45		

Table 36. Results for DOW 2.

t_{EXP} (min)	**x_{mj}**						**X_j**		**S^E_j**	**Y^E_j**	
	1B	t2B	c2b	2ButOH	LA	SBL	X_{1B}	X_{LA}	S_{1B}^{SBL}	Y_{1B}^{SBL}	Y_{LA}^{SBL}
0	0.6598	0.0000	0.0000	0.0000	0.3402	0.0000					
9	0.3475	0.0048	0.0041	0.0024	0.6399	0.0013	0.0351	0.0020	0.1039	0.0036	0.0020
35	0.3406	0.0133	0.0163	0.0106	0.5947	0.0244	0.1596	0.0395	0.3779	0.0603	0.0395
115	0.3578	0.0924	0.0923	0.0178	0.3994	0.0403	0.4043	0.0917	0.1661	0.0672	0.0917
141	0.2765	0.0710	0.0742	0.0219	0.5006	0.0558	0.4463	0.1002	0.2502	0.1117	0.1002
171	0.3169	0.1328	0.0000	0.0258	0.4160	0.1085	0.4573	0.2068	0.4061	0.1857	0.2068
201	0.3301	0.1598	0.1511	0.0212	0.2435	0.0943	0.5636	0.2792	0.2212	0.1246	0.2792
230	0.2319	0.1347	0.1218	0.0348	0.3485	0.1283	0.6441	0.2692	0.3058	0.1970	0.2692

Table 35. Area results for DOW 2.

t_{EXP} (min)	**1B**	**t2b**	**c2B**	**2ButOH**	**Minority**	**LA**	**SBL**	**Σ%minority**
0							0	
9	0.1061	0.0015	0.0012	0.0008	0.0097	0.8415	0.0393	1.0414%
35	0.0935	0.0037	0.0045	0.0030	0.0000	0.7032	0.1896	0.5576%
115	0.0985	0.0254	0.0254	0.0050	0.1175	0.4738	0.2513	12.5539%
141	0.0693	0.0178	0.0186	0.0056	0.0600	0.5406	0.2858	6.7977%
171	0.0653	0.0274	0.0000	0.0054	0.1579	0.3694	0.3715	16.3376%
201	0.1036	0.0502	0.0474	0.0068	0.0247	0.3293	0.4346	3.4936%
230	0.0489	0.0284	0.0257	0.0075	0.1566	0.3168	0.4135	16.6640%