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Obtaining levulinic acid from fructose over acidic ion-exchange resins catalysts

Obtenció d'àcid levulinic a partir de fructosa utilitzant resines àcides de bescanvi iònic com a catalitzadors

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No tot el que conta pot ser quantificat, i no tot el que pot ser quantificat conta.

Albert Einstein

Primerament vull agrair l'ajuda, la dedicació, l'impuls, les ganes, els ànims i consells de la meva tutora la Dra. Iborra que m'ha ensenyat molt del TFG però més a créixer com a persona. També vull agrair al Dr. Tejero per transmetre'm els seus coneixements i per la seva insistència.

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REPORT

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1. SUMMARY

Diesel compositions must be reformulated in order to fulfil new EU standards, where oxygen content must be, of at least, 15% by 2020. By other way, the new diesels can reach the consideration of biofuels if they are obtained from biomass. An important platform chemical obtained from biomass is levulinic acid, which is the most widely used reactant to obtain alkyl levulinates. These alkyl levulinates are found to be possible oxygenated chemicals additives that could upgrade fuel's quality, turning into in "greener" ones.

The absence in the literature of information of acid ion-exchange resins as catalysts for the dehydration of fructose to 5-hydroxymethylfurfural and subsequent rehydration to obtain levulinic acid, make the study of the behaviour of these catalysts useful and interesting.

The reaction system was studied using dioxane as solvent, a fixed composition of reactants (14% wt. fructose and 4% wt. water) and in the temperature range between 90 ºC and 110 ºC. Two sets of resins are used during the study in the catalysts screening: a set of macroreticular resins (Amberlyst 15 and Amberlyst 39) and another one of gel-type (Dowex 50x8, Dowex 50x4 and Dowex 50x2). The experimental set was a discontinuous pressurized batch reactor and high-performance liquid chromatography.

Fructose conversion, selectivity towards levulinic acid (LA) and 5-hydroxymethylfurfural (HMF), and yields of each product are calculated. The gel-type resin Dowex 50x2 is the most selective resin between the studied operation conditions. From the results of two sets of resins it can be concluded that less content of cross-linker divinylbenzene leads to higher yields. Yield of HMF and global yield reaction are better at lower temperatures, while LA yield increase at higher temperatures. Humic acids formation is the cause of the noticeable reduction of the global reaction yield. The highest yield reached for HMF is 72,4% at 90 ºC with Dowex 50x4 and 34,4% for LA at 100 with Dowex 50x2.

Keywords: ion-exchange resins, fructose, levulinic acid, HMF, hydrolysis, biomass

2. RESUM

Per a complir els nous estàndards de les composicions del dièsel imposades per la UE, aquestes han de ser re-formulades per tal de que el contingut d'oxigen sigui, com a mínim, del 15% al 2020. A més, els nous dièsels poden obtenir la condició de biodièsel si són obtinguts a partir de biomassa. Una molècula important obtinguda a partir de biomassa i que pot derivar en moltes d'altres és l'àcid levulinic, el qual es el reactant més important d'on s'obtenen alquil levulinats. Aquests alquil levulinats es troben entre els possibles additius del dièsel que podrien millorar la seva qualitat en transformar-los en dièsels més "verds".

La absència d'informació a la bibliografia sobre resines acides de bescanvi iònic com a catalitzadors per la deshidratació de la fructosa cap a 5-hidroximetilfurfural i la posterior rehidratació per obtenir àcid levulinic, fa que l'estudi del comportament d'aquests catalitzadors sigui útil i interesant.

El sistema de reacció s'ha estudiat utilitzant dioxà com a dissolvent, amb composicions fixes dels reactants (14% fructosa i 4% aigua en pes) entre un rang de temperatures de 90 ºC fins a 110 ºC. Dos conjunts de resines han estat utilitzades per a l'screening. Un conjunt de resines macroreticulars (Amberlyst 15 and Amberlyst 39) i un altre de resines tipus gel (Dowex 50x8, Dowex 50x4 i Dowex 50x2). L'equip experimental consta d'un reactor discontinu a pressió i un cromatògraf HPLC.

S'ha estudiat la conversió de fructosa, la selectivitat en ver l'àcid levulinic i el HMF, i els rendiments obtinguts per a cada producte. La resina Dowex 50x2 tipus gel es la resina més selectiva donades les condicions d'operació. Del resultat dels dos conjunts de resines es pot extreure que quan menys contingut de divinilbenzè hi ha en les resines s'obtenen rendiments més superiors. El rendiment de HMF i el global són millors a temperatures baixes, mentre que el d'àcid levulinic creix a temperatures altes. Degut a que la formació d'humines redueix notablement el rendiment global. Els millors rendiments obtinguts han estat per el HMF del 72,4% a 90 ºC amb la Dowex 50x4 **I** per el àcid levulinic del 34,4% a 100 ºC amb Dowex 50x2.

Paraules clau: resines de bescanvi iònic, fructosa, acid levulinic, HMF, hidròlisi, biomassa

3. INTRODUCTION

The chemical industry of today is under increased pressure to develop novel green and sustainable materials as well as bio-fuels and chemicals. Indeed, the endeavor to move towards more eco-friendly cost efficient production processes and technologies, as well as chemical transformation of renewables has a central role considering the future supply sustainable of chemicals and energy needed by society (1).

3.1. USING BIOMASS TO OBTAIN BIOFUELS

The world's primary source of energy for the transport is oil, having a demand of approximately 84 million barrels a day and which is projected to increase to about 116 million barrels a day by 2030 (2). In order to reduce the dependence on oil and mitigate the climate change in transport and chemical sectors it is necessary to find new production chains and introduce innovative fuels and technologies (3).

Biomass is recognized as a possible resource for the sustainable production of chemicals and fuels. Currently, transportation fuels based on biomass, biofuels, are identified as 1st and 2nd generation biofuels. First generation biofuels are produced from sugar, starch, vegetable oil or animal fats using conventional technologies. The basic feedstocks are often seeds and grains such as wheat, corn and rapeseed. The most common first generation biofuels are bioethanol, biodiesel and starch-derived biogas, but also straight vegetable oils, biomethanol and bioethers may be included in this category. The main advantage of first generation biofuels is their easy conversion into biofuel. However usually refer to biofuels produced from raw materials in competition with food, fertile land and feed industries. Because of this competition, these biofuels give rise to ethical, political and environmental concerns. In order to overcome these issues, production of second generation biofuels (i.e. from raw materials based on waste residues or non-food crop biomass) gained increasing worldwide interest in the last few years as a possible “greener” alternative to fossil fuels and 1st generation biofuels. Recent literature reviews give an idea of the intense research activity currently performed on the production of chemical platforms from biomass, and many different routes give a wide variety of chemicals (4), (5), (6), (7).

Second generation biofuels are produced from nonedible biomass. This includes the use of lignocellulosic materials, such as residues from agriculture or forestry. Most processes and technologies for 2nd generation biofuels are still at a pre-commercial stage, but could enter the market within 10-15 years (8) from now if corresponding investments (R&D, infrastructure) are achieved.

One kind of these second generation biofuels is based on additives like alkyl levulinates. Alkyl levulinates are of particular interest due to their specific physicochemical properties. Indeed, they could find applications as specialty chemicals and in the chemical and petrochemical industries (9), (10). Alkyl levulinates have a lot of different applications: they can be used as solvents because they are all soluble in classical solvents (alcohol, ethers and chloroform) except water (methyl levulinates excepted) (8). Their use has been patented for mineral oil refinement (11). Although they could be of interest, for example, in polymers, perfume or flavoring preparations and latex coating compositions, (12), (13), (14) the main potential applications seems to concern fuel formulations at the moment.

Alkyl levulinates are proposed as additives to conventional diesel (15), (16), (17) or gasoline (15), (16), (18) fuels, (Fischer-Tropsch) gas oil-based fuels, (19), (20) and even biodiesels (15), (16), (21). Among possible candidates, long alkyl chain levulinates (4-10 carbons) are currently mainly studied due to greater solubility in the hydrocarbonated fraction concomitant to lower water solubility (22). 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 (17). For that, ethyl to butyl levulinates seem to be the main studied esters, and 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 (16), (17). It has been shown that the presence of these oxygenated compounds leads to cleaner combustion processes with fewer smoke or NO_x (nitrogen oxides) emissions (20). Another reported advantage is that butyl levulinates cause lower degradations to some elastomeric constituents of the engine (swelling) than other additives (19). Examples concern miscibility of ethyl to butyl levulinates with various diesel fuels, along with phase separation temperature determination,

(19) fuel consumption, particles, NO_x emissions, cetane number, lubricity, miscibility, and stability of ethyl levulinate blending with biodiesel or conventional diesel (ULSD) (23).

One of the most important parameters in a diesel fuel is the *cetane number*. Cetane number or CN is an indicator of the combustion speed of diesel fuel. It is an inverse of the similar octane rating for gasoline. The CN is an important factor in determining the quality of a diesel. A computer-based study from Kashinath et al. (24) confirmed that **butyl levulinate** possesses a **cetane number of 48**. The quality of European diesel fuels is specified by de EN 590 standard (Directive 2009/30/EC) (Table 1).

Table 1. EN 590:2009 Diesel Fuel Specification.

Fuel Property	Unit	Specification Min	Specification Max	Test
Cetane Number		**49**		ISO 5165
Cetane Index		46		ISO 4264
Density @15ºC	kg/m^3	820	860	ISO 3675/ASTM D4052
Sulfur	% (wt.)	-	0,20	EN 24260/ISO 8754
Flash Point	ºC	55	-	ISO 2719
Carbon residue(10% btms)	% (wt.)	-	0,30[a]	ISO 10370
Ash	% (wt.)	-	0,01	EN 26245
Water Content	mg/kg	-	200	ASTM D1744
Copper strip corrosion, 3h @50ºC		-	Class1	ISO 2160
Oxidation stability	g/m^3	-	25	ASTM D2247
Viscosity @40ºC	mm^2/s	2,00	4,50	ISO 3104
Distillation (vol. % recovered)				ISO 3405
10% point	ºC	report		
50% point		report		
65% point		250	-	
85% point		-	350	
95% point		-	370	

a-limit does not apply if ignition improver additives are used

While these specifications are not mandatory, they are followed by fuel suppliers in Europe.

Alkyl levulinates can be obtained through different reaction pathways (Figure 1). One synthetic route is the reaction of furfuryl alcohol with an alcohol in the presence of acid, which forms the consequent alkyl levulinate. Furfuryl alcohol is formed by the reduction of furfural, obtained from the xylan hemicellulose, a pentose and component of lignocellulosic biomass.

Nevertheless, the first studies used purified levulinic acid Sah (25) and then Schuete et al. (26) published the formation of several alkyl levulinates in the corresponding alcohol in the presence of HCl. The etherification of levulinic acid with alcohols is probably the most important way of obtaining alkyl levulinates.

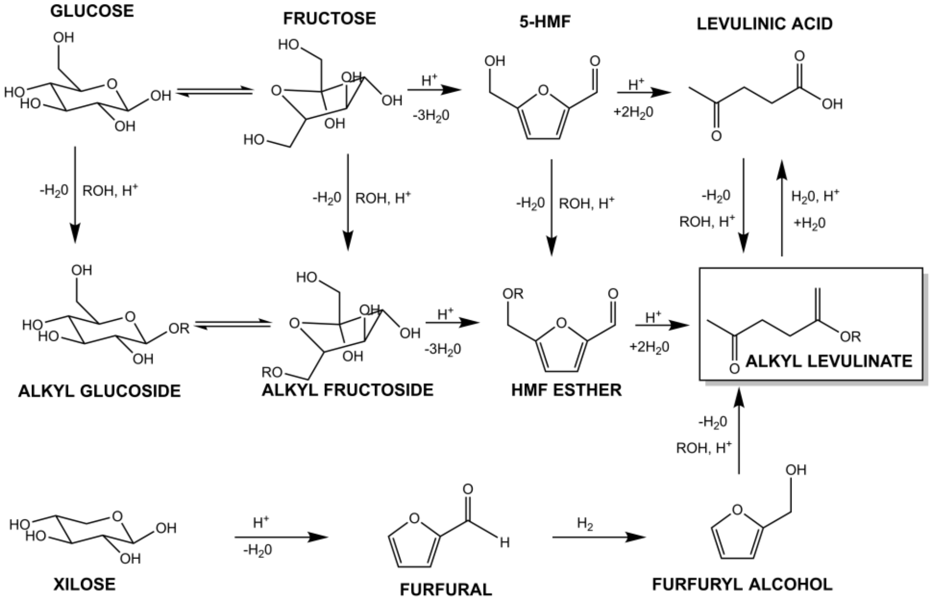

Figure 1. Main synthesis pathways for alkyl levulinates

3.2. OBTAINING LEVULINIC ACID. STATE OF THE ART

Lignocellulose is the most important source of biomass. It is mainly composed of lignin, cellulose, and hemicellulose. Lignin is a three-dimensional polymer formed of methoxylated phenyl propane structures. Therefore, lignin is regarded as source of aromatic molecules. Cellulose and hemicellulose are polymers composed of glucose or different carbohydrate units, respectively. Depolymerization of hemicellulose and cellulose can therefore give sugars (i.e., xylose, mannose, glucose) from nonedible and widely available renewable resources. Simple sugars and derivatives are of crucial importance due to their large potential for use and transformation to important commodity (e.g., sorbitol, furans) or *platform chemicals* (27).

Some of the common pretreatment technologies are *hydrothermal treatments*, *alkaline treatments*, *alternative organic solvents* and *acid hydrolysis*. Acid hydrolysis is the oldest known method. It can be derived into two general approaches, based on concentrated acid/low temperature, or dilute acid/high temperature. Concentrated acid-based processes are not more typically used, because of the expensiveness, causing significant operational problems related to corrosion and high salt concentrations after neutralization, and being environmentally not acceptable. Diluted sulphuric acid process is widely used industrially.

Levulinic acid, formed from deep hydrolysis of (ligno)cellulose, belongs to the class of platform chemicals. Levulinic acid has been highlighted by the United States Department of Energy in 2004 and again in 2010 as a promising building block for chemistry (28).

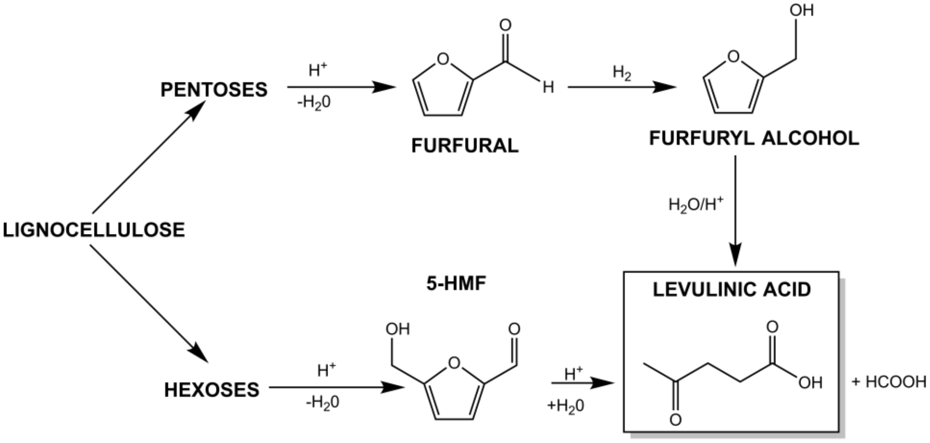

Figure 2. Products obtained by deep hydrolysis of biomass.

Levulinic acid is industrially produced by the Biofine process, which uses diluted sulphuric acid as catalyst (8). Thanks to different functional groups, valorization of levulinic acid can lead to various important products for the polymer industry, to γ-valerolactone and its derivative methyl tetrahydrofuran for fuel and solvent applications and to alkyl levulinates (8). However, the recent interest for biomass transformation and the discovery of new applications for biobased products have considerably increased this literature. Consequently, the majority of the publications have appeared during the last five years, similarly to those related to other biomass-issued, very important, sugar-derived compounds. A couple of interesting papers describing advances in levulinic acid derivatives chemistry have therefore appeared very recently (8).

In the literature can be find many different operating conditions, temperature ranges and different types of catalysts (see Table 2 and 3.).

Attending to catalysis type, homogeneous catalysis was the first type used. There are some disadvantages if working with a homogeneous catalyst, due to the blend cannot be separated easily. However heterogeneous catalysis is more interesting and was studied using a lot of different catalysts: metal oxides, zeolites, polymeric resins, etc..

By other way, the temperature conditions founded are severe; various authors focus on HMF optimizing; try to produce alkyl levulinates from sugars directly or study the humins minimization (29). The literature examined leads to three themes that can be studied:

1. Authors that use heterogeneous catalysis do not focus on levulinic acid as the goal point.
2. Temperature ranges must be decreased in order to economize a hypothetic industrial process.
3. There are few articles over polymeric resins.

Table 2. Working conditions and yields obtained by homogeneous catalysis

Reference	Catalyst	Cat. quantity	Reagent	Solvent	T ºC	Reaction time	HMF yield %	LA yield %
30	H_2SO_4	1,5ml (0,001; 0,001; 0,1; 1; 5 and 10 mol/L)	Fructose Glucose Sucrose	DMSO THF GVL Acetone DMC MeCN	70, 100, 130,160	10 min	2% to 58 %	0% to 62%
31	HCl	4,5% v/v	Rice husks	water	170	60 min	-	59,4%
32	H_2SO_4	1%, 3%, 5% wt.	Glucose	water	170-190	60 min	-	80,7 %
33	$CrCl_3$ + HCl	Cr-reactant 3:100 molar ratio	Glucose	water	140	3 h	59%	46%
Gallezot	H_2SO_4 HCl	-	Fructose	DMSO Water/acetone n-butanol extractive.	165	-	63 %	-

Table 3. Working conditions and yields obtained by heterogeneous catalysis

Reference	Catalyst	Cat. quantity	Reagent	Solvent	T ºC	Reaction time	HMF yield %	LA yield %
34	Zirconium dioxide	2 wt. %	Cellulose	water	180	3h	-	53,9%
35	Amberlyst 70	6 wt. %	Fructose	water GVL/water	160	4h/16h	-	46/54 %
36	Polyoxometalate salts (IL-POMS)	25 mg per 50mg fruct.	Fructose	DMSO	100	1h	99%	-
37	Amberlyst 70,31,121,15,35 and 36	50 mg per 300 mg fruct.	Fructose	2-methyltetrahydrofurane	130	1h	68%	-
38	(C-SO_3H)	1/10 fruct(wt.).	Fructose	DMSO	120	30 min	89%	-
39	Acid Y-zeolite	2g to 20g per 150 ml	Glucose	water	110-160	24h	9%	21%
40	Amberlyst 15	10g per 0,75g fruct	Fructose syrup	Dioxane DMSO, DMF, acetonitrile, 2-propanol	100	3h	80%	-
41	Various catalysts (NB_2O_5, TiO_2, Ta_2O_5, lewis acids…)		Glucose Fructose	water	150	2h	64%	-

3.3. SULPHONIC POLYSTYRENE-DIVINYLBENZENE (PS-DVB) ION-EXCHANGE RESINS AS CATALYSTS

Heterogeneous catalysis is the most common kind of catalysis, because they present fewer problems from an engineering point of view. Approximately 80% of industrial catalytic processes are based on heterogeneous catalysis and of those; 90% are catalyzed by solids (42).

The typical properties for a catalyst are selectivity, reusability and activity, exposed in relative importance order for industrial processes. So that a solid can act as catalysts it is important that at least one of the reagents must interact with his surface and be fixed on it (adsorption). Having a large surface where the reactants can be adsorbed is essential for a solid catalyst. Therefore porous solids are typically used, which have a large surface per mass of solid. The structure of solid particles (number, size and pore volume) is fundamental in catalyst performance. Chemical composition is also important, because the interaction of the reactant with the surface is of chemical nature.

Typically, a solid catalyst is formed by an active phase or component, the support on one or more promotors.

The active component is responsible of accelerating the main reaction. There are many different substances which can be used as active components. These substances can be transition metals, metallic oxides, metallic sulfurs and metallic salts, acidic solids like zeolites (principally silica and/or alumina) and functionalized polymers like ion-exchange resins (42).

Ion exchange resins are functionalized polymeric materials capable of exchanging ions with the media where are dipped. The polymeric matrix is formed by hydrocarbon chains and by a cross-linking agent, providing a hydrophobic 3D structure. Furthermore the polymeric matrix contains functional groups that provide characteristics of acidity, basicity or even both, depending on the functional group nature, to the resins. The thermal and mechanical resistances of these catalysts depend on the cross-linking rate and de nature of the functional groups.

There are many advantages of ion-exchange resins against other catalysts. First of all they are easy to handle and store. They are equally appropriate for working in continuous and batch reactors. Because their density is very similar to the most common organic solvents they can easily remain in suspension even at low stirring speeds. Corrosion problems can be avoided because most protons are inside the particle and waste treatments are much simple by the reduced acidity or basicity of waste products. They are easily separated from mixtures by filtering, which leads to higher purity products and yields. This simplifies industrial processes by doing away with several separation steps and units, which has a great impact in costs. These catalysts have acceptable duration and the possibility of regeneration can always be done. Moreover, obtaining products free of water is easier because these resins can work even in non-polar media.

From among the different kinds of resins, are widely used those formed by a matrix of styrene-divinylbenzene (PS-DVB) showed in figure 3. The obtaining of this resin is performed by a styrene polymerization process (by polystyrene is produced) and the subsequent addition of a specific amount of divinylbenzene, which provides the 3D structure and insolubility of the polymer. Additionally, resins must be submitted to a functionalization process. In the case of acidic resins, are sulfonated with a concentrated sulphuric acid.

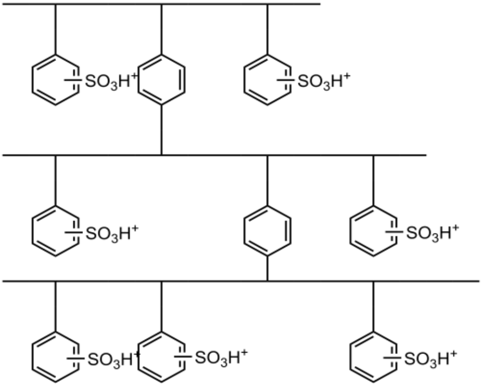

Figure 3. Structure of a sulphonated resin

Depending on the synthesis process of the resins, these can present different reticulation degree, structure, swelling, particle diameter, acid capacity, density, humidity and stability.

PS-DVB resins can be divided in macroreticular and gel-type resins depending on its polymer physical structure, which is related to the synthesis process.

Gel-type resins contain a 2-8% of DVB, they are synthesized by copolymerization in absence of any porogen agent and thus, they only show porosity when they are swollen in polar media. Its structure is very elastic and they have high swelling capacity in polar solvents.

Macroreticular resins are synthesized with a porogen agent in the copolymerization process (such as heptane or C_4-C_{10} alcohols) that dissolves the monomer but not the polymer. As a result, a permanent porous structure is showed in dry state or in absence of any polar solvent. Macroreticular resins have higher DVB content (8-20% or even more) and its permanent porous structure gives these resins additional physical resistance. However, the higher cross-liking degree confers stiffness to the polymeric matrix, making these resins less capable of swelling (Figure 4).

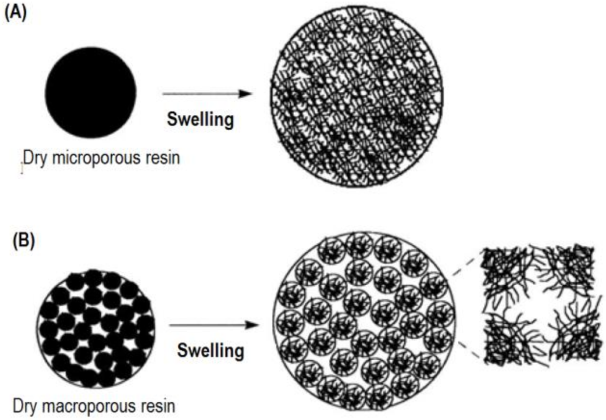

Figure 4. Schematic representation of changes in the morphology of gel type bead (A) and macroreticular bead (B) during swelling.

Macroreticular resins consist of agglomerates of gel phase microspheres. Between the agglomerates of microspheres a family of macropores (30-80 nm) is found. Macropores are permanent and are responsible of large specific pore volumes of these resins. Mesopores (8-20 nm) are found between gel phase microspheres. They are placed between the nodules of gel phase (Figure 5). Macropores can be detected by conventional pore characterization techniques such as nitrogen adsorption or mercury porosimetry. However, mesopores and micropores only appear when the resin is swollen in polar media and they require other techniques to be detected.

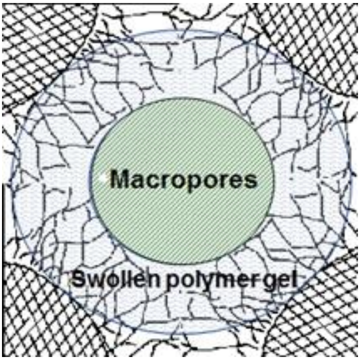

Figure 5. Representation of swollen state morphology. Courtesy of K. Jerabek.

Until now, only ISEC (Inverse Steric Exclusion Chromatography) technique has been able to characterize the swollen structure of PS-DVB resins. The technique consists on measuring the elution volumes of different solutes of known molecular size, by using a chromatographic column filled with the investigated swollen polymer (44).

4. OBJECTIVES

As shown in the introduction section, literature shows that using heterogeneous catalysis do not focus on levulinic acid as the target product, temperature ranges must be decreased in order to economize a future industrial process and there are few articles over polymeric resins. So the aim of the current experimental work is to do a preliminary approach to the study of obtaining levulinic acid from fructose, port of a larger project interested in the synthesis of biomass-derived products, using PS-DVB ion exchange resins as catalysts.

First of all, in order to obtain valuable information of the reaction system, an experimental procedure must be redesigned by adapting procedure to use an “available” batch reactor system with a GC integrated analysis.

The second goal is to do a catalyst screening, is it to say, to ascertain whether sulphonated polystyrene-divinylbenzene acidic resins can be used in the synthesis of LA from fructose, paying attention to fructose dehydration to 5-hydroxymethylfurfal and subsequent hydration of 5-HMF to levulinic.

The screening will be done by comparing conversion and selectivity for different catalysts, and relating those with the resins properties.

Finally, it will be checked the influence of the temperature on the selectivity and yield of the reaction system for one of the most promising catalyst.

5. EXPERIMENTAL SECTION

5.1. EXPERIMENTAL SET

5.1.1. Materials

The reagent for the synthesis of levulinic acid was fructose analytical grade (Labkem, FRUC-00A-250) with a purity of 99%. The dissolvent used were dioxane (Acros Organics, 270490025) with a purity of and 99,5% and water (Milli-Q, Millipore).

Table 4. Important properties of main components of the reaction system.

Properties	Fructose	HMF	LA	Dioxane
Molecular mass (g/mole)	180,16	126,11	116,12	88,11
Density (g/cm3)	1,69	1,29	1,130	1,084
Melting point (ºC)	103	30 to 34	33 to 35	11,8
Boiling point (ºC)	-	114 to 116(1mbar)	245 to 246	101,1

*except where otherwise noted, data given for materials in their Standard State (25 ºC, 1 atm)

To chromatographic calibrates 5-hydroxymethylfurfural (HMF) (Acros Organics, 121460050) with a purity of 98%, levulinic acid (LA) (Acros Organics, 125140010) with a purity of 98+%, formic acid (Labkem,, 00153-1a103991305) with a purity of 98% and finally furfuraldehyde (Acros Organics, 181100010) with a purity of 99%.

5.1.2. Auxiliary gases and liquids

To pressurize the reactor nitrogen as inert gas was used with a 99,9995% of purity and the carrier gas of the gas chromatograph was helium with a 99,998% of purity, both supplied by *Abelló Linde* (Barcelona, España).

The eluent of the high-performance liquid chromatography (HPLC) is a 0,5mmol solution of sulphuric acid (PREGUNTAR A HPLC) in Milli-Q water.

5.1.3. Catalysts

The PS-DVB resins used were Rohm and Haas Amberlyst-15, Amberlyst-16, Amberlyst-36, Amberlyst-39, and Aldrich Dowex 50x8, Dowex 50x4 and Dowex 50x2. Table 5 gives some of the most important properties of each used resins (45).

Table 5. Properties of PS-DVB resin catalysts used in this study.

Catalysts	**Type**	**Acid capacity (mmol H^+/g)**	**% DVB**	**T_{max} (ºC)**	**V_{sp}^a (cm^3/g)**
Amberlyst 15	macro	4,81	20	120	0,823
Amberlyst 16	macro	4,80	12	130	1,245
Amberylst 36	macro	5.40	12	150	0,999
Amberlyst 39	macro	4,82	8	130	1,451
Dowex 50x8	gel	4,83	8	150	1,627
Dowex 50x4	gel	4,95	4	150	1,92
Dowex 50x2	gel	4,83	2	150	2,655

(a) Specific volume of swollen phase in water, measured by ISEC technique

Figure 6 illustrates the flow diagram of used installation and coming up next the units are detailed separately.

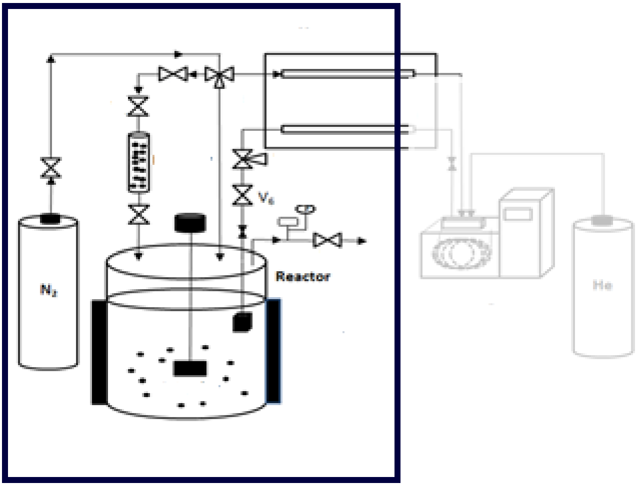

Figure 6. Diagram of the installation.

The system consist in a stirred tank reactor made of stainless steel 316 SS Autoclave Engineers, prepared to work in batch, whose nominal volume is 100 ml and the extern and intern diameter measure 53 y 46 mm respectively. The maximum operation pressure is 76 bar at 454 ºC, while the minimal design temperature is -29 ºC at 76 bar.

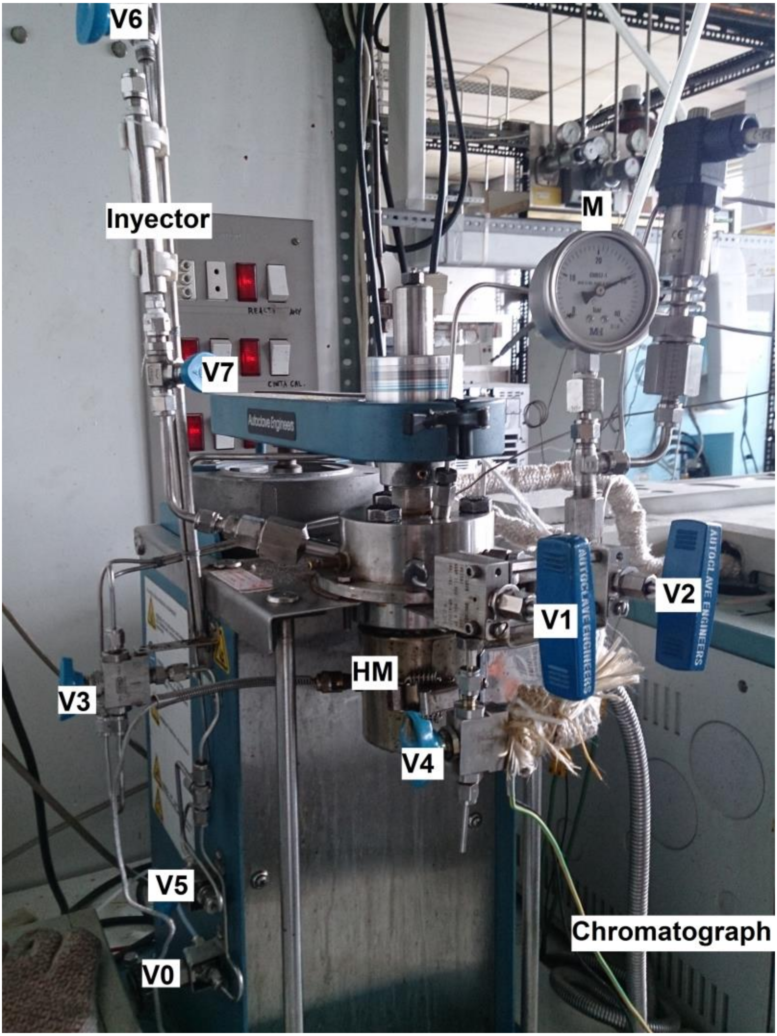

Figure 7. Experimental setup with accessories and valves specified

The tank head has the necessary connections so that the catalyst can be injected and the samples could have been taken. A sintered iron filter with a mesh of 0,5µm prevents that solid in particles inthe reaction system (catalysts or humins) escape while sampling. In the tank head can also be found the stirrer, a relief valve, a thermocouple, a baffle and a rupture disc.

Figure 8 and 9. Tank head with internal accessories.

The stirrer contents four paddles turbine type *axial u disperser* mounted on the agitation system, model *Magnedrive II Series 0.7501*. The agitation/stirring velocity is controlled with a frequency inverter *T-Verter N2 Series*, which regulate the spin speed of the motor axis.

Parallel to the axis agitation is found a stainless steel 316 SS baffle. Its function is contribute to the homogenization of the reaction system breaking possible vortexes created by the stirring, achieving that the flux model of the reactor resembles to the mixed flow model.

In the opposite side there is a thermocouple, protected with a sheath. Its function is to measure the temperature inside the reactor, and additionally it works as a baffle. The thermocouple used is of type K (cromel-alumel) and belongs to a proportional integral derivative (PID) control system.

The pressure meter, type *Labon Druckmessumformer CB6020*, is founded between the relief valve and the reactor body. It contains a metallic tube from *Bourdon* where the measure is taken and is calibrated between 0 and 30 bars. Pressure reads are made visually with sphere-kind manometer (M) located above the reactor which gives gauge pressures.

To the depressurization of the reactor is used a relief or vent valve. It is used if there is an uncontrolled increase of pressure or when sampling to return the products.

The rupture disc can withstand a maximum pressure between 50,1 and 54,8 bar with an error of 5%. Operation pressure cannot overpass the rupture pressure, in order to avoid the rupture by fatigue before time. This last condition is fulfilled because the operation pressure is 30 bars.

As heating system is available an electric oven TC-22 Pro 9, controlled from the internal reactor temperature (TC-22) and its external wall, which is also measured by a thermocouple. The reactor temperature stabilizes and it remains constant with an error of ±0,1 ºC.

Injections system of the catalyst comprises of a stainless steel 316 SS cylinder, where the amount of catalyst is loaded, and a nitrogen line to boost the catalyst into the reactor by pneumatic transportation generating pressure changes between the reactor and the injector, using the proper valves.

5.1.4. SAMPLING AND ANALYSIS SYSTEM

The installation has a gas chromatograph connected online with the reactor so that all system can be closed, and samples losses can be reduced. The information of this analysis system is explained by R. Bringué (43). Nevertheless samples are taken from the tube connected to the filter using the controlling valve carefully. Samples were collected in 1,5 ml Eppendorf so that it could be measured by high performance-liquid chromatography.

The HPLC chromatograph *Waters*, were samples are analysed. Sample injection is taken automatically, whose volume is of 0,1 ml. The separation column used is a *Biorrad HPX-87H* used to separate organic acids. The detector counts with a refractive index (RI) detector.

Eluent of chromatograph is a prepared solution of 5 mmol/L of sulphuric acid Milli-Q Water. Flow conditions are 0,8 ml/min at 60 ºC of temperature. Each analysis last 50 min in order that all the compounds reach the detector.

5.2. EXPERIMENTAL SETUP

5.2.1. CATALYST PRE-TREATMENT

The resins are very hygroscopic with high humidity content, which is necessary to remove, because it can introduce error in water precedent form the reactor evaluation an in the catalyst mass used. On the other hand water can contribute to the resin inhibition.

Water removing consists of a firs mechanical drying at atmosphere temperature, followed by a drying in an atmospheric stove at 110 ºC for two hours. Finally the catalyst remains between 12 and 15 hours at 10 mbar pressure in a vacuum stove at 100 ºC.

5.2.2. LOAD AND SEALED OF THE REACTOR

1. The feed blend is prepared in the correspondent proportion weighting the reagent amount and the solvents (70 ml) and it is introduced into the reactor.
2. Reactor is sealed using the screws of the tank head with the sealing rubber placed.
3. Dispositive is pressurized to 30 bar of supplied pressure. Valve 0 must be opened to lead the nitrogen pass inside the reactor. When the pressure is achieved, valve 0 must be closed in order to check the tightness verifying that the pressure remains constant in the manometer M lecture.
4. After checking that there are no leaks, valve 0 is opened once again. The heating mantle (HM), is placed around the reactor and subjected with a pin. The installation is ready to work.

5.2.3. START UP

1. All the switches of the electric panel are turned on, and the stirring (500 rpm) is connected. Control computer also must be ready.
2. The program *Microreactor Catalitic* from *LabView* is loaded in the control computer and the working temperature is set to the desired temperature. The setpoint of the heating mantel (PRO-)) must be over 20ºC above the working temperature. In this way reactor will reach the working temperature fast but the gradient will not be very accentuated to prevent the degradation of fructose.

5.2.4. CATALYST INJECTION

When the operation temperature is reached in the inside of reactor, proceeds to the catalyst injection. The steps to follow are:

1. Nut of the injection cylinder is unscrewed and a funnel is placed subjected by an iron stick.
2. Catalyst desired mass is weighed and as fast as possible is placed in the injector and the nut screwed.
3. Valve 3 is set in position 1 and valve 5 is opened. Then valve 6, so that the nitrogen flows to the injector.

4. To the injection, pressure inside of the reactor is dropped to 10 bars using the relief valve 2. Then valve 7 is opened and closed instantaneity. This step is repeated 3 or 5 times and the chronometer is started, due to the reaction has begun.
5. Then valve 5 and 6 are closed and valve 2 is placed in position 2.
6. The system is purged by opening valve 4.
7. Finally the nut is unscrewed another time that there is no catalyst left inside the reactor.

5.2.5. SAMPLING

1. Open valve 1 carefully and collect the sample in a 1,5 ml Eppendorf (the original connection between valve 1 and the gas chromatograph must be un removed, which contains valve 4.
2. Close valve 1 when finished sampling and connect the tube from chromatograph.
3. Turn the valve 3 to position 1 and open valve 7.
4. With valve 2, pressure must be dropped 10 bars so that the remaining sample in the tube can return to the reactor. Wait until the pressure has reached the initial value and repeat it for 3 times.
5. Close valve1, turn valve 3 to position 2 and purge the system with valve 4.
6. Unscrew valve 4 from valve 1 for the following sample.
7. Sample mass must be weighed and fast kept in the fried well labelled.

5.2.6. ANALYSING SAMPLES

1. This time the first step is go to the HPLC analysis department of Scientific Park. There the HPLC chromatograph will be prepared by the expert technician.
2. Samples must be diluted 10 times in water in order to do not saturate the RI detector.
3. The analysing program must be loaded.
4. Wait for the results and analyse the chromatograms there in order to collect all data.

5.2.7. DISCHARGE AND CLEANING OF THE REACTOR

Once the temperature of the reactor has dropped sufficiently to manipulate it the discharge and cleaning is performed

1. Depressurize completely the reactor
2. Unscrew all of the head screws, placing a pin under the ring that holds the reactor.

3. After taking away the sealing rubber, the reactor content is spilled into a prepared container with a funnel and a paper filter where resin will be collected.
4. Reactor is cleaned with proper solvent and deionized water. After is it dried with synthetic air to ensure that there are not substances inside.
5. Filter is unscrewed and laced in a beaker with hexane. It is placed in an ultrasonic bath for 20 min. After that the filter must be cleaned with solvent and dried with synthetic air for three times.
6. To eliminate resin wastes in the injection zone: valve 3 to position 1 and then valves 5 6 and 7 must be open in this order. Later valve 0 must be opened and closed repeatedly to let pas nitrogen through the injector. Then valves must be closed and valve 3 returned to position 2.
7. Wash the inside parts of the reactor with deionized water and let them dry with air until the next assay.
8. Finally, place the filter. Reactor is clean to work again.

5.3. EXPERIMENTAL CONDITIONS

To reach stablished objectives the following values for the variables have been used:

Composition of the initial load remained constant all over the experiments. Proportions were calculated in order to overpass the 70 ml, so that the filter was completely dipped but not to overpass the nominal volume of the reactor 100 ml due to there are the baffle, the thermocouple and the stirrer that occupy some space.

The wt. % for each component was fructose 14% ; dioxane 82%; water 4%.

Pressure was 30 bars because it allowed to have all the substances in liquid phase at the operating temperature and enhanced the dissolving water and formic acid.

Temperature for the screening was set to 100 ºC. 100 ºC is a moderate temperature that could be used in an industrial process because reduces the energy costs. In bibliography temperatures appear to be high and this lead to the formation of humins, which are not desired.

For the study of temperature were chosen temperatures around 100 ºC that not over pass the maximal temperature of the resins. 80 ºC, 90ºC 110ºC and 120ºC were the values.

Catalysts studied were Amberlyst-15, Amberlyst-16, Amberlyst-39, Dowex 50x8, Dowex 50x4 and Dowex 50x2 where the chosen ones. They have different DVB% but more or less the same acid capacity. Ameberlyst resins are macroreticular and Dowex series are gel-type resins. In literature has been found the use of Amberlyst-15 and Amberlyst-70 mostly, but not a very large spectrum.

Catalyst mass was chosen as 3 g in order to observe a noticeably velocity in the reaction.

6. RESULTS AND DISCUSSION

6.1. SETTING CONDITIONS

Mass quantities seem not to have a reason to follow. Nevertheless are selected by experience and bibliography. So that the samples could be analysed with the gas chromatograph, humins would be decreased and the second step of reaction enhanced, fructose mass proportion was increased rather than bibliography said, dioxane was chosen to reduce humins, and over stoichiometry water charged.

6.2. RUN ANALYSIS

Dehydration of fructose with dioxane as dissolvent catalysed by acidic ion-exchange resins lead to the expected products, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA).

First methodology, taken by literature (1) (47), consisted in using gas chromatography (GC-TCD), to control the moles of products. GC is online with the reactor and samples circulate through little tubes towards the chromatograph, were the temperature injection valve was 250ºC.

During an experiment the mole number of the intermediate HMF, and the product LA, water and dioxane were measured. Also were measured furfural, by-product from the main reaction, and formic acid (FA), formed in the second step of the reaction. However, fructose and known byproducts named humic acids, or humins couldn’t be measured.

Fructose cannot be analysed in a gas chromatograph because fructose decomposes into ashes before reaching the gas phase

These humins consist in a furan-rich polynetwork containing different oxygen functional groups (46) that arise by the condensation reactions of sugars, HMF and furfural. They are soluble or insoluble in water, depending on the number of molecules that form the polymer and a black solid when dry. At the end of an experiment can be observed after filtration. In figure 10 can be observed the solid rests of humins. Black spheres are wasted catalyst but the smaller ones and with no defined form are humins.

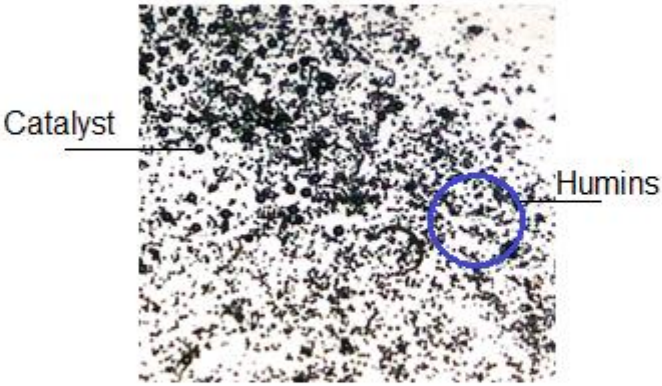

Figure 10. Humic acids format after 8 hours reaction.

After a week, the compounds of the installation started to muffle up and become dirty. These problems made that the sample analyses were not reproducible and obtained results did not follow a logical trajectory.

These analysing conditions were not lead to correct results. So the decision taken was to change the analytical method for HPLC, in order to improve the quality of the samples analysis.

External HPLC analysis solved the analysis of fructose and operation problems but water could not be followed due to it was used as eluent.

HPLC results were coherent and reproducible. The peaks observed were compared with each patron component. The correspondence is evident and can be ensured that components are separated sufficiently; therefore they can be quantified properly. The solvent used during the reaction, dioxane, is oversaturated and cannot be quantified. In figure 11 are observed LA and HMF. At time fructose was almost all reacted and the peak is funded in 8,05 min of retention time. The peak before LA is FA, retention time 11,3 min, and over 40 min can be observed a flattened peak corresponding to furfural.

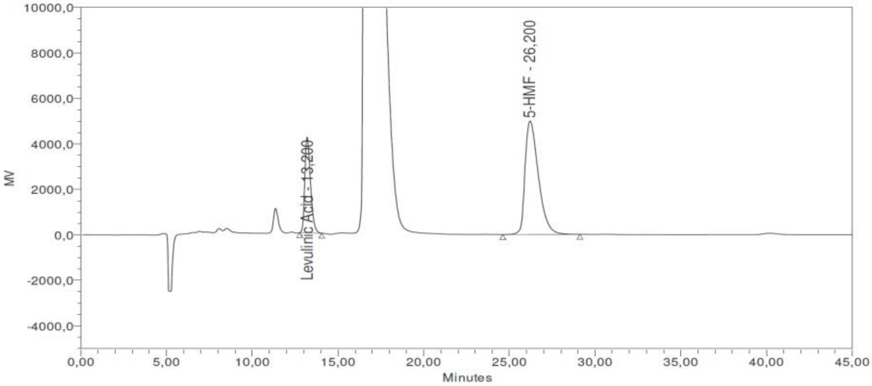

Figure 11. HPLC Chromatogram at reaction time 2h 40 min (Catalyst Dowex 50x2, 3,5% wt.)

Figure 12 illustrates an essay with Dowex 50x2 as catalysts, which is representative of the main behaviour of the rest of the experiments. HMF as intermediate increases to a maximum and then it decreases. Meanwhile LA increases steadily. Stoichiometry moles of FA should be the same formed as LA. As it can be observed moles of FA are a little higher than LA. It could be explained because when furfural is formed the reaction also gives formaldehyde. There should be an oxidant to obtain FA, but this oxidant remains unknown. However the route to furfural could be different and form FA in another way.

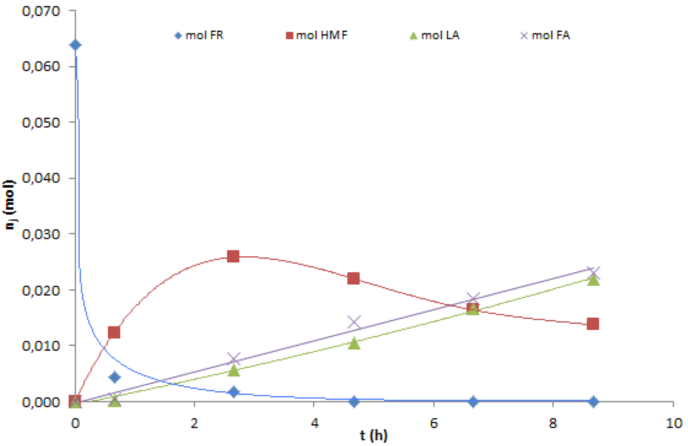

Figure 12. Moles of Fructose, HMF and LA over the reaction time (Catalyst Dowex 50x2, 3,5% wt.)

6.3. SCREENING AND TEMPERATURE INFLUENCE

The literature researched did not mention which type of resins could be better in the reaction system, so the different catalysts are selected in order to have a wide spectrum of properties that can influence the reaction.

In order to compare the different catalysts it is important to calculate the fructose conversion and the selectivity of fructose to HMF or LA. The conversion equation in a batch reactor is defined as:

$$X_{fructose} = \frac{\mathrm{n}^{0}_{fructose} - n_{fructose}}{\mathrm{n}^{0}_{fructose}} \tag{1}$$

Selectivity to HMF and LA is defined as the quotient of moles of each product per the total moles of fructose consumed. Yield is defined as the formed moles of each product per the initial fructose moles. The expressions are:

$$S^{HMF}_{Fruct} = \frac{n_{HMF}}{\mathrm{n}^{0}_{fructose} - n_{fructose}} \tag{2}$$

$$S^{LA}_{Fruct} = \frac{n_{LA}}{\mathrm{n}^{0}_{fructose} - n_{fructose}} \tag{3}$$

$$\mathrm{Y}_{HMF} = \frac{n_{HMF}}{\mathrm{n}^{0}_{fructose}} \tag{4}$$

$$\mathrm{Y}_{LA} = \frac{n_{LA}}{\mathrm{n}^{0}_{fructose}} \tag{5}$$

Subsequent figures present the evolution of these parameters in front of operation time, acid capacity and volume of swollen porous (V_{sp}) of resins and with the relation between acid capacity and $V_{sp.}$

First must be pointed that in a blank test, where the initial mixture was heated to 100ºC during 2 h was proved that no products or byproducts were formed.

During the experimental it has been observed that at the end of every experiment fructose is almost over. However (see figure 13) not all the resins have the same trajectory to the fully fructose conversion. Hence, the velocity of the reaction varies upon the used resin.

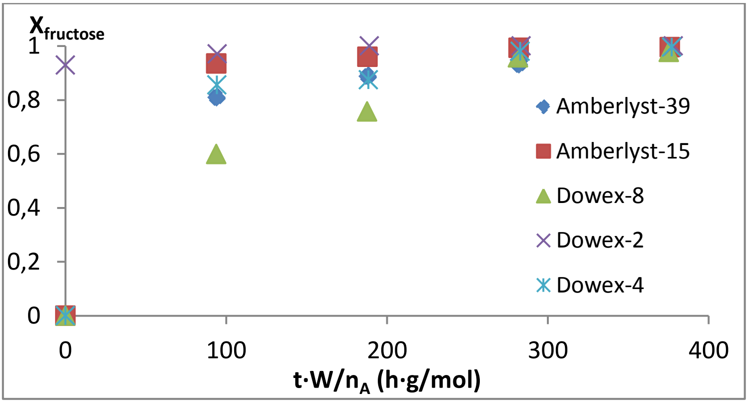

Figure 13. Conversion of fructose over time for different catalysts at 100ºC.

There is an experiment which has a particularity in front of the others. The experiment carried with Dowex 50x2, the resin was charged with the reagents before heating due to Dowex 50x2 created problems of injection in previous essays.

As can be observed in these results, conversion of fructose for 8h of reaction is almost complete. It means that selectivity of the desired products is more import. Because of conversion is not a limiting parameter, the best resin will be the one that leads to highest selectivity to HMF or LA.

Table 6 shows the selectivity and yield towards HMF and LA in two different reaction times. 4 hours of reaction correspond to the maximum of the selectivity towards HMF for all the used catalysts. On the other hand, 8 hour reaction corresponds to the maximum selectivity to LA because LA is the last product of the reaction chain and that means that the more reaction time, the more LA can be achieved until fructose and HMF are over.

Table 6. Selectivity values for HMF and LA at 4h and 8h reaction time

Catalysts	**t = 4h**		**t=8h**	
	S^{HMF}_{Fruct}	Y_{HMF} %	S^{HMF}_{Fruct}	Y_{LA} %
Amberlyst 15	0,28	4,7	0,08	2,3
Amberlyst 39	0,35	31,1	0,26	24,6
Dowex 50x8	0,36	26,9	0,29	20,2
Dowex 50x4	0,40	35,1	0,24	30,9
Dowex 50x2	0,42	40,7	0,21	34,4

Despite of LA is the desired product of the study, HMF production is important due to this chemical is also a platform molecule that can be used to synthetize another chemicals. Also, if production of levulinic is wanted to be carried in an industrial way, HMF obtaining could be of interest because a more optimized reactor system could be a two reactor system working in different conditions.

From Figures 14 to 17, selectivity to HMF and LA is represented in front of resins properties in order to check its influence. Results correspond to HMF and LA, when they reach their maximal selectivity. This is of interest in order to find the best resin and HMF and LA production.

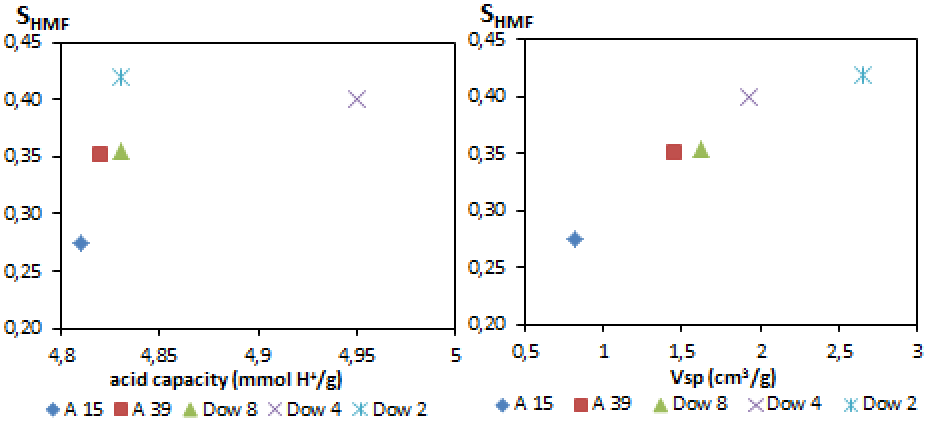

Figura 14 and 15. Influence of acid capacity and V_{sp} on HMF selectivity (t=4h).

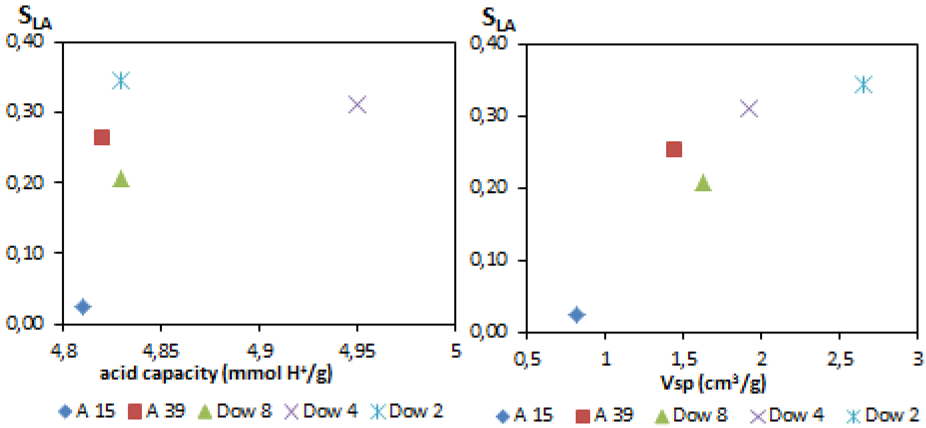

Figure 16 and 17. Influence of acid capacity and V_{sp} on LA selectivity (t=8h)

Attending to resin structure, it seems that the difference between macro and gel type resins (A39 and Dowex 50x8) with the same DVB content (8%) and approximately the same acidity, do not give any advantage to one or another towards HMF selectivity but in the case of levulinic selectivity seems that the macroporous resin A-39 is more selective (see Figures 14 and 15).

Also must be pointed that:

1. There is a high influence in a narrow range of the studied acidities and seems to not have little influence at higher one.
2. The volume of swollen phase V_{sp}, does have influence on the selectivity. Experimental data shows that the more V_{sp} the resin have, the more selective is

However, in order to give an idea of how many actives cites can be accessible to the molecules is better analyse the acid capacity versus V_{sp} ratio. As can be seen in figure 18 and 19, accessibility of acid sites influence noticeably in the selectivity towards HMF and LA.

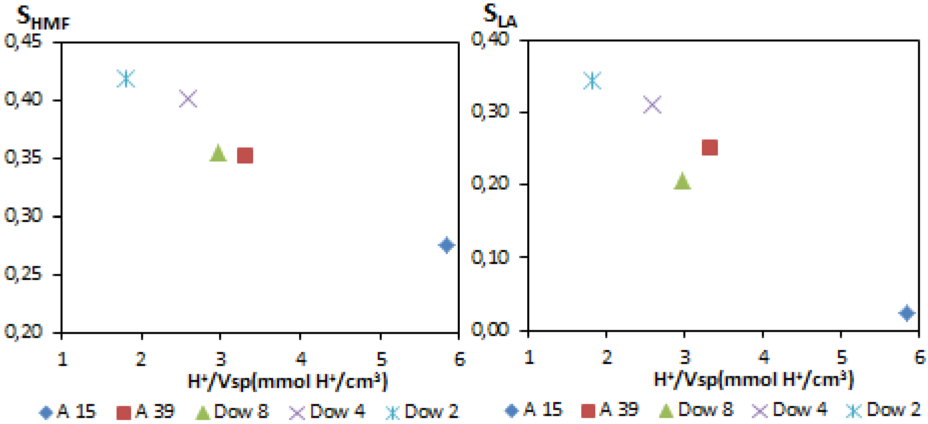

Figure 18 and 19. Influence of H^+/V_{sp} on HMF and LA selectivity (t=4h and t=8h respectively)

Analysing the gel-type resins results, it can be deduced that the lower DSB %, the better selectivity. Dowex 50x2 is the most efficient catalyst for obtaining HMF and LA. Additionally, regarding macroreticular ones, Amberlyst-15, the resin with higher DVB content, shows less accessibility to acid sites, which is the expect behaviour. So, in both types of resin structures (macroreticular and gel), accessibility increases with diminishing DSB% and in consequence selectivity increases. Resins with an intermediate 8% DVB content, macroreticular A-39 and gel-type Dowex 50x8, give the same selectivity to HMF and slightly different to LA. The different structure could explain why levulinic acid selectivity is better in the macroreticular resin A-39. The change in medium polarity, originated because of the second reaction step consume of water, probably do not let Dowex 50x8 completely swell, while A-39 rests less affected because it has permanent porous.

Best selectivity for gel-type resins with low DVB % could be explained because that allows a great swelling and originates larger spaces between polymer chains (“porosity”). As molecules in the reaction systems are relatively large, they can reach more acid centres from the inside of the resins as more swollen the resin is.

The last important products in the reaction system, although not the most desired, are humins. They are important because they decrease the yield of the reaction system. Higher temperatures promote the reaction toward humins. Certainly, humins cannot be quantified, and also cannot be ensured that all of the fructose that react but not to HMF or LA is transformed to humins. However, they are reflected into LA formation yield and the global velocity reaction.

Unfortunately humins have not been quantified because they rest mixed with the catalyst and resins wastes are difficult to separate; they are retained in filters and walls; and some of them are soluble in the medium. However, an approximated measure from residual humins could be obtained by weighing solid residues (catalyst and solid humins together).

Temperature effect was studied at 90 ºC, 100 ºC, 110ºC with gel-type resin Dowex 50x4 as catalyst. To give an idea for the general yield of the reaction towards the desired products, can be considered that all the HMF measured in a moment, could react to only to LA over time. Truly it is not correct but allows adding up the two products as one. To sum up, the behaviour through the different temperature (Figure 20), confirm that lower temperatures have better global yields because humins are produced in lower amounts.

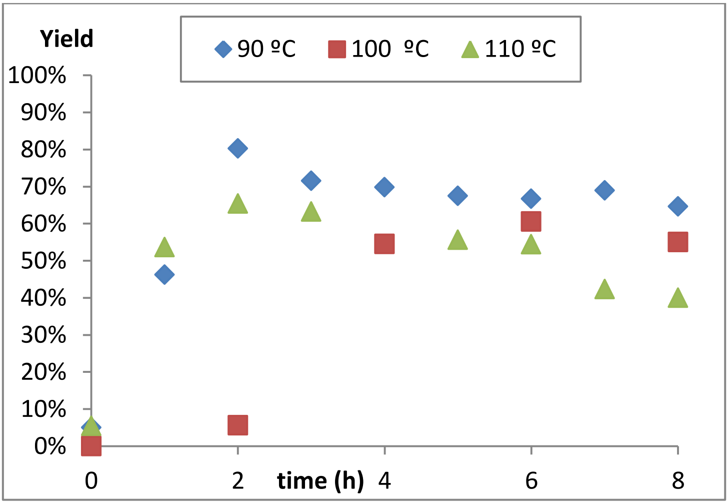

Figure 20. Reaction global yield over time in different temperatures (Catalyst Dowex 50x4)

As can be seen in Table 7, HMF yield at low temperatures improves significantly. HMF is the molecule responsible of humin formation and minimizing humin lead to good yields of this platform molecule. Focusing on LA yield, it increases while the temperature does to. Because reaction has two steps, the second step should be favoured for high temperatures and that corresponds to the results.

Table 7 Yields of HMF and LA in different reaction times

Temperature (ºC)	t = 2h		t = 4h		t = 6h		t=8h	
	Y_{HMF} %	Y_{LA} %	Y_{HMF} %	Y_{LA} %	Y_{HMF} %	Y_{LA} %	Y_{HMF} %	Y_{LA} %
90	72,4	7,9	58,0	11,9	51,6	15,1	45,9	18,8
100	2,5	3,2	35,1	19,5	32,9	27,6	24,2	30,9
110	45,5	8,1	17,9	28,9	13,7	40,8	6,2	33,8

It could be concluded that the higher temperature, the higher yield of LA. For the point of view of obtaining levulinic acid it could be beneficial, but to the whole reaction system is not profitable.

It can be summarized that, the best yields achieved in the present work are, towards the HMF 72,4% at 90 ºC with Dowex50x4 and towards LA 34,4% at 100ºC with Dowex 50x2.

Table 8. Yields of HMF and LA with heterogeneous catalysis

Reference	**Catalyst**	**HMF yield %**	**LA yield %**
34	Zirconium dioxide	-	53,9%
35	Amberlyst 70	-	46/54 %
36	Polyoxometalate salts (IL-POMS)	99%	-
37	Amberlyst 70,31,121,15,35 and 36	68%	-
38	(C-SO_3H)	89%	-
39	Acid Y-zeolite	9%	21%
40	Amberlyst 15	80%	-
41	Various catalysts (NB_2O_5, TiO_2, Ta_2O_5, lewis acids…)	64%	-

Table 8 shows the best yields achieved by authors in literature. Comparison with the ones obtained in the present work, sets then in the middle. Attending to the fact that they are obtained in higher fructose concentrations and lower temperature than literature ones, lets us to be confident in the use of the gel-type resins in an industrial way, because that could generate processes more cost-efficient than performed for the others.

7. CONCLUSIONS

This study has proven that de dehydration of fructose into levulinic acid can take place with PS-DVB resins as catalyst with similar yields found in literature, though there is a lot of improvement that can be reached by changing the operation conditions.

Gel type resins with lower DSB content are more suitable to enhance the reaction to desired products. Of the catalysts tested, Dowex 50x2 appears to be the most selective in the sampled conditions.

The access to acid sides, and hence, swelling capacity of the resin, are the catalyst properties that control the most over catalyst efficiency. Reaction rates increase when the swollen volume phase is higher and there are parts with lower polymer density, having a behaviour related with the content of cross-linker (DVB %). However, on the other side, acid capacity does not seem to be significant against reaction rates, although more experiments are needed to prove this conclusion.

Humins have been more significant than expected. Nonetheless, their formation seems to be very sensitive to temperature, because the experiments carried at 90 ºC improved the general yield reaction towards desired product in a significant way.

The highest yield reached during the experimental towards HMF is 72,4% at 90 ºC with Dowex 50x4, and towards LA, is 34,4% at 100 ºC with Dowex 50x2 as catalyst. Although these two results are not obtained for equal conditions, the comparison with literature shows that similar yields are reached, though probably not in the optimal conditions.

Further testing could be applied to this field of resin type catalyst in order to ascertain whether they are suitable or not to catalyse the reaction system in an industrial plant. Studies to optimizing conditions and to life-long reusability of the resins would be necessary.

8. RECOMMENDATIONS

In order to improve the analytical method there are several considerations that could help if someone carries on with this reaction system:

1. Enlarge temperature ranges to low temperatures in order to enhance HMF production and study the possibility of working with temperature ramps to force the step to levulinic acid, minimalizing humins.
2. Optimize initial reagent concentrations and solvent. For example, to reach greater LA yields.
3. Fit operation setups:
    a. Cleaning up the tube after each assay with hot pressured water due to the easily muffling of the system because of fructose and humic acids.
    b. Heating process must not be done with the heating mantle over 110ºC because of the decomposition of fructose on the walls, and thus, reducing yield.
    c. Samples must be closed and kept into the fridge as fast as possible. Consider covering the Eppendorf with aluminium foil in order to protect the photosensitive substances.

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10. ACRONYMS

HMF	5-hydroxymethylfurfural
CN	cetane number
DMC	Dimethyl carbonate
DMF	Dimethylfuran
DMSO	Dimethyl sulfoxide
DVB	Divinylbenzene
FA	Formic acid
GC	Gas chromatography
GVL	*γ*-valerolctane
HM	Heating mantle
HPLC	High-performance líquid chromatography
LA	Levulinic acid
M	manometer
MeCN	methyl cyanide
PS	Polystyrene
THF	Tetrahydrofuran
V_{sp}	volume of swollen phase

APPENDICES

APPENDIX 1: CHROMATOGRAPHIC ANALYSIS

Table 8. Retention times for the substances detected by HPLC

Substances	Retention time (min)
Fructose	8,25
FA	11,35
LA	13,15
HMF	26,15

Table 9. Vials prepared for the calibration

Vials	Fructose (mg/ml)	HMF (mg/ml)	LA (mg/ml)	FA (mg/ml)
Stock	10,075	1,43	8,5	10
Std. 1	0,504	0,715	4,250	1
Std. 2	0,252	0,358	2,125	2
Std. 3	0,126	0,179	1,063	3
Std. 4	0,063	0,107	0,638	0,5
Std. 5	-	-	0,425	-

Table 10. Area obained for fructose by HPLC

Vials	Fructose (mg/ml)	Area (10^{-6})
Std. 1	0,504	29,0
Std. 2	0,252	14,6
Std. 3	0,126	7,16
Std. 4	0,063	3,56

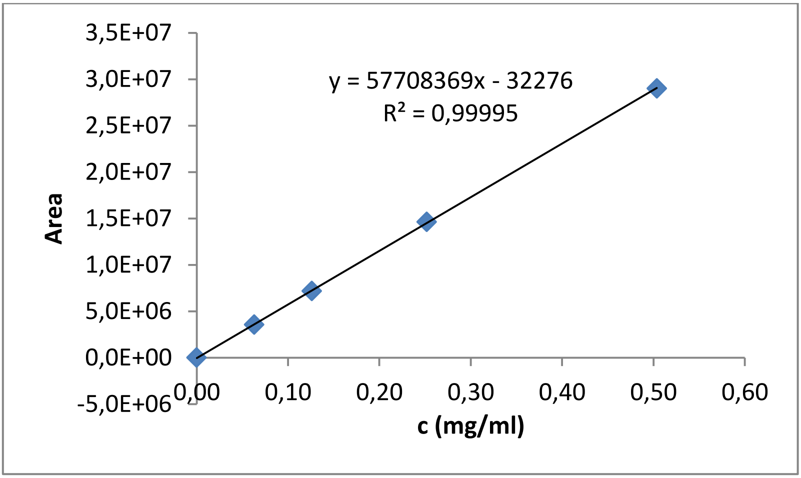
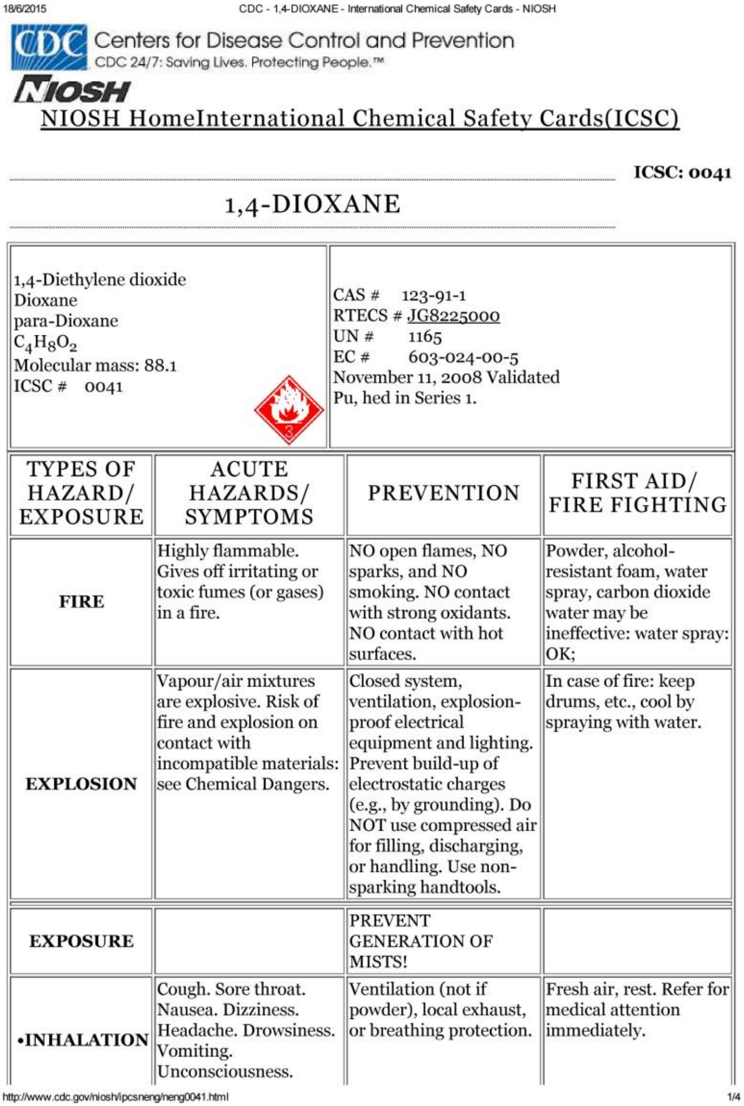


Figure 21. Example of linear regression for the calibration of fructose.

Table 11. Calibration straight obtain where y is area and x is concentration (mg/ml).

Substance	**Equation**	**R^2**
Fructose	y=(57708369±72236)x-(32276±187535)	0,9999
HMF	y=(67254085±2117677)x+(734368±1564040)	0,9997
LA	y=(42682496±595172)x+(2908756±1311921)	0,9999
FA	y=(23253922±311142)x-(896561±1357726)	0,9999

APPENDIX 2: SAFETY DATA SHEETS



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Centers for Disease Control and Prevention
CDC 24/7: Saving Lives. Protecting People.™

NIOSH HomeInternational Chemical Safety Cards(ICSC)

ICSC: 0041

1,4-DIOXANE

1,4-Diethylene dioxide Dioxane para-Dioxane $C_4H_8O_2$ Molecular mass: 88.1 ICSC # 0041	CAS # 123-91-1 RTECS # JG8225000 UN # 1165 EC # 603-024-00-5 November 11, 2008 Validated Pu, hed in Series 1.

TYPES OF HAZARD/ EXPOSURE	ACUTE HAZARDS/ SYMPTOMS	PREVENTION	FIRST AID/ FIRE FIGHTING
FIRE	Highly flammable. Gives off irritating or toxic fumes (or gases) in a fire.	NO open flames, NO sparks, and NO smoking. NO contact with strong oxidants. NO contact with hot surfaces.	Powder, alcohol-resistant foam, water spray, carbon dioxide water may be ineffective: water spray: OK;
EXPLOSION	Vapour/air mixtures are explosive. Risk of fire and explosion on contact with incompatible materials: see Chemical Dangers.	Closed system, ventilation, explosion-proof electrical equipment and lighting. Prevent build-up of electrostatic charges (e.g., by grounding). Do NOT use compressed air for filling, discharging, or handling. Use non-sparking handtools.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		PREVENT GENERATION OF MISTS!	
•INHALATION	Cough. Sore throat. Nausea. Dizziness. Headache. Drowsiness. Vomiting. Unconsciousness.	Ventilation (not if powder), local exhaust, or breathing protection.	Fresh air, rest. Refer for medical attention immediately.

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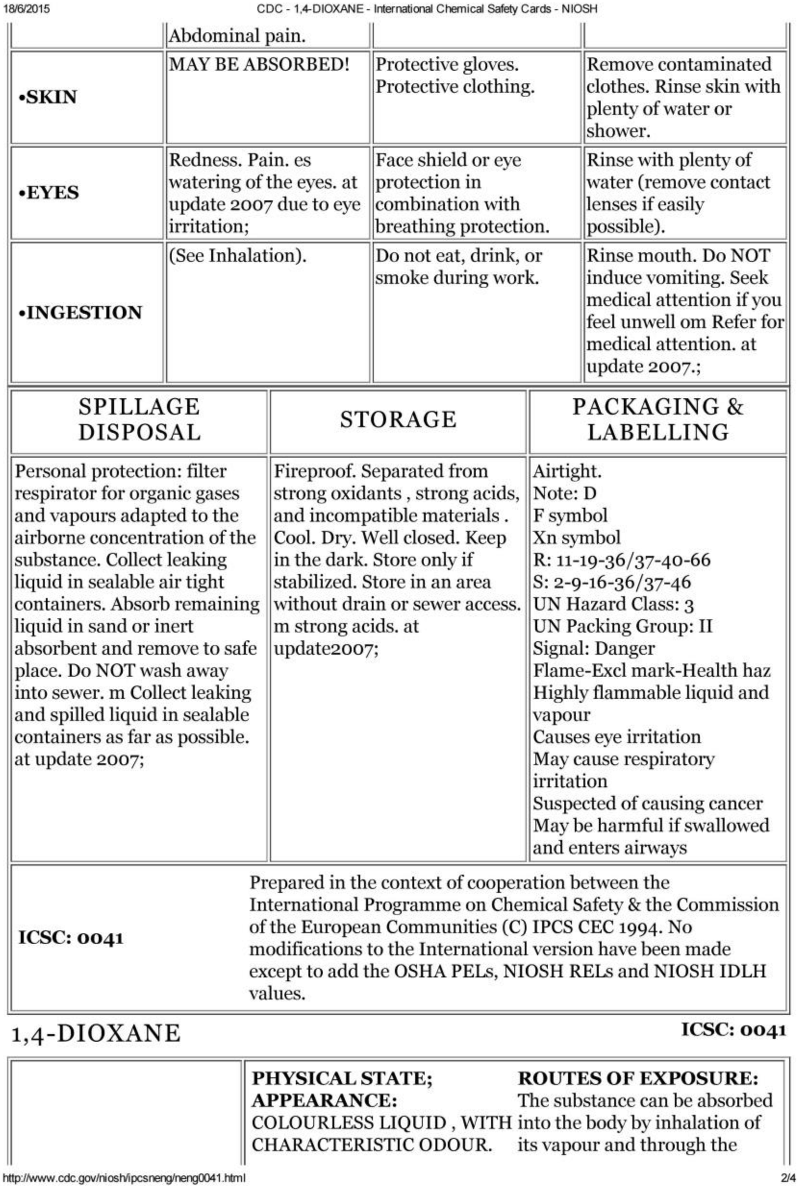

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	Abdominal pain.		
•SKIN	MAY BE ABSORBED!	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower.
•EYES	Redness. Pain. es watering of the eyes. at update 2007 due to eye irritation;	Face shield or eye protection in combination with breathing protection.	Rinse with plenty of water (remove contact lenses if easily possible).
•INGESTION	(See Inhalation).	Do not eat, drink, or smoke during work.	Rinse mouth. Do NOT induce vomiting. Seek medical attention if you feel unwell om Refer for medical attention. at update 2007.;

SPILLAGE DISPOSAL	STORAGE	PACKAGING & LABELLING
Personal protection: filter respirator for organic gases and vapours adapted to the airborne concentration of the substance. Collect leaking liquid in sealable air tight containers. Absorb remaining liquid in sand or inert absorbent and remove to safe place. Do NOT wash away into sewer. m Collect leaking and spilled liquid in sealable containers as far as possible. at update 2007;	Fireproof. Separated from strong oxidants , strong acids, and incompatible materials . Cool. Dry. Well closed. Keep in the dark. Store only if stabilized. Store in an area without drain or sewer access. m strong acids. at update2007;	Airtight. Note: D F symbol Xn symbol R: 11-19-36/37-40-66 S: 2-9-16-36/37-46 UN Hazard Class: 3 UN Packing Group: II Signal: Danger Flame-Excl mark-Health haz Highly flammable liquid and vapour Causes eye irritation May cause respiratory irritation Suspected of causing cancer May be harmful if swallowed and enters airways

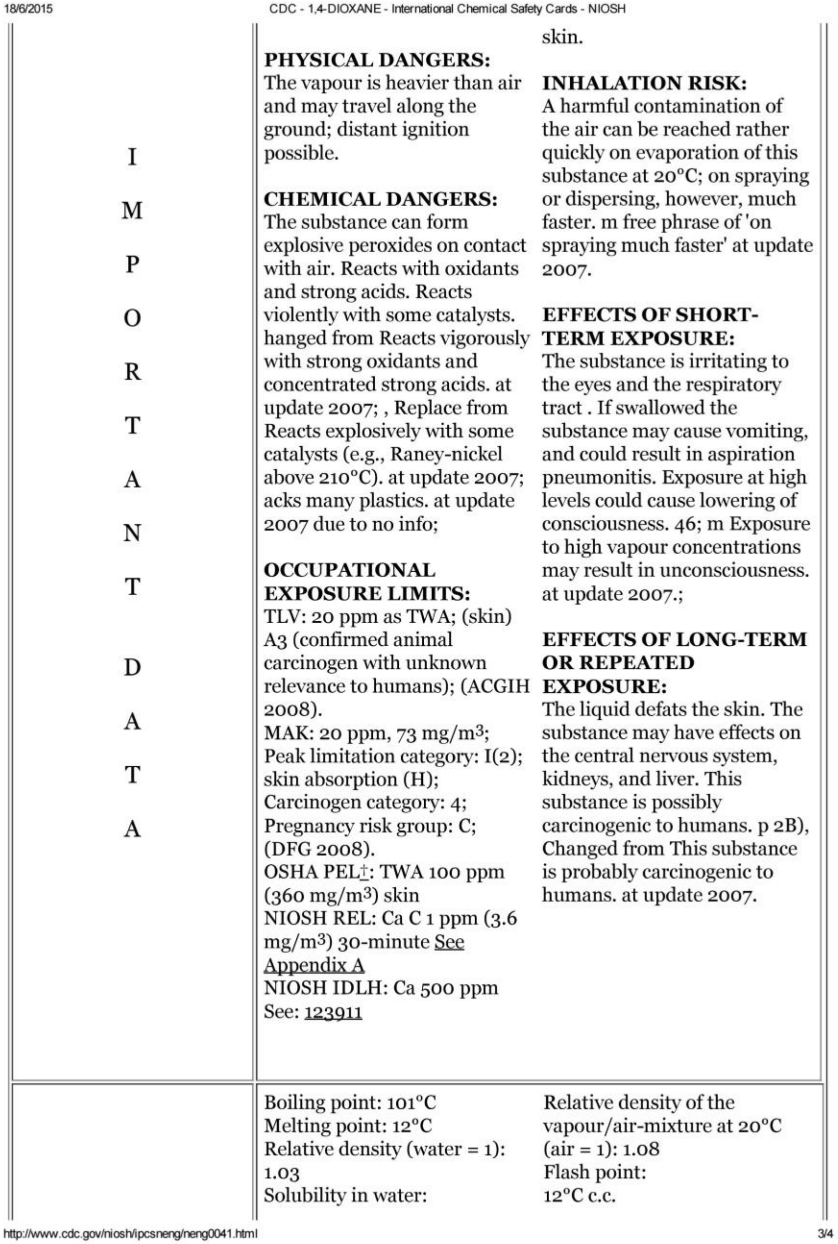
ICSC: 0041	Prepared in the context of cooperation between the International Programme on Chemical Safety & the Commission of the European Communities (C) IPCS CEC 1994. No modifications to the International version have been made except to add the OSHA PELs, NIOSH RELs and NIOSH IDLH values.

1,4-DIOXANE

ICSC: 0041

	PHYSICAL STATE; APPEARANCE: COLOURLESS LIQUID , WITH CHARACTERISTIC ODOUR.	**ROUTES OF EXPOSURE:** The substance can be absorbed into the body by inhalation of its vapour and through the

http://www.cdc.gov/niosh/ipcsneng/neng0041.html 2/4



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IMPORTANT DATA

PHYSICAL DANGERS:
The vapour is heavier than air and may travel along the ground; distant ignition possible.

CHEMICAL DANGERS:
The substance can form explosive peroxides on contact with air. Reacts with oxidants and strong acids. Reacts violently with some catalysts. hanged from Reacts vigorously with strong oxidants and concentrated strong acids. at update 2007; , Replace from Reacts explosively with some catalysts (e.g., Raney-nickel above 210°C). at update 2007; acks many plastics. at update 2007 due to no info;

OCCUPATIONAL EXPOSURE LIMITS:
TLV: 20 ppm as TWA; (skin) A3 (confirmed animal carcinogen with unknown relevance to humans); (ACGIH 2008).
MAK: 20 ppm, 73 mg/m^3;
Peak limitation category: I(2); skin absorption (H);
Carcinogen category: 4;
Pregnancy risk group: C;
(DFG 2008).
OSHA PEL†: TWA 100 ppm (360 mg/m^3) skin
NIOSH REL: Ca C 1 ppm (3.6 mg/m^3) 30-minute See Appendix A
NIOSH IDLH: Ca 500 ppm
See: 123911

skin.

INHALATION RISK:
A harmful contamination of the air can be reached rather quickly on evaporation of this substance at 20°C; on spraying or dispersing, however, much faster. m free phrase of 'on spraying much faster' at update 2007.

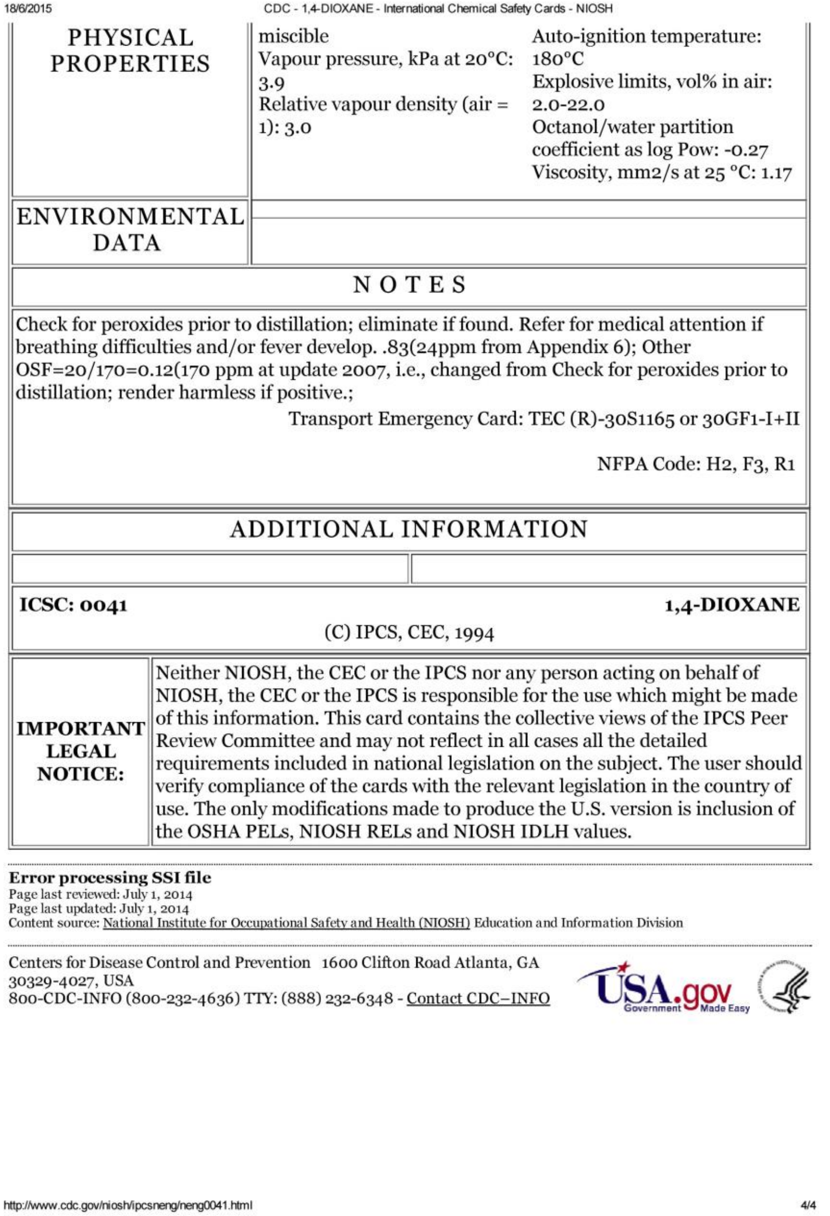
EFFECTS OF SHORT-TERM EXPOSURE:
The substance is irritating to the eyes and the respiratory tract . If swallowed the substance may cause vomiting, and could result in aspiration pneumonitis. Exposure at high levels could cause lowering of consciousness. 46; m Exposure to high vapour concentrations may result in unconsciousness. at update 2007.;

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:
The liquid defats the skin. The substance may have effects on the central nervous system, kidneys, and liver. This substance is possibly carcinogenic to humans. p 2B), Changed from This substance is probably carcinogenic to humans. at update 2007.

Boiling point: 101°C
Melting point: 12°C
Relative density (water = 1): 1.03
Solubility in water:

Relative density of the vapour/air-mixture at 20°C (air = 1): 1.08
Flash point:
12°C c.c.

http://www.cdc.gov/niosh/ipcsneng/neng0041.html 3/4



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PHYSICAL PROPERTIES	miscible Vapour pressure, kPa at 20°C: 3.9 Relative vapour density (air = 1): 3.0	Auto-ignition temperature: 180°C Explosive limits, vol% in air: 2.0-22.0 Octanol/water partition coefficient as log Pow: -0.27 Viscosity, mm2/s at 25 °C: 1.17
ENVIRONMENTAL DATA		

NOTES

Check for peroxides prior to distillation; eliminate if found. Refer for medical attention if breathing difficulties and/or fever develop. .83(24ppm from Appendix 6); Other OSF=20/170=0.12(170 ppm at update 2007, i.e., changed from Check for peroxides prior to distillation; render harmless if positive.;

Transport Emergency Card: TEC (R)-30S1165 or 30GF1-I+II

NFPA Code: H2, F3, R1

ADDITIONAL INFORMATION

ICSC: 0041 **1,4-DIOXANE**

(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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Chemicals & Laboratory Equipment

Health	2
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Levulinic acid MSDS

Section 1: Chemical Product and Company Identification

Product Name: Levulinic acid

Catalog Codes: SLL1693

CAS#: 123-76-2

RTECS: OI1575000

TSCA: TSCA 8(b) inventory: Levulinic acid

CI#: Not available.

Synonym: 4-Oxopentanoic acid

Chemical Name: Not available.

Chemical Formula: $C_5H_8O_3$

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396
US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**
Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Levulinic acid	123-76-2	100

Toxicological Data on Ingredients: Levulinic acid: ORAL (LD50): Acute: 1850 mg/kg [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant). Hazardous in case of ingestion, of inhalation. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant). Hazardous in case of ingestion, of inhalation. CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to mucous membranes. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated or prolonged inhalation of dust may lead to chronic respiratory irritation.

Section 4: First Aid Measures

Eye Contact: Check for and remove any contact lenses. Do not use an eye ointment. Seek medical attention.

Skin Contact:
After contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation: Not available.

Ingestion:
Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however, is not conclusive. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: 137°C (278.6°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances: Not available.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

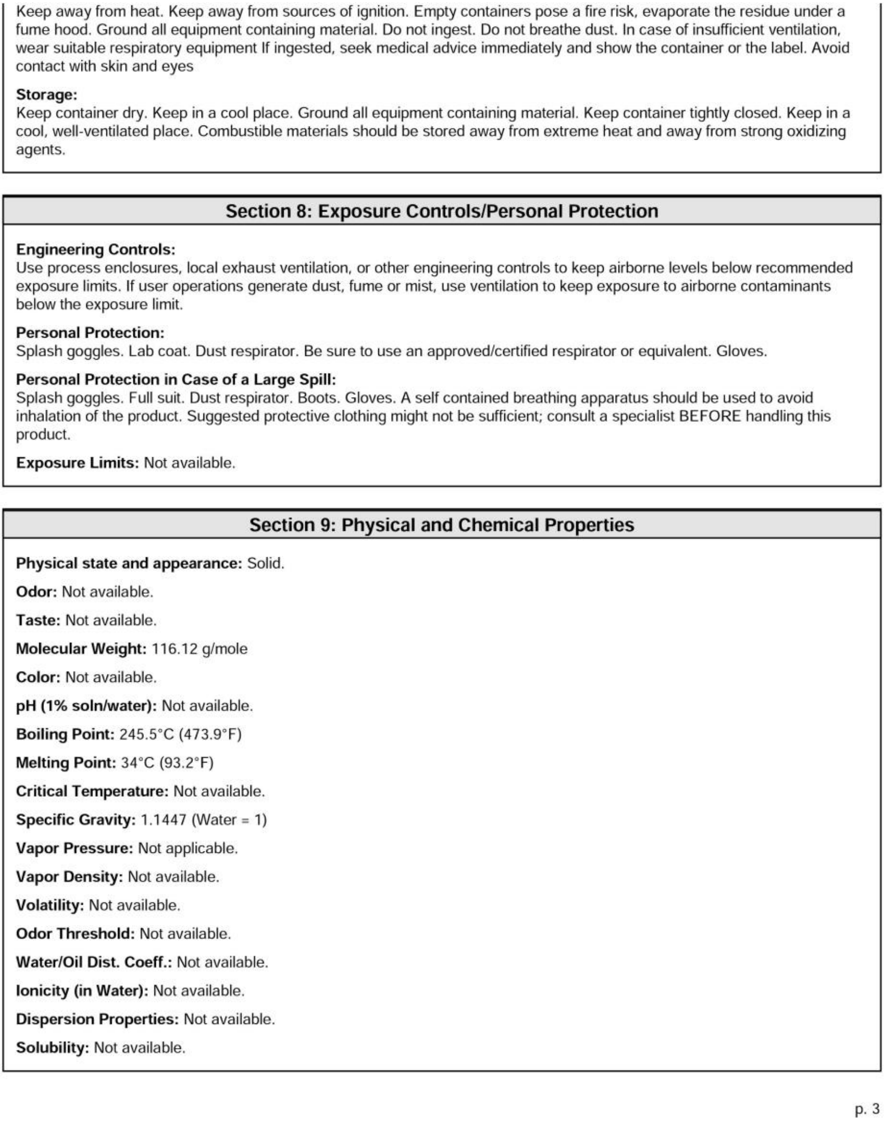
Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
If the product is in its solid form: Use a shovel to put the material into a convenient waste disposal container. If the product is in its liquid form: Absorb with an inert material and put the spilled material in an appropriate waste disposal. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions:



Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes

Storage:
Keep container dry. Keep in a cool place. Ground all equipment containing material. Keep container tightly closed. Keep in a cool, well-ventilated place. Combustible materials should be stored away from extreme heat and away from strong oxidizing agents.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid.

Odor: Not available.

Taste: Not available.

Molecular Weight: 116.12 g/mole

Color: Not available.

pH (1% soln/water): Not available.

Boiling Point: 245.5°C (473.9°F)

Melting Point: 34°C (93.2°F)

Critical Temperature: Not available.

Specific Gravity: 1.1447 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: Not available.

Solubility: Not available.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Not available.

Incompatibility with various substances: Not available.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Eye contact. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 1850 mg/kg [Rat].

Chronic Effects on Humans: The substance is toxic to mucous membranes.

Other Toxic Effects on Humans:
Very hazardous in case of skin contact (irritant). Hazardous in case of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans: Not available.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are more toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

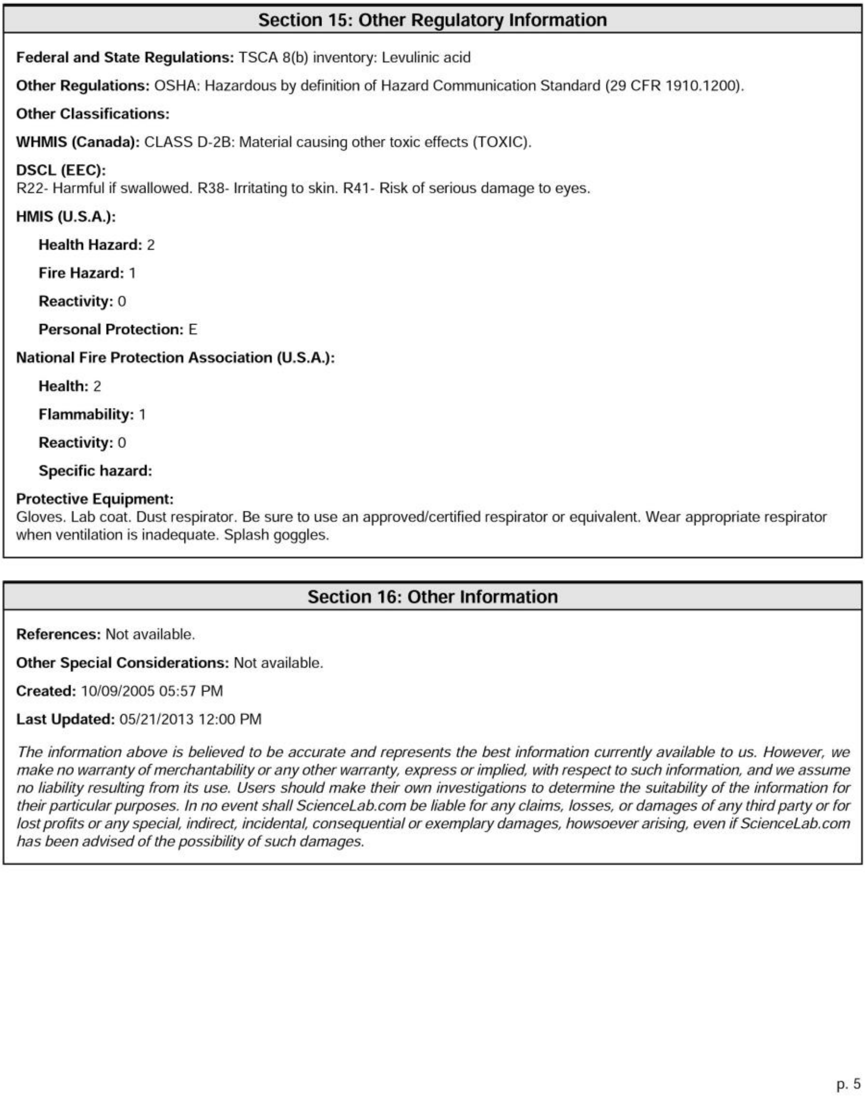
Waste Disposal:

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.



Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Levulinic acid

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other Classifications:

WHMIS (Canada): CLASS D-2B: Material causing other toxic effects (TOXIC).

DSCL (EEC):
R22- Harmful if swallowed. R38- Irritating to skin. R41- Risk of serious damage to eyes.

HMIS (U.S.A.):

- **Health Hazard:** 2
- **Fire Hazard:** 1
- **Reactivity:** 0
- **Personal Protection:** E

National Fire Protection Association (U.S.A.):

- **Health:** 2
- **Flammability:** 1
- **Reactivity:** 0
- **Specific hazard:**

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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