



Treball Final de Grau

**Catalytic assessment of ion exchange-based bifunctional catalysts
for the hydrogenation of levulinic acid to γ -valerolactone.**

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*Science never solves a problem without creating
ten more.*

George Bernard Shaw

REPORT

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1. SUMMARY

Nowadays, most of the energy and chemicals come from fossil fuels. Nevertheless, there is a growing concern about the depletion of fossil resources and the respective environmental problems they cause in terms of the greenhouse effect. Lignocellulose-derived platform molecules are being investigated as a possible solution. Among the platform molecules derived from biomass we can distinguish levulinic acid, which through a hydrogenation reaction can produce γ -valerolactone, which has multiple applications.

On this research, the hydrogenation reaction of levulinic acid to produce γ -valerolactone has been catalysed with bifunctional ion exchange resins.

An initial assessment of the operating conditions has been carried out with Amberlyst CH28 catalyst. As a result of the evaluation, it was found that it is better to work with a water-diluted LA feed, at a temperature of 120 °C and that the catalyst loading, when the hydrogen pressure is limited to 7 bar, does not favour the catalytic activity.

The LA hydrogenation reaction has also been performed to produce GVL with 4 bifunctional copper and palladium resins, which have been doped in the faculty's laboratory. From this study it has been observed that copper doped resins show a higher conversion. Palladium resins, on the other hand, are more selective. In addition, it has been noted that resins with macroreticular structure show higher LA conversion than gel-type resins. Despite this fact, gel-type resins show better selectivity to produce GVL.

Lastly, it should be noted that both the levulinic conversion and the GVL selectivity of the reaction under the conditions tested were very low and need to be further studied.

Keywords: γ -valerolactone (GVL), Amberlyst CH28, levulinic acid (LA), bifunctional ion exchange resin, hydrogenation, lignocellulose-derived platform molecules, biomass.

2. RESUM

Avui en dia, la major part de l'energia i dels productes químics provenen de combustibles fòssils. No obstant això, la preocupació per l'esgotament dels recursos fòssils i els respectius problemes ambientals que provoquen en termes d'efecte hivernacle va creixent. Les molècules de plataforma derivades de la lignocel·lulosa s'estan investigant com a possible solució. Entre les molècules plataforma derivades de la biomassa es pot distingir l'àcid levulínic, el qual mitjançant una reacció d'hidrogenació, pot produir la γ -valerolactona, la qual disposa de múltiples aplicacions.

En aquest treball, la reacció d'hidrogenació de l'àcid levulínic per produir la γ -valerolactona s'ha catalitzat amb resines d'intercanvi iònic bifuncionals.

S'ha realitzat una avaluació inicial de les condicions de funcionament amb el catalitzador Amberlyst CH28. Com a resultat de l'avaluació, s'ha pogut comprovar que és millor treballar amb un aliment de LA diluït en aigua, a una temperatura de 120 °C i que la càrrega del catalitzador, quan la pressió d'hidrogen es limita a 7 bar, no afavoreix l'activitat catalítica.

També s'ha realitzat la reacció d'hidrogenació LA per produir GVL amb 4 resines bifuncionals de coure i pal·ladi, les quals han estat dopades al laboratori de la facultat. A partir d'aquest estudi s'ha observat que les resines dopades amb coure mostren una conversió més elevada. Les resines de pal·ladi, en canvi, són més selectives. A més, s'ha notat que les resines amb estructura macrorreticular presenten una conversió de LA més alta que les resines de tipus gel. Malgrat això, les resines de tipus gel mostren una millor selectivitat per produir GVL.

Finalment, cal tenir en compte que tant la conversió del àcid levulínic com la selectivitat en GVL de la reacció, en les condicions provades, han estat molt baixes i s'han de seguir estudiant.

Paraules clau: γ -valerolactona (GVL), Amberlyst CH28, àcid levulínic (LA), resines bifuncionals d'intercanvi iònic, hidrogenació, molècules plataforma derivades de la lignocel·lulosa, biomassa.

3. INTRODUCTION

For years now, the world's population has been growing and developing economically due to the improvement in life quality. Consequently, the world's energy consumption has increased drastically. According to Tian et al., (2021), almost 90% of the energy consumed in 2018 came from fossil fuels, confirming the fact that fossil fuels are still dominating the energy market. Nevertheless, there is a growing concern about the depletion of fossil resources and the respective environmental problems they cause in terms of the greenhouse effect. For this reason, there is a need to investigate new renewable alternatives and developing sustainable processes to produce chemicals, fuels, and polymers which are irreplaceable in our lives.

After coal, oil, and natural gas, biomass is becoming the focus of research attention because whereas solar radiation, wind, and tides can be used as a renewable source of energy, biomass can also produce chemicals and materials. In addition, biomass is not only committed to the development of efficient and environmentally friendly technologies but also to solving the problem of agricultural and forestry waste reuse.

3.1. BIOMASS

Biomass is defined as any organic matter that is available on a recurring basis. There are several types of biomass of which, wood and crops (e.g. wheat, maize, and rice), usually stand out. Another very important type of biomass is waste (e.g. food waste, manure, etc.). These resources are often considered renewable, as they can be regrown or regenerated at any time. They also absorb carbon dioxide from the air while growing (through photosynthesis) and return it to the air at the end of their life, thus creating a closed-loop.

Although the provenance of biomass may be diverse, not all of them provide valid biomass for biorefinery feedstock. This feedstock must be cheap, available in abundance and it must be able to be chemically converted. From the different forms in which biomass can be presented, lignocellulose, chitin, and microalgae stand out as being more accessible for further processing.

According to the US Department of Energy (DOE), a biorefinery is an overall concept of processing plants where biomass feedstock is converted into a broad spectrum of valuable

products that are typically produced from petrochemical refining. (Shinde et al., 2019) Figure 1 shows the analogy between the traditional refinery and the biorefinery.

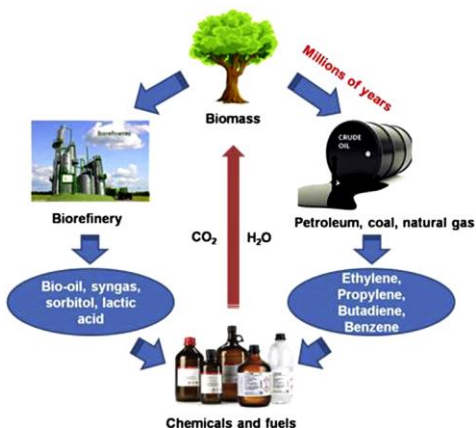


Figure 1. Opposite routes for obtaining chemicals.

(Shinde et al., 2019)

Biorefineries are classified into:

First generation biorefinery: edible and dried grains are milled to produce ethanol. This generation is in serious competition with the food chain. It has a fixed processing capacity. For this reason, it is a technology that can only be used for restricted purposes.

Second generation biorefinery: wet grains are milled producing a variety of end products such as starch, corn syrup, ethanol, corn oil, animal feed, and corn gluten meal.

Third generation biorefinery: This is a more advanced version of the biorefinery. This generation uses agricultural and/or forestry biomass to produce a multitude of product streams.

3.1.1. Lignocellulosic biomass

Anything coming from plant origin that is not used as food or feed is considered lignocellulosic biomass. It is the most abundant source of organic carbon available on Earth that can be used as feedstock. Lignocellulosic biomass consists of polymeric carbohydrates such as cellulose, hemicellulose, and polymeric aromatics (lignin). Polymeric carbohydrates are the units found at the C6 and C5 carbons that are tightly bound to lignin. It can be classified into virgin biomass, waste biomass, and energy crops. Virgin biomass includes all naturally occurring terrestrial plants (trees, shrubs, and grasses). Waste biomass is produced as a low-value by-product of various

industrial sectors such as agriculture (corn stover, sugar cane bagasse, straw, etc.) and forestry (discards from sawmills and paper mills). Lignocellulosic biomass usually consists of approximately 40%-50% cellulose, 20%-30% hemicellulose, and 10%-25% lignin (Shinde et al., 2019).

3.1.1.1. Lignocellulose-derived platform molecules

In the last decade, it was proposed to define a chemical platform as an intermediate molecule with a flexible structure to enable a wide range of derivatives. In addition, it must be cost-competitive at the platform level and at the derivative level, be able to generate economies of scale and scope in the value chain, be organized within an innovation ecosystem, and have well-developed governance mechanisms associated with it (Bomtempo et al., 2017).

Many chemically varying functionalized molecules can be obtained from the decomposition of lignocellulose. From these numerous molecules, a team from the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) identified a list of 12 chemicals with potentially industrial applications.

These 12 chemical building blocks (Figure 2) can be produced from sugar through biological and chemical reactions. Furthermore, these building blocks can be further converted into various high-value chemicals and/or materials. The unique characteristics of these building block chemicals are that they are molecules with multiple functional groups with the potential to be transformed into new families of useful molecules. The broad classification of these 12 sugar-based building blocks includes the 1,4-diacids (e.g., succinic, fumaric, and malic), 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinito.

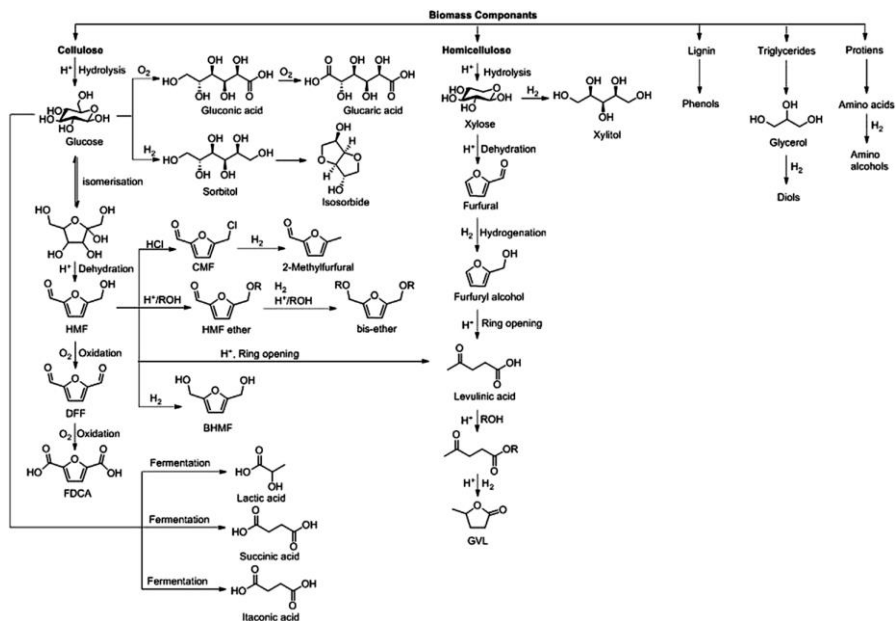


Figure 2. Synthesis of platform chemicals and some of their respective by-products.

(Shinde et al., 2019)

3.1.1.1.1. Levulinic acid

Levulinic acid (LA) is also known as keto acid. The molecular formula of the compound is $C_5H_8O_3$. LA is a white crystalline solid under $30\text{ }^\circ\text{C}$ and is soluble in aqueous and common organic solvents including the polar ones. Moreover, it is an organic intermediate for the synthesis of several chemicals for applications in fuel additives, fragrances, solvents, oil additives, pharmaceuticals, and plasticizers. Levulinate esters, γ -valerolactone, acrylic acid, 1,4-pentadiol, angelica lactone, 2-methyltetrahydrofuran, d-aminolevulinic acid, nonanone, pyrrolidones, etc., are the possible derivatives produced from levulinic acid (Figure 3).

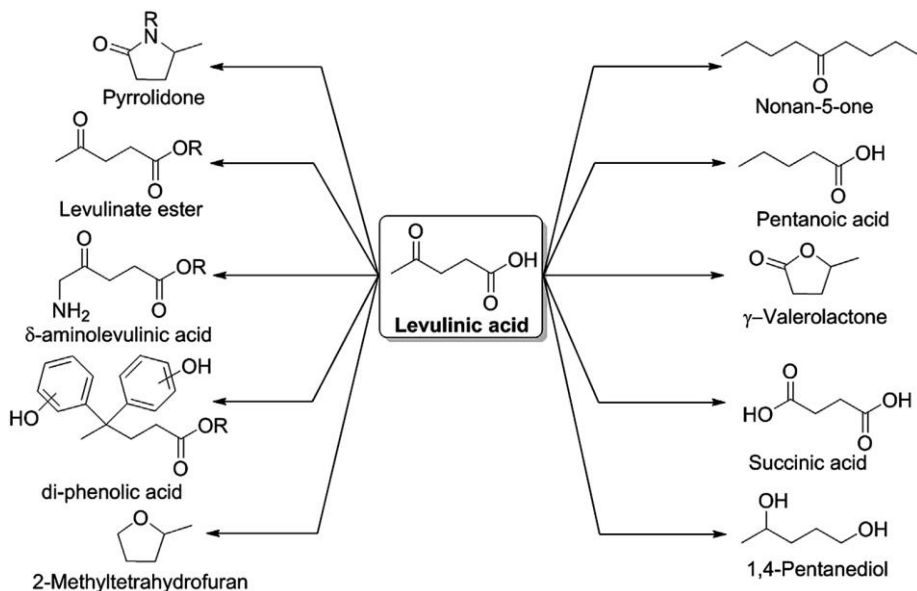


Figure 3. Different compounds that can be obtained from levulinic acid. (Shinde et al., 2019)

One route used to produce levulinic acid is from glucose, which is a derivative of cellulose. The process consists of two steps. First, glucose is isomerized to fructose and then dehydrated to hydroxymethylfurfural (HMF). Secondly, HMF under hydrolysis in an aqueous medium forms LA together with formic acid as a by-product (Figure 4).

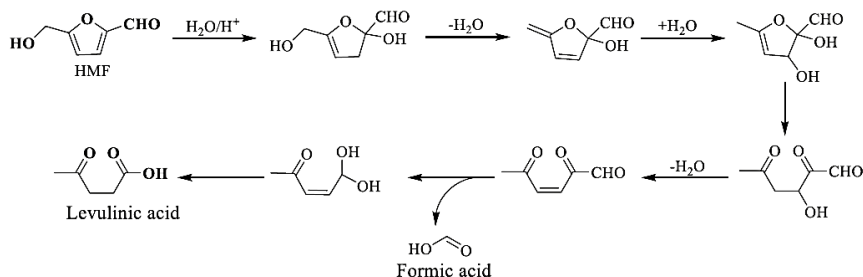


Figure 4. Reaction mechanism for the production of LA from glucose.

(K. K., Pant; Sanjay Kumar, Gupta; Ejaz, Ahmad. *Catalysis for Clean Energy and Environmental Sustainability. Biomass Conversion and Green Chemistry - Volume 1.* Springer: Switzerland, 2021.)

3.1.1.1.1. γ -valerolactone (GVL)

γ -valerolactone (GVL) is an organic compound whose molecular formula is $C_5H_8O_2$. It is a 5-carbon cyclic ester (valero-) with 5 atoms (4 carbons and 1 oxygen) in the ring (γ -lactone). GVL is a colourless liquid, which is stable under normal conditions and has a sweet, herbaceous odour. For this reason, it is a suitable substance for the production of perfumes and food additives. The properties of GVL make it stable and reactive enough to produce a variety of compounds including butene, valeric acid and 5-nonanone (Figure 5). It is also used as a green solvent. Under normal conditions it is a liquid and has a high boiling point. It does not decompose or degrade over time, even in presence of water or oxygen, is stable at moderate temperatures and does not form peroxides in air. It is a low toxicity compound (LD_{50} Oral rat = 8800 mg/kg), and the main hazard is flammability ($T_{\text{flammability}} = 96\text{ }^\circ\text{C}$). Nevertheless, the low volatility (3,5 kPa at $80\text{ }^\circ\text{C}$) of GVL means that the flammability risk under normal conditions is low.

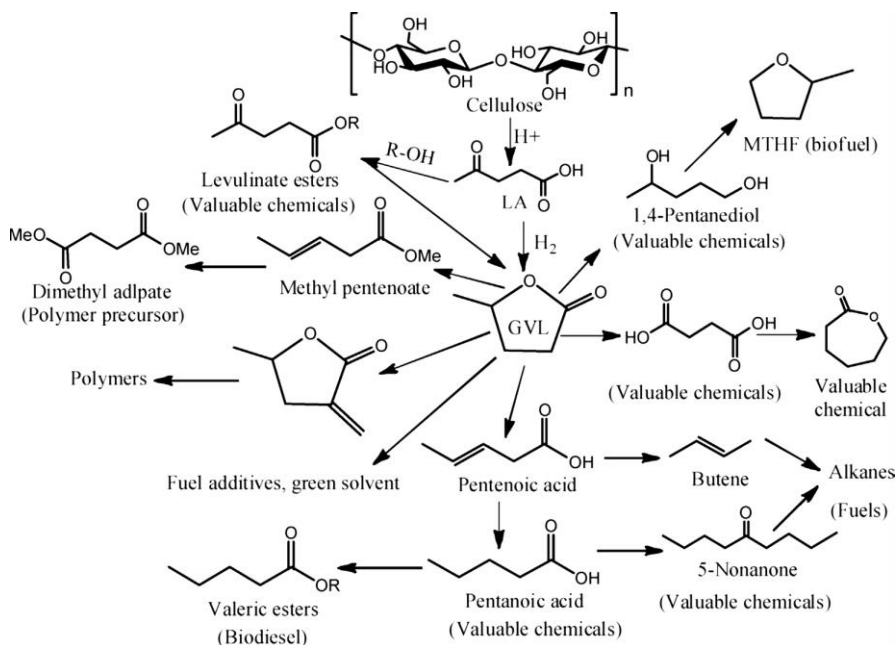


Figure 5. Different compounds that can be obtained from GVL. (Yan et al., 2015)

Given the large number of applications of γ -valerolactone, it has been decided to focus this work on its production from LA.

GVL can be produced in multiple pathways (Figure 6). On the one hand, the hydrogenation of levulinic acid produces γ -hydroxyvaleric acid, an unstable intermediate, which ring closes by intramolecular esterification and loses a water molecule spontaneously to produce GVL.

A second possibility could be the dehydration of LA to form α -angelica lactone followed by hydrogenation to produce GVL. This pathway requires the presence of an acid functionality, and usually results in lower yields as coke is formed from the α -angelica lactone catalysed by the acid.

In the third possible pathway, the levulinic acid ester is hydrogenated to make the hydroxy levulinic ester, which ring-close by intramolecular transesterification to produce GVL and its corresponding alcohol. Normally, when water is present, the ester is first hydrolyzed producing an alcohol and LA, which would then proceed through the previously described route. The last possible pathway to produce lactones is to ring-close the corresponding olefinic acid which in the case of the GVL, would be 4-pentenoic acid.

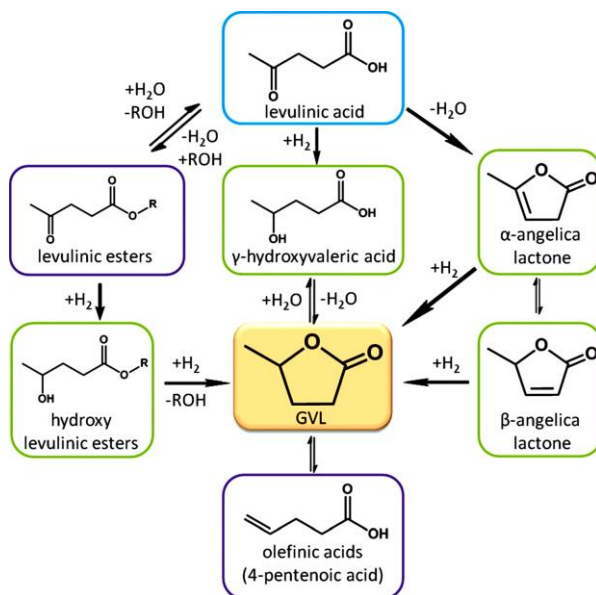


Figure 6. Multiple reaction pathways to produce GVL. (Alonso et al., 2013)

3.2. CATALYSIS OF THE GVL PRODUCTION REACTION

In the chemical industry there are many reactions that need to be catalysed. Catalysis can be homogeneous or heterogeneous. The main difference between the two catalyses is the phase in which the catalyst is located in relation to the phase of the chemical reaction. They also differ in the downstream separation in industrial processes, in the recovery of catalysts, in the selectivity of the reaction, among others. The main differences between the two types are presented in Table 1.

Table 1. Comparison of the main characteristics between homogeneous and heterogeneous catalysis. (Schirru, 2020)

Homogeneous catalysis	Heterogeneous catalysis
Same phases	Different solid phase
Arduous separation	Easily separated
High-priced recycling	Easily regenerated and recycled
Frequently high rates	Not as fast rates as homogeneous
Free diffusion	Limited diffusion
Resistance to poisons	Sensitivity to poisons
Elevated selectivity	Low selectivity
Short-lasting	Long-lasting
Mild conditions	Frequently high energy conditions
Well understood mechanism	Poorly understood mechanism

3.2.1. Homogeneous catalysis

Recently, homogeneous catalysts have been widely used as they allow easy access to the catalytic active centre. Homogeneous catalysts based on ruthenium (Ru) have been the most prominent and researched for the production of GVL from LA. Some of them are: $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{Ru}(\text{acac})_3/\text{PBU}_3$, and $\text{Ru}(\text{acac})_3/\text{P}(\text{n-Oct})_3$. Some of them have been tested under various reaction conditions giving the results shown in the Table 2.

Table 2. Homogeneous hydrogenation of levulinic acid using some catalysts mentioned above. (Yan et al., 2015)

Catalyst	Solvent	T (°C)	H2 source	t (h)	Y _{GVL} (%)
$\text{Ru}(\text{acac})_3 + \text{TPPTS}$	H ₂ O	140	69 bar H ₂	12	95
$\text{Ru}(\text{acac})_3 + \text{Pn-Oct}_3 + \text{NH}_4\text{PF}_6$	-	160	100 bar H ₂	18	>99
$\text{RuCl}_2(\text{PPh}_3)_3$	-	180	12 kg/cm ² H ₂	24	99
$\text{RuH}_2(\text{PPh}_3)_4$	-	180	12 kg/cm ² H ₂	24	58
Shvo (Ru)	-	-	-	-	99,9

Note: T: temperature, t: time and Y_{GVL}: yield to GVL.

One of the typical ways to produce GVL with homogeneous catalysis is by Shvo catalyst (Figure 7). (Valentini et al., 2019) This reaction usually involves hydrogenation of LA to intermediate 4-hydroxyvaleric acid followed by ring closure and formation of GVL.

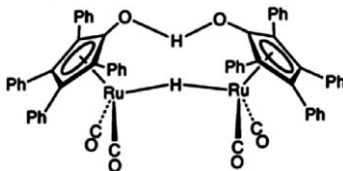


Figure 7. Shvo catalyst. (Yan et al., 2015)

Another typical form of homogeneous catalysis is the use of a multifunctional homogeneous catalysis system, which is composed of a metal-organic precursor $\text{Ru}(\text{acac})_3$, ligands, and acid additives. This type of system provides a highly selective catalytic conversion and quantitative yield of LA to produce GVL (see Table 2).

Despite the good results of homogeneous catalysts, some homogeneous catalysts require several steps to be synthesised, which can lead to increased cost and additional production efforts. Also, the recycling of such catalysts and their durability needs to be further studied.

3.2.2. Heterogeneous catalysis

Heterogeneous catalysis differs from homogeneous catalysis in that it is usually easy to separate, allows efficient recycling, minimises metal leaching, and improves handling and process control.

3.2.2.1. Supported noble metal catalysts

Supported metal nanoparticles of noble metals tend to provide good hydrogenation performance, as they have a large surface area and there is a synergistic effect between metal nanoparticle and support. Even so, the cost of these catalysts, the use of volatile organic additives, the requirements of high-pressure operation and the involvement of other rigid reaction parameters, limit their application in the industry.

The most commonly used supported noble metals in the hydrogenation reaction of levulinic acid to γ -valerolactone are Ru, Rh, Pd, Pt and Au and they can be supported on different substrates. Some noble metal supported catalysts were tested under different reaction conditions and the results are shown in Table 3.

Table 3. Heterogenous hydrogenation of levulinic acid using some noble metal catalysts. (Yan et al., 2015)

Catalyst	Solvent	T (°C)	H ₂ source	t (h)	Y _{GVL} (%)
Ru/C	H ₂ O	150	40 bar H ₂	1	30
Pd/Al ₂ O ₃	-	220	HCOOH	12	29
5 % Rh/C	Dioxane	141	H ₂ + CO ₂ (247 bar)	N. D.	73
Au/ZrO ₂ -VS	H ₂ O	180	HCOOH	3	99

Note: T: temperature, t: time, Y_{GVL}: yield to GVL, N.D: not defined, and ZrO₂-VS: acid-tolerant ZrO₂.

3.2.2.2. Supported non-noble metal catalysts

The production of GVL using non-noble metal catalysts has proved to be a focus of study (Yan et al., 2015). This is due to the lower manufacturing cost of such catalysts.

On the other hand, such catalysts have problems with active metal leaching and the high yield of coke produced during the process.

The most commonly used supported non-noble metals in the hydrogenation reaction of levulinic acid to γ -valerolactone are Ni, Co, Cu, and Fe and they can be supported on different substrates such as Al₂O₃, SiO₂, ZnO, ZrO₂, TiO₂ and MgO. Some Co, Cu and Ni supported catalysts were tested under different reaction conditions and the results are shown in the Table 4.

Table 4. Heterogenous hydrogenation of levulinic acid using some non-noble metal catalysts. (Yan et al., 2015)

Catalyst	Solvent	T (°C)	Pressure H ₂ (bar)	t (h)	Y _{GVL} (%)
Ni/TiO ₂	-	140	8	5	38
Ni-MoOx/C	Toluene	140	8	5	21
Cu-ZrO ₂	H ₂ O	200	34,5	5	100
Cu-Al ₂ O ₃	H ₂ O	200	34,5	5	100

Note: T: temperature, t: time, and Y_{GVL}: yield to GVL.

3.2.2.3. Bifunctional ion exchange resins

As explained above (Figure 6), the reaction under study takes place in two steps, which depend on the reaction route. One reaction pathway consists of the hydrogenation of levulinic acid to give the reaction intermediate γ -hydroxivaleric acid, followed by dehydration of this γ -hydroxivaleric acid to give GVL.

To synthesise one-pot GVL, it is necessary to catalyse both reactions at the same time. For this purpose, bifunctional metal-acid resins are frequently used. The metal acts as a catalyst in the hydrogenation reaction, while the acid centre accelerates the dehydration reaction.

Ion exchange resins (IER) consist of solid organic cross-linked polymer with uniform distributions of active groups onto the surface. The active group and the support will determine the characteristics of the IER.

Bifunctional resins have two types of active sites in their structure, which allow different reactions to occur subsequently.

We can consider those resins anionic or cationic depending on whether the active group is acidic (sulphonic, carboxylic groups...) or basic (amino, hydroxyl groups...).

Moreover, the characteristics of the support will be determined according to the polymer that constitutes it and its structure. The support can be made of addition polymers (polystyrene, acrylics...) or condensation polymers (phenolics, epoxy-amines...) but styrene-divinylbenzene matrices are the most commonly used. (Giménez Farreras, 1985) The type of polymer provides some properties to the resin. However, the structure depends on the crosslinking agent used and the way in which the polymerisation reaction has been carried out.

They could be classified as gel or macroreticular ion exchange resin by its structure (Figure 8). Gel-type resins can also be named as microporous resins. These resins are produced by a copolymerisation reaction between a monomer (styrene (ST) or/and methacrylic acid (MAA)) and a crosslinking co-monomer (divinyl benzene (DVB)) in the presence of an initiator and a porogenic agent. The matrices made of styrene-divinyl benzene and methacrylicacid-divinyl benzene copolymer beads are designated as ST-DVB and MA-DVB. Commonly, commercial ion exchange resins content between 8-12 % of DVB. (Schirru, 2020)

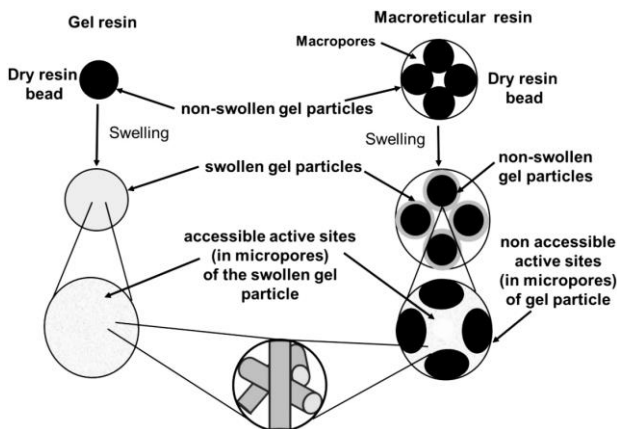


Figure 8. Differences in structure between gel and macroporous resins. (Schirru, 2020)

On the one hand, gel-type resins are thermally stable and exhibit high exchange capacity. Gel resins contain a low degree of crosslinking, and its porosity can only be observed when the swelling medium is convenient. Resins swell when they interact with a solvent. This process generates temporary voids, which would form part of the gel phase. This phase is the part of the resin structure that is altered depending on the polarity of the medium in which it is found. IERs' catalytic performance depends on the solvent used in the reaction. Dry gel-types show extremely low specific surface area (fewer than $10\text{m}^2/\text{g}$) but they have a higher swelling degree.

On the other hand, macroreticular resins contain higher degree of crosslinking, and have macropores. For this reason, it is not necessary for the resins to swell since the easy access is already guaranteed. This permanent porosity is introduced by using a porogenic agent during the copolymerisation stage. Although this type of resin tends to have a lower exchange capacity, it has the advantage of having a longer service life.

Macroreticular resins are composed of macropores and embedded microparticles. The microgel particles swell moderately with a polar solvent. However, the size of the macropores does not vary significantly in the medium. As macroreticular resins exhibit limited swelling behaviour compared to gel resins, their catalytic activity is independent of the type of solvent.

IERs are normally insoluble in water and are commercialised in spherical or bead form with an effective size of between 0.3 mm and 1.2 mm. They have the advantage over other catalysts of avoiding secondary reactions. Resins are also easily separable from the other reaction components, they have a long life and can be regenerated. This last factor allows them to be used in continuous flow.

Since there are articles, which show that Amberlyst CH28 resin works well in accelerating the hydrogenation reaction of mesityl oxide to obtain methyl isobutyl ketone (Talwalkar & Mahajani, 2006), it has been decided to test it in the hydrogenation reaction of LA to obtain GVL.

Another reason why it has been chosen to follow the procedure of this article is that catalysts containing metals usually require treatment before use. This treatment is called activation and consists of the reduction of the oxidation state of the metal. Although the Amberlyst CH28 manufacturer recommends a separate activation protocol, in the procedure followed in the article the activation is carried out simultaneously with the reaction.

For these reasons, the commercial bifunctional metal/acid catalyst Amberlyst CH28, which contains palladium, has been initially used as reference. Two additional commercial ion exchange resins (Amberlyst 15 and Dowex 50WX2) have been used as support to prepare copper- and palladium-doped ion exchange resins. These have been doped in the kinetics and catalysis laboratory of the chemistry faculty of the University of Barcelona with copper and palladium.

The resins used can be classified according to their morphology into: macroreticular (Amberlyst CH28 and Amberlyst 15) and gel type (Dowex 50WX2).

4. OBJECTIVES

The main objective of this study is to contribute to the study of the hydrogenation of levulinic acid to produce γ -valerolactone using bifunctional resins as catalyst.

The other objectives for this project are:

- To test the activity of Amberlyst CH28 in the hydrogenation of levulinic acid to obtain γ -valerolactone.
- To evaluate the effect of feed, temperature and catalyst loading on the reaction.
- Decide on the best reaction conditions among those tested.
- Test the catalytic activity of four catalysts prepared by another person in the laboratory.
- To assess the effect of the type of embedded metal and the type of resin support on the reaction.
- Decide whether the catalysts tested are a good choice for producing γ -valerolactone from levulinic acid hydrogenation.

5. EXPERIMENTAL SECTION

5.1. MATERIALS

Experiments for the hydrogenation reaction of levulinic acid to γ -valerolactone were carried out using levulinic acid with purity of 98 +% supplied by Arcos Organics and hydrogen gas of 99,9995 % purity supplied by Abelló Linde as reactants.

The main properties of the reactants are listed in the Table 5.

Table 5. Summary of the main properties of reactants.

Properties	Levulinic acid	Hydrogen gas
CAS number	123-76-2	1333-74-0
Molecular formula	C ₅ H ₈ O ₃	H ₂
Molecular mass (g/mol)	116,12	2
Density (kg/m³)	1,130	0,089
Melting point (°C)	33 - 35	-259,2
Boiling point (°C, at 760mmHg)	245,0 - 246,0	-252,9
Flammability point (°C)	98	Not available
Explosion limits (vol %)	Not available	4 - 77
Hazard statements	H302 + H315 + H319	H220 + H280

The same levulinic acid as specified above, water (Mili-Q, Millipore), γ -valerolactone supplied by Aldrich with purity 99 %, α -angelica lactone supplied by Tokyo Chemical Industry CO. LTD with purity > 98,0 % and valeric acid supplied by Sigma-Aldrich with purity \geq 99 % were used in the chromatographic calibration.

A summary of properties of the substances mentioned above is given in the following table.

Table 6. Summary of the main properties of chromatographic calibration substances.

Properties	α -angelica lactone	γ -valerolactone	Valeric acid
CAS number	591-12-8	108-29-2	109-52-4
Molecular formula	C ₅ H ₆ O ₂	C ₅ H ₈ O ₂	C ₅ H ₁₀ O ₂
Molecular mass (g/mol)	98,10	100,12	102,13
Density at 25 °C (kg/m³)	1,092	1,05	0,94
Melting point (°C)	13 - 17	-31	-35
Boiling point (°C)	55 - 56 (at 12 mmHg)	207 – 208	185
Flammability point (°C)	68	96	86
Explosion limits (vol %)	Not available	Not available	1,6 - 7,3
Hazard statements	H317	-	H314 + H318 + H414

Three different commercial ion exchange resins have been used in this study: Amberlyst CH28 and Amberlyst 15 both supplied by Dow France S.A.S, and Dowex 50WX2 100-200 mesh supplied by Acros Organics. All chosen resins are strongly acidic, sulphonic, polymeric resins and their matrices consist of cross-linked styrene-divinylbenzene copolymers. A brief summary of properties for the three resins is shown in Table 7.

Table 7. Comparison of the main characteristics of the three commercial resins used.

Catalyst	Type	Acid capacity (eq H ⁺ /L)	%DVB	Moisture (% in H ⁺ form)	MOT (°C)
ACH28	macro	1,6	N/A	52-58	130
A15	macro	1,7	20	52-57	120
Dowex 50WX2	gel	0,6	2	74-82	150

Note: N/A: not available, MOT: Maximum Operation Temperature recommended by manufacturer

The commercial resin Amberlyst CH28 has a nominal palladium value of 0,7 % dry basis.

Four doped resins [Amberlyst 15 (1 %Cu), Dowex 50WX2 (1 %Cu), Amberlyst 15 (1 %Pd) and Dowex 50WX2 (1 %Pd)] have been prepared in the laboratory: two copper and two palladium, one for each of the above-mentioned commercial supports (Amberlyst 15 and Dowex 50WX2). These prepared resins have been assigned a nominal metal value of 1 %, but they have not been characterised as it was first necessary to check if they had catalytic activity.

5.2. EXPERIMENTAL SETUP

A schematic of the system used to carry out the reaction is shown in the Figure 9. The reactor is equipped with an agitator, a thermometric probe, a manometer to measure the pressure, a sampling device, internal filters, hydrogen and nitrogen inlets and an electric oven.

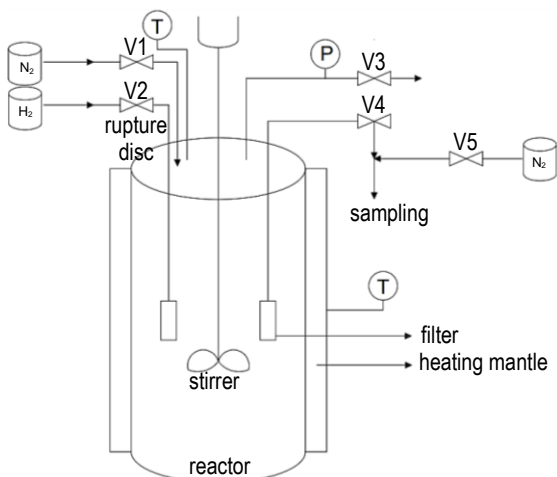


Figure 9. Scheme of the experimental setup.

The system consists in a 100 mL nominal stainless steel (316 SS Autoclave Engineers) batch reactor with 150 bar as maximum operating pressure and 232°C as maximum operating temperature. At the head of the reactor is found the rupture disc. The reactor also has a stirring, a thermocouple, and a pressure gauge.

The stirring speed is controlled by an external tachometer (IB-40 Reactor Controller, Iberfluid instruments). The heating system is based on an electric oven with two controllers and two temperature sensors type K (chromel – alumel) that measure the internal temperature of the outer wall. The thermocouple, and the two filters are placed in the form of a cross around the agitator, and they act as an internal baffle.

5.2.1. Analytical system

To analyse the reaction pathway of the production of GVL from LA followed in the experiments, the distribution of substances over time was analysed using a gas chromatograph (Agilent Technologies, 7820A).

To analyse each sample, 0,2 μ L are withdrawn using a chromatographic syringe and injected into the gas chromatograph. Before starting each analysis, it is necessary to check that the equipment is operating at the required conditions.

The injected substance is rapidly vaporised at the injection port. Consequently, the mixture enters the chromatographic column in the vapour phase, where the different components advance at characteristic velocities for each compound because they are entrained by a carrier gas (helium) into the capillary column. This column is placed in a thermal controlled oven and the separation takes place in it thanks to the difference in travelling speeds. These velocities depend on the oven conditions and the interaction between the compounds present in the sample, so that the lightest component is the one that leaves the column first. The separated analytes flow through the thermal conductivity detector (TCD). Consequently, a response is emitted and is captured by the computer. Finally, the computer draws the chromatogram of the mixture.

Each compound has a specific chromatographic peak associated with it and a corresponding retention time. This is the time it takes for the sample to generate the maximum response from its injection time. The area of a chromatographic peak is directly proportional to the amount of the corresponding component, so that the composition of the sample can be obtained.

An initial calibration of levulinic acid, water, γ -valerolactone, α -angelica lactone and, finally, valeric acid was carried out to determine which peak corresponded to which substance. 4-hydroxyvaleric acid has not been calibrated as it is not commercially available in the laboratory and it was considered that its response in the chromatograph would be similar to that produced by valeric acid.

5.3. EXPERIMENTAL PROCEDURE

5.3.1. Catalyst pre-treatment

First of all, it is necessary to remove any moisture that the catalyst may have retained. In order to do that, two steps have been followed: drying in a conventional oven at 100 °C and atmospheric pressure for at least 4h and then transferring the container containing the catalyst to a vacuum oven at 100 °C as well for at least 12h.

5.3.2. Reactor loading and reaction start-up

Once the catalyst is as dry as possible, it is weighed on an analytical balance using the difference weighing method. The catalyst is then introduced into the reactor. After that, the necessary mass of levulinic acid and water is added to the reactor in each case, depending on the conditions of each experiment. However, it should be borne in mind that the reactor cannot be filled completely, only 80 % (approximately 80 mL) of its volume is usable. To follow up, the

O-ring is fitted to the reactor and the reactor is screwed onto the reactor support. It is then necessary to check the vessel for leaks and to make sure that it is not leaking. For this purpose, nitrogen is introduced by opening valve V1 up to a pressure of 15 bar. If the reactor leaks, it is necessary to reopen it and start again from the beginning until the pressure remains constant. After this, all the air must be displaced to the outside, so the V3 valve is opened. While leaving valve V3 open, valve V1 is opened again, and a stream of nitrogen is allowed to circulate for a few seconds. Once all the air inside the reactor has been displaced, valve V1 is closed to stop the nitrogen inlet and, once the pressure gauge has reached atmospheric pressure, the vent valve V3 is closed. At this point, the reactor jacket is fitted. Then, the stirrer is started at 500 rpm with the control screen and the heating system is also tuned on up to the desired temperature. Once the reactor reaches the temperature set-point, valve V2 is opened together with V3 to displace any remaining nitrogen to the outside. Once all the nitrogen has been displaced, the purge valve V3 is closed and the valve V2 is closed, stopping the hydrogen inlet flow, when the pressure gauge reaches the working pressure of the experiment. From this moment on, the activation/reaction time is counted.

5.3.3. Sampling

Sampling is performed every hour after the reaction time has started. A higher number of samples has not been performed in the experiments reported, because the reaction volume is small (75-80) mL and that would alter the reaction conditions too much. Closed, pre-labelled 1 mL vials were used for sampling. The procedure consists of opening the valve V5 to clean everything inside the sampling tube and then closing it. After that it has to insert the tip of the sampling tube into the vial and quickly open and close the valve V4. The vial is then removed. Finally, prick the sample into the chromatograph with a chromatographic needle and analyse the result.

5.3.4. Clean-up

For the cleaning of the reactor, initially both the stirring and the heating system are stopped. It is also necessary to depressurise it with the purge (valve V3). Once it is at ambient conditions, it is unscrewed from the support, the reaction system inside is filtered and the waste is managed. The vessel and the agitator are initially rinsed with water. Finally, they are cleaned with acetone by loading the reactor with acetone and leaving it to stir for a period. After cleaning, the reactor is dismantled until the next experiment.

5.4. EXPERIMENTAL CONDITIONS

This research presents a first part where the effect of feed, temperature and catalyst loading are analysed only with the commercial resin Amberlyst CH28. A distinction has been made between pure levulinic acid feed and aqueous solution of levulinic acid at 50 % by weight. To evaluate the temperature, three different temperatures were set: 120 °C, 150 °C and 180 °C and, finally, to compare the catalyst load, experiments were carried out with 0.5 % and 5 % catalyst load. The following tables show the experimental design that has been carried out to compare these three factors. It should be noted that in order to compare the effect of one variable, the rest have been kept constant.

Table 8. Experimental design to compare the effect of feed.

Experiment	Catalyst	T (°C)	P (bar H ₂)	Feed type (% wt.)	Catalyst load (% wt.)
1	ACH28	180	7	50	4,6
2, 3 and 4*	ACH28	180	7	100	4,6

*Experiment 2 is triplicated.

Table 9. Experimental design to compare the effect of temperature.

Experiment	Catalyst	T (°C)	P (bar H ₂)	Feed type (% wt.)	Catalyst load (% wt.)
1	ACH28	180	7	50	4,8
5	ACH28	150	7	50	4,8
6	ACH28	120	7	50	4,8

Table 10. Experimental design to compare the effect of catalyst load.

Experiment	Catalyst	T (°C)	P (bar H ₂)	Feed type (% wt.)	Catalyst load (% wt.)
7	ACH28	120	7	50	0,5
8	ACH28	120	7	50	5

Since the facility available in the kinetics laboratory has a hydrogen pressure limited to 7 bar, all experiments had to be carried out at a working pressure of 5-7 bar. In contrast, the article works at about 30 bar (Talwalkar & Mahajani, 2006).

As far as the stirring speed is concerned, it has been set at 500 rpm since no substantial changes in conversion are observed in the article Talwalkar & Mahajani, (2006) and vortex formation is not of interest.

In the second part, the intention is to compare the commercial resin with four resins doped in the laboratory. A15 and Dowex 50WX2 resins have been doped with copper and palladium, in order to compare the resin support (macroreticular or gel) and the type of metal (noble or non-noble). In addition, it will be possible to observe whether the prepared resins have a lower or

higher catalytic activity than the commercial resin. The following table show the experimental design that has been carried out to compare these factors.

Table 11. Experimental design to compare the effect of support and the metal type.

Experiment	Catalyst	T (°C)	P (bar H ₂)	Feed type (% wt.)	Catalyst load (% wt.)
9	A15 (1 %Cu)	120	5	50	1,3
10	A15 (1 %Pd)	120	5	50	1,3
11	Dowex 50WX2 (1 %Cu)	120	5	50	1,3
12	Dowex 50WX2 (1 %Pd)	120	5	50	1,3

Before starting the experiments shown in this study, a test was carried out and it was observed that after 6h the conversion of levulinic acid to the desired product (GVL) did not increase considerably, which is why the experiments were all carried out for a duration of 6h.

6. RESULTS AND DISCUSSION

6.1. MATHEMATICAL DEFINITIONS OF VARIABLES

It is necessary to comment on which mathematical definitions have been taken into account to analyse and compare the results of the different experiments carried out.

The expression 1 is used for calculating the catalyst load:

$$\text{catalyst load} = \frac{\text{catalyst mass}}{\text{catalyst mass} + \text{feed mass}} \cdot 100 \quad [1]$$

The levulinic acid conversion (X_{LA}) is calculated through the moles of reactant with the expression 2, where mol LA₀ refers to the fed moles and mol LA at a given time t.

$$\text{conversion } (X_{LA}) = \frac{\text{mol LA}_0 - \text{mol LA}}{\text{mol LA}_0} \cdot 100 \quad [2]$$

As it cannot be completely certain that all products formed from levulinic acid have been detected, expression 3 has been used to calculate the GVL selectivity (S_{LA}^{GVL}):

$$\text{selectivity } (S_{LA}^{GVL}) = \frac{\text{mol GVL}}{\text{mol LA}_0 - \text{mol LA}} \cdot 100 \quad [3]$$

The expressions for calculating GVL yield (Y_{LA}^{GVL}) is given below:

$$\text{yield } (Y_{LA}^{GVL}) = \frac{X_{LA} \cdot S_{LA}^{GVL}}{100} \quad [4]$$

Turnover number (TON) specifies the maximum use that can be made of a catalyst for a special reaction under defined reaction conditions by the number of molecular reactions or reaction cycles occurring at the reactive centre up to the decay of activity. TON was obtained through the expression 5:

$$\text{TON} = \frac{\text{mol LA}_0 - \text{mol LA}}{\text{metal mol}} \quad [5]$$

6.2. CALIBRATION OF THE SUBSTANCES IN THE GAS CHROMATOGRAPH

The retention times obtained for the calibrated substances are given in Table 12:

Table 12. Retention time for de possible substances involved in the hydrogenation reaction from LA to GVL.

Compound	Mixture compound retention time [min]
Water	3,45
α -angelica lactone	7,39
Valeric acid	7,70
γ -valerolactone	8,08
Levulinic acid	9,06

The calibration equations used are shown in Table 13. These relate the percentage obtained in area of each substance in the chromatogram (x) to the percentage by weight of the mixture (y). From this weight percentage, the mass and moles of each compound can be calculated. (Details of the calibration can be found in the annex).

Table 13. Gas chromatograph calibration equations.

Compound	Equation
Water	$y = (0,003 \pm 0,001) \cdot x^2 + (0,67 \pm 0,06) \cdot x$
α -angelica lactone	$y = (1,3 \pm 0,1) \cdot x$
Valeric acid	$y = (1,2 \pm 0,1) \cdot x$
γ -valerolactone	$y = (-0,01 \pm 0,03) \cdot x^2 + (1,2 \pm 0,2) \cdot x$
Levulinic acid	$y = (-0,003 \pm 0,001) \cdot x^2 + (1,28 \pm 0,08) \cdot x$

6.3. EXPERIMENTAL REACTION MONITORING

After all the experiments, it was found that the reaction route was that which first hydrogenates levulinic acid to give 4-hydroxyvaleric acid and, secondly, dehydrates 4-hydroxyvaleric acid to give γ -valerolactone. This is because no signal has been detected for α -angelica lactone. The figures 10a and 10b show the general species monitoring for an experiment using Amberlyst CH28 for a duration of 6 h at 180 °C, with a hydrogen pressure of 7 bar, a catalyst loading of 4.7 % and a pure feed (98 %LA).

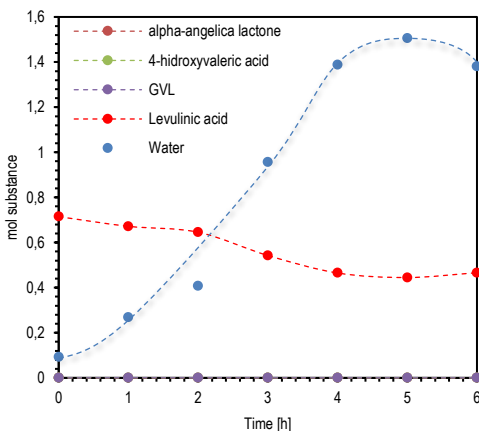


Figure 10a. Distribution of substances throughout the experiment.

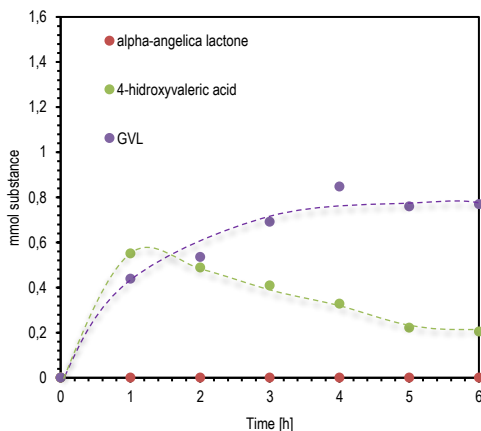


Figure 10b. Rescaling of the product distribution for the reaction intermediates and the reaction product in order to make it more visible.

Figures 10a and 10b show how the reactant (LA) decreases with time until hour 4 of reaction, after which it does not seem to react anymore.

On the other hand, it is observed how the reaction intermediate (4-hydroxyvaleric acid) is formed until it reaches a peak and, subsequently, it starts to decrease to form γ -valerolactone.

The water increases with time as a result of the dehydration of 4-hydroxyvaleric acid to form γ -valerolactone.

Finally, γ -valerolactone is observed to increase over time. Its curve initially grows very fast because enough reaction intermediate has been formed, but as the reaction progresses, it increases more slowly, as there is fewer and fewer intermediate.

6.3.1. Experimental error

Material balances have been carried out in all experiments. An experiment with deviation fewer than 5% in the material balance is considered acceptable.

In all the different experiments carried out, this fact is fulfilled with the exception of experiments carried out with pure levulinic acid feed and at 180 °C (experiments 1, 2, 3 and 4). This may be because the reaction has not stopped at the production of γ -valerolactone. As a sufficiently high temperature (180 °C) was available, the GVL was further hydrogenated to give rise to valeric acid. The production of the valeric acid is followed by the formation of n-butane

(produced by decarboxylation of valeric acid over metal sites, with the release of stoichiometric amounts of CO_2), along with n-pentane (as a result of successive hydrogenations and dehydrations of valeric acid over metal and acid sites, respectively). (Figure 11) The formation of these unwanted products and the yield up to produce valeric acid were found to be controlled by varying the metal loading of the catalyst. No obstante, en este trabajo se pretendía parar la hidrogenación en la formación de la GVL. (Serrano-Ruiz et al., 2010) (Simakova & Murzin, 2016)

To check this, the loss of matter has been assimilated to CO_2 , since it is a compound that cannot be quantified with the established analytical method.

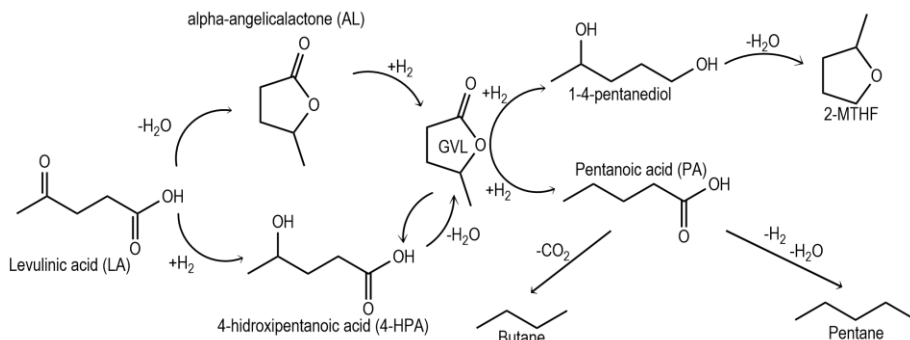


Figure 11. Hydrogenation reaction of gamma-valerolactone to form 1,4-pentadiol and valeric acid, and their respective by-products.

Since it has been observed that these are the reaction conditions that have represented the greatest imbalance of matter, it has been decided to carry out triplicates under these conditions in order to analyse the reproducibility of the experiments. Also, performing the triplicates under these reaction conditions gives the highest error that could be obtained among the conditions that have been used. The confidence intervals obtained for the different parameters corresponding to the triplicates are shown in Table 14.

Table 14. Confidence intervals for a reaction time of 6 h (left) and 4 h (right).

	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	TON ($\frac{\text{mol LA}}{\text{mol metal}}$)	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	TON ($\frac{\text{mol LA}}{\text{mol metal}}$)
Average	40	0,4	0,15	2200	34,4	0,4	0,14	2030
±	10	0,3	0,07	500	2,4	0,2	0,06	60

As a general trend it can be observed that the confidence interval increases during the course of the reaction, i.e., it is higher for a reaction time of 6 h than for a reaction time of 4 h. This could

be due to the fact that during the experiment a larger number of samples have been extracted and therefore the amount of matter differs more from the initial amount. In consequence, whenever it has been necessary, it has been used the data from the 4 or 5 h experiment rather than the 6 h.

6.3.2. Results of the experiments

Before analysing the effect of each variable, the results of the experiments are presented in Table 15. As a general trend it is observed that the experiments do not exceed 20 % LA conversion. However, experiments 2, 3 and 4 do but they do not show the desirable conversion either.

On the other hand, the selectivities are very low and consequently, so are the yields.

Finally, the TON value varies between [0-4000].

Table 15. Catalytic results of the experiments.

Experiment	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	TON $\left(\frac{\text{mol LA}}{\text{mol metal}}\right)$
1	18,4	9,3	1,7	524
2	31,4	0,7	0,2	1935
3	34,8	0,3	0,1	2017
4	48,2	0,2	0,1	2781
5	5,3*	11,6*	0,6*	150*
6	3,6	19,7	0,7	106
7	12,4	1,5	0,2	3551
8	6,3	1,8	0,1	141
9	13,6	1,0	0,1	275
10	5,2	5,6	0,3	184
11	3,5	4,3	0,2	74
12	0,7	56,7	0,4	24

*All data are taken at 6 h of reaction except the experiment 5 data which are taken at 5 h.

6.4. EFFECT OF VARIABLES ON CATALYTIC ACTIVITY

This section is divided into three parts. Firstly, I want to test whether the Amberlyst CH28 catalyst is suitable for accelerating the hydrogenation reaction of LA to form GVL.

Also, in this first part, a preliminary study of three operating variables has been carried out: feed type, temperature, and catalyst load. This has been done to decide on the operating conditions. It should be remembered that the pressure cannot be varied because the installation is limited to 7 bar.

Secondly, the reaction with the four doped resins was carried out in the laboratory. The aim is to check whether the catalysts show catalytic activity in the hydrogenation reaction of LA to form GVL. On the other hand, I want to analyse the catalytic activities of the noble metals

compared to that of the non-noble metals and that of the gel type support compared to the macroporous one.

Thirdly, a general assessment of the experiments and the catalytic activity of the catalysts is going to be made.

6.4.1. Effect of operating variables

6.4.1.1. Effect of feed concentration

Firstly, the effect of the initial concentration of levulinic acid was analysed. This has an important impact because in the biorefineries the LA streams are not pure, but diluted with about 50 % water. We worked with pure acid and with a 50 %wt. aqueous solution. The experiments were carried out using Amberlyst CH28 as catalyst at 180 °C and 7 bar hydrogen pressure. Table 16 shows the results of the two experiments (Experiment 1 and the average of 2, 3 and 4 because they were triplicates) carried out. All experiments lasted 6 hours.

Table 16. Results of the experiments to assess the effect of feed.

Feed type (% wt.)	Catalyst load (% wt.)	X _{LA} (%)	S _{LA} ^{GVL} (%)	Y _{LA} ^{GVL} (%)	TON ($\frac{\text{mol LA}}{\text{mol metal}}$)
51	4,9	18,4	9,3	1,7	524
98	4,7	48,2	0,2	0,1	2781

To make it more visual, the results have been plotted in Figure 12. It can be seen that for the pure feed the conversion is higher than for the diluted feed. However, the diluted feed shows a better selectivity towards the desired product, γ -valerolactone. Finally, the γ -valerolactone yield of the reaction is higher when the feed is diluted.

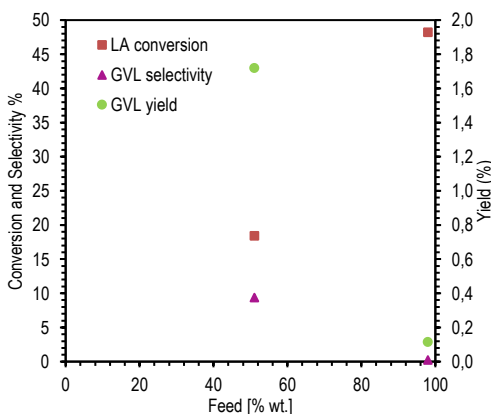


Figure 12. Comparison of conversion, selectivity, and yield for two different feed types.

The difference in conversion could be due to the initial concentration. Since the pure feed has a higher concentration, levulinic acid is more rapidly hydrogenated and therefore more easily consumed. Nevertheless, the higher concentration does not favour the formation of GVL, since as explained in Figure 12, the reaction has not stopped in the formation of GVL and if the reaction rate is higher, valeric acid and its respective products will also be formed more easily.

The pure feed has a higher conversion rate, and this implies a higher consumption of LA, which is why the TON is higher in this case.

As the aim of this research is to produce GVL, it has been decided that the rest of the experiments will be done with an LA feed diluted to 50% by weight.

6.4.1.2. Effect of reaction temperature

To analyse the effect of temperature, three temperatures have been chosen: 120 °C, 150 °C and 180 °C. The experiments were carried out using Amberlyst CH28 at 7 bar hydrogen pressure and with a diluted feed. Table 17 shows the results obtained for experiments 1, 5 and 6.

Table 17. Results of the experiments to assess the effect of temperature.

Temperature (°C)	Catalyst load (% wt.)	X _{LA} (%)	S _{LA} ^{GVL} (%)	Y _{LA} ^{GVL} (%)	TON ($\frac{\text{mol LA}}{\text{mol metal}}$)
120	4,9	3,6	19,7	0,7	106
150	5,0	5,3*	11,6*	0,6*	150*
180	4,9	18,4	9,3	1,7	524

*All data are taken at 6h of reaction except for the experiment carried out at 150 °C which are taken at 5h.

Figure 13 shows how conversion, selectivity and performance depend on temperature. On the one hand, the higher the temperature, the higher the conversion. Secondly, the higher the temperature, the lower the selectivity to GVL and, finally, the higher the temperature, the higher the yield. For this last statement, it must be remembered that the data at 150°C are for one hour less reaction time.

In general, it can be said that the rate of a reaction increases with increasing temperature. This is because the increase in temperature increases the average energy and velocity of the reacting molecules, increasing the number of collisions between them and the number of molecules that reach or exceed the activation energy.

Depending on the reaction temperature, the hydrogenation reaction of LA to produce GVL can continue until VA is produced. Thus, it is observed that as the temperature increases, valeric acid is produced and, therefore, matter is lost in the form of CO₂.

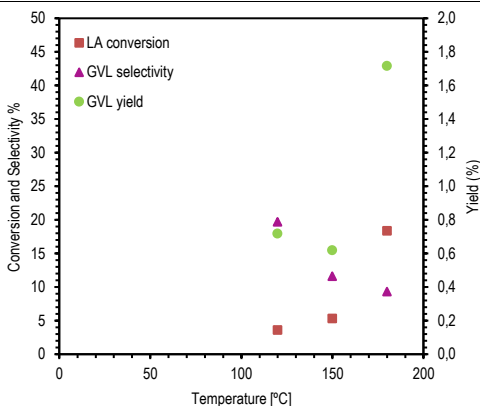


Figure 13. Comparison of conversion, selectivity, and yield for three temperatures (see reaction conditions in Table 17).

Using selectivity criteria, the rest of the experiments have been carried out at 120 °C.

6.4.1.3. Effect of catalyst load

The effect of the catalyst load (Expresion 1) on the reaction was investigated by means of two different catalyst loading: 0,5 % and 6 %. The experiments were carried out at 120 °C, 5 bar hydrogen, 50 %wt LA feed and using the catalyst Amberlyst CH28. Table 18 shows the results of both experiments (Experiments 7 and 8).

Table 18. Results of the experiments to assess the effect of catalyst load.

Catalyst load (% wt.)	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	TON $\left(\frac{\text{mol LA}}{\text{mol metal}}\right)$
0,5	12,4	1,5	0,2	3551
6,0	6,3	1,8	0,1	141

It can be seen in Figure 14 that the higher the catalyst load, the lower the conversion. Nevertheless, both the selectivity and the yield of the reaction to produce GVL are practically the same.

Normally it would be expected that the higher the catalyst load, the more reactant would be converted, but this is not the case here. This could be due to the low solubility of hydrogen in water. It could be that 5 bar of hydrogen is not enough pressure for the hydrogen to dissolve in the solution and, as a consequence, using a larger amount of catalyst is not beneficial.

For this reason, a catalyst loading of less than 6 % has been used in all other experiments.

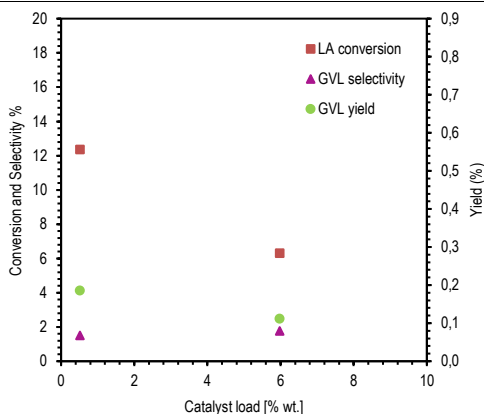


Figure 14. Comparison of conversion, selectivity, and yield for 2 different catalyst loads.

6.4.2. Effect of the catalyst

In this section, four different catalysts have been used. These catalysts have been doped in the laboratory with copper and palladium. The resin supports were commercial, namely Amberlyst 15 and Dowex 50WX2.

6.4.2.1. Effect of metal

In order to compare the effect of the type of metal (noble or non-noble) on the LA hydrogenation reaction to produce GVL, both resins have been doped with both metals. In this way it will be possible to compare the metals with each other for each support and to analyse if there is a general trend for each metal. These experiments have been carried out with 50 % wt. diluted LA feed, at 120 °C, 5 bar hydrogen pressure, and with a catalyst loading of 1.3 %.

Table 19 shows that in the case of Amberlyst 15, the Cu-doped catalyst has a higher conversion. However, this does not imply that it is better because it has a lower selectivity towards GVL. The same happens when the Dowex 50WX2 support is doped. It should be noted that in the latter case, the palladium-doped catalyst has a considerably higher selectivity than the rest.

Table 19. Results of the experiments to assess the effect of metal.

Catalyst	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	Y_{LA}^{VA} (%)	TON $\left(\frac{\text{mol LA}}{\text{mol metal}}\right)$
A15 (1 % Cu)	13,6	1,0	0,1	0,06	275
A15 (1 % Pd)	5,2	5,6	0,3	0,00	184
Dowex 50WX2 (1 % Cu)	3,5	4,3	0,2	0,04	74
Dowex 50WX2 (1 % Pd)	0,7	56,7	0,4	0,00	24

*Note: All data are taken at 5h of reaction.

A possible explanation for the above data would be the fact that copper is much more active in the LA hydrogenation stage than palladium, so that 4-hydroxivaleric acid is formed but it quickly passes to GVL and, at the same time, copper, being so active, is able to continue hydrogenating GVL to give rise to valeric acid, while palladium, for the same reaction time, does not. Thus, the copper-doped catalyst selectivity is lower. This explanation would also be applicable to TON, since the higher the conversion, the greater the number of moles of reactant reacted with respect to the moles of metal contained in the added catalyst. GVL production yields are low.

6.4.2.2. Effect of support

In this section, the same experiments are used as in the previous section (6.6.1), but in this case different supports with the same metal are compared. The experiments were carried out with 50 % wt. diluted LA feed, at 120 °C, 5 bar hydrogen pressure, and with a catalyst loading of 1.3 %.

Table 20 shows that A15 supported catalyst (macroreticular) gives a higher conversion. On the other hand, the gel catalyst (Dowex 50WX2) provides better selectivity towards γ -valerolactone production.

The fact that the A15 support provides a higher conversion at 5h of reaction could be attributed to the fact that a macro-reticular structure allows a distribution of the metal in smaller particles, in such a way that they represent a larger surface area of metal catalysing the hydrogenation reaction.

On the other hand, the Dowex 50WX2 support is more selective in producing GVL. In fact, the generation of downstream products such as valeric acid has not been detected (Y_{LA}^{VA}). This higher selectivity may be because the dehydration reaction requires better accessibility to the acid centres of the resin, that is, a higher degree of swelling, and gel-like structures such as Dowex provide a higher degree of swelling.

Table 20. Results of the experiments to assess the effect of support.

Catalyst	X_{LA} (%)	S_{LA}^{GVL} (%)	Y_{LA}^{GVL} (%)	Y_{LA}^{VA} (%)	TON $\left(\frac{\text{mol LA}}{\text{mol metal}}\right)$
Dowex 50WX2 (1 % Cu)	3,5	4,3	0,2	0,04	74
A15 (1 % Cu)	13,6	1,0	0,1	0,06	275
Dowex 50WX2 (1 % Pd)	0,7	56,7	0,4	0,00	24
A15 (1 % Pd)	5,2	5,6	0,3	0,00	184

*Note: All data are taken at 5h of reaction.

6.4.3. Global analysis of the different catalysts

In the different conditions of temperature (120, 150 and 180) °C, pressure (5-7) bar H₂, feed (pure or 50 % aqueous), catalyst loading (0.5-6) % used, the hydrogenation reaction of levulinic acid to produce γ -valerolactone had hardly any yield in GVL. Conversions are very low and the desired product is not selectively formed.

The commercial resin ACH28, which is doped with palladium, has shown the best γ -valerolactone yield (Y = 0.7 % at 120 °C, 7 bar H₂, 50 % feed and 4.9 % catalyst loading). However, it is still not a viable catalyst under the conditions tested.

Bifunctional resins doped in the laboratory did not show good catalytic activity. This could be attributed to the fact that the support did not retain enough metal or that the metal was not optimally distributed.

At the moment, none of the catalysts used would be a good option to produce GVL from levulinic acid in industry.

6.5. PROPOSALS FOR THE FUTURE

In the introduction to this work, we have presented a number of data from the literature with reasonable conversions in the production of γ -valerolactone from levulinic acid. However, the main difference between the reaction conditions of those experiments and the experiments performed in this study was the pressure. For this reason, I propose to carry out the reaction with a minimum hydrogen pressure of 30 bar to ensure its solubility in the reaction medium and to ensure the contact between reactants.

On the other hand, I also propose the use of thermosetting ion exchange resins in order to increase the temperature while ensuring that the resin structure remains stable.

Another proposal would be to perform a protocol of activation and reduction of the metal before using the catalyst in the reaction.

Finally, to improve the production of GVL regarding the other by-products as valeric acid, a continuous piston flow reactor could be used, since it is analogous to the batch reactor.

7. CONCLUSIONS

To sum up, Amberlyst CH28 resin did not exhibit the same catalytic activity in the hydrogenation reaction of levulinic acid to produce γ -valerolactone as it did in the hydrogenation reaction of mesityl oxide to obtain methyl isobutyl ketone (Talwalkar & Mahajani, 2006).

The type of feed has the expected effect on the hydrogenation reaction. The higher the feed, the higher the conversion but the lower the GVL selectivity and, consequently, the lower the yield.

Temperature plays a fundamental role in the reaction. It has been observed that the higher the reaction temperature, the more levulinic has been consumed. Despite the increase in conversion, the selectivity has decreased. This has been attributed to the fact that at elevated temperatures γ -valerolactone continues hydrogenating itself to produce valeric acid.

The catalyst loading did not improve catalytic activity so it was concluded that it was not cost effective to use large amounts of catalyst.

Considering the three operating variables studied, the best operating conditions are with 50 % diluted feed, the lowest temperature (120 °C) and low catalyst loading.

The laboratory Cu-doped catalysts have higher conversion than the Pd-doped. Nevertheless, this does not imply that it is better because it has a lower selectivity towards GVL. The Pd-doped Dowex 50WX2 catalyst has a considerably higher selectivity than the rest. At the same time, copper, being so active, is able to continue hydrogenating GVL to give rise to valeric acid, while palladium, for the same reaction time, does not. Thus, the copper-doped catalyst selectivity is lower.

A15 supported catalyst (macroreticular) gives a higher conversion. On the other hand, the gel catalyst (Dowex 50WX2) provides better selectivity towards γ -valerolactone production.

Further testing could be applied to bifunctional ion exchange resins in order to prove whether or not they are suitable to catalyze this reaction in an industrial environment.

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9. ACRONYMS

AL: α -angelica lactone

A15: Amberlyst 15

ACH28: Amberlyst CH28

C5: carbon five

C6: carbon 6

DOE: Department of energy

DVB: Divinylbenzene

IER: Ion exchange resin

GVL: γ -Valerolactone

GC: Gas chromatograph

HMF: Hydroxymethylfurfural

LA: Levulinic acid

MOT: Maximum operation temperature

MTHF: 2-Methyltetrahydrofuran

NREL: National Renewable Energy Laboratory

PNNL: Pacific Northwest National Laboratory

S: Selectivity

TCD: Thermal conductivity detector

TON: Turnover number

VA: Valeric acid.

X: Conversion

Y: Yield

4-HVA: 4-hydroxyvaleric acid

APPENDICES

APPENDIX 1: GAS CHROMATOGRAPH CALIBRATION

To obtain the GC calibration, 25 vials of known concentration were prepared, and each vial was injected three times into the chromatograph. The following tables show the concentration of each vial and the response generated for each substance.

Vial	LA	
	%mass	%area (average)
1	98,0	99,0
2	0,0	0,0
3	0,0	0,0
4	0,0	0,0
5	0,0	0,0
6	9,6	8,0
7	20,3	18,4
8	29,5	25,1
9	38,2	32,0
10	35,9	32,5
11	46,5	37,3
12	0,0	0,0
13	16,8	15,1
14	23,5	21,9
15	44,7	42,6
16	0,0	0,0
17	4,8	3,9
18	12,3	13,2
19	83,6	79,4
20	93,0	92,2
21	59,2	47,3
22	49,2	40,2
23	43,3	35,5
24	34,3	25,4
25	88,0	85,2

Vial	Water	
	%mass	%area (average)
1	2,0	1,0
2	1,0	0,6
3	0,0	0,0
4	1,0	0,2
5	100,0	100,0
6	11,1	16,9
7	20,6	25,9
8	32,9	41,0
9	40,2	49,6
10	30,3	35,9
11	53,5	62,7
12	0,0	0,0
13	15,9	20,2
14	1,1	0,9
15	1,4	1,0
16	24,8	32,7
17	16,4	24,1
18	5,5	10,8
19	13,3	19,3
20	1,9	3,1
21	35,4	48,0
22	49,2	58,3
23	45,7	55,2
24	65,4	74,4
25	11,8	14,6

Vial	GVL	
	%mass	%area (average)
1	0,0	0,0
2	99,0	99,4
3	0,0	0,0
4	0,0	0,0
5	0,0	0,0
6	69,8	67,9
7	19,5	19,4
8	17,5	16,6
9	10,4	9,6
10	27,0	26,4
11	0,0	0,0
12	0,0	0,0
13	38,4	20,2
14	56,8	60,3
15	48,8	52,3
16	49,8	46,7
17	57,9	55,0
18	64,2	67,2
19	2,0	0,4
20	2,6	1,6
21	2,1	2,1
22	1,6	1,5
23	4,9	4,8
24	0,1	0,1
25	0,1	0,1

Vial	AL	
	%mass	%area (average)
1	0,0	0,0
2	0,0	0,0
3	100,0	100,0
4	0,0	0,0
5	0,0	0,0
6	4,8	3,6
7	19,8	18,0
8	10,1	8,7
9	5,5	4,5
10	3,5	2,5
11	0,0	0,0
12	0,0	0,0
13	12,7	38,7
14	18,6	17,0
15	3,1	2,6
16	10,7	8,0
17	11,5	8,5
18	13,3	7,0
19	0,0	0,0
20	1,5	2,3
21	1,1	0,9
22	0,0	0,0
23	1,8	1,4
24	0,1	0,1
25	0,1	0,0

Vial	VA	
	%mass	%area (average)
1	0,0	0,0
2	0,0	0,0
3	0,0	0,0
4	99,0	99,8
5	0,0	0,0
6	4,7	3,6
7	19,8	18,3
8	10,1	8,7
9	5,6	4,3
10	3,3	2,7
11	0,0	0,0
12	0,0	0,0
13	16,3	15,4
14	0,0	0,0
15	1,9	1,5
16	14,7	12,7
17	9,4	8,5
18	4,7	4,8
19	1,1	0,9
20	1,0	0,8
21	2,2	1,7
22	0,0	0,0
23	4,4	3,0
24	0,0	0,0
25	0,1	0,0

