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Grau en Enginyeria Química

Treball Final de Grau

Nonane production from levulinic acid as raw material from lignocellulosic biomass.

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Hem de tindre constància i sobretot confiança amb nosaltres mateixos. Hem de creure que estem dotats per alguna cosa.

Marie Curie

Vull agrair a totes les persones que m'han ajudat a recopilar dades i informació per aquest treball de fi de grau. Aquest treball no hauria assolit la seva forma actual sense la seva inestimable ajuda. En particular, vull agrair tots els membres del departament d'Enginyeria Química i Química Analítica per oferir-me aquest treball.

Per sobre de tot, als meus tutors, la Dra. Montserrat Iborra Urios i al Dr. Javier Tejero Salvador, no només per transmetrem els seus coneixements, sinó també el seu entusiasme pel tema en qüestió i l'ajuda obtinguda per a realitzar el treball final de grau.

Espero que aquest projecte contribueixi a una comprensió més clara de lo que es pot obtenir a partir de la biomassa.

Agraeixo també el suport de la meva família, inclòs el meu pare, mare, germà i la meva parella. M'han ajudat en els moments més difícils .

CONTENTS

SUMMARY

In order to comply with the criteria of sustainability that society and industry demand today, it is necessary to work with ecoefficient processes, that is, "producing more with less", so as to promote better management of resources and energy and at the same time minimizing environmental impacts. Therefore, it is important for the term "biomass".

Biomass can efficiently replace or complement petroleum in the production of fuels for the transport sector. One of the effective strategies for the processing of complex raw materials of biomass consists of the pre-conversion into simpler compounds (platform molecules) that are more easily transformed into subsequent update reactions.

This work intends to cover the most relevant catalytic strategies designed for the conversion of levulnic acid as raw material to Nonano as biofuel. Therefore, it is shown which is the best pretreatment to separate lignocellulose biomass, the posterior hydrolysis of cellulose to glucose (or to other C_6 sugars), as from this sugar obtained levulinic acid and how this acid is reached the Nonano molecule with gamma-valerolactone and pentanoic acid as intermediate.

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RESUM

Per complir amb els criteris de sostenibilitat que demanda avui en dia la societat i la pròpia indústria, cal treballar amb processos ecoeficients, és a dir, "produint més amb menys", de manera que es fomenti una millor gestió dels recursos i energia, i al mateix temps minimitzant els impactes mediambientals. Per això, és important el terme "biomassa".

La biomassa pot substituir o complementar eficientment el petroli en la producció de combustibles per al sector del transport. Una de les estratègies efectives pel processament de matèries primeres complexes de biomassa consisteix en la conversió prèvia en compostos més simples (molècules de plataforma) que es transformen més fàcilment en posteriors reaccions d'actualització.

El present treball té la intenció de cobrir les estratègies catalítiques més rellevants dissenyades per a la conversió de l'àcid levulínic com a matèria primera a nonano com a biocombustible. Per tant es mostra quin és el millor pretractament per separa la biomassa lignocel·lulòsica, la posteriro hidròlisi de la cel·lulosa a glucosa (o a altres sucres C_6), com a partir d'aquest sucre s'obté l'àcid levulínic i com d'aquest àcid s'arriba a la molècula de nonano amb la gamma-valerolactona i l'àcid pentanoic com a intermedis.

1. INTRODUCTION

Nowadays, high global population growth, progressive growth in the first-world half-life years, and the rapid and voracious growth in emerging economies have led to the excessive use of fossil resources to obtain fuels and chemical derivatives, which has mainly generated two types of problems: on the one hand, the associated environmental impacts, and in particular its effects on climate change and the consequent degradation of our ecosystem, and on the other hand, the limitation of existing reserves and their future depletion. Therefore, concerns about the decline in fossil fuel reserves, coupled with the effects of global warming caused by rising greenhouse gas levels, are pushing society towards finding new renewable energy sources that can replace current fossil sources.

Biomass was the most important energy source in humanity until the Industrial Revolution when it was massively replaced by fossil fuels. Until this stage, the energy use of this source was developed by direct combustion of biomass. In recent decades, due to the problems presented by the global energy landscape, interest in this renewable raw material has resurfaced and, increasingly efficient, reliable, and clean biomass harvesting systems have been developed, causing industries to begin to consider this energy source as an alternative to fossil fuels.

The fact that 90% of oil is used as a raw material to produce energy for transport, makes this sector one of the most studied to reduce pollution and there is so much interest in the production of biofuels from biomass as raw material. These biofuels are considered a renewable and sustainable energy source that complies with the three intertwined development policies: global energy security, economic development, and protection.

2. BIOFUELS FROM BIOMASS

A viable alternative to combating the disadvantages of using oil and natural gas is to obtain biofuels from biomass. Liquid biofuels derived from sugars, starch, or wood are, by their similarity, are currently the ones preferred. The parameters of cultivation, treatment, transport, and conversion of biomass to fuels are important for the production of greenhouse gases. In this sense, the increase in biomass cultivation favors the absorption of CO_2 thereby reducing the net intensity of greenhouse gases (1).

2.1. BIOMASS

Among the alternative sources, biomass is a very interesting option, since unlike products derived from fossil raw materials, biomass has a neutral balance of carbon dioxide. That is because the amount that is released into the atmosphere at the end of the life cycle of bioproducts is identical to the amount of atmospheric CO_2 that was captured and fixed by the photosynthetic organisms during the formation of that biomass.

The carbon used to build biomass is absorbed from the atmosphere in the form of carbon dioxide (CO2) by plant life, using solar energy. Plants can then be eaten by animals and therefore converted into animal biomass. However, primary absorption is carried out by plants. When this biomass breaks down, depending on the process involved, carbon is released into the atmosphere basically in the form of carbon dioxide (CO_2) or methane (CH_4). These processes are known as the Carbon Cycle (Figure 1.) (2).
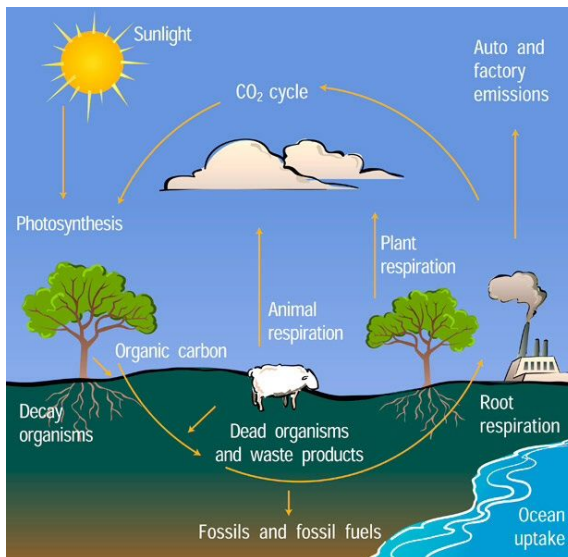
Figure 1. Carbon Cycle
(Image take from https://scied.ucar.edu/carbon-cycle)

Biomass is the organic matter that originated in a biological process, excluding organic matter that has undergone profound changes in its composition, such as those that have taken place during the mineralization processes that occurred in the formation of coal, oil, or gas. The term biomass refers to all organic matter from forest waste (trees, branches, bark, splinters, pruning, etc.), agricultural waste (waste from food crops, such as olive pruning, cereal straw, corn bagasse, etc.), energy crops, urban waste (frying oils, food scraps, sewage treatment sludge, etc.) and waste from paper pulp industries.

As mentioned above, biomass could provide a renewable alternative to fossil resources through the combination of its low environmental impact and new technologies. Being able to establish a new sustainable supply chain for the production of high-value chemicals, fuels.

Biomass, like oil, has a complex composition so its use requires its initial separation into a number of intermediate product groups. The subsequent treatment and processing of these intermediate products will lead to a whole range of end products (3,4,10).

This constitutes the basic principle of biorefinery as an extension of the principle of operation of oil refineries, Section 3 shall define the concept of biorefinery.

Depending on the predominant fraction, or of interest for its final use, biomass can be distinguished in lignocellulosic biomass, amylose, sugary or-oilseed.

2.2. TYPES OF BIOFUEL

Depending on this nature, source, production techniques, and stages of development, biofuels were classified in several ways.

Biofuels are classified as first-generation biofuels using starch raw materials (including sugars) and triglyceride raw materials, second-generation biofuels using raw materials of lignocellulosic origin, and third-generation biofuels that use microalgae as raw materials (5,6).
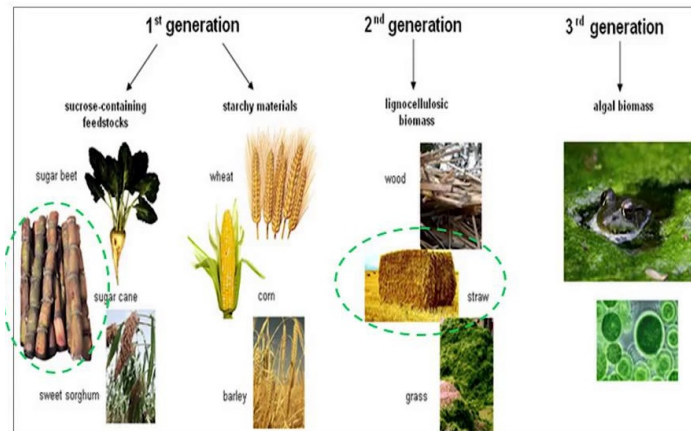

Figure 2. Biofuels and their types
(Image take from https://simranias.com/biofuel-fuel-vs-food/)

2.2.1. First-generation biofuels

First-generation biofuels are produced directly from food crops: starch, sugar, or easily accessible oils, but also contain small amounts of oil.

These biofuels have played an important role in the establishment of infrastructure and in the adoption of energy policies. However, when emissions are included in the use of a life cycle analysis on greenhouse gases the benefits are highly variable, and not always the result is as good as anticipated. The production of biofuels usually includes the use of fossil fuels and fertilizers necessary for the production of biomass, thus causing the emission of both N_2O and CO_2. According to entities such as Greenpeace they are considered unsustainable, as they can compete with food production, either directly by diverting food crops for biofuel production or indirectly by competing for land and agricultural labor (8).

The main challenge in research with first-generation biofuels is the optimization of processes to reduce costs so that green fuels can be competitive with those produced from oil (7).

The most commonly used are biodiesel, bioethanol, and biogas.

2.2.1.1. Bioethanol

Bioethanol is generated by microbial fermentation from glucose to ethanol followed by distillation and dehydration. It can be a complete substitute for gasoline or mingle with it. It is the most produced biofuel, accounting for more than 94% of total biofuel production. Also, ethanol production continues to increase, as its demand is expected to grow to more than twice that of today. This rapid growth is possible because ethanol and gasoline mixtures can be used in modern gasoline engines without any modification. The areas that are driving the most production are North America, Europe, and Asia-Oceania. Despite the decline in production in Central and South America, Brazil is the country that produces the most bioethanol after the United States (8,7,11).

2.2.1.2. Biodiesel

Biodiesel is produced by transesterification of triglycerides with ethanol or methanol to a lesser degree. It can be mixed with fossil diesel or as a complete substitute. It is the second most abundant renewable liquid fuel, with annual production exceeding 4 million barrels per day, used in injection engines in a wide range of mixtures with gasoline-diesel or as a pure fuel. It is not flammable or explosive, in contrast to petroleum diesel, which has a lower flash point. This property makes vehicles that use biodiesel as fuel much safer from accidents than vehicles that run on diesel or gasoline.

Biodiesel is better than diesel in terms of lower sulfur content, flash point, aromatic content, and higher biodegradability. However, biodiesel produces slightly lower energy and torque per unit of mass, leading to higher fuel consumption. Germany led biodiesel production in Europe with 0.63 million barrels per day in 2011 becoming the world's top producer. Other countries such as France, Italy, and Austria are increasing their biodiesel production (8,7).

2.2.1.3. Biogas

Biogas is a mixture of mainly CH_4 and CO_2 that can be used in vehicles as feed. Anaerobic digestion of organic waste is used to produce biogas. Biogas production is common in most countries around the world, especially European countries where biogas production is subsidized to generate electricity, on the contrary, in India and China it is produced on a small scale. In Germany and Denmark, biogas is used as biofuel for transport, after being transformed into biomethane (7,8).

2.2.2.   Second Secondgenerations

The production of biofuels from lignocellulosic biomass-derived from plants, such as agricultural and forestry waste, could fulfill the dual function of renewable energy production and waste reduction.

These biofuels are an alternative to be able to produce biofuel without needing raw materials from food crops (12).

Lignocellulosic biomass, which comes from the structural part of plants, can be hydrolyzed to produce chemical components that in turn can be used as renewable sources of carbon to produce biofuels and chemical compounds. Second-generation biofuels made of lignocellulosic raw material, which is composed of cellulose (40 to 50%), hemicellulose (25 to 35%), and lignin (15 to 20%).

Cellulose is the most abundant organic polymer in the world. It is a linear polysaccharide of high molecular weight and a high degree of polymerization, in addition to being the main component in the cell walls of plants. The higher the degree of polymerization, the harder cellulose to hydrolyze (25).

Hemicellulose is composed of polymers of different sugars with shorter and branched chains, which makes it more amorphous and easier to hydrolyze in its constituent sugars than cellulose. The main monosaccharides found in hemicellulose are five: glucose, mannose, and galactose which are hexose, and xylose and arabinose which are pentoses. Its role is to supply the bond between lignin and cellulose to provide rigidity to the cell wall and are insoluble in water (49).

Lignin is the third most abundant biopolymer on Earth behind cellulose and hemicellulose. It is found mainly in the middle sheet of the cell wall and the cell wall layers forming together with the hemicellulose a matrix around the microfibers of cellulose (23,24).

Lignocellulosic biomass also contains smaller amounts of other minority components such as; proteins (3-10%), lipids (1.5%), soluble sugars, and minerals (10.5%), which in chemical analyses are estimated as ash.
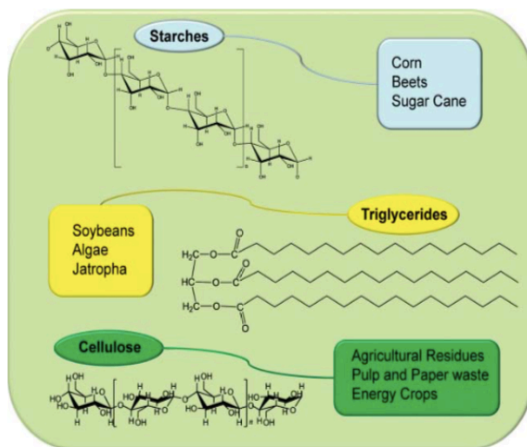
Figure 3. Chemical structure of biomass feedstocks
(Image take from Green Chem., 2010, 12, 1493–1513)

These components interact and become tangled to form the lignin-carbohydrate complex. The breakdown of these results in the formation of chemical compounds that can be used for the production of biofuels and chemical compounds. Cellulose is a glucose polymer that can be depolymerized through hydrolysis in monomers, these obtained sugars can be transformed into bioproducts through fermentation o chemical transformation into biorefineries.

The U.S. Department of Energy has selected twelve reference molecules, which can be produced from sugars contained in biomass through biological or chemical conversions and could replace intermediate petroleum-derived compounds in the production of chemicals and materials. These reference molecules that may represent the future of a bio-based economy are 1.4-diacids (succinic, smoke and malic), dicarboxylic acid 2.5-furan, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutylactone, glycerol, sorbitol, and xylitol/arabinitol, to which itaconic and glucaric acids, 3-hydroxibutrilolactone and 5-hydroxymethylfurfural have been recently added.

In this work several platform molecules are covered, from which the furfural is highlighted, as a coproduct and 5-hydroxymethyl-furfural (HMF) as an intermediate in the production of levulinic acid (LA), levulinic acid as the first material to obtain gamma-valerolactone which subsequently becomes pentanoic acid, which becomes the final nonanone product by 5-nonanone and the formation does not want n-butene and n-pentene. It should be noted that all these molecules have more applications apart from that of this work, some of them will be detailed in the sections 4.3.1 and 4.4.1.

2.2.3. Third-generation biofuels

Third generation biofuels are also called advanced biofuels due to raw materials and technological processes used for their production, the raw material of third-generation fuels are microalgae.

Microalgae have the ability to mitigate CO_2 emissions and produce lipids, so they are considered to be potential for third-generation biofuels. Photosynthetic microalgae fix CO_2 in the presence of water and light in biomass. Carbohydrates, present in the cell wall and microalgae plastics, can be used as a source of carbon for the fermenting production of ethanol and biodiesel.

Many authors conclude that although the behavior of microalgae in the face of physiological stress conditions is variable between species; the limitation of nutrients especially nitrogen and phosphorus, associated with heterotrophic growth or high luminous intensities in phototrophic are considered as the most efficient strategies to increase lipid content in microalgae, in particular triglycerides consisting of saturated and monounsaturated fatty acids, ideal for the production of biodiesel.

The use of microalgae as a raw material for biofuel production has many advantages over terrestrial plants, such as a faster growth rate of algae, efficient carbon dioxide capture, very short harvest cycle, absence of lignin, low hemicellulose content in the raw material and growth in areas not suitable for agricultural purposes. But carbohydrates in microalgae, starch (present in chloroplasts), and cellulose or polysaccharides (present in the cell wall) cannot be easily fermented by microorganisms and must, therefore, be hydrolyzed to fermentable sugars before fermentation with ethanol.

In general, for biofuel production, microalgae cultivation takes place on a large scale in open pools and bioreactors, in marine habitats near the coast, in open ponds, and sed bioreactors. Therefore, the successful growth of desired microalgae is likely to require drastic changes in ocean composition.

Oil extracted from microalgae is another potential source of biomass for biodiesel production. These algae raw materials can be used directly to generate combustion energy after drying or can be processed for liquid and gaseous biofuels using biochemical and thermochemical conversions (15-17).

However, despite the promising results that have been obtained, on an industrial scale, it is necessary to develop the ability to grow high-production strains of oils and the ability to extract the lipids generated.

Actually, out of 300.000 strains of algae, only a few give the high production that is required. To obtain good results a high growth control and optimization would be necessary.

Moreover, to commercially produce biodiesel from microalgae, more research is needed for the mass production of species identified as potential, because of their high lipid productivity and their proper fatty acid profile.

3. BIOREFINERY

With the use of biomass as a renewable resource the concept of the biorefinery is born, such as the refining industry for the production of energy, fuels, materials, and chemicals from plant biomass. This seeks to develop technologies that allow the production of, from the different components of biomass, energy, biofuels, and families of basic products that can be useful to different production industries. An integrated biorefinery is a facility where all types of biomass from forestry, agriculture, aquaculture and waste from industry and households, including wood, crops, organic waste (derived from plants and animals), forest waste and aquatic biomass (algae and seaweed) can be used to produce a wide variety of products including energy (electricity), heat), biofuels, chemicals, and biomaterials.

This will increase the profitability of biomass use and achieve greater flexibility in the face of potential market fluctuations and changes in consumer needs. Also, the concept of integrated biorefinery has associated complex conversion methods, both biochemical and thermochemical, to obtain a wide range of products.

These conversion processes will have greater energy efficiency, increasing the sustainability of the overall process (18,14,20).

Biorefineries are named by analogy with conventional refineries that also process a complex raw material, and in both cases give rise to a wide variety of chemicals and fuels with maximum use of raw materials. There is a wide variety of definitions of biorefinery, one of the most accepted definitions has been made by the National Renewable Energy Laboratory (NREL) of USA: "A biorefinery is a facility that facilitates the processes of integral conversion of biomass and equipment to produce fuels, energy and value-added chemicals from biomass". Another definition has been proposed by the U.S. Department of Energy (US-DOE): "A biorefinery is a general concept of a processing plant where biomass is converted into a spectrum of value-added products". The International Energy Agency (IEA) defines biorefinery as the facility where a broad spectrum of products of commercial interest from biomass is generated sustainably.

The choice of given biomass as a raw material for obtaining energy and other products (biofuels, biopolymers, and base chemical molecules) will be determined by the characteristics and activities of the region in which it occurs: availability and edaphoclimatic characteristics of the territory, predominant activities of the agricultural and industrial sectors, population size, etc. The composition of the selected biomass shall determine the processing processes applicable in a biorefinery (26).

For the above reasons, a biorefinery is not a typical installation, but depending on the type of biomass you have to process it consists of several basic units. Much of the biorefinery studies have focused on obtaining fuel and energy from biomass.

In a biorefinery a series of processes take place. First, a series of homogenization and uniformization operations are necessary at the entrance of the treatment plants to facilitate subsequent transformations since as explained above the structure of the biomass is very complex. Initial treatment operations include drying, pressing, crushing, chipping, chopping, grinding, etc.

Once the treatment is carried out, depending on which final product is to be obtained and what type of biomass is used as raw material there are different conversion technologies: thermochemical platform, lipid platform, biogas platform, protein platform, and sugar and lignocellulose platform.

A Thermochemical biorefinery is a facility based on the decomposition by thermochemical processes of biomass for processing into chemicals of interest or fuels. This decomposition can be divided into three large blocks: liquefaction, pyrolysis, and gasification.

Lipid platforms are based on the use and transformation of biomass oils and fats (plants and animals). The first products and possibly the best-known example is the production of 1st generation biodiesel by transesterification of vegetable oils.

The biogas platform is based on the obtaining and use of the so-called biogas, which is a mixture of gases contained as main components: methane and carbon dioxide. Biomass undergoes the action of anaerobic microorganisms to obtain biogas. Biogas can be used to obtain energy and other products.

The protein platform is based on the use and use of proteins present in biomass. The most common plant sources of protein are soybeans, corn, rapeseed, and wheat gluten. Virtually all protein production goes to the food industry, but new applications, such as the synthesis of fibers and polymers from plant proteins or polyamines, are being investigated. It is also possible to genetically modify the properties of these proteins to adapt them to later applications. They also have an interest in the fields of pharmacy, cosmetics, and agrochemicals.

The lignocellulosic biorefineries or sugar and lignocellulose platform, such as those used for nonane production, shall be explained in more detail in Section 4.

Finally, once the products have been obtained regardless of the conversion technology, the separation and purification of the final product take place.

A disadvantage of biorefineries to oil refineries is that a relatively greater number of processing technologies are required, some of which are still in the process of being developed, in particular those needed to convert lignocellulosic-type biomass into carbohydrates and other products, which requires further work in research and development in this area.

On the contrary, the wide geographical distribution, abundance, and variety of biomass will tend to reduce the risks of availability in the supply of raw materials and the price volatility that characterizes the current oil economy (21,22).
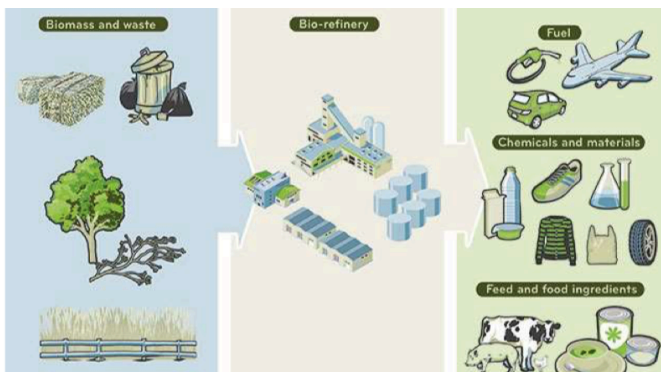

Figure 4. Biorefinery processes
(Image take from https://biconsortium.eu/bio-based-industries-consortium)

4. BIOREFINERY LIGNOCELLULOSIC TO PRODUCE NONANE

In recent years, the interest in not using raw materials in conflict with the food supply coupled with the need for forest preservation has made the use of lignocellulosic materials for the manufacture of fuels and chemicals a strategic objective.

Biorefinery of lignocellulosic materials can process a wide variety of low-cost raw materials (straw, reeds, wood, paper waste, etc.) and its conversion products are well placed both in the traditional petrochemical market and in future bioproduct markets.

As specified in Section 2.2.2 lignocellulosic biomass consists of three primary chemical components or precursors that may be the source of a wide range of chemicals: hemicellulose, cellulose, and lignin. Therefore, the objective of the biorefinery of lignocellulosic materials is the fractionation of the lignocellulosic biomass into these three components and the subsequent processing of these for the production of various final products (19,48).

The objective of this work is to study the production of the nonane as biofuel.

Today it does not exist any biorefinery that produces nonane as the final product, so the following considers the possible procedures that such biorefinery would have. It is important to note that if there are pilot plants for the production of levulinic acid which is the raw material for nonane production. An example of these plants will be detailed in Section 4.3.2.

Therefore, the pretreatment needed to separate the lignocellulosic biomass will be discussed below, from the hydrolysis of cellulose to glucose (or C_6 sugars), from the production of levulinic acid from glucose, from obtaining gamma-valerolactone by hydrogenation of the levulinic acid and the production of pentanoic acid for obtaining the star product, the nonano in a possible biorefinery.

4.1. PRETREATMENT OF LIGNOCELLULOSIC BIOMASS

Fractionation is the key stage as it greatly conditions the performance and effectiveness of subsequent treatments in each of the separate fractions. The separation of lignin and hemicellulose, the reduction of cellulose crystallinity as well as the increase in the porosity of the materials will be the objectives to achieve with pretreatment to promote hydrolysis of cellulose (Figure 5).

The success of pretreated depends to a large extent on the conditions applied, but also significantly on the composition of the raw material and its resistance to treatment. Thus, woody biomass (e.g. forest crops, fruit tree pruning, etc.) in addition to different physical properties has a higher lignin content than non-woody (straw, grass, etc.) which makes it more resistant to enzymatic and microbial digestion.

For effective pretreatment, several characteristics must be followed: reduction of biomass particle size, limited degradation product formation that inhibits the growth of fermentative microorganisms, energy minimization, low catalyst cost, and a balance between biomass cost, downstream processing cost, operating cost and cost of capital.

A wide variety of processes have been proposed for the pretreating of lignocellulosic materials, including physical, physicochemical, chemical, or biological processes.

Physical pretreatment includes crushing and hydrothermolysis. Crushing is the reduction of biomass particle size by mechanical means that can be of different types, such as dry grinding, wet, vibratory, and compression grinding.T he physicochemical can be vapor explosion, CO_2 explosion, or ammonia fiber explosion. The chemical includes acids and bases. The most commonly used acids and bases are H_2SO_4 and NaOH respectively. The category of chemical additives mainly involves cellulose solvents that can greatly improve the alteration of biomass structure before hydrolysis. Alkaline H_2O_2, ozone, glycerol, dioxane, phenol, and ethylene glycol are few of the solvents of cellulose. Finally, biological pretreating is based on the use of fungi (25, 28,34,49). As can be seen in Section 4.3.2, physical and mechanical pretreatments are the most common, including combining them.
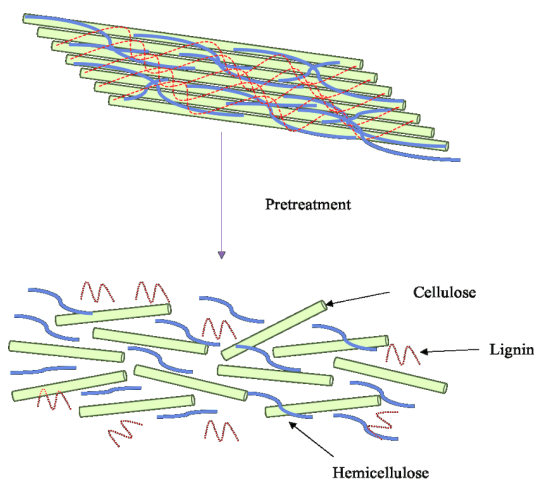

Figure 5. Pretreatment of lignocellulosic biomass
(REF https://www.researchgate.net/figure/Effect-of-pretreatment-on-lignocellulosic-biomass_fig5_326732180)

4.2. HYDROLYSIS OF CELLULOSE

Once the cellulose is separated from lignin and hemicellulose, the hydrolysis of cellulose can be continued. Cellulose is forming a structure of microfiber chains, which in turn are linked by numerous hydrogen bridges between them, which makes it very difficult to hydrolyze (25,27). The cellulose polymer is composed of monomers glucopyranosyl bound by glycosidic bonds, and these bonds can break down in the presence of an acid catalyst. So the simplest way to chemically hydrolyze cellulose into glucose is by using an acid catalyst.

Hydrolysis of chemically catalyzed cellulose has seen several periods of rebirth and has occasionally been combined with biocatalytic fermentation stages to convert sugars into secondary chemical compounds. Industrially speaking, the most important process is hydrolysis with concentrated or diluted mineral acids, predominantly sulfuric acid. One advantage of this process over enzymatic hydrolysis is its high hydrolysis rate. However, depending on reaction conditions, glucose can be transformed into other smaller molecules, thus decreasing efficiency (Figure 6) (28,29,34,49).
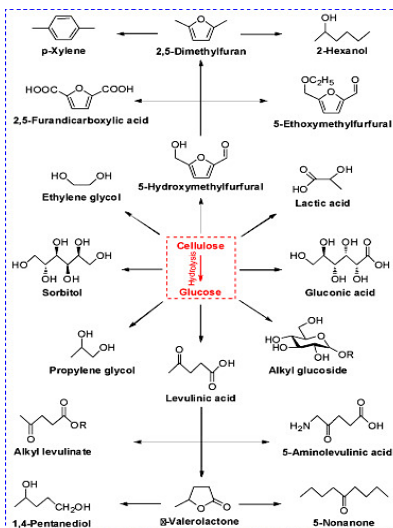
Figure 6. Selective transformation of cellulose into various chemicals and fuels via glucose.
(Hu, L., Lin, L., Wu, Z., Zhou, S., & Liu, S. (2015). Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. Applied Catalysis B: Environmental, 174-175 225–243. doi:10.1016/j.apcatb.2015.03.003)

The dissolution of cellulose or lignocellulosic biomass in ionic liquids makes it extremely easy to hydrolysis biopolymers (cellulose and hemicellulose) due to the removal of structural protection barriers, interactions of Van der Wals and hydrogen bridges, from hydrolysis centers. Thus, once dissolved in ion liquid, acid hydrolysis occurs even at temperatures below 100ºC.

In the first stage, cellulose is hydrolyzed towards oligomers (1.4-glucans) and glucose. Glucose is not stable enough under acidic conditions and is prone to dehydration towards 5-hydroxymethyl furfural (5-HMF) and other different products. 5-HMF, in turn, can be broken down into two molecules: in levulinic acid and formic acid in aqueous media. Figure 7 shows the possible products that are produced with the hydrolysis of lignocellulose biomass.
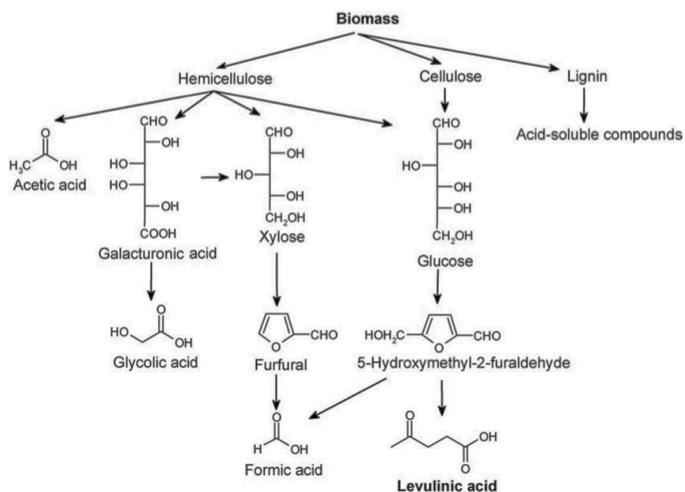
Figure 7. Possible products of the acid-catalysed hydrolysis of a
lignocellulosic material
*(Image take from The Empty Palm Oil Fruit Bunch as the Potential Source of
Biomass in Furfural Production in Indonesia: Preliminary Process Design
and Environmental Perspective
Article (PDF Available) in Journal of Physics Conference Series)
1363:012096 · November 2019)*

4.3. LEVULINIC ACID

4.3.1.   Levulinic acid features and applications

The levulinic acid (LA) also known as 4-oxopentanoic acid or ketovaleric acid is an organic compound with chemical formula $C_5H_8O_3$. It is a promising platform molecule, which can be produced from cellulosic biomass, first described in 1870.

LA is a crystalline solid-structure polar compound that is easily soluble in water, ethanol, diethyl ether, acetone, and many other organic solvents.
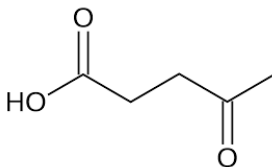
Figure 8. Levulinic acid structure

The double C-O bond has a strong polarity, the oxygen atom has a strong attraction of electrons compared to the carbon atom so that the electron will be transferred to the oxygen atom, leaving this electronegative and forming a positive charge center in the carbon atom. For this reason, LA has a greater dissociation constant than other saturated acids, being a stronger acid.

The presence of ketone and carboxylic acid functional groups highly increases its reactivity compared to linear chain carboxylic alkyl acids. These functional groups also cause difficulties to control LA reactivity towards specific compounds. To control it, the strategy is the initial reduction of the oxygen content in the molecule, leading to the production of less reactive intermediate products (46,49).

Different chemicals and fuels can be obtained from levulinic acid. The importance of this chemical platform is partly due to its potential capacity to serve as an intermediate biochemical for fuel production through conventional petrochemical technology, thus constituting a renewable raw material that can be used in today's petrochemical industry (55,43,52).

Levulinic acid can be used for example, as a raw material for the production of transport fuels (petrol and diesel). Thanks to the special structure of LA, various types of products can be obtained by esterification, halogenation, hydrogenation, and condensation.

For example, in the pharmaceutical industry, calcium levulinate is a new calcium supplement that can become pastilles, capsules, or injections for oil enhancement and muscle excitability. It is used in anti-inflammatory drugs, anti-allergenic drugs, as well as mineral supplements.

As for applications in agriculture, d-aminolevulinate acid (DALA) is a new photoactivation herbicide that is harmless to crops and human health.

In the food industry, levulinic acid esters are often used as food additives as flavor enhancers. Levulinic acid and its derivatives are also used for personal care in natural cosmetics, in perfumes and pH regulators for the skin (39).

The levulinic acid can be added to polyester resins and polyester polyols, thus increasing the scratch resistance of the coatings obtained.

Esterification of levulinic acid with C_1-C_2 alcohols results in levulinic esters. These esters, produced from methanol or ethanol, have great potential as mixing components in diesel formulations. LA esters are similar to biodiesel fatty acid methyl esters (FAME), which are used in some low-sulfur diesel formulations but do not have their main drawbacks: cold flow properties and rubber formation (39).

The addition of ethyl levulinate or methyl levulinate could solve these two problems.

It has also been shown that this acid can be hydrogenated in the presence of a bifunctional catalyst to produce methyl-tetrahydrofuran (MTHF) at a stage and with relatively high yields. This MTHF can serve directly as a mixing component for gasoline. High energy density, lower flammability, hydrophobic nature, low toxicity, and a high specific gravity of 2-MTHF make it suitable for use as fuel; thus, 2-MTHF has been identified as a liquid non-oil fuel that can be replaced or mixed with gasoline. It has also been reported that 2-MTHF is a better mixture with gasoline than methanol and can be more easily integrated into the distribution flow of a refinery.

A very important derivative of its selective hydrogenation is gamma-valerolactone (GVL). It has physical and chemical properties that make it considered a sustainable liquid. Section 5.4 will further detail this derivative as it is a product necessary to obtain the nonane.
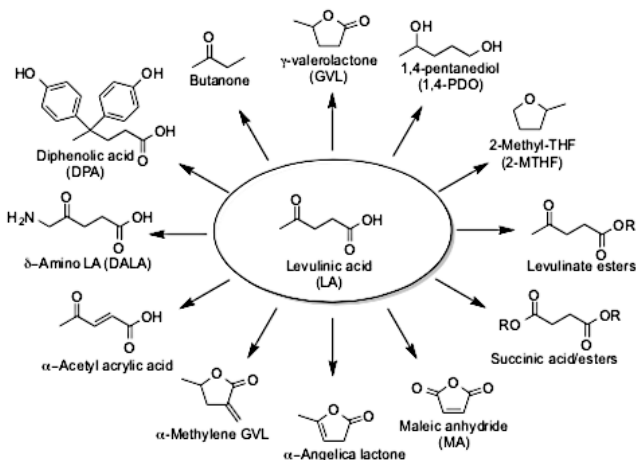
Figure 9. A selection of products that can be derived from levulinic
acid
*(Image take from
https://www.aimspress.com/fileOther/PDF/energy/energy-07-02-
165.pdf)*

4.3.2. Levulinic acid production

As mentioned above, the formation of LA from cellulose consists first of the degradation of cellulose to glucose or other sugars of six carbons. Then these C_6 sugars are dehydrated at 5-hydroxymethylfurfural (HMF), and finally, this furanic intermediate is transformed by hydration with two water molecules, to levulinic acid and formic acid in equimolar amounts. Unwanted by-products called humines that originate from polymerization are also formed, soluble or insoluble (brown or black).

On the other hand, C$_5$ sugars (hemicellulosic fraction) dehydration give furfural, which in turn can be used directly as a product or converted into levulinic acid (Figure 10). Lignin along with some degraded cellulose and hemicellulose and some inerts, come out of the process as a carbon-rich solid (biochar) that can be energy-valued (28,29,31,34).
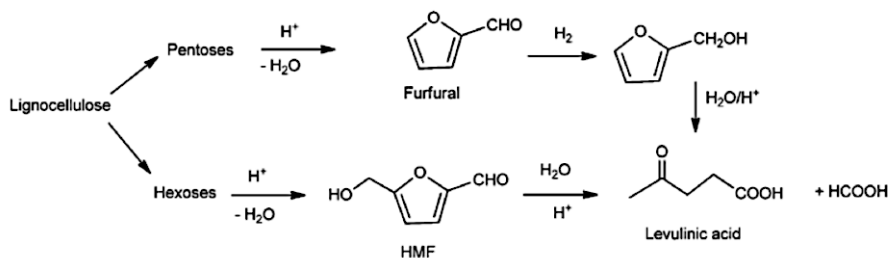

Figure 10. Conversion of lignocellulosic biomass to levulinic acid
(Image take from http://e-spacio.uned.es/fez/eserv/bibliuned:master-Ciencias-CyTQ-Fhabela/Habela_Sanz_Federico_TFM.pdf)

It has been shown that when working with continuous flow reactors, higher LA production performance is achieved compared to discontinuous reactors.

The following LA production companies have developed their technology based on this model: Biofine, DSM, GFBiochemical, Segetis (acquired by the previous one), and the Spanish Reunited Techniques.

Biofine Renewables, LLC is a company that develops technology for biorefinery processes and has established a commercial process for the continuous production of levulinic acid. The Biofine process is one of the most famous technologies currently available for the industrial production of such acid.

This technology was proposed by Fitzpatrick, using diluted sulfuric acid as a catalyst in a two-stage conversion chain. The process is designed to obtain high production yields of levulinic acid and furfural acid (2-FA) from the degradation of hexose and pentose from lignocellulosic biomass. In particular, approximately 50% of sugars with 6 carbons in cellulose and hemicellulose become LA, 20% is converted to formic acid (FA), and 30% form tar. Also, it enables the conversion of 50% (mass) of sugars with 5 carbons (pentose) to furfural.

Raw materials such as paper, wood and other lignocellulosic materials are initially crushed to ensure efficient hydrolysis and optimal yields, and biomass particles are transported by high-pressure air injection to a tank. There, they are mixed with a recycled diluted sulphuric acid solution (1.5-3%, depending on the raw material and its alkalinity). The Biofine process (figure 8) then consists of two distinct steps catalyzed by acid. In the first step, the biomass and the sulphuric acid solution is continuously mixed and supplied to a tubular reactor that operates at a typical temperature of 210-220ºC and a pressure of 25 bar, and a residence time of only 12 s to hydrolyze the polysaccharides (breaking the lignocellulose) obtaining their soluble monomers (hexose, pentose, and HMF). Since it operates continuously and with a short residence time is required a very small reactor diameter. It's important to consider that with a serial reaction using a plug reactor the production of the intermediate product is favorable. In other words, the production of HMF by minimizing the production of humine. According to patent claims, a small amount of sodium sulfite (or potassium) is added to the reaction mixture to prevent obstruction of this kind of reactor (13).

The output flow of the first reactor is fed to a continuous agitated tank reactor (CSTR) that operates at lower temperature and pressure (190-200ºC and 14 bar), this reactor is considerably larger than the first and the residence time is approximately 20 minutes. At this stage, complete hydrolysis to the levulinic acid and evaporation of formic acid and furfural takes place to condense them externally and collect them as secondary products. Volatile products tend to be disposed of at this stage when the tarted mixture of LA and the waste passes into a gravity separator. From here, the insoluble mixture goes to a unit of dehydration where water and volatile evaporates. Heating the LA boiling mixture is carried out at reduced pressure and results in the tartrate material cracking, to give a powdered substance ("char").

Solid by-products (humines) are removed from the LA solution in a press filter unit and the gross product of 75% LA can be purified up to a purity of 98% per distillation. The acid is recovered in the final stage of recycling, allowing its reuse in the System (Figure 8).

It should be noted that a study from the University of Pisa showed that highly diluted HCl was a better catalyst than H_2SO_4, as the latter generated a significant amount of humien by-product on the reactor walls. This change produced a better yield of 95-97%.

The advantages offered by this process over other technologies are the use of a small continuous volume reactor, offering high performance with short residence times; the great flexibility of raw materials, and the low energy input required because the temperatures and pressures that are worked are not high.
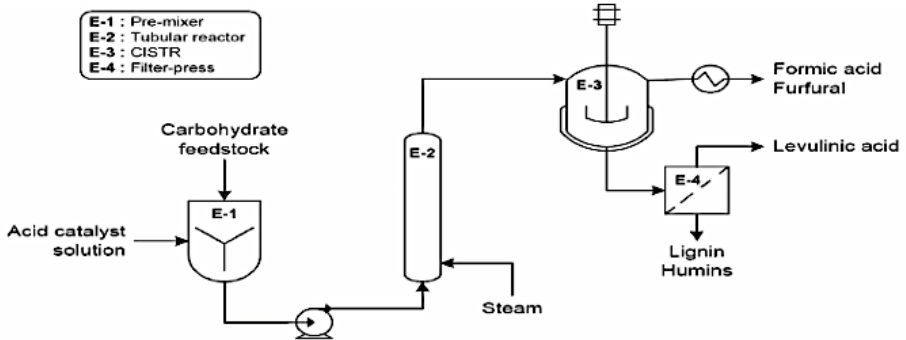

Figure 11. Biofine process scheme
(Image take from https://www.researchgate.net/figure/The-Biofine-process-Girisuta-2007_fig3_245419109)

On the other hand, the Spanish company techniques gathered has created a pilot plant to produce levulinic acid through the LIFE+WALEVA (From Whatever Residue into Levulinic Acid – an innovative way to turn waste into a resource) process, from rice straw as raw material. The procedure is similar to that of the Biofine process. The main difference is that it uses rice straw as raw materials instead of wood and obtains a yield of 90% and 95%.

The WALEVA Project demonstrates that alternative sustainable solutions can be found for agricultural waste that, in this case, affect the rice industry in Spanish regions such as Extremadura, Andalusia, the Ebro Delta, and Albufera de Valencia. Also, it has the support of the Farmers Association of the Region of Don Benito, the main area of rice production in Extremadura, and could be extended to other rice regions inside and outside Spain, which face the same difficulty in sustainably getting rid of the waste produced by the rice harvest (36).

Traditionally, farmers remove waste from the rice crop by burning straw, producing carbon dioxide emissions into the atmosphere of around 1.7 kg of CO_2 per kilo of straw.

According to data provided by the European Union, in 2012 rice production in Europe exceeded 3 million tonnes, generating 0.8 tonnes of straw waste per tonne of rice, representing about 2.4 million tonnes of waste each year, emitting more than 4 million tonnes of CO_2 into the atmosphere.

In Spain, there are approximately 105,000 hectares of land for rice cultivation, which is 577,000 tonnes of rice straw each year and, therefore, the emission of almost one million tonnes of CO- during the burning of waste.

The WALEVA project consortium proposed a solution to this problem on the principles of circular bioeconomy. His strategy was to pave the way for the development of a new value chain based on a high value-added product: levulinic acid (LA).

Thus, by transforming rice straw into levulinic acid, the use of raw materials and energy resources to produce goods would be reduced while achieving a sustainable solution for waste management. This project has focused on reducing CO_2 emissions by burning activities and reducing the impact of rice on the total emission of greenhouse gases that determines the amount of carbon dioxide produced by Waleva technology and other possible alternatives to reduce its emission.

As the main result of this project, in addition to the economic viability taking into account the final yield of LA, the final degree of LA, it has been observed that the carbon dioxide emitted by the use of Waleva technology is lower than the greenhouse gas emissions generated by the common incineration of rice straw by each rice producer in the world. Waleva technology has been shown to reduce CO_2 emissions by nearly 80%.
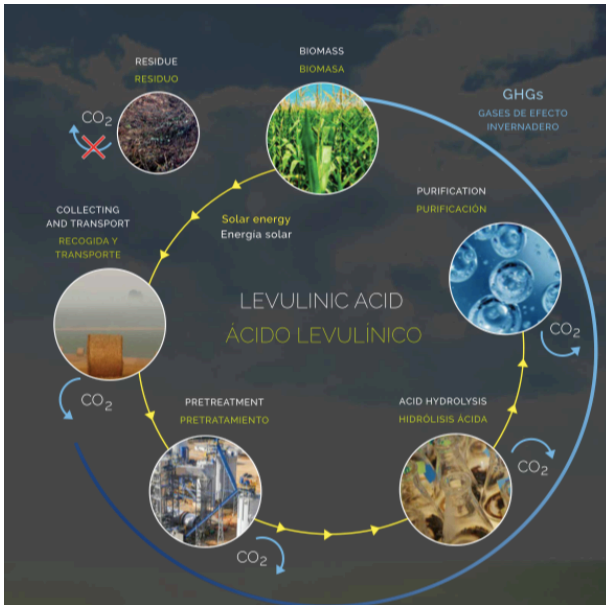
Figure 12. Waleva process outline
(*Image take from http://waleva.eu/wp-
content/uploads/2016/02/Panel-Waleva-Vertical-
TR.compressed.pdf*)

Technique	Reactor types	Number of reactors	Residence time (s)	Working conditions	Raw materials	Yield [%]
Biofine	continuous agitated tank and Tubular reactor	2	First reactor: 12 Second reactor: 1.200	First reactor: 483-493K 25 bar Second reactor: 463-473K 14 bar	Wood rice straw	95-97 90-95 (WALEVA)

Table 1. Comparison of the two projects

4.3.3. Types of catalysts used in the hydrolysis

A catalyst is a chemical, simple or compound, that modifies the speed of a chemical reaction, intervening in it, without becoming part of the products resulting from it. The catalyst is combined with one of the reagents forming an intermediate compound that reacts with the other more easily. The catalyst does not change the thermodynamic balance, it only increases the speed of those that can be given (with Gibbs-free energy greater than zero). The catalyst allows us to reach the same products, but in another way, that is, through other intermediate reactions, which also present a "summation" of energies of less activation to the non-catalyzed reaction.

The design of highly active and selective catalysts for the production of high value-added compounds has experienced a significant boom in recent decades. This is due to society's awareness of environmental issues, the search for new processes and methodologies that are both more efficient and environmentally benign, and the need for the improvement of chemical processes, both economically and from the activity and selectivity of catalysts.

The design and selection of catalysts on an industrial scale involve evaluating catalyst performance under real reaction and feed conditions during long reaction periods and several reactive cycles.

In this process, the selectivity, activity, stability (thermal and mechanical), and catalyst cost are carefully evaluated until catalyst formulation and optimal process operating conditions are achieved. This point is so critical that on numerous occasions therein lies the technical viability or not of a process.

On the other hand, the type of catalyst used in biomass (and LA processing processes in this particular case) in industrially applied products has a crucial effect, not only on the reaction itself but also on the sustainability of the process if we are governed by the fundamentals of green chemistry. In this way, these materials are increasingly synthesized using less aggressive preparation methods, including the use of benign solvents (water, ethanol, supercritical CO_2) thus following the principles of sustainable chemistry.

Therefore, the ideal catalyst design will be based on a process capable of modifying the material surface, the appropriate chemical, the electronic and geometric configuration that maximizes catalyst yields and stability, but also using Materials Safe for Nature.

Catalysts can be distinguished from two types: homogeneous and heterogeneous. The homogeneous are those that the catalyst and reagent(s) are in the same phase, while in the heterogeneous they are in different phases.

Currently, there are many studies on how the performance of LA production varies from which catalyst is used, then a few will be detailed in table 2.

Author	Raw materials	Solvent	Catalyst	Operating temperature	Yield [%]	Favoring humine production
Horvat	glucose	H_2O	HCl, H2SO4, H3PO4	-	85	Yes
Jow	fructose	-	Zeolite LZY	383-433K	56	Yes
Dumesic	glucose	-	H-ZSH-5	-	70	No
Wang	glucose	-	TiO_2	-	32	Yes
Chen	glucose	-	S2O8/Zr2-SiO2-Sn2O3	473K	58	Yes
Schraufinagel and Rase	glucose	-	Dowex MSC and Amberlysts	373K	24	Yes
Sanborn	fructose	-	Amberlysts 35	423K	62	Yes
Smith	fructose	Acetone-agua	Dowex 50 x 8-100	-	73,4	Yes
Ebitani	fructose	agua	Amberlysts 15	393K	52	Yes
Dumesic	fructose	90%GVL-10%H2O	Amberlysts 70	-	69	No
Kuster and Van Der Van	fructose	-	Zeolite LZY	413K		Yes
Lai	glucose	-	modified sulfonated mesoporous silica	-	38	Yes

Table 2: Summary of the different studies
(29-31,42-46,49,51-54).

The first author to appear in the table, Horvat, obtained levulinic acid through a consecutive process of dehydration and rehydration in the presence of homogeneous catalysts (HCl, H_2SO_4, H_3PO_4...) due to its immediate availability, easy application, short reaction times and high catalytic activity.

However, I conclude that the catalyst recovery process needed a lot of energy and that these acid catalysts generated residues that were difficult to remove due to their environmental impact.

Jow and his Companions have used LZY zeolite as a catalyst to dehydrate fructose to LA (383-433 K), obtaining a yield of 56%. They reasoned that this low yield was due to Lewis' strong acidity of the Silica/Alumina support, as well as the molecular sieving capacity of type Y zeolite.

Dumesic and his colleagues produced AL in a THF-H2O single-phase solvent with furfural alcohol using H-ZSH-5 as a catalyst obtaining a selectivity of 70%.

Wang and his collaborators used sulfated TiO_2 for dewatering cellulose to LA, with a yield of 32% under their optimal conditions. This low performance is attributed to the low stability of the catalyst.

Chen and his colleagues used a solid super acid (S_2O_8/Zr_2-SiO_2-Sn_2O_3) at 473K to produce LA from Rice Straw with a yield of 58%. They also conducted a study of catalyst recycling and realized that it was losing its activity by 50% in the second use.

Schraufinagel and Rase used the Dowex MSC and Amberlysts exchange resins as catalysts for HMF and LA formation with a yield of 24%.

Sanborn and his collaborators used a solid acid cathode exchange resin, Amberlysts 35, for the production of LA from Corn Syrup. They performed better than Schraufinagel and Rase's study, 62%.

Smith and his collaborators produced LA using Dowex 50 (8-100 from fructose in acetone-water using a microwave heating technique. The yield was 73.4% which was reduced to 54.3% probably due to humines also showed that using a microwave as a heat source reduced reaction time.

Ebitani and his collaborators used Amberlyst 15 (393K) for LA synthesis, obtaining 52%.

Dumesic Group converted cellulose to LA with Amberlyst 70 as a catalyst in a mixture of 90% GVL and 10% water obtaining a yield of 69%. This showed that GVL is the selection solvent for solubilizing carbons or humines formed during cellulose decomposition by improving biomass conversion.

Kuster and Van Der Van dehydrated the fructose to HMF with hydrochloric acid and then dehydrated HMF back to LA also with hydrochloric acid. They used as a catalyst the Zeolite LZY type Y. They concluded that high LA performance is possible, but that at 140°C the thermal decomposition of fructose and the catalyzed acid decomposition of HMF and LA produced humines that reduced yield.

Lai used modified sulfonated mesoporous silica, with magnetic iron oxide particles for LA production from cellulose. It was able to separate and recycle the magnetic catalyst after the reaction when a magnetic field is applied. But it achieved only a yield of 38%.

Other authors reported that gamma-valerolactone (GVL), a product of LA hydrogenation can be used as a solvent to extract LA and AF from aqueous solutions. Water and GVL mixtures are usually single-phase; however, the system became biphasic if the aqueous phase contains specific solutes, such as salts and sugars, and most os is divided into the organic phase. THE LA and GVL can be separated, for example, by distillation (normal boiling points of LA and GVL equal to 518 and 481 K, respectively). This method provides an important advantage when using GVL as a solvent as this is also the final product, and this eliminates the need to separate the final product from the solvent. This method was also shown to solve the humine problem.
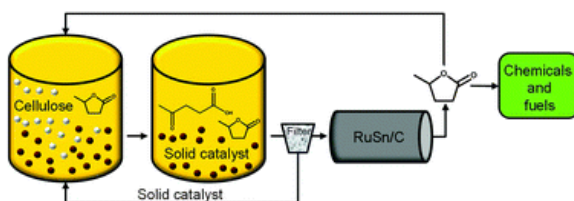

Figure 13. Conversion of LA from GVL as solvent
(Alonso, D. M., Gallo, J. M. R., Mellmer, M. A., Wettstein, S. G., &
Dumesic, J. A. (2013). Direct conversion of cellulose to levulinic acid and
gamma-valerolactone using solid acid catalysts. Catalysis Science &
Technology, 3(4), 927-931)

As seen above the type of catalyst is essential for good performance in the formation of levulinic acid. The sulfuric acid used in the Biofine process is a homogeneous catalyst. Extensive studies have been conducted for the conversion of biomass raw materials into levulinic acid using homogeneous catalysts, including mineral acids and metal chlorides. Good results have been achieved with these catalysts, however, the elimination of these liquid inorganic acids causes environmental problems, containment, and manipulation, as well as not being able to be regenerated on numerous occasions due to their toxic and corrosive nature.

Alternatively, it would be desirable to use solid acid catalysts that exhibit activities and selectivity comparable to homogeneous catalysts for aqueous-phase dehydration reactions, such as heterogeneous catalysts (LZY zeolites, HY, MFI, and $CrCl_3$).

The key to these heterogeneous catalysts lies in the easy separation of products and unreacted reagents, allowing continuous use or reuse, reducing waste, and better amortizing their cost.

As seen in the different researches, one of the most commonly used catalysts is zeolites. These catalysts are solid compounds with a defined porous structure. They are aluminum-silicates, being precisely the silica/alumina ratio one of the criteria used to distinguish the different types. On the one hand, the zeolites of high alumina content are cationic and have hydrophilic character, while on the other hand those of high silica content are non-cationic, hydrophobic, and are the ones that are most catalytically important, as they prevent the fermentation of fructose.

Another type of catalyst commonly used in LA catalytic transformation processes to industrially applied products are the supported catalysts. A supported catalyst is a system that combines the selectivity properties of a homogeneous catalyst and those of insolubility of a heterogeneous one, thus allowing the separation of reaction products. They are usually made up of 3 components; an active phase (noble metals, metal oxides, or metal sulfides) a promoter (metal oxides), and a carrier or support (metal oxides or stable coals).

Acidic polymeric ion exchange resins, such as Nafion and Amberlite, are also being investigated, which are shown catalytic effectiveness for a wide range of reactions, due to their high concentration of acidic sites of Brönsted.

Thus, it is preferable to use heterogeneous catalytic processes to homogeneous ones, to avoid having to use subsequent processes of separation and purification of the catalyst, which involve an added expense, in addition to generating corrosion problems in industrial equipment. Consequently, the use of active, selective, stable, recoverable, and recyclable heterogeneous catalysts represents a future solution for obtaining chemicals, petrochemicals, and fine chemistry cost-effectively and sustainably.

4.4. GAMMA-VALEROLACTONE

4.4.1. Gamma-valerolactone features and applications

The γ -Valerolactone (GVL) is a non-hazardous, high-boiling, low-toxicity liquid that has been identified as a green solvent.

It can be considered a renewable hydrocarbon resource for energy and carbon-based consumer products for the chemical industry. It has been shown to be a suitable replacement for ethanol in mixtures of gasoline and ethanol because the water separation of the GVL requires less energy since the GVL does not form an azeotropic with water while ethanol does (56).

It is also used in the food industry, as it is a very safe material because it has a low vapor pressure even at high temperatures, it does not hydrolyze at neutral pH and does not form peroxides under the air.

Although it contains a chiral center, it is usually produced and used in a racemic form. It is easy and safe to store and transport. Due to its characteristic odor leaks and spills are easily detected.
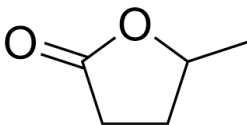

Figure 14. Gamma-valerolactone structure

Due to its characteristic smell of herbs, it can be used as an additive for the manufacture of perfumes. However its most important applications a liquid fuel.

Continuous hydrogenation of GVL produces valeric acid that can be esterified with alcohols to produce a new class of cellulosic transport fuels, called "valérico biofuels (61).

Moreover, an integrated catalytic process has been developed to convert GVL to liquid alkenes tween C_8 and C_{24}) that can be mixed with gasoline, diesel,o aviation fuels. Specifically for this work the GVL intermediates to obtain the nonane (C_9) as aa second-generation biofuel (62).
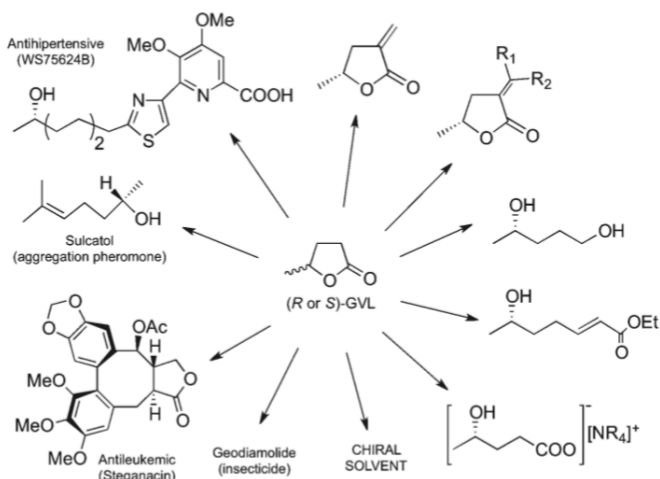

Figure 15. Selected Applications of optically pure GVL
(Image take from Green Chem., 2015, 17, 5189–5195)

4.4.2. Gamma-valerolactone production

There are two routes for the production of gamma-valerolactone, one in which the levulinic acid is dehydrated and cycled in the presence of an acid to the α-angelica lactone and subsequently hydrogenated to the γ-valerolactone. And the other where the leulinic acid is hydrogenated to 4-hydroxypentanoic acid (4-HVA) and then dehydrated to obtain the γ-valerolactone, as shown in figure 11. This second path is recommended since it produces neither coke nor tar.
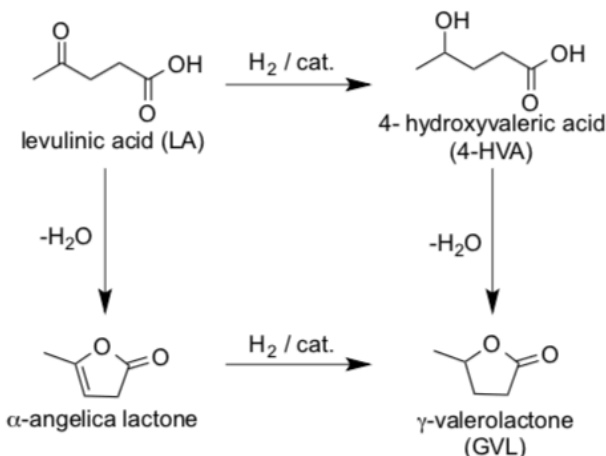

Figure 16. Synthesis of GVL from LA via either α-angelica lactone or 4-HVA
(Image take from Department of Chemistry, Imperial College London, South Kensington, London, 2016)

The hydrogenation of the levulinic acid can be with molecular hydrogen or with formic acid. Using formic acid as a source of hydrogen not only prevents the external hydrogen sub-supply but also generates usable high-pressure CO_2 to mitigate greenhouse gas emissions.

It should also be noted that using molecular hydrogen as an external source causes an excess of hydrogen, and this inevitably produces a little 2-methyltetrahydrofuran, which can form peroxides during storage and that makes it a risk of explosion. That is why researchers have recently minimized the demand for an external source of hydrogen by using formic acid formed in equimolecular amounts with levulinic acid (33).

Regarding the right catalyst for this reaction, there are many studies, then a few will be detailed in table 3.

Author	Catalyst	Solvent	Working conditions	Yield [%]
Manzer	Ru supported by carbon inert materials	1,4-dioxane	473-488K 55 bar	97
Gong	Ru/C	methanol	403K 12 bar	92
AL-Shaal	RU/C	1,4-dioxane	403K 12 bar	89,1
Other researchers	Ni-Ru	-	473 K 8 bar	97
Other researchers	Pt/TiO$_2$ Pt/ZrO$_2$	-	473K 40 bar	99,5
Horváth	RU/ PnBu$_3$	NH$_4$PF$_6$		95
Yang	CuO-CuOAl2O4	-	473K <70 bar	91
Hengne and Rode	Cu/Al2O3 Cu/ZrO2	-	473K 34 bar	100

Table 3: summary of the different studies
(32,35,36,38,40,41,42,45,47,50,58,59,61)

In a series of publications, Manzer studied the catalytic activity of a series of noble metals (Ru, Rh, Pd, Pt, Go, Re and Ni) supported on inert (carbon) materials with a 50% LA weight feed at 1,4 – dioxane. With Ru catalysts, the highest yields (97%) under operating conditions ranging from 150 to 215ºC temperature, 55 bar hydrogen pressure, and 2 to 4 h reaction time.

Gong et al. obtained 92% yield with the Ru catalyst (5%)/C using methanol as a solvent in a solution with 5% LA weight, 130 ºC and under 12 bar hydrogen pressure. They also studied performance while maintaining the catalyst but changing the solvent, in n-butanol, benzaldehyde, 1.4-dioxane, or dimethylsulfoxide but no appreciable reaction was observed.

Al-Shaal and col. studied the effect of different alcohols as solvents on reducing LA to GVL. Tests of 160 min reaction time were conducted with Ru catalyst (5%) /C at 130ºC and under 12 bar hydrogen pressure, with a feed of 500 mg LA in 10 mL of solvent. This research showed that the best solvent for this reaction was 1,4-dioxane (yield 95.9%), followed by water (86.2%), methanol (84.4%), ethanol (61%,) and butanol (31%). Excluding 1,4-dioxane, these results can be explained by the decreasing solubility of H2 in solvents (Henry constants of 7500, 596, 4,52 a, and 358 MPa, respectively). In addition, these authors compared performance when using Ru-(5%) /C with other catalysts that use different supports such as: Ru-(5%) /SiO$_2$, Ru-(5%)/Al2O3 and Ru-(5%)/TiO$_2$. The first has proven to be superior (GVL yield of 89.1% versus 74.9%, 76,.2% and 71.2%, respectively) from a LA (5% by weight) pet-ethanol solution (10% v of water) as a solvent at 130ºC

In more recent articles for the Ru case, they studied the production of GVL with Ni-Ru catalysts on carbon obtaining yields of 97% using temperatures above 200ºC and 8 bars of hydrogen pressure. Besides, in the case of Ni with a mixture with Cu over alumina the production of GVL has also been achieved, achieving 96% yield with reaction parameters of 250ºC and 6.5 MPa of hydrogen pressure.

Other noble metal catalysts have also been the subject of research for this reaction. This is the case of Pt, which is supposed to be one of the best hydrogenation metals on inorganic supports, although it requires higher temperatures than Ru.

Other researchers conducted trials using catalysts with various noble metals (1% Re, Au, Pd, Ru, Pt and some 50:50 alloys two of them) and different supports (TiO_2, ZrO_2, C, SiO_2) at 200ºC and 40 bar pressure H_2, concluding that Pt-(1%)/-TiO_2 and Pt (1%)/ZrO_2 are the most active catalysts reducing a LA solution to 89% by weight in GVL. Yields of up to 99.5% were achieved with little deactivation for more than 100 hours of permanent operation.

Horváth and his colleagues demonstrated the use of an on-site Ru catalyst using a combination of Ru and $PnBu_3$ phosphine that strongly donates electrons in the presence of NH_4PF_6 for LA to GVL hydrogenation. The reaction demonstrated the quantitative conversion from LA to with an iht yield of 95%.

Information on the use of non-noble metals as catalysts for GVL production is scarce compared to the use of noble metals.

Yan et al. achieved the reduction of an aqueous mixture with 16% by weight from LA to GVL with a yield of up to 91%, to 200(C and below 70 bar of H_2, with a Catalyst of CuO-$CuCr_2O_4$. Other catalysts provided lower yields: CuO- $CuOAl_2O_4$ (86%) and CuO-$CuOFe2O4$ (81%) (molar ratio Cu/metal 2 in each case) after 10 h of reaction.

A document prepared by Hengne and Rode includes the reduction of an aqueous solution with 5% by weight from LA to 200ºC under 34 bar of H_2 in 5 h. In contrast to Yan and cabbage results, they report 100% GVL performance using catalysts with Cu/Al_2O_3 and Cu/ZrO_2, while Cu/Cr_2O_3 catalysts only achieved 9% performance.

The production of GVL without the need for additional reaction solvent, such as agitation of fry acid mixtures with Ru-C as a catalyst under a hydrogen atmosphere resulting in a complete conversion, has also been investigated.

The Ru-C catalyst was removed from the product mixture by filtration and was observed to be recycled. It was observed that at low temperatures the catalyst has a better service life.

As it's known using formic acid as a source of hydrogen will prevent costly purification of fry acid. One aspect that has not been taken into account before is that this acid has to be removed before contactingcatalyst.yst..

Another important aspect is that during LA generation by hydrolysis of lignocellulosic biomass results in LA product currents that inevitably contain water, the presence of water in the currents of levulinic acid products could create an additional challenge concerning catalyst stability, so water-tolerant catalysts (such as Ru supported with TiO_2, A,l_2O_3 and SiO_2) were identified, eliminating the costly need to separate water from LA food before hydrogenation.

For the use of these catalysts, it is important to take into account the support structure of the catalyst support since the higher the specific area better will be the catalysis because it facilitates the absorption of the substrate and allows a greater dispersion of the Ru.

As a result of these studies, it can be concluded that the commercial catalyst Ru (5%) /C is the most used for this reaction, as Ru is a particularly active and selective metal for the hydrogenation process. It is also concluded that noble metals, including Ru, Re, Pd and, Pt, show excellent catalytic activity in converting formic acid to hydrogen, making them suitable for GVL production. But because the costs of these catalysts are very high in consideration with production costs have been considered other cheaper catalysts such as catalysts for noble metal alloys such as ZrO_2.

Despite the high efficiency of homogeneous catalysts, the need to separate catalysts from products can be a problem limiting their application on an industrial scale. Therefore, attention must be paid to heterogeneous catalysts, due to the ease of recovery of the product and the recycling of the catalyst associated with these systems makes them both economical and practical for large-scale processes.

One method considered for commercial-scale manufacturing of the a-valerolactone is the hydrogenation of the steam-phase fry acid. The main advantage of this system is that they are especially suitable for continuous processing. However, this methodology is energy-intensive, as the evaporation of LA requires high energy input. In general, the process could be facilitated by the development of a liquid phase hydrogenation system that can directly convert aqueous streams of levulinic acid products into GVL. The simplest uses hydrogen alongside a heterogeneous transition metal catalyst.

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4.5. NONANE OBTAINING

The strategy to produce nonane from the GVL is through the production of pentanoic acid, a hydrophobic product that is spontaneously separated from the water.

GVL solutions can be converted into pentanoic acid using combined ring-opening reactions (in acid sites) and hydrogenation (in metal sites) on a bifunctional (ZrO_2 +Pt/ Al_2O_3) catalyst, water-stable at moderate temperature and pressures.
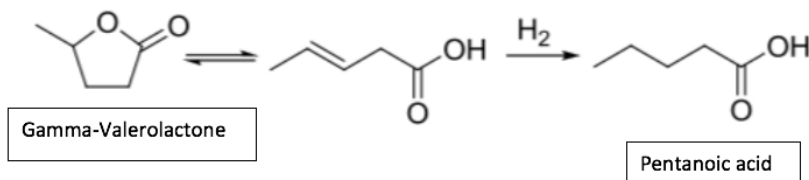

Figure 17. Production of pentanoic acid

The production of pentanoic acid is accompanied by the formation of n-butane, produced by the decarboxylation of pentanoic acid on metal sites with the release of stylometric amounts of CO_2, and the formation of n-pentane, as a result of successive hydrogenations and dehydrations of pentanoic acid on metal sites and acids respectively. The formation of these unwanted products and the performance of pentanoic acid is controlled by varying the load of the catalyst metal. A decrease in the metal contained in the catalyzer causes a significant increase in the performance of pentanoic ado under the same temperature and pressure conditions (62,37).
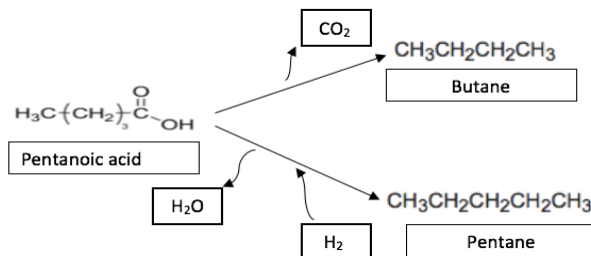
Figure 18. Butane and pentane production

Once the pentanoic acid has been produced, the star (nonane) product can already be produced by a double catalytic bed process.

In the first bed, 5-nonanone is formed by cetonation of pentanoic acid. The ketone decarboxylation reaction is a reaction involving the coupling of two molecules of carboxylic acids to give a ketone, water, and carbon dioxide. This reaction reduces the amount of oxygen in the final product in addition to eliminating the acidic function that in most cases implies disadvantages if you want to use biomass as fuel.

In ketonesylation of pentanoic acid first two pentanoic acid molecules react to give a molecule with nine carbon atoms in the chain, 5-nonanone (figure 15).
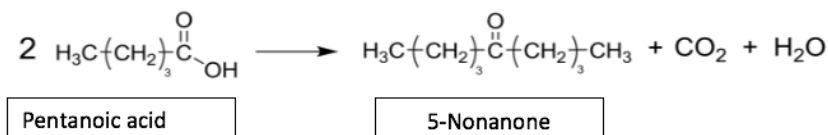

Figure 19. 5-Nonane production

This transformation can be carried out on a ZrO_2 catalyst. With this substrate, the acid conversion is greater than 80% to 350°C and increases as the temperature rises until 400°C. At this temperature the conversion is complete. Selectivity at 5-nonanone is around 90%, has a maximum of 95% (63).

Then the ketones formed in the first bed (5-nonanone) pass to the second bed of heterogeneous catalyst with a noble metal supported on metal oxide or active carbon ($2\%Pt/Al_2O_3$) for hydrooxygenate ketone to nonane which is the desired final product.

Hydro-oxygenation consists of a series of three reactions (figure 16), ketone hydrogenation, alcohol dehydratio,n, and alkene hydrogenation, which can cascade over a multifunctional catalyst. This hydroxygenationon is carried out on a catalyst of 2%Pt/Al$_2$O$_3$ (64).
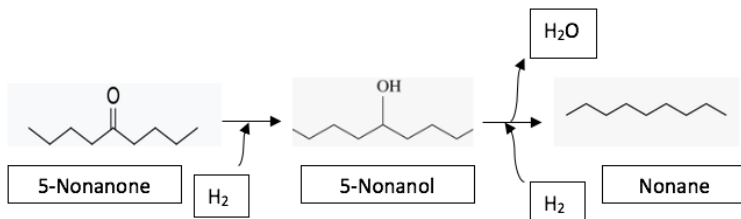

Figure 20. Hydro-oxgenation of 5-nonane

Cetone in the presence of hydrogen and by a catalyst that activates the reaction is hydrogenated obtaining the corresponding secondary alcohol, 5-nonanol. Hydrogenation is carried out at a hydrogen pressure of 40 bar as hydrogenations are favored when working under pressure (increases hydrogen concentration and adsorption are favored over active centers). Besides, ketonesic decarboxylation is not supposed to be affected by increased pressure during the reaction. Therefore, as a priori, it is likely that the two catalytic beds are active under the same temperature and pressure conditions, successive reactions in the same reactor are intended to be chained together and work with both beds in series.

Then 5-nonanol is dehydrated and the alkene is formed by the loss of the water molecule. Finally, the 4-nonene alkene is hydrogenated to alcano(nanano). This reaction is carried out cascading and on the same multifunctional catalyst of 2%Pt/Al$_2$O$_3$. The nonane desired product is a good liquid fuel.

The use of these two catalysts (ZrO$_2$ +2%Pt/Al$_2$O$_3$) as Optimus is demonstrated in a study, which obtained a non-ane selectivity of 80%, a fraction of hydrocarbons between C10 and C15 with 10% selectivity, a selectivity of 5-nonanone insignificant and the remaining 10% of the selectivity corresponded to other (non-oxygenated) hydrocarbons. All of this showed that metal support plays a key role in hydrosoxygenation. In the case of alumina the catalyst hydrogens ketone and alchein and dehydrates alcohol very effectively. Also, it is observed that the catalyst is stable and does not suffer appreciable deactivation during the testing period (65).
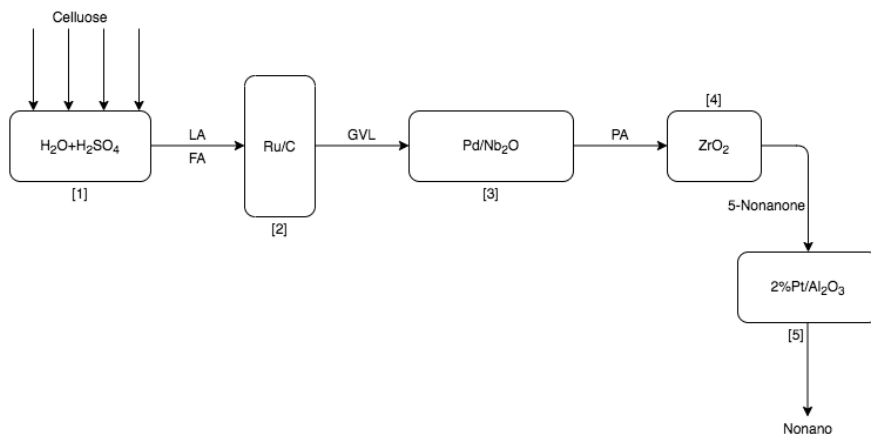
5. PROCESS PROPOSAL

Figure 21. Process proposal

[1] Cellulose is introduced gradually first, as it has been shown that this favors the reduction of humines. The subsequent procedures of obtaining the allynic acid are the same as in section 4.3.2., where a plug flow reactor is first used to promote the production of the HMF intermediate and then a perfect mixing reactor.

[2] The formed LA is hydrogenated to 4-hodroxipentanoic using the FA as a source of hydrogen and subsequently dehydrated to the GVL using Ru/C as a catalyst and 1,4 dioxane as solvent at 403-488K and 12-55 bar.

[3] Pentatonic acid is produced using the Pd/Nb_2O bifunctional catalyst.

[4] In this bed 5-nonanone is formed by the cetonation of pentanoic acid with a ZrO_2 catalyst with a temperature of 623-673K and 40 bar.

[5] The formed cetones pass to the second bed for hydrodesoxgenaring 5-nonanone to nonano with a catalitzador 2 %Pt/Al_2O_3 at temperature 623-673K at 40 bar.

6. CONCLUSIONS

According to the above throughout this document, it can be concluded that this is an interesting field due to the importance and the number of applications that LA acid has nowadays. Thanks to the research and bibliographic collection of the most relevant aspects of lignocellulosic biomass and existing technologies for processing, as well as by previous studies regarding the conversion of LA and GVL to nonane, it can be concluded that nonane could be a good alternative and a substitute of the "fòssil resources" to produce biofuel.

Obtaining nonane could bring social benefits because the lignocellulosic biomass used as raw material is a renewable resource that does not participate in food markets. Also, nonane is a less polluting product than oil, which means that it is more economical and environmentally friendly.

As for the implementation of the project, it is proven that it is feasible as there are already some studies carried out, although there is still a lack of knowledge to carry it on a commercial scale. The fact that there is already a pilot plant in Spain that produces levulinic acid from biomass is a good start since this acid is the raw material, therefore, half the procedure for obtaining the nonane would already be carried out, only more investment and research in the use of heterogeneous catalysts would be lacking.

Most of the studies claim that the optimal catalyst for gamma-valerolactone synthesis from fryulin acid is Ru/C, the problem is that these catalysts are very expensive therefore ZrO_2 would be a good substitute as a catalyst due to its lower price and that it is also a good catalyst for obtaining 5-nonanone from the pentanoic. In Section 5, the Ru/C catalyst has been proposed instead of ZrO_2, as much research of these catalysts is still lacking and most studies found to continue to use Ru/C as a catalyst.

On the other hand, the bifunctional catalyst Pt/ Al_2O_3 is the one that has been reported for the conversion of 5-nonanone to nonane since it is the one that produced the highest nonane performance in the bibliography found, although much more research is needed.

In this work, only the theory of the process has been deepened and not so much in the economy, although the fact that the majority of the products involved have many applications apart from the production of the nonane makes this process of firsts profitable.

All this concludes that more research is needed in the synthesis of nonane from levulinic acid. No experiments have been performed in this work but the information described has been taken from other studies. This work gives a standard of guidelines that could be carried out in a laboratory.

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ACRONYMS

LA: Levulinic Acid

FA: Formic Acid

HMF: 5-hydroxymethyl-furfural

NREL: National Renewable Energy Laboratory

US-DOE: U.S.Department of Energy

IEA: The International Energy Agency

DALA: D-aminolevulinate

FAME: Falty Acid Methyl Esters

MTHF: Methyl-tetrahydrofuran

CSIR: Continuous Agitated Tank Reactor

WALEVA: From Whatever Residue Into Levulinic Acid