Tutor/s

Dra. Montserrat Iborra Urios
Departament d'Enginyeria Química I Química Analítica

Dr. Javier Tejero Salvador
Departament d'Enginyeria Química I Química Analítica

Grau en Enginyeria Química

Treball Final de Grau

Obtaining butyl levulinate from fructose over acid solid catalysts with water removal.

Daniel Valdés Martín

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En primer lloc, m'agradaria agrair a la Dra. Iborra per tot el seu temps dedicat i per haver-me donat la oportunitat de fer aquest treball en el que he pogut aprendre no només nous coneixements, sinó també a valorar la recerca i el seu paper fonamental dins de la nostre societat. També a l'ajuda prestada per el Dr. Tejero, a qui li estic molt agraït per tota l'atenció i preocupació que ha mostrat durant tots aquests mesos i que tant m'han ajudat. Al Parc Científic de la Universitat de Barcelona, i en concret a l'Esther Miralles per dedicar-me part del seu temps que ha estat de molta ajuda.

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1. SUMMARY

Fossil resources are running out on our planet, while environment and sustainability concerns are gaining importance year by year. New targets have been settled in Europe in order to reduce emission of pollutants and particles to the atmosphere. In order to fulfill with these targets, a reformulation in transport fuels is needed since they are the principals originators.

Butyl levulinate is an ester which seems to be a potential additive in biodiesel blends. Its properties as boil point, viscosity or miscibility in water and in diesel, make it a suitable candidate. Its presence in biodiesel blends reduce significantly the emissions, and in addition, improve their cold flow properties. Synthesis of butyl levulinate is obtained through esterification of levuinic acid with butanol, which can be achieved from dehydration of monosaccharides like fructose or glucose, from alcoholysis of furfural alcohol or from levulinic acid.

Levulinic acid is a platform molecule which have a significant interest in industry. Is obtained by Biofine process, in which biomass is used as raw material. Nowadays, tarting from biomass is interesting. This is why it is being studied the feasibility of butyl levulinate synthesis from fructose or glucose. Previous studies have been made in order to evaluate the type of catalyst that can enhance the most butyl levulinate formation, with a temperatures range between 100 and 130 ºC and in atmospheric pressure. In this study, same conditions were settled in order to test which proportions between fructose and butanol, and which quantity of catalyst, can obtain the best results.

It has been observed the importance that water presence in initial mixture have regarding humins formation. Reducing the viscosity of the initial mixture enhances butyl levulinate formation and decreases humins presence. Molar rations between butanol and fructose around 6 gave better results than the others, and excepting one case, yields increased according with catalyst dosage.

.

Keywords: butyl levulinate, esterification reaction, fructose, alkyl levulinates, biofuels, biomass

2. RESUM

Els recursos fòssils del nostre planeta s'estan esgotant I la preocupació per la sostenibilitat I el medi ambient va agafant un paper més important any rere any en la nostre societat. A Europa s'han establert objectius per reduir la emissió de contaminants i partícules en suspensió a l'atmosfera. Per tal de complir aquests objectius, és necessari plantejar-se una reformulació dels combustibles utilitzats en el transport ja que són els principals emissors.

El butil levulinat és un èster que té interès com a additiu per les mescles de biodièsel. Les seves propietats com el punt d'ebullició, la viscositat o la miscibilitat en aigua i en dièsel, el fan un candidat perfecte. La seva presencia en les mescles de biodièsel, fa que les emissions a l'atmosfera es vegin reduïdes, i a més millora les propietats en fred del combustible. La seva síntesi passa per l'esterificació de l'àcid levulínic amb butanol, que es pot dur a terme a partir de la deshidratació de monosacàrids com la glucosa o la fructosa, a partir de l'alcohol furfural o bé partint del propi àcid levulínic.

L'àcid levulínic és una molècula plataforma que té un gran interès a nivell industrial. S'obté a partir del procés *Biofine* en el qual s'utilitza biomassa com a matèria prima. Partir directament de la biomassa és de gran interès. És per això que s'està investigant la viabilitat de la obtenció del butil levulinat partint directament de la fructosa. S'han realitzat estudis previs per avaluar quin tipus de catalitzador afavoreix més la formació del butil levulinat, en un rang de temperatures entre 100 i 130 ºC i a pressió atmosfèrica. En aquest estudi s'ha treballat en les mateixes condicions per avaluar quines proporcions entre fructosa i butanol, i amb quina quantitat de catalitzador, es poden aconseguir millors resultats.

S'ha observat la importància que té la presència inicial d'aigua en el sistema per la formació de humins. Reduint la viscositat de la mescla afavoreix la formació de butil levulinat i disminueix la presència final de humins. Relacions molars entre butanol i fructosa properes a 6 han donat millors resultats que la resta, i exceptuant un cas, els rendiments augmenten amb la massa de catalitzador.

Paraules clau: butyl levulinat, reacció d'esterificació, alquil levulinats, biocombustibles, biomassa.

3. INTRODUCTION

3.1. CURRENT ROLE OF BIOFUELS

Nowadays, an unsustainable situation is generated as energy demand increases along with the world population. In turn, this situation accelerates global warming. The main originator of that issue is the emission of the GHG, greenhouse gases. It is known that in the EU, an estimated 21% of the greenhouse gas emissions are produced by transport [1].

One of the first's steps of the European Community to start facing that issue was the Regulation No 443/2009 of the European Parliament and of the Council, in which the standards emissions for new passenger cars as part of the Community's integrated approach to reduce CO_2 emissions from light-duty vehicles were settled. The objective was the achievement, before 2020, of a 20% reduction of GHG emissions compared to 1990 levels [2]. The following regulations have established long-term emission reductions targets for 2030 and 2050, with a 40% and an 80% reduction respectively [3]. In order to fulfill these targets, there must be a reconsideration on fuels formulation.

Among all kinds of fuels, fossil fuels have been considered the most appropriate due to their high energy density and their availability. Besides, it was found that these fuels were the best option thanks to the advances made in their processing technology and their availability. This concern about sustainability though, have made consider the possibility of replacing fossil fuels for biofuels so it has been proved that fossil fuels are not a good solution in terms of reducing global warming. In addition, it is estimated that if human keep this consumption rate, crude oil will run out in 45 years [4]. Facing all these problems, biofuels seem to be the solution, considering that they pollute less than fossil fuels and they are made from biomass, which means that unlike fossil fuels they are made from renewable feedstock. Among all renewable energy sources, biomass is differentiated by two aspects: a low conversion efficiency of sunlight into energy stored in plants (1-3%) and the fact that any change in the biomass production will have an impact in any organism's life [5]. Four different generations of biofuels have been developed, according to their feedstock and sustainability level [1].

First generation biofuels are produced from food carbohydrates, vegetable oils, and animal fats [1]. They show some benefits regarding CO_2 emissions, such as cleaner and greener combustion, and they are also good blenders with petroleum-based fuels. Biodiesel, bioethanol, and biogas are the main biofuels of this group. They are getting increasingly competitive as the oil price has risen this last decade [6]. Biodiesel is produced by transesterification of vegetable oils and has a lot of profits: it can be blended with fossil diesel or as a full substitute as well. Bioethanol can have an important role, namely as a gasoline substitute. Although it can be a full substitute, it can also serve to produce ethyl tert-butyl ether [6], which blends more easily with gasoline. The problem with these first generation biofuels is the competitiveness with food crops, the dilemma of food versus fuel that made them an unsustainable choice. As mentioned before, the population on Earth keeps growing and so the demand of commodities as well, so betting on first-generation biofuels would mean use land that is potentially viable for food crops, to produce fuel, and consequently, the price of food would be affected [7].

Taking into account the first-generation drawbacks, more suitable and sustainable alternatives must be considered in order to confront the emission of GHG. Second generation biofuels are made from lignocellulosic feedstock which is totally viable since cellulose and hemicellulose can be converted to sugars through biochemical or thermochemical pathways [8].

One of the most promising thermochemical processes to obtain biofuels is the Fischer-Tropsch process, also referred to as Biomass-to-liquids (BTL) which its product, a syngas, is free of sulfur, nitrogen and aromatics content [9]. This process consists of a pre-treatment

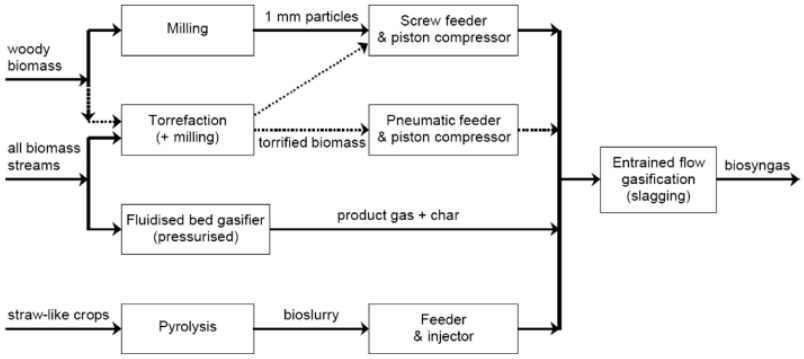


Figure 1. Four possible specific pre-treatment and feeding options for different biomass streams [59].

followed by three stages: gasification, cleaning, and conditioning. According to the type of biomass, the pre-treatment will be different as it is shown in *Figure 1*. Although there have been made many tests run in pilot plants, biomass-to-liquids is not very commercially expanded yet due to the lack of industrial development. In fact, in Europe, in 2013 the first biomass gasification plant was built in Vaasa, Finland, whereas when it comes to pyrolysis, there are a total of seven operational plants in Europe [10]. As biochemical routes, fermentation and transesterification are the choices to obtain bioethanol and biodiesel. With fermentation, the pretreated biomass is hydrolyzed by cellulose enzymes to obtain fermentable sugars [11]. The other option is to subject biomass to esterification and transesterification of free fatty acids and triglycerides, respectively [12]. These methods though, still have many drawbacks like low fermentability of mixed sugar stream or the generation of inhibitory soluble compounds *i.e.* 5-hydroxymethylfurfural [13].

In conclusion, even though second generation biofuels feedstock has a lower impact on total costs than the first generation biofuels (45-58%) [8], advanced technologies are needed to make them cost-competitive with fossil fuels, due to the current expensive costs that lignin treatment requires.

With second-generation biofuels, the land competitiveness between fuels and food remains solved, but the equipment and technologies to produce biofuels that are developed and well-established for first-generation feedstock, are not for the second generation. That is when a new kind of sources is needed and third generation biofuels are introduced. In this case, macro and micro algae are the feedstock. These organisms are surrounded by a lot of benefits, such as they don't need arable land (so fertilizers neither) and they can be cultivated all over the year [1]. Besides, higher photosynthetic efficiency than terrestrial plants makes them more potentially biomass producers, with a faster growth rate [7]. Among all types of algae, microalgae consist of lipids, proteins, and carbohydrates, and depending on the cultivation and the type of nutrients, their lipid content can be enhanced and reach up high levels (80% of weight). There are two main processes to produce biofuels from algae, anaerobic digestion, and trans-esterification. As shown in *Figure 2*, the first is able to produce methane, carbon dioxide, new biomass, and inorganic residues, and with trans-esterification of algae, methyl ester is produced, which is the most common component of biodiesel [14]. Huang et al. [15] produced microbial oil from sulphuric acid-treated rice straw hydrolysate by the cultivation of the

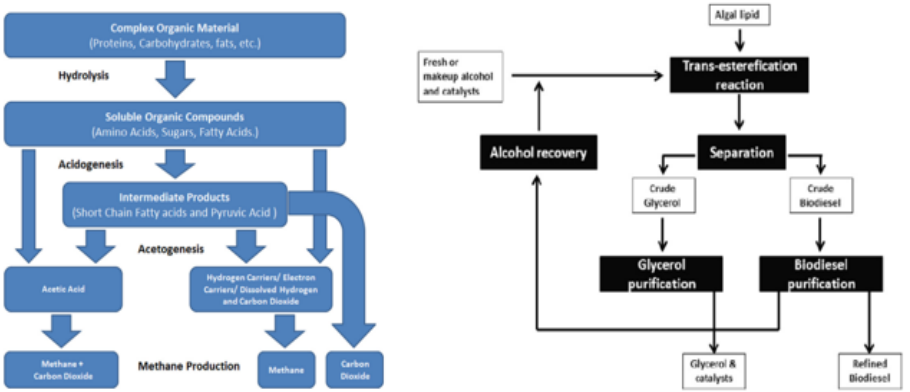


Figure 2. Schemes of anaerobic digestion process (left) and trans-esterification (right) [14].

microorganism *Trichosporon fermentans*, with lipid yield of 11.5 g/l which proves that this organism is capable of accumulate lipid with a high yield. However, it still needs more research to do in order to make them economically viable, and more investigating is needed since this new source of biofuels has been drawing attention as a promising sustainable source.

Finally, the fourth generation of biofuels, keeping the basis of the third generation which is the use of the capacity of algae to store high content of lipids, it enhances it with metabolic and genetic engineering of microalgae. There is some debate about whether the third generation includes metabolic engineering so then fourth-generation does not really exist. In any case, in this work, both are distinguished as two different generations of biofuels.

The aim is to acquire specific desired properties for micro algae in order to make them more efficient. These organisms can be cultivated in two ways, outdoor and indoor, with its benefits and drawbacks. Uncontained cultivation (outdoor) is done in open-pond systems and even though it is more difficult to control all variables of the process, the low energy requirements and the low operation costs, make outdoor cultivation the chosen operating mode for most companies [16]. Indoor cultivation is carried out in closed photobioreactor systems where variables like temperature, pressure and medium composition are controlled [17], so energy demand is higher which means that operating costs are also higher. Since this field is still under development, it has to be completely studied in order to prevent any possible damage, whether in human or environmental health [18].

At the moment, only the first generation of biofuels is at a commercial level since their technological advances and industry are well-known. Regarding the feedstock, both first generation and second generation are easier to obtain, but when it comes to processing it, second-generation biofuels feedstock still presents some difficulties. Nevertheless, the current production of biofuels is not as sustainable as desired. Therefore, many researchers keep working on finding more environmentally friendly alternatives. Since a complete substitution of fossil fuels it is not yet possible, blending them with biofuels is the most appropriate solution. Biodiesel can work both as a single fuel and in fossil diesel mixtures, which is the most common option. However, bioethanol must be blended since it would require many modifications in diesel engines [19].

3.2. ALKYL LEVULINATES AS BLENDERS

As it has been mentioned, blends of diesel and biodiesel are the provisional solution in order to reduce GHG emissions and start to replace fossil fuels. However, there is the possibility to improve the properties of these blends by adding other substances, additives that increase their oxygen content. Alkyl esters from levulinic acid are suitable as they can also improve the lubricity of the mixture, which prevents the engine from wear.

Biodiesel can present some important drawbacks when it is blended alone with fossil diesel, especially at low temperatures, where it can begin to gel and thereby clog filters and even increase its viscosity so it cannot be pumped from the tank fuel to the engine [20]. Cold flow properties are a key aspect of fuels performance, but first of all, a few important concepts need to be highlighted. When the temperature is decreasing, fuels nucleate and form wax crystals that remain suspended, then those with higher melt points start to crystallize until crystals are visible (0.5 μm), that temperature is the Cloud Point of the substance [21]. As the temperature keeps decreasing, the growth rate of crystals is accelerated and once they are have turned bigger, they can form agglomerates. When fuel no longer flows or turns solid is called Pour Point.

Different pathways to obtain alkyl levulinates are defined by the raw materials used and the type of reaction that occurs (Figure 3). Among all the possible sources, the most commons are cellulose, saccharides, chloromethyl furfural and alcohol furfural, from which many techniques have been developed in order to produce alkyl levulinates [22]. In this work, some of these sources are defined.

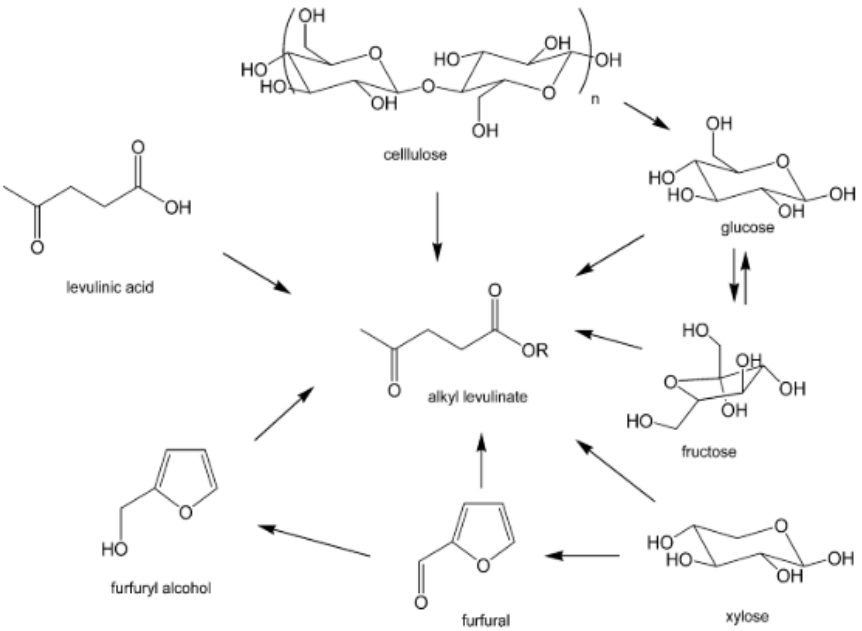


Figure 3. Synthesis of alkyl levulinates from various biomass reactants [23].

Alkyl levulinates can be produced through alcoholysis of furfuryl alcohol. This intermediate is produced by the reduction of furfural, which is obtained from xylose, a hemicellulose component of lignocellulosic biomass [23]. High conversions and selectivities are generally obtained through this reaction. Some research has been made, testing many different kinds of catalysts to find which is more suitable for this reaction. Srinivasa et al. [22] used titanium exchanged heteropoly tungstate catalyst for the production of ethyl levulinate, achieving a full conversion of furfuryl alcohol and product yield of 98%. Carbon-based ArSO3H catalysts with hollow mesoporous spherical morphologies were tested by Song et al. [24] and showed interesting results as well, with an 81.3% of ethyl levulinate yield. As furfural can be produced in high yields in a continuous flow, furfuryl alcohol can also be synthesized through continuous flow hydrogenation of furfural. This alternative was studied by Zhao et al. [25] using a catalytic bed-packed with zeolites and 80% of methyl levulinate yield was obtained, which proves that it has the potential to be industrially developed as well.

Another important pathway to obtain alkyl levulinates is by the esterification of levulinic acid with the corresponding alcohol (see Figure 4). One of the firsts direct esterifications of levulinic acid reported was carried out by Schuette et al. [26], where many alkyl esters were synthesized from levulinic acid in order to evaluate their vapor pressure. There is not an established and determined system for the production of alkyl levulinates from levulinic acid since a lot of catalysts and initial conditions have been proved. Russo et al. [27] studied the kinetics of levulinic acid esterification in a batch reactor and in two continuous bed reactors, with homogeneous (sulfuric acid) and heterogeneous (Smopex-101) catalyst respectively, and were able to estimate parameters and thus, run some simulations to compare them with experimental data. Another kinetics analysis was recently carried out by Zainol et al. [28] using lignin-furfural carbon cryogel catalyst.

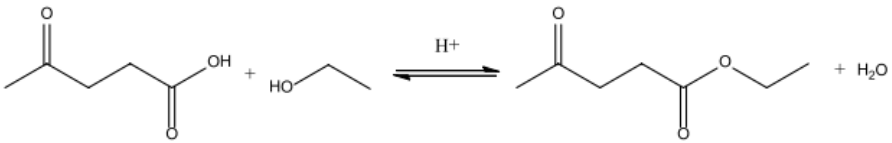


Figure 4. Esterification of levulinic acid with ethanol to produce ethyl levulinate [27].

Finally, there are some important sources that bring some great interest to the scientific community. Monosaccharides like glucose and fructose can be a feasible choice due to its availability and low-market price that make them easy to acquire, so they seem to be a perfect raw material. The reaction route goes through the formation of the intermediate *5-hydroxymethylfurfural* (5-HMF) to produce levulinic acid and then, by esterification with the corresponding alcohol, the formation of alkyl levulinates. The formation of ether species from 5-HMF can bring alkyl levulinates as well, by dehydration and rehydration [23]. The yield in this case though is lower than the other pathways mentioned above. The reason is that is a complex reaction system with multiple side-reactions that give undesired products.

As it is a promising source of some chemicals platforms production, namely alkyl levulinates, recently it has gained important attention for researchers. Liu et al. [29] used carbon nanotubes and nanofibers with sulfonic groups to produce 5-HMF and ethyl levulinate from fructose. The effect of temperature was studied testing the same experiment at 80, 100

and 120ºC, and could be observed how both, the yield of ethyl levulinate and conversion of fructose increased with temperature, reaching a top 86% of product yield with a full conversion of fructose. Ionic liquids with sulfonic acid-functionalized were also used to carry out the production of ethyl levulinate from sucrose, glucose, and fructose by Saravanamurugan et al. [30]. This study showed that selectivity towards ethyl levulinate decreased increasing fructose initial concentration, while selectivity towards di-ethyl-ether increased, with a full conversion of fructose.

A lot of research has been done to study the feasibility of ethyl levulinate as it seemed to be the most suitable alkyl levulinate to be blended with diesel. It shows good properties as low and high solubility in water and diesel, respectively, low cloud point, and density and viscosity values inside an acceptable range for diesel blends (see Table 1). But butyl levulinate has gained recently more attention due to the improved properties of blending it in comparison with ethyl levulinate blends. Christensen et al. [31] evaluated the properties of butyl levulinate and its blends with diesel to compare them with ethyl levulinate, and it showed less solubility in water and more miscibility with diesel. The only drawback detected is the increase in NOx emissions, due to the fact that blends with butyl levulinate have a lower cetane number than the ones with ethyl levulinate.

EN 14214-Property	Units	Low. Limit	Up. Limit	Test-Method
Ester content	% (m/m)	96.5	-	EN 14103
Density at 15ºC	kg/ m3	560	900	EN ISO 12185
Viscosity at 40ºC	mm2/ s	3.5	5	EN ISO 3104
Flash Point	ºC	>101	-	EN 22719
Sulfur content	mg kg-1	-	10	UV Fluorescence
Cetane number	-	51.0	-	EN ISO 5165
Phosphorus content	mg kg-1	-	10	EN 14107
Water content	mg kg-1	-	500	EN ISO 12937
Acid Value	mg KOHg-1	-	0.5	EN 12634
Oxidation stability at 110ºC	hours	6	-	EN 14112

Table 1.Limits and methods of testing for EN 14214 standard of B100 biodiesel [57]

3.3. ACID SOLID CATALYSTS FOR ESTERIFICATION OF LEVULINIC ACID

Solid catalysts have taken a fundamental role in the chemical industry since they are easy to separate from the rest of the products and reactants and easy to reuse them. Also, it is estimated that 90% of all the chemical processes use heterogeneous catalysts [32]. Among the heterogeneous catalysts, heteropoly acids (HPA), and namely zeolites play an important role in the research of biomass to biofuels, but more recently ion-exchange resins have gained attention as well.

3.3.1. Heteropoly acids and zeolites

Heteropoly compounds, also known as polyoxometalates, make reference to their heteropolyanion hierarchy. This kind of catalyst has a lot of benefits due to their polyanion structure mentioned before, and their acid and redox properties [33].

That structure is classified into three levels: primary structure, secondary structure, and tertiary structure. The primary structure comprises the polyanion structure, a central metal atom bonded to four oxygen atoms. Generally, there are two types of HPA regarding the primary

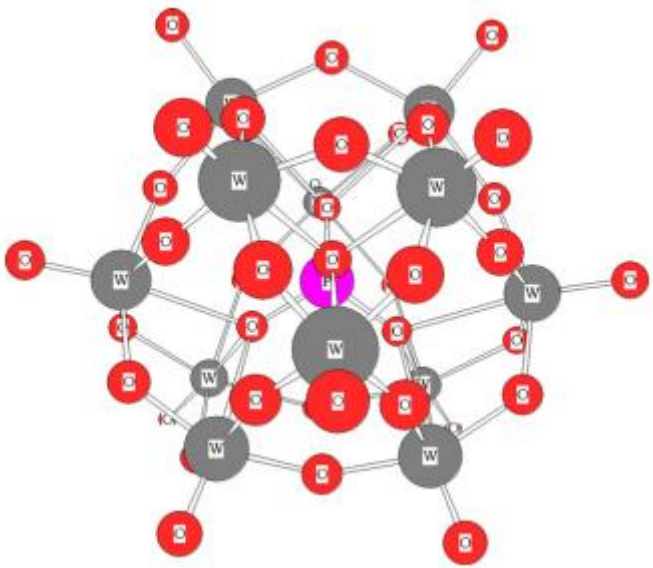


Figure 5. Representation of HPA with Keggin structure $[PW_{12}O_{40}]^{3-}$ *[58].*

structure type, those with Keggin units and those with Dawson units. HPA with Keggin structure (see Figure 5) is more used as a catalyst than the ones with Dawson, though [33]. The secondary structure is the three-dimensional sequence of polyanions, cations, and additional molecules, and it is variable and flexible. Finally, the tertiary structure shows how secondary structures are assembled to form solid particles.

Zeolites can be described as heteropoly compounds since they are a three-dimensional tetrahedral molecule, composed by one center atom of Si, surrounded by four oxygen atoms. This Si atom though, can be replaced for an Al atom and create a negative charge. These aluminosilicates framework material have microporous channels which interconnect cavities, and they can be readily synthesized offering good control over both pore size and three-dimensional structure [34]. Zeolites can have a wide range of applications, not only as a catalyst but also as ion-exchangers and adsorbents. When they are composed by the same amount of Al and Si atoms, their cation exchange capacity is maximum and can be used in detergents. For catalytic applications, a framework mostly composed by Si atoms is more appropriate since high temperatures are needed for catalytic and regeneration cycles [35].

Kalpana et al. [36] tested various acidic zeolites for the esterification of levulinic acid and it was founded that the most suitable zeolite was H-BETA, with large pores, giving an 82.2% of LA conversion with a 100% selectivity towards butyl-levulinate. Saravanamurugan et al. [37] went further and tested zeolites for direct transformation of glucose to methyl levulinate and ethyl levulinate, achieving 49% and 41% of product yield, respectively.

Heteropolyacids can present some drawbacks as a catalyst like low surface area, poor mechanical strengths or solubility in polar solvents [33]. It has been found that zeolites can offer good performance as support of HPA since they are hydrothermally stable and present a larger surface area [38]. Manikandan et al. [38] found that silicate-1 offers better performance as support of HPA with intracrystalline nanovoids, since they increase the external surface area and enhance dispersion of HPA as well. There are other substances that can work as support of HPA too, like organic polymers, active carbon, SiO_2, TiO_2 or ZrO_2. However, those with high silica content appear to be the favorite used in experimental literature [39].

3.3.2. Ion-exchange resins

Ion-exchange resins have a crucial role in today's chemical industry, especially in water treatments. They are very abundant in dehydration processes, i.e. condensation of alcohols to ethers, alcohols to alkenes, conversion of carboxylic acids to acid anhydride or amides to nitriles. Ion-exchange resins also take part in hydrogenation and alkylation reactions, and very important in esterification for the production of value added petrochemicals and oleochemicals, among others [40].

They have a cross-linked functional polymer matrix composed of copolymers of divinylbenzene and styrene, with sulfonated acid groups grafted on its benzene rings [41]. There are two morphological types of functional resins: gel-type and macroreticular. Gel-type resins in dry state do not offer any kind of porosity which means zero internal surface area, and only a few catalytic sites are appreciable on the surface. These conditions in dry state indicate that they need a swelling medium. Therefore in swollen state, they present mesopores that make the interior of the resin accessible, besides micropores (for inaccessible parts of the matrix). Macroreticular resins already present macropores in dry state, but they also have micropores due to the swelling of the polymer matrix.

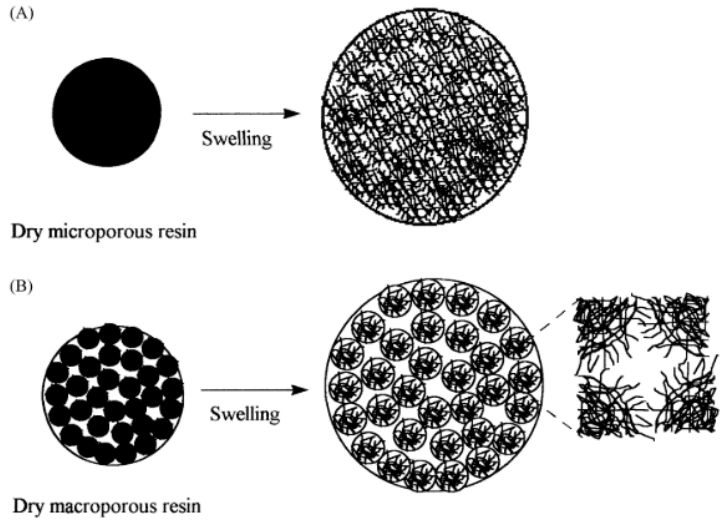


Figure 6. Representation of dry and swelling state of gel-type (A) and macroreticular (B) resins *[42]*.

The difference in both types of resins is made when copolymerization of the matrix is carried out, wherein macroreticular resins this happens in the presence of a certain solvent that gives these permanents pores to the resin. The main parameter that characterizes the resin is the cross-linking content (divinylbenzene), which determines the surface area and the pore size distribution. These values will rule the three main stages of ion-exchange resin catalysis, absorption, reaction, and desorption. Both gel-type and macroreticular are supplied as spherical beads between 0.3-1.25 mm of diameter, but some types also can be supplied as powder, particles with less than 0.22 mm of diameter [42].

Ion-exchange resins have always been object of study, since they are potentially useful in a wide range of applications. Alexandratos et al. [43] studied their feasibility for selective complexation of metal ions, synthetizing bifunctional ion-exchange resins with different cross-linking degrees to see which one gave the rigidity needed for these kind of reactions. Also and as mentioned before, ion-exchange resins are very used in catalysis of esterification and transesterification. Wang et al. [44] studied the upgrading of bio-oil properties such as viscosity, stability and heating value, converting the organic acids that were present into their corresponding esters. They utilized 732 and NKC-9 resins, both macroreticular. Another study, carried out by Özbay et al. [45], tested Amberlyst and Dowex resins in order to reduce free fatty acid content of waste cooking oils, which can cause undesired saponification reactions when transesterification of waste cooking oils is needed to produce biodiesel. They also studied the effect of catalyst amount, concluding that conversion increased with increasing reaction temperature and catalyst mass. Regarding to alkyl levulinates, as it has been said that some esters of levulinic acid are high potential additives for biodiesel, ion-exchange resins have been used to study their behavior in esterification of levulinic acid. Tejero et al. [46] concluded that, even though Amberlyst resins (macroreticular) presented great accessibility of their surface active sites, their low number make Dowex resins (gel-type) more suitable due to their higher reaction rates. Furthermore, reaction rates increased with reduction on cross-linking degree, so the resin that showed better results was the one with less divinylbenzene content (Dowex 50Wx2, 2% DVB).

4. OBJECTIVES

Biomass to biofuels is a new step that society must take in order to reach all the objectives settled. Alkyl levulinates are already known as a potentials biodiesel additives but there is still a lack of study in their production to rise them on a commercial level.

Along with other works, this study is a contribution of a larger project focused on the synthesis of fuel additives derived from biomass. The aim of this current study is to set the conditions which are the most suitable for the production of butyl levulinate from fructose, regarding the proportions of the reactants and the mass of catalyst used.

These experiments will be carried out with water removal, which is expected to enhance the reaction since it moves the equilibrium towards the production of butyl levulinate. Besides, the presence of water in this kind of reaction systems can be harmful, since the production of humins might be promoted by water presence.

5. EXPERIMENTAL SECTION

5.1. MATERIALS: REACTANTS AND CATALYST

For all the experimental part of this work, various substances have been used. As reactants, 1-butanol (99.5%, ACROS ORGANICS, Code: 232080025) and D-Fructose (99%, Alfa Aesar, Lot: 10207896 and Labkem).

As there are already other studies that have focused on evaluate which catalyst can offer better performance in the synthesis of butyl levulinate [47] [48] [49], this work has not tested more than one catalyst, because the effects to study were others as has been said in the objectives. The catalyst that has been used in all experiments is an ion-exchange resin polystyrene-divinylbenzene conventionally sulfonated (CS) and gel-type, Dowex 50Wx4 (Dow France S.A.S., Code 20580).

For the Gas Chromatograph (GC) calibration, the same butanol has been used with butyl levulinate (98%, Aldrich Chemistry, Code: 101495705), Di-n-butyl ether (99+%, ACROS ORGANICS, Code: 149690010) and butyl formate (98%, ACROS ORGANICS, Code: 403541000).

To heat the mixture as a hot fluid, it has been used silicone oil for heating baths LBSil 100 AUX (Labkem, Batch no.: 18C24485ABM). Finally, grease is used in order to lubricate the joints and make easier the dismantling of the equipment.

5.2. EXPERIMENTAL SETUP

All the experiments have been carried out in the same installation composed by a distilling flask, a Dean-Stark connected (AFORA, 5366/2E) and a Dimroth condenser (DRA). The distilling flask contains the mixture throughout the experiment and has one liter of capacity and three ground-necked. The angle-neck is used for a sounding line to measure temperature, the central neck for loading the reactants and the other one is connected to the Dean-Stark.

The Dean-Stark apparatus consists of a vertical tube with a stopcock on the bottom and a protruding tube which goes connected to the distilling flask, all made of glass. The top is opened to get engaged with the condenser. The principal tube is graduated with a total volume of 25 mL. This piece has a lot of importance because is the one responsible for the water removal. During an experiment, the vapor gets condensed and is deposited on the principal tube where two layers are formed. The upper layer is the organic, and the lower is the aqueous, due to the fact that water has a higher density than the organic compounds condensed. As water remains at the bottom, the stopcock allows remove it so it has no way back to the distilling flask.

The Dimroth condenser is a wide tube of glass with a cooling coil inside. This cooling coil has its enter and exit on the upper part of the tube while the top is opened. It is recommended that the condensed front does not get over a quarter of the tube length, so this must be controlled with the cooling water flow.

There are other essentials devices that make the installation works. The temperature meter (CRISON thermometer 621) able to handle six sounding lines (although only one it has been used), by which the temperature of the mixture inside the distilling flask is measured. To heat up the mixture, a heat-stir SB162 (StuartR) is used, so it also supplies the stirring. Thereby the temperature and the stirring can be regulated up to 300ºC and 900 rpm respectively.

Figure 7. Installation used and its parts indicated.

Samples analysis are carried out in a gas chromatograph 6890N Network GC System (Agilent Technologies). The column where the samples are injected within it is 20 micrometers of internal diameter, 0.5 micrometers stationary thickness, and 50 meters length. Helium gas is used as a carrier gas and methyl siloxane as the stationary phase.

GC runs analysis method FRUCTOSA_BUOH_MANUAL.M, where initially the oven is at 60ºC and holds it 2 minutes. Then the first ramp starts and oven temperature begins to increase with a 10ºC/min rate until it reaches 120ºC when the second ramp starts with a 15ºC/min rate until it reaches 250ºC. Once the oven is at 250ºC, it holds this temperature 8 minutes, then the analysis is over with a total of 24.67 minutes of running time.

5.3. EXPERIMENTAL PROCEDURE

5.3.1. Catalyst treatment

An acidic ion-exchange resin has a very sensible behavior so it needs to be treated carefully. This resin is commercially sold in a very wet state, so it must be dried before use it. With the help of a spatula, the desired quantity of resin is deposited in a porcelain plate. Then it must be putted in the oven between 14 and 24 hours before use it. It has to be known that approximately, for 4-5 grams of wet resin, there is 1 dried, so if 3 grams of resin is needed, between 12 and 15 grams of wet resin must be taken.

Once the resin is taken out of the oven, it must be saved in a closed glass because is very hydrophilic and it can absorb easily the humidity of the air. To weight the desired quantity of resin, a box of paper is used. Finally, when it is time to load it to the reactor, a funnel of paper can help if the neck is so tight that there is danger of throw it out of the flask.

5.3.2. Reactor loading

It will be tried that the volume mixture is always 400 mL approximately, so with a fixed ratio of reactants, their quantities can be known. First, all reactants are weighted before to put them in the reactor. As has been said above, the central neck will be used to load both reactants and catalyst. Butanol must be loaded first with the magnetic stirring device switched on, so then fructose can get mixed avoiding stirring issues due to the viscosity of the mixture. It must be loaded bit by bit anyway.

5.3.3. Experimental launching

When all reactants are already loaded, a final check to the installation must be done. All the joints must be checked so they are enough closed to avoid any possible leak. The level of the oil bath must be over the level of the mixture in the distilling flask, in such a way that it stays immersed. Also, the stopcock of the Dean-Stark must be closed. As said before, the stirring is already working so only the heat must be switched on at 225ºC approximately. The refrigeration valve is opened too.

The mixture will take between 20 and 30 minutes to reach 99-100ºC and then the first drop falls into the Dean-Stark. This is considered time zero, so the experiment starts at this moment.

5.3.4. Sampling

When time begins to count, temperature and volume of the aqueous phase in the Dean-Stark are measured every 5 minutes and every 10 minutes when the rate has decreased enough. Every time the level of the aqueous phase reaches 20 mL, the stopcock is opened and 10-12 mL are removed and saved in a glass pot.

The experiment ends after 8 hours from time zero and then the heat is shut down. It is recommended that the stirring keeps working because if it is switched off too it may cause some turbulence inside the flask that can get to the Dean-Stark and contaminate the organic phase. Once the mixture is no longer boiling, the stirring can be switched off. Then, the aqueous and organic phases are saved both in different glass pots. The installation is dismantled and the remainder inside the flask is saved in another pot as well. All samples are weighted once they are collected.

5.3.5. Samples analysis

All three samples are analyzed in the gas chromatograph. Three replicates are done for each sample. As it has been said, the method loaded for analysis is FRUCTOSA_BUOH_MANUAL.M. Only 0.2 µL is needed for each analysis. When the GC is ready, the syringe is putted in the manual injector, and button Start is pressed. The syringe piston is not pushed yet until the time analyzed does not reach 0.1 minutes, then is pushed with one and fast movement, trying to make it as an impulse input. When the time passes 0.5 minutes, the syringe is extracted from the injector.

When samples from the flask are analyzed, after each injection the syringe must be cleaned with acetone. That is because these samples can content different viscous polymers that might damage the inside of the syringe.

In order to analyze all compound, those samples extracted from the flask are taken to the Separation Techniques Unit inside Scientifics and Technological Services from the University of Barcelona. An HPLC column is used, composed by a 2695 Separations Module, a 2414 Refractive Index Detector, and a 2996 Photodiode array detector, all from Waters.

5.3.6. Clean-up

Regarding the gas chromatograph, once all samples have been analyzed low-consumption mode is activated. All samples are labeled and stored in the fridge. The distilling flask is cleaned and prepared for the next experiment. A chromium mixture can be used to clean it if it is necessary.

5.4. EXPERIMENTAL CONDITIONS

All the experiments carried out had a duration of 8 hours as said before. The pressure was the atmospheric and the temperature was started at 20ºC ad up to a range of 115-120ºC. The stirring was settled at 300 rpm, but at the beginning, the stirring could not work at this rate due to the viscosity inside the flask. Thus, initially stirring was settled at a low rate, and then while the mixture is starting to heat up, increased slowly. As the aim of this study is to optimize all reactants and catalyst proportions in order to have the maximum butyl levulinate production, their quantities were varied through all the experiments. Butanol mass though was fixed at 355 mL which corresponds to 288 g.

The mass of water used to dissolve fructose was limited due to its immiscibility with butanol at some proportions. At 20ºC, the solubility of water in 1-butanol is 20.1 w/w% [50] so this means that with a mass of 288 g of butanol, the maximum quantity of water avoiding a two-phase formation inside the flask would be 60.5 g. The formation of two phases inside the flask is an undesired fact because it would affect directly the reaction, making the system less homogeneous. Besides, to analyze the sample of the flask, as the composition would not be the same at every point, the output of the analysis would not be reliable. So all of this can be avoided adding the correct amount of water and also with the removal of water thanks to the Dean-Stark.

6. RESULTS AND DISCUSSION

6.1. CALCULATIONS

Some parameters of the reaction must be calculated in order to obtain a quantitative analysis of the experimental part of this work. Selectivities and conversions could not be calculated due to the composition and nature of the samples, which contaminated the output signal of HPLC (*see Appendix 4*). The yield of a product was calculated with the following equation:

$$Y_k = \frac{moles\ of\ k\ produced}{initial\ moles\ of\ fructose}$$

where k can be any product such as butyl levulinate, butyl formate, 5-HMF, levulinic acid, formic acid, dibutyl ether or butoxymethyl furfural. Due to the issue regarding the HPLC, only butyl levulinate and butyl formate yields could be calculated.

In order to compare all the experimental outputs, time must be normalized with the expression below:

$$standardised\ time = time\ [min] \times \frac{catalyst\ mass\ [g]}{initials\ moles\ of\ fructose\ [mol]}$$

which gives an approach of contact time between catalyst and reactant, and it has to be taken into account since every experiment had different initial conditions.

Concentrations of water, butanol, butyl levulinate, butyl formate, dibutyl ether, and butoxymethyl furfural were calculated by the expressions from the gas chromatograph calibration (*see Appendix 2*). Samples were measured three times to minimize experimental error. Also, it was revised that all experiments had shown less than 10% of mass balance error, so their results could be reliable.

6.2. SETTING INITIAL CONDITIONS

The first experiments were carried out to observe and study the behavior of the system. A molar ratio of 10 between butanol and fructose was settled on the firsts 5 experiments, and no water was loaded on the first 3. Due to that, the first problem that was detected was the viscosity. The magnetic stirrer was not able to spin with the mixture only composed by butanol and fructose, and a huge presence of humins was detected so adding water was considered as solution.

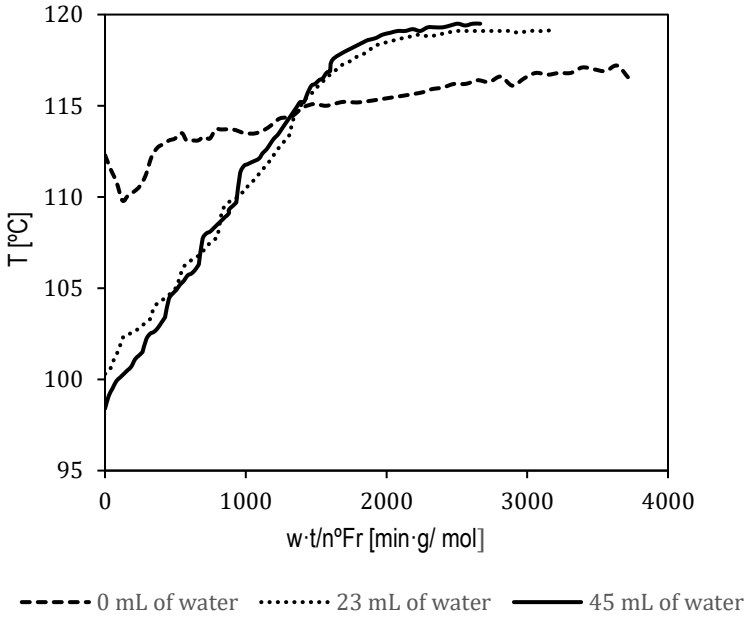


Figure 8. Temperature monitoring of the reaction varying the amount of water loaded. Between 2 and 3 g of catalyst was used.

As can be shown in Figure 6, the boiling point of the mixture decreases with the increase of water loaded. That is expected because without water, the boiling point of butanol which is the reactant in excess, is 118ºC, so when fructose is reacting producing water, in the experiment with 0 mL of water added, the boiling point of the mixture is 112.3ºC. Another point that can be noticed, is that the progression of temperature without water is lower than the others. As it has been said above, the problem of viscosity prevented the mixture from a fluency stirring. That harms the reaction and is traduced in a low maximum temperature, which corresponds with a

low production on butyl levulinate (which have a boiling point of 130ºC approximately). The minimum amount of water necessary will be added since its presence moves the equilibrium towards reactants, which is the reason of why is then removed in the Dean Stark. When fructose undergoes dehydration to produce intermediate 5-HMF, three molecules of water are released for each molecule of fructose, so less content of water enhances this reaction [51]. Although two molecules of water are consumed for each of 5-HMF in order to form levulinic and formic acid, water is released again in esterification of both organic acids. Besides, butanol is in excess so part of it can go through dehydration to form dibutyl ether, where another molecule of water is produced. Butene formation can also be considered, which would release another molecule of water, but its formation cannot be detected due to its high volatility.

The presence of humins was detected but even though it is known that having water in the system favors its production, an increase of butyl levulinate production was observed so for the next experiments an amount of 45 mL of water approximately, was added. In the following table, it is shown the initial conditions of all experiments (see also Appendix 1).

Experiment	$\mathbf{R_{BuOH\text{-}Fr}}$ [mol/mol]	$\mathbf{R_{BuOH\text{-}Water}}$ [mol/mol]	**Catalyst** [g]
2	9.84	-	2.988
3	9.93	-	3.194
4	9.96	2.99	2.456
5	10.02	1.61	2.046
6	5.98	1.52	3.622
7	4.95	1.51	3.717
8	4.92	1.54	7.105
9	5.99	1.54	7.002
10	5.37	1.47	3.018
11	5.55	1.59	7.064
12	6.90	1.53	3.521
13	5.90	1.53	7.131

Table 2. Initial conditions for all the experiments.

6.3. DESCRIPTION OF A TYPICAL EXPERIMENT

Figure 7 shows an example of an experiment, with its evolution of both temperature and water recollected. The evolution is quite similar in all experiments, as temperature varies between 100 and 119ºC (it never reaches 120ºC). Water must be removed every time that aqueous phase level is approaching the upper zone of the Dean-Stark, in order to avoid its recirculation. When this is done, the level of organic phase is reduced and recirculation is interrupted until it is reached again. That causes little increases of temperature which can be

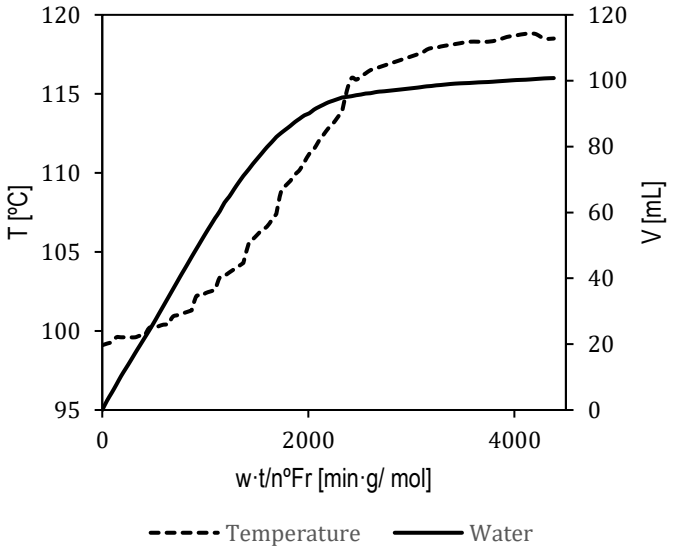


Figure 9. Evolution of experiment 8.

observed in temperature line. It can be observed that the first half of the experiment, the production of water follows a lineal tendency, while temperature has more an exponential behavior. When water production rate is slowed down, it means that reaction is ending, so temperature progression is interrupted as well.

While composition inside the flasks were different, organic phase were similar and aqueous phase almost equal in every experiment. That is expected to happen, because the same volatile compounds were always present in the mixture so they are going to boil with the same fraction. Butanol is in excess in every experiment and is miscible in little quantities with water,

so will be detected in every aqueous sample. Butyl formate is more volatile and is a product of esterification of formic acid. It can also be produced from butoxymethyl furfural, but in a less portion. That can explain that its fraction will be more sensible as will vary in organic phase more than butanol in aqueous phase. In figure 10 it can be seen examples of typical compositions of both aqueous and organic phases.

Regarding the flask samples, their composition had an important fraction of butanol non reacted (because it was loaded in excess) of approximately 80% in mass. The rest of compounds such as butyl formate, butyl levulinate, dibutyl ether, and buthoxymethyl furfural were detected with more varied fractions. As organic acids cannot be well detected in a gas chromatograph, formic and levulinic acid were not quantified but it could be observed their presence with little peaks at 5 and 15 minutes of elapsed time, respectively.

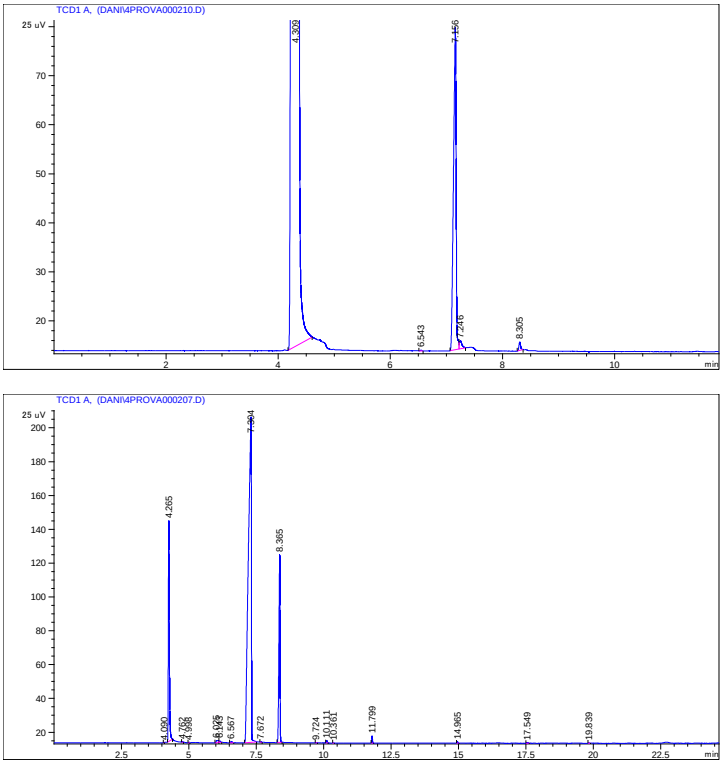


Figure 10. Composition of experiment 13, aqueous phase (above) and organic phase (below).

6.4. EFFECT OF CATALYST MASS

Besides the quantity of reactants, different amounts of catalyst were also chosen to evaluate its optimal load for the production of butyl levulinate. Mostly of experiments have been tested with 3-3.5 g and 7 g of catalyst. First thing to take into account is that increasing the mass of catalyst, increases the contact time between catalyst and reactant, and this can be shown in Figure 10.

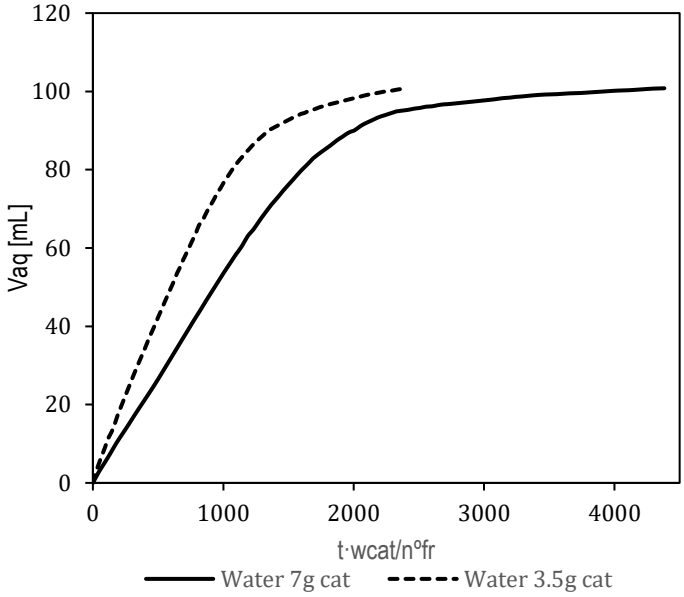


Figure 11.Comparison of water recollected of experiment 7 (3.5 g of catalyst) and experiment 8 (7 g of catalyst).

With the same physic time (8 hours), it can be observed that the line corresponding to 7 g of catalyst has more contact time for reacting (lower slope), so therefore is expected to enhance butyl levulinate production. The effect on temperature is the same, as it increases according with the reaction evolution. Maxim temperature and total water recollected values do not have any appreciable change or increase by increasing mass catalyst

As it has been said, it is expected for butyl levulinate production to be enhanced increasing contact time between catalyst and reactants. Next figure shows the butyl formate and levulinate concentration obtained in the flask regarding to catalyst and fructose loaded.

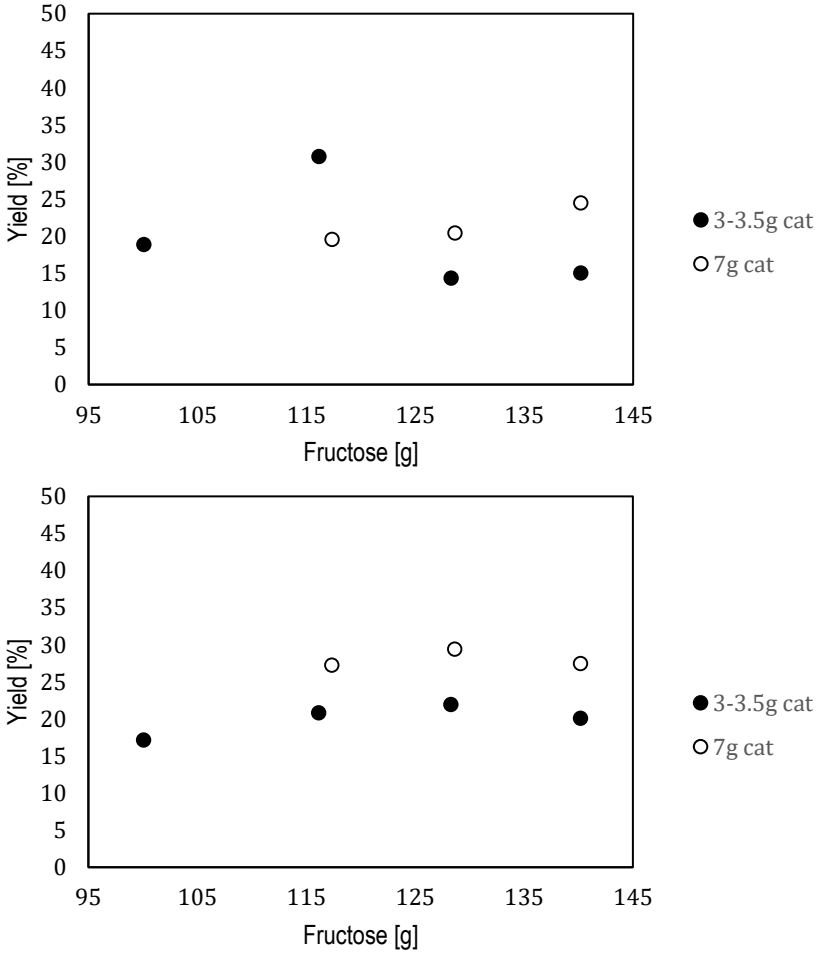


Figure 12.Yields of BL (above) and BF (below) regarding the catalyst mass.

It can be observed that results are quite as expected. With more catalyst dosage, yields for butyl formate are higher than with less dosage. For butyl levulinate, although at higher fructose loads yields increase according catalyst mass, there is one case in which its yield is quite higher with less catalyst. No explanation has been found for this isolate case

6.5. BUTANOL-FRUCTOSE MOLAR RATIO

The primary objective of this work was to set the proportions between fructose, butanol, and catalyst that could give better results, and it has been already seen how the amount of catalyst affects the reaction yield. The total of butanol loaded was fixed at 355 mL, so the amount of fructose was the manipulated variable. As explained before, viscosity had an important role on the feasibility of the experiments, so it could not be loaded a huge quantity of fructose because it would have required a bigger quantity of water to avoid stirring problems, and the amount of water was restricted for its miscibility with butanol. Hence, as it can be shown in Table 2, the fructose loaded went from 69 g to 140 g.

With the quantity of butanol fixed, it is about to study which quantity of fructose favors more the desired reaction. In the following figure, it is shown the yield of butyl levulinate and butyl formate for each experiment. Also this results can be read in Table 3.

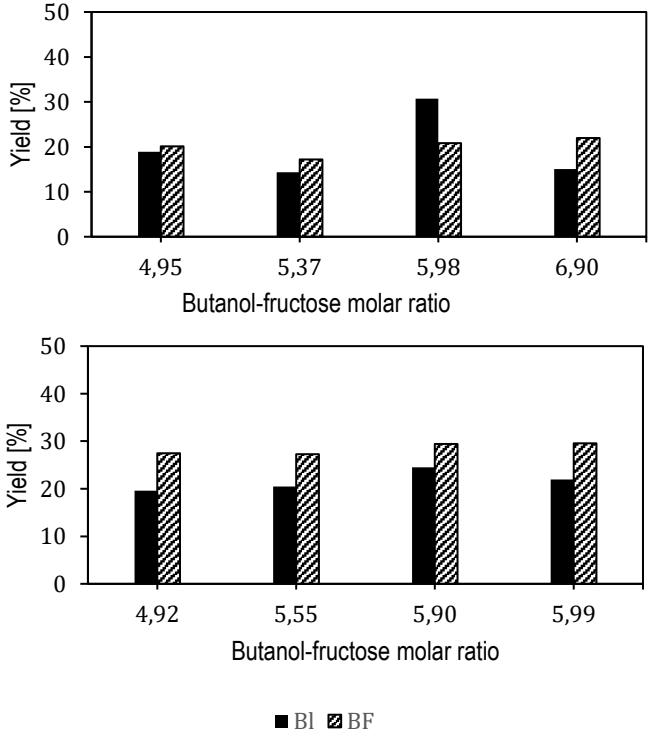


Figure 13. Different yields of butyl levulinate and butyl formate with 3-3.5g (above) and 7g (below) of catalyst.

By observing this plot, it can be easily seen that higher yields are around a molar ratio between butanol and fructose of 6. Regarding butyl formate, there is no appreciable variation as all yields are quite similar.

Experiment	**Fructose** [g]	**Catalyst** [g]	**BL Yield** [%]	**BF Yield** [%]
6	5.98	3.622	30.72	20.83
7	4.95	3.717	18.90	20.09
8	4.92	7.105	19.56	27.47
9	5.99	7.002	21.98	29.56
10	5.37	3.018	14.35	17.17
11	5.55	7.064	20.44	27.27
12	6.90	3.521	15.05	21.94
13	5.90	7.131	24.49	29.40

Table 3. Different yields of butyl levulinate and butyl formate of each experiment

6.6. HUMINS FORMATION

As it has been commented, humins were detected in all experiments carried out. It is an important part of this work to try to minimize any aspect that can harm the reaction yield, so humins production deserves to be discussed. Literature about char formation during this kind of reactions has been searched in order to compare it with the results obtained in this work.

Formation of humins is not exactly understood yet, but everything seems to indicate that is a condensation cross-polymerization of 5-HMF with fructose [52]. Dee et al. [53] proposed a mechanism for the formation of humins, in which an oxocarbonium ion is formed after protonation of an aldehyde group of 5-HMF reacted with a fructose molecule. Then a cyclic compound is formed when the oxocarbonium ion reacts with a cis-hydroxyl group of fructose. Then, another oxocarbonium ion is formed by protonation in the hydroxyl group of 5-HMF or fructose. This will allow propagating the molecule in order to form higher molecular weight products. A schematic vision of this mechanism is shown in the following figure.

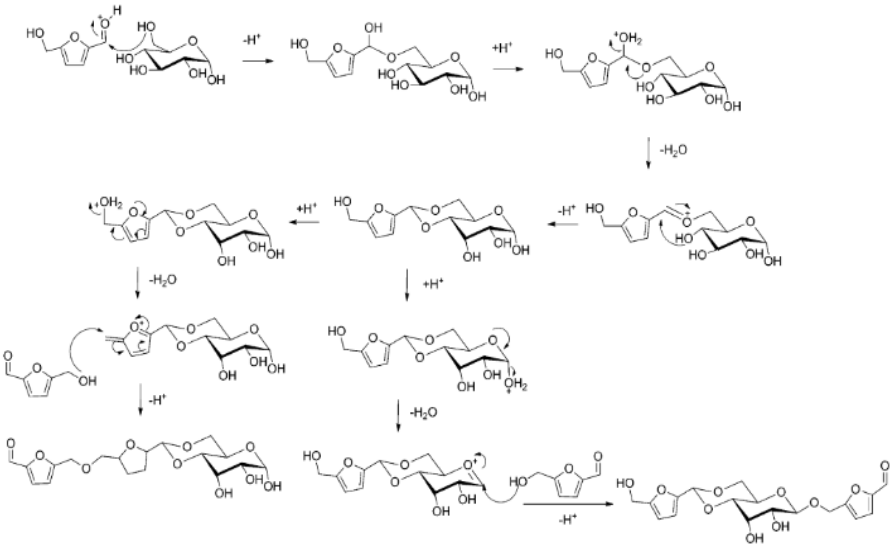


Figure 14. Mechanism suggested by Dee et al. *[53]* for the production of humins.

Chuntanapum et al. [54] studied the role of the intermediate 5-HMF in humins formation, and they observed that polymerization occurred more from glucose dehydration than from 5-HMF as reactant. This suggests that it is more important the interaction between glucose and fructose with 5-HMF, than other compounds that can be formed just with the presence of 5-HMF. This study gives credit to mechanism proposed by Dee (Figure 14). Humins formation just from 5-HMF, without interacting with a monosaccharide, was studied by Patil et al. [55] and they could support a proposed model which says that humins from 5-HMF are formed from 2,5-dioxo-6-hydroxy-hexanal, instead of being formed from levulinic or formic acid.

In this work, humins could not be quantified and their visual detection was quite similar in all experiments**.** Their presence though, can be detected in chromatograms of HPLC. Since these polymers are formed from 5-HMF and fructose, their molecules have similarities with the others and their response in the analysis is expected to have the same features.

Fructose could only be detected by RI detector, whereas 5-HMF was detected by UV absorbance detectors in a wavelength of 285 nm. Their retention times were 8.83 minutes and 27.86 minutes, respectively. All signals had numerous peaks that did not correspond to the compounds of patterns. In addition, in some cases the peak expected to be found at some

retention time is covered by a heavier peak with a similar retention time that is superimposed, which is the main reason that any compound could not be quantified with HPLC analysis. Dilutions were made and less quantity of sample were injected in order to have cleaner signals but it was not enough and peaks were still covered. A detailed purification study would be required in order to isolate the desired peaks, taking into account the nature of every compound, but this would involve more research which escapes from this work's magnitude. Two chromatograms are shown in the next figure to appreciate the humins presence surrounding fructose and 5-HMF peaks:

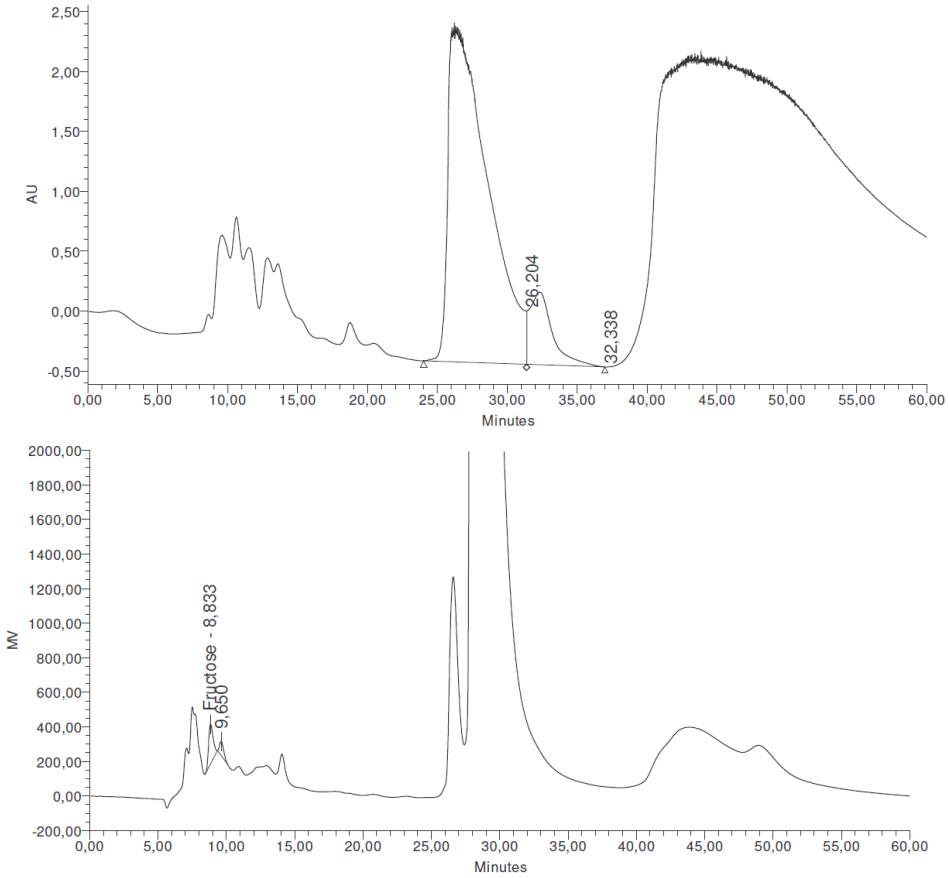


Figure 15. HPLC analysis for experiment with 128.64 g of fructose, 44.96 ml of water, 362.37 ml of butanol, and 7.064 g of catalyst. Chromatogram of 5-HMF (above) and fructose (below).

In the first chromatogram, as it has been said, the corresponding peak of 5-HMF is missing due to an overlap with a heavier peak near. Unlike 5-HMF, fructose gives an appreciable peak distinguished from the others, although is also surrounded by various peaks. A little bit of sound can be observed in both diagrams (see also Appendix 4 for the rest of chromatograms) which can be attributed to the complex composition of the samples analyzed.

There are some authors that have investigated the effects of reaction parameters in humins formation. Hu et al. [56] studied the humin-type polymer formation in dehydration of glucose with methanol. Their results concluded that with an initial methanol:water ratio of 10 (methanol rich medium), humins formation was significantly lowered. In this work, since it was tried to load the same quantity of butanol, and water amount was also fixed at 45 mL, variations in butanol:water ratio were negligible (from 6.06 to 6.35) and this effect could not be studied. Regarding catalyst dosage, Hu et al. did not find any appreciable change in polymer formation, testing from 1 to 10 wt.%. Comparison of chromatograms between experiments with same initial conditions but with different catalyst load are shown in the following figures:

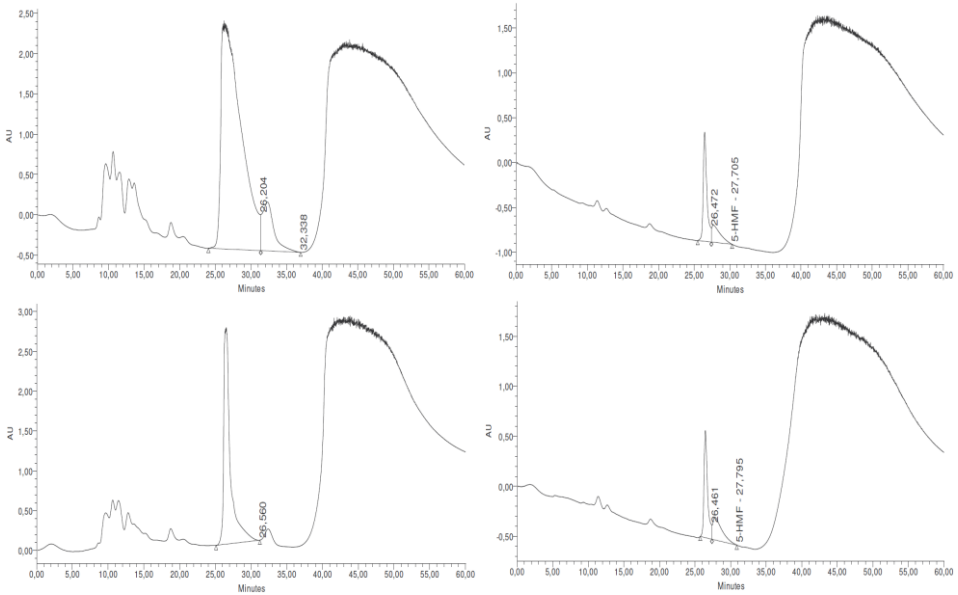


Figure 16. Above: 128 g of fructose with 3.0 (left) and 7.1 (right) g of catalyst.
Below: 140 g of fructose with 3.7 (left) and 7.1 (right) g of catalyst

It can be observed the differences between diagrams from the left than from the right. The two diagrams on the left correspond to experiments with less amount of catalyst (3-3.7). The other two on the right are diagrams of experiments with the same amount of reactants than the ones on the left, but with the double dosage of catalyst approximately. It can be quickly seen that with less catalyst, there is more area from other compounds, other peaks with different retention times than 5-HMF. Furthermore, with less catalyst, the peak that should correspond to 5-HMF is missing, and in the diagrams with more catalyst, these peaks are found and recognized by the program. This suggests that more dosage of catalyst hinders polymerization of 5-HMF by-products with fructose. Namely it can be observed that there is one peak on the left of 5-HMF peak, which is highly increased with catalyst dosage decrease.

Humins analysis is normally carried out by IR spectroscopy, i.e. FT-IR or Raman spectroscopy, with wavenumbers between 600 and 4000 cm^{-1}, and a resolution of 2-4 cm^{-1}.

7. CONCLUSIONS AND RECOMMENDATIONS

This study has proven that synthesis of butyl levulinate can be obtained directly from fructose, at atmospheric pressure with a temperature range of 115 to 120ºC, in the presence of butanol and with water removal since it shifts the equilibrium towards butyl levulinate production.

In this system, water addition was found to be an important aspect since, without it, the viscosity of the mixture became a problem, prevent it from a fluency stirring. Water does not favor the reaction and that is why it is removed. But its initial addition diluted fructose and therefore, mixture viscosity was reduced so the magnetic stirrer was able to spin properly and this was traduced in higher yields of butyl levulinate.

Molar ratios from 5 to 10 between butanol and fructose were tested and the results obtained were varied which suggests that plays a very important role in reaction yield. Molar ratios near 6 gave the highest butyl levulinate yields. Regarding the catalyst mass effect, yields seemed to increase accordingly to the catalyst amount, excluding some case.

Humins formation has been an important topic in this work. Although in previous similar works [47] they were not detected, their presence was noticed in every experiment. Some authors [56] concluded that alcohol-water initial molar ratio was a determinant factor to reduce humins formation, and that catalyst dosage did not seem to be influential. In results from HPLC analysis, it could be seen that chromatograms from experiments with less catalyst dosage, had more and heavier peaks surrounding 5-HMF and fructose peaks, which seems to correspond with humin-type polymers formed during the reaction. On the contrary, those experiments with more catalyst dosage showed less and cleaner peaks. Then, it can be suggested that more load of catalyst can reduce humins formation, but this cannot be confirmed in this work since none of these compounds were quantified.

In order to achieve more accurate results, this study could be done in a reactor with a mechanic stirrer, which have more power so the initial mixture can be homogenized without having to add water. In addition, various experiments could be carried out with a time reaction from 1 hour, and adding two hours of reaction time on the next experiment, so it can be studied the progression of both the reaction, and the products concentration.

8. REFERENCES AND NOTES

[1] S. Darda, T. Papalas and A. Zabaniotou, "Biofuels journey in Europe: Currently the way to low carbon economy sustainability is still a challenge," *Journal of Cleaner Production,* vol. 208, pp. 575-588, 2019.

[2] European Comission, *Regulation (EC) No 443/2009 - Reduction in CO2 emissions of new passenger cars,* 2009.

[3] European Comission, "Climate action rogress report," Brussels, 2018.

[4] International Energy Agency, Resources to Reserves, Paris: IEA Publications, 2013.

[5] U. R. Fritsche, "Direct and indirect land-use competition issues for energy crops and their sustainable production – an overview," *Biofuels, bioproducts & biorefining,* pp. 692-704, 2010.

[6] S. N. Naik, V. V. Goud, P. K. Rout and A. K. Dalai, "Production of first and second generation biofuels: A comprehensive review.," ElSevier, 2010.

[7] K. G. Satyanarayana, A. B. Mariano and J. V. C. Vargas, "A review on microalgae, a versatile source for sustainable energy and materials.," *International Journal of Energy Research,* pp. 291-311, 2011.

[8] M. A. Carriquiry, X. Du and G. R. Timilsina, "Second generation biofuels: Economics and policies," *Energy Policy,* vol. 39, no. 7, pp. 4222-4234, 2011.

[9] A. Lappas and E. Heracleous, "Production of biofuels via Fischer-Tropsch synthesis: biomass-to-liquids," *Handbook of Biofuels production,* pp. 493-529, 2011.

[10] Bioenergy2020+, "Commercializing Liquid Biofuels from Biomass," [Online]. Available: https://demoplants.bioenergy2020.eu/. [Accessed 12th June 2019].

[11] Y. Sun and J. Cheng, "Hydrolysis of lignocellulosic materials for ethanol production: a review," *BioResource Technology,* vol. 83, pp. 1-11, 2002.

[12] R. Luque and J. Clark, "Biodiesel-Like Biofuels from Simultaneous Transesterification / Esterification of Waste Oils with a Biomass-Derived Solid Acid Catalyst," *ChemCatChem,* pp. 594-597, 2011.

[13] P. Munasinghe and S. Khanal, "Bioresource Technology Biomass-derived syngas fermentation into biofuels : Opportunities and challenges," *BioResource Technology,* vol. 101, pp. 5013-5022, 2010.

[14] A. Alaswad, M. Dassisti, P. T and A. G. Olabi, "Technologies and developments of third generation biofuel production," *Renewable and Sustainable Energy Reviews,* vol. 51, pp. 1446-1460, 2015.

[15] C. Huang, M. Zong, H. Wu and Q. Liu, "Bioresource Technology Microbial oil production from rice straw hydrolysate by Trichosporon fermentans," *Bioresource Technology,* vol. 100, no. 19, pp. 4535-4538, 2009.

[16] B. Abdullah, S. Anuar, S. Muhammad, Z. Shokravi and S. Ismail, "Fourth generation biofuel : A review on risks and mitigation strategies," *Renewable and Sustainable Energy Reviews,* vol. 107, pp. 37-50, 2019.

[17] J. Lü, C. Sheahan and P. Fu, "Environmental Science Metabolic engineering of algae for fourth generation biofuels production," *Energy & Environmental Science,* pp. 2451-2466, 2011.

[18] A. A. Snow and V. H. Smith, "Genetically Engineered Algae for Biofuels : A Key Role for Ecologists," *BioScience,* vol. 62, no. 8, pp. 765-768, 2012.

[19] S. A. Shahir, H. H. Masjuki, M. A. Kalam, A. Imran and A. M. Ashraful, "Performance and emission assessment of diesel – biodiesel – ethanol / bioethanol blend as a fuel in diesel engines : A review," *Renewable and Sustainable Energy Reviews,* vol. 48, pp. 62-78, 2015.

[20] R. Joshi and M. Pegg, "Flow properties of biodiesel fuel blends at low temperatures," *Fuel,* vol. 86, pp. 143-151,

2007.

[21] P. Taylor and R. Dunn, "Cold flow properties of biodiesel : a guide to getting an accurate analysis.," *Biofuels,* 2015.

[22] B. Srinivasa Rao, P. Krishna Kumari, D. Dhana Lakshmi and N. Lingaiah, "One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts," *Catalysis Today,* vol. 309, pp. 269-275, 2018.

[23] A. Démolis, N. Essayem and F. Rataboul, "Synthesis and Applications of Alkyl Levulinates," *ACS Sustainable Chemistry & Engineering,* pp. 1338-1352, 2014.

[24] D. Song, S. An, B. Lu, Y. Guo and J. Leng, "Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate.," *Applied Catalysis B: Environmental,* vol. 179, pp. 445-457, 2015.

[25] D. Zhao, P. Prinsen, Y. Wang, W. Ouyang, F. Delbecq, C. Len and R. Luque, "Continuous flow alcoholysis of furfuryl alcohol to alkyl levulinates using zeolites.," *ACS Sustainable Chemistry & Engineering,* pp. 1-36, 2018.

[26] H. A. Schuette and A. Cowley, "Levulinic acid. II. The vapor pressures of its alkyl esters.," vol. 53, pp. 3485-3489, 1931.

[27] V. Russo, V. Hrobar, P. Makl-Arvela, K. Eranen, F. Sandelin, M. Di Serio and T. Salmi, "Kinetics and Modelling of Levulinic Acid Esterification in Batch and Continuous Reactors.," *Topics in Catalysts,* pp. 1-10, 2018.

[28] M. Mohammad Zainol, N. A. Saidina Amin and M. Asmadi, "Kinetics and thermodynamic analysis of levulinic acid esterification using lignin-furfural carbon cryogel catalyst," *Renewable Energy,* vol. 130, pp. 547-557, 2018.

[29] R. Liu, J. Chen, X. Huang, L. Chen, L. Ma and X. Li, "Conversion of fructose into 5-hydroxymethylfurfural and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials.," *Green Chemistry,* vol. 15, pp. 2895-2903, 2013.

[30] S. Saravanamurugan, O. Van Buu and A. Riisager, "Conversion of Mono- and Disaccharides to Ethyl Levulinate and Ethyl Pyranoside with Sulfonic Acid-Functionalized Ionic Liquids," *Chemsuschem,* pp. 723-726, 2011.

[31] E. Christensen, A. Williams, S. Paul, S. Burton and R. Mccormick, "Properties and Performance of Levulinate Esters as Diesel Blend Components," *Energy & Fuels,* pp. 5422-5428, 2011.

[32] G. Ertl, H. Knoezinger, F. Schueth and J. Weitkamp, Handbook of Heterogeneous Catalysis, Weinheim, Germany: Wiley-VCH, 2008.

[33] M. Misono, Heterogeneous Catalysis of Mixed Oxides: Perovskite and Heteropoly Catalysts, Amsterdam, the Netherlands: Elsevier, 2013.

[34] R. A. Van Santen and M. Neurock, Molecular Heterogeneous Catalysis. A Conceptual and Computational Approach., Weinheim: Wiley-VCH, 2006.

[35] J. Cejka, H. Van Bekkum, A. Corma and F. Schüth, Introduction to zeolite science and practice, Amsterdam: ElSevier B.V. , 2007.

[36] M. Kalpana and J. Kozinski, "Esterification of Levulinic Acid to n -Butyl Levulinate Over Various Acidic Zeolites," *Catalysis Letters,* vol. 143, pp. 1220-1225, 2013.

[37] S. saravanamurugan and A. Riisager, "Zeolite Catalyzed Transformation of Carbohydrates to Alkyl Levulinates," *ChemCatchem,* vol. 5, pp. 1754-1757, 2013.

[38] K. Manikandan and K. K. Cheralathan, "Heteropoly acid supported on silicalite−1 possesing intracrystalline nanovoids prepared using biomass − an efficient and recyclable catalyst for esterification of levulinic acid," *Applied Catalysis A: General,* pp. 1-38, 2017.

[39] R. Van Santen and M. Neurock, Molecular Heterogeneous Catalysis. A Conceptual and Computational Approach., Weinheim: WILEY-VCH, 2006.

[40] A. Asiri and T. Rangreez, Applications of Ion Exchange Materials in Chemical and Food Industries, Cham, Switzerland: Springer, 2019.

[41] E. Ramírez, R. Bringué, C. Fité, M. Iborra, J. Tejero and F. Cunill, "Role of ion-exchange resins as catalyst in the reaction-network of transformation of biomass into biofuels.," in *Ion Exchange Resins 2017*, Cambridge, 2017.

[42] B. Corain, M. Zecca and K. Jerabek, "Catalysis and polymer networks — the role of morphology and molecular accessibility," *Journal of Molecular Catalysis A,* vol. 177, pp. 3-20, 2001.

[43] S. Alexandratos, A. Trochimczuk, E. Horwitz and R. Gatrone, "Synthesis and Characterization of a Bifunctional Ion

Exchange Resin with Polystyrene-Immobilized Diphosphonic Acid Ligands," *Journal of Applied Polymer Science,* vol. 61, pp. 273-278, 1996.

[44] J. Wang, J. Chang and J. Fan, "Catalytic esterification of bio-oil by ion exchange resins," *Journal of Fuel Chemistry and Technology,* vol. 38, no. 5, pp. 560-564, 2010.

[45] N. Özbay, N. Oktar and A. Tapan, "Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins," *Fuel,* vol. 87, pp. 1789-1798, 2007.

[46] M. Tejero, E. Ramírez, C. Fité, J. Tejero and F. Cunill, "Applied Catalysis A : General Esterification of levulinic acid with butanol over ion exchange resins," *Applied Catalysis A, General,* vol. 517, pp. 56-66, 2016.

[47] R. Sharma, M. Iborra and E. Ramírez, "A contribution to the study of acidic ion-exchange resins to produce butyl levulinate from fructose and butyl alcohol.," 2012.

[48] M. d. M. Planas, M. Iborra and J. Tejero, "Liquid-phase synthessis of butl levulinate with simultaneous water removal.," 2017.

[49] Tejero, M. Àngels and F. Cunill, "A contribution to the study of butyl levulinate synthesis in the liquid-phase on ion-exchange resins.," 2012.

[50] Z. Muzikova, P. Simacek, M. Pospisil and G. Sebor, "Density, Viscosity and Water Phase Stability of 1-Butanol-Gasoline Blends," *Journal of Fuels,* vol. 2014, pp. 1-8, 2014.

[51] R. Musau and R. Munavu, "The Preparation of 5-Hydroxymethyi-2-Furaldehyde (HMF) from D-Fructose in the Presence of DMSO," *Biomass,* vol. 13, pp. 67-74, 1987.

[52] C. Sievers, I. Musin, T. Marzialetti, M. Olarte, P. Agrawal and C. Jones, "Acid-Catalyzed Conversion of Sugars and Furfurals in an Ionic-Liquid Phase," *ChemSusChem,* vol. 0100, pp. 665-671, 2009.

[53] S. Dee and A. Bell, "A Study of the Acid-Catalyzed Hydrolysis of Cellulose Dissolved in Ionic Liquids and the Factors Influencing the Dehydration of Glucose and the Formation of Humins," *ChemSusChem,* vol. 4, pp. 1166-1173, 2011.

[54] A. Chuntanapum and Y. Matsumura, "Char Formation Mechanism in Supercritical Water Gasification Process: A Study of Model Compounds," *Ind. Eng. Chem. Res.,* vol. 49, pp. 4055-4062, 2010.

[55] S. Patil and C. Lund, "Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural," *energy&fuels,* vol. 25, pp. 4745-4755, 2011.

[56] X. Hu, C. Lievens, A. Larcher and C. Li, "Reaction pathways of glucose during esterification : Effects of reaction parameters on the formation of humin type polymers," *Bioresource Technology,* vol. 102, no. 21, pp. 10104-10113, 2011.

[57] O. Tyagi, N. Atray, B. Kumar and A. Datta, "Production, Characterization and Development of Standards for Biodiesel- A Review.," *Journal of Metrology Society of India,* vol. 25, no. 3, pp. 197-218, 2010.

[58] F. Meng, N. Aieta, S. Dec, J. W. D. Horan, M. Frey, P. Pham, J. Turner, M. Yandrasits, S. Hamrock and A. Herring, "Structural and transport effects of doping perfluorosulfonic acid polymers with the heteropoly acids, H3PW12O40 or H4SiW12O40.," *Electrochimica Acta,* vol. 53, pp. 1372-1378, 2007.

[59] R. Zwart and R. Van Ree, "Bio-based Fischer-Tropsch Diesel Production Technologies," in *Biofuels*, John Wiley & Sons, 2009, pp. 95-116.

9. ACRONYMS

BL	Butyl levulinate
BF	Butyl formate
5-HMF	5-hidroxymethyl furfural
EL	Ethyl levulinate
LA	Levulinic acid
FA	Formic acid
BuOH	Butanol
BMF	Buthoxymethyl furfural
DBE	Dibutyl eter
$\mathbf{Y_k}$	Yield of reagent k
$\mathbf{R_{k-j}}$	Molar ratio between k and j
$\mathbf{m_{cat}}$	Catalyst mass, g
V	Volume, mL
T	Temperature, ºC
t	Time
IR	Infrared spectrum
FT-IR	Fourier transform-infrared spectroscopy
UV	Ultraviolet
RI	Refractor Index

APPENDICES

APPENDIX 1: EXPERIMENTAL DESIGN

It was tried to test as much experimental conditions as possible in order to fill all possibilities inside the boundaries conditions like solubility and viscosity. This 3D graphic shows the initial conditions of all experiments carried out. as a complement of Table 1.

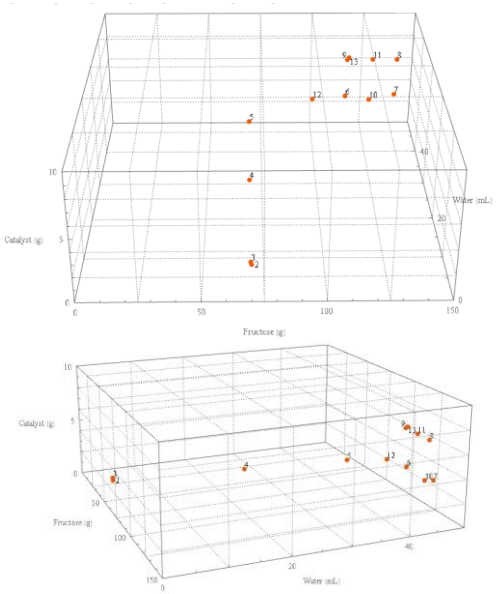


Figure 17. 3D graphic of experimental design. Done it with Wolfram Mathematica 11.3Student Edition.

APPENDIX 2: GC CALIBRATION

Ten vials were prepared in order to simulate all proportions of substances that could appear on the samples. Using the same method in the gas chromatograph. vials were analyzed three times. All results were adjusted with the linear expression of which parameters fitted better. Five expressions were obtained for water. butanol. butyl formate. butyl levulinate and dibutyl ether. The same expression of butyl levulinate was used to quantify the butoxymethyl furfural.

	Mass [%]				
Vial	**Water**	**Butanol**	**BF**	**BL**	**DBE**
1	0	83.3	0	15.7	1.0
2	8.7	75.2	2.1	14.0	0
3	14.1	68.4	2.9	12.7	1.9
4	17.1	61.4	4.5	12.2	4.8
5	21.2	51.5	8.2	12.1	7.0
6	82.1	1.8	6.5	9.1	0.5
7	2.3	40.7	4.2	8.1	44.7
8	85.1	2.1	12.1	0	0.7
9	93.6	0	5.5	0	0.9
10	44.7	28.5	11.7	15.1	0

Table 4. Mass composition of all vials.

Component	Equation	R^2
Water	%Mass=(1.00±0.03)·%Area+(-0.36±1.35)	0.994
Butanol	%Mass=(0.99±0.02)·%Area+(-1.03±1.01)	0.997
Butyl formate	%Mass=(0.90±0.06)·%Area+(0.96±0.39)	0.963
Butyl levulinate	%Mass=(1.09±0.06)·%Area+(0.60±0.58)	0.974
Dibu		

Table 5. Equations from GC calibration.

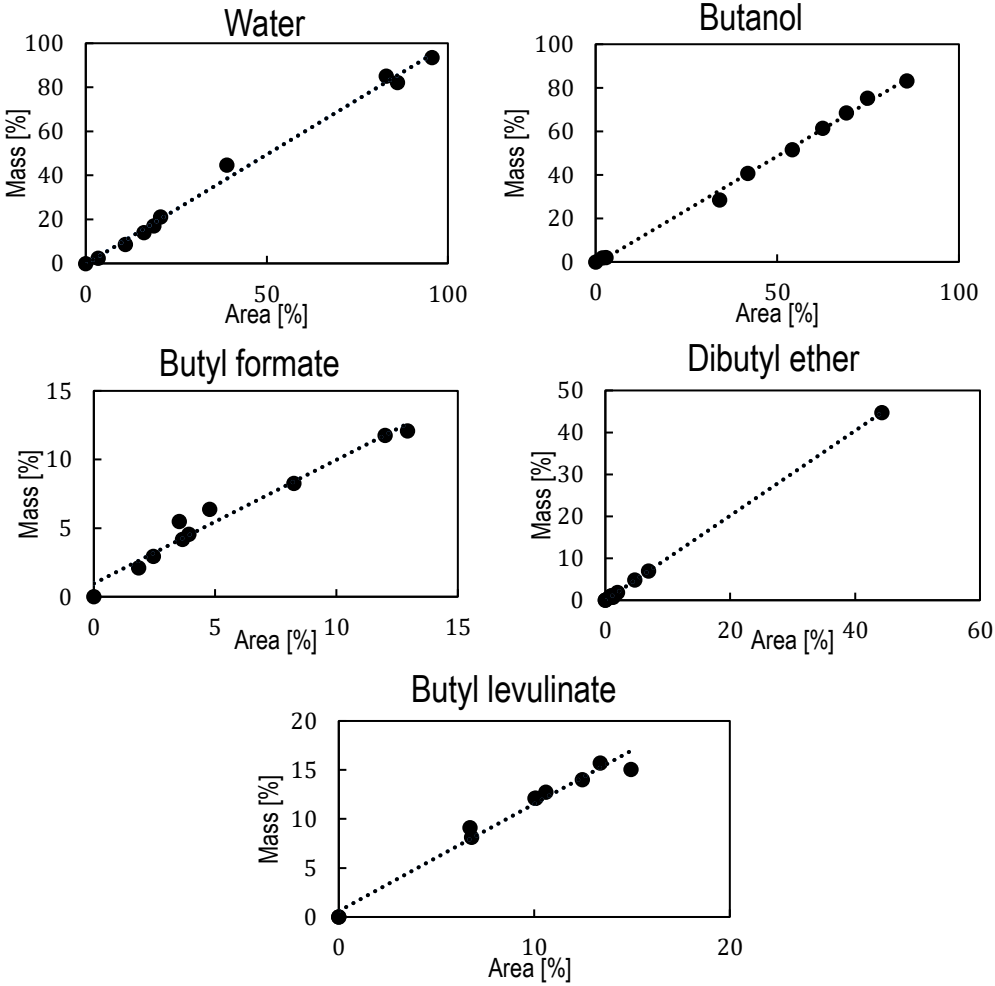


Figure 18. Graphics from GC calibration.

APPENDIX 3: EXPERIMENTAL DATA

Experiment 2

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Molar ratio BuOh-Fr**
283.02	69.9	2.988	9.84

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	91,76	6,00	1,23	0,00	0,00	0,00
Organic phase	16,28	66,68	14,51	0,00	0,00	0,00
Flask	2,12	84,11	1,88	4,40	0,00	8,49

Table 6. Experimental data of experiment 2.

Experiment 3

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Molar ratio BuOh-Fr**
284,1	69,57	3,19	9,93

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,11	5,08	0,00	0,00	0,00	0,00
Organic phase	93,11	5,08	0,00	0,00	0,00	0,00
Flask	0,75	90,79	1,55	3,56	0,00	3,89

Table 7. Experimental data of experiment 3.

Experiment 4

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
283,63	69,19	2,46	23,07	9,96

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	92,90	5,34	0,00	0,00	0,00	0,00
Organic phase	15,10	75,82	7,30	0,00	0,00	0,00
Flask	0,00	84,38	2,99	7,80	0,58	3,64

Table 8. Experimental data of experiment 4.

Experiment 5

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
284,94	69,12	2,05	42,85	10,02

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	92,85	5,32	0,97	0,00	0,00	0,66
Organic phase	19,24	73,39	5,28	0,00	0,00	0,00
Flask	0,00	85,92	2,56	7,72	0,21	4,64

Table 9. Experimental data of experiment 5.

Experiment 6

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
285,58	116,15	3,62	45,69	5,98

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,51	4,74	0,00	0,00	0,00	0,00
Organic phase	16,75	70,25	10,74	0,00	0,10	0,00
Flask	0,00	74,94	3,93	11,13	0,34	9,30

Table 10. Experimental data of experiment 6.

Experiment 7

Butanol [g]	**Fructose [g]**	**Catalyst [g]**	**Water [mL]**	**Molar ratio BuOh-Fr**
285,58	140,20	3,72	45,85	4,95

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,07	5,18	0,00	0,00	0,00	0,00
Organic phase	19,36	66,30	12,07	0,00	0,00	0,00
Flask	0,00	77,20	4,34	7,80	0,00	11,66

Table 11. Experimental data of experiment 7.

Experiment 8

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
283,64	140,2	7,1053	44,74	4,92

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,70	4,55	0,00	0,00	0,00	0,00
Organic phase	21,41	62,31	10,56	2,50	0,36	3,48
Flask	0,33	72,86	6,36	8,75	0,73	11,55

Table 12. Experimental data of experiment 8.

Experiment 9

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
286,92	116,48	7,00	45,17	5,99

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,69	4,56	0,00	0,00	0,00	0,00
Flask phase	1,13	75,12	5,99	7,72	0,91	9,15

Table 13. Experimental data of experiment 9.

Experiment 10

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
283,53	128,30	3,02	46,75	5,37

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,46	4,79	0,00	0,00	0,00	0,00
Organic phase	17,84	70,88	9,32	0,00	0,00	0,00
Flask	0,89	81,10	3,32	5,35	0,00	10,28

Table 14. Experimental data of experiment 10.

Experiment 11

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
293,52	128,64	7,06	44,96	5,55

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,69	4,56	0,00	0,00	0,00	0,00
Organic phase	16,57	67,11	13,78	0,00	0,03	0,00
Flask	0,00	75,70	5,49	8,14	0,46	11,24

Table 15. Experimental data of experiment 11.

Experiment 12

Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
284,17	100,08	3,52	45,02	6,90

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,49	4,76	0,00	0,00	0,00	0,00
Organic phase	17,90	84,32	9,63	0,00	0,00	0,00
Flask	0,00	84,32	3,46	4,88	0,11	11,38

Table 16. Experimental data of experiment 12.

Experiment 13

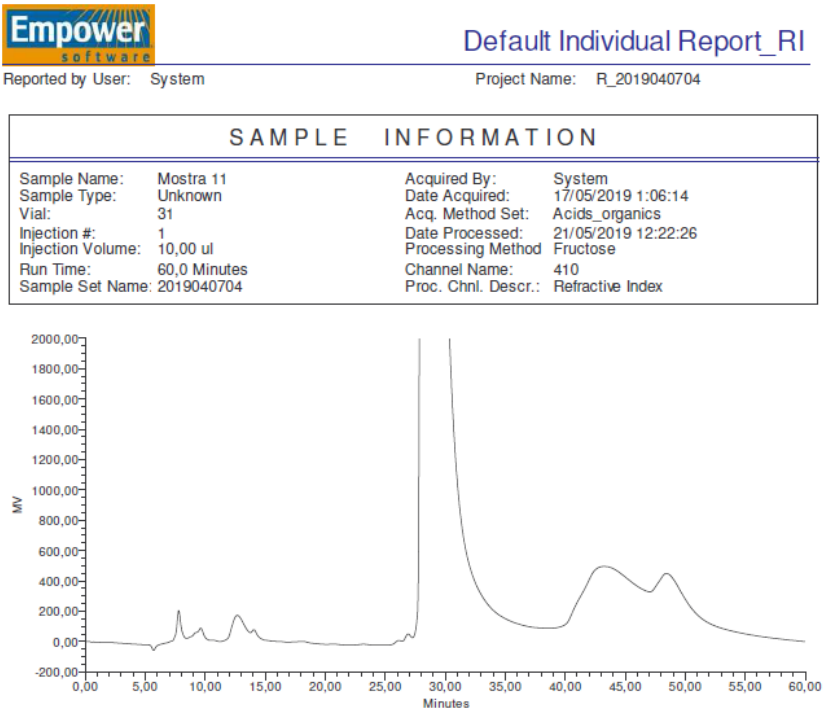
Butanol [g]	**Fructose** [g]	**Catalyst** [g]	**Water** [mL]	**Molar ratio BuOh-Fr**
284,95	117,35	7,13	45,37	5,90

	Mass fraction [%]					
	Water	Butanol	BF	BL	DBE	BMF
Aqueous phase	93,76	4,49	0,00	0,00	0,00	0,00
Organic phase	15,38	67,19	14,67	0,00	0,20	0,00
Flask	0,00	75,32	5,48	9,49	0,91	8,97

Table 17. Experimental data of experiment 13.

APPENDIX 4: HPLC CHROMATOGRAMS

HPLC analysis was carried out in order to trying to quantify fructose, 5-HMF, levulinic acid, and formic acid. Fructose was analyzed by RI detector while the rest were analyzed by UV detector. 5-HMF was detected at 285 nm, levulinic acida t 265 nm, and formic acida t 210 nm. In the next figures, some examples of HPLC chromatograms are shown.



	Peak Name	RT
1	Fructose	8,800

Figure 18. HPLC detection of fructose of experiment 11.

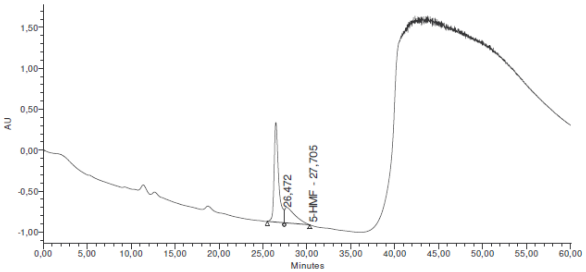
Empower software

Default Individual Report_UV

Reported by User: System Project Name: R_2019040704

SAMPLE INFORMATION

Sample Name:	Mostra 11	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17/05/2019 1:06:14
Vial:	31	Acq. Method Set:	Acids_organics
Injection #:	1	Date Processed:	21/05/2019 12:36:04
Injection Volume:	10,00 ul	Processing Method	5_HMF
Run Time:	60,0 Minutes	Channel Name:	285 nm
Sample Set Name:	2019040704	Proc. Chnl. Descr.:	PDA 285,0 nm



	Peak Name	RT	Area	% Area	Height	Peak Type
1		26,472	43776316	73,43	1216244	Unknown
2	5-HMF	27,705	15840269	26,57	191169	Found

Figure 20. HPLC detection of 5-HMF of experiment 11.

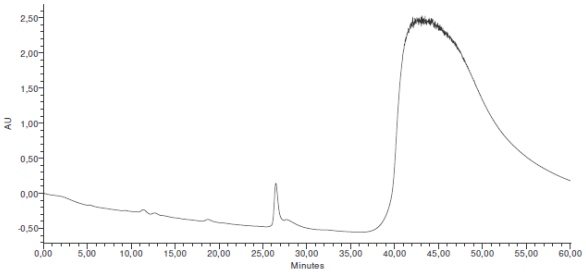
Empower software

Default Individual Report_UV

Reported by User: System Project Name: R_2019040704

SAMPLE INFORMATION

Sample Name:	Mostra 11	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17/05/2019 1:06:14
Vial:	31	Acq. Method Set:	Acids_organics
Injection #:	1	Date Processed:	21/05/2019 12:32:05
Injection Volume:	10,00 ul	Processing Method	Levulinic
Run Time:	60,0 Minutes	Channel Name:	265 nm
Sample Set Name:	2019040704	Proc. Chnl. Descr.:	PDA 265,0 nm



	Peak Name	RT	Peak Type
1	Levulinic Acid	13,788	Missing

Figure 19. HPLC detection of LA of experiment 11.

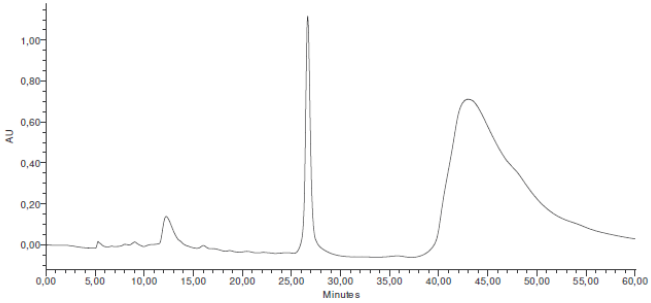
Empower software

Default Individual Report_UV

Reported by User: System Project Name: R_2019040704

SAMPLE INFORMATION

Sample Name:	Mostra 11	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17/05/2019 1:06:14
Vial:	31	Acq. Method Set:	Acids_organics
Injection #:	1	Date Processed:	21/05/2019 12:28:08
Injection Volume:	10,00 ul	Processing Method	Formic
Run Time:	60,0 Minutes	Channel Name:	210 nm
Sample Set Name:	2019040704	Proc. Chnl. Descr.:	PDA 210,0 nm



	Peak Name	RT	Peak Type
1	Formic Acid	11,838	Missing

Figure 21. HPLC detection of FA of experiment 11.