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Master's Degree in Chemical Engineering

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Study of thermostable resins for the production of butyl levulinate from fructose and butyl alcohol.

Estudio de resinas termoestables para la producción de butil levulinato a partir de fructosa y alcohol butílico.

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"An experiment is a question which science poses to Nature,

and a measurement is the recording of Nature's answer".

Max Planck

Al culminar con esta etapa de mi vida, agradezco primeramente a Dios y mis padres por ser los principales promotores de mis aspiraciones, labores, metas cumplidas y logros por conseguir.

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REPORT

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1 SUMMARY

Today we get around 70,000 direct products from oil, which gives us an idea of the importance that it has in our economy. Approximately 90 % of the oil is used as raw material to produce energy and the rest for others chemical products. It is for this reason that the search for petroleum substitutes has been proposed for more than 100 years, with the use of biomass as a raw material being of major importance today, as biomass is the only source of carbon renewable from which it is possible to obtain biofuel and chemical products.

Nowadays, studies are increasingly demanding towards the development of biofuels, focusing on the development of second- generation fuels. A good starting point is the lignocellulosic biomass, since it contains more than 50 % by weight of sugars, which can be transformed to very valuable platform molecules chemicals such as of levulinic acid. In this context, we propose to study the reaction between fructose and 1-butanol to produce butyl levulinate over thermostable ion exchange resins, a chemical candidate to be blended with diesel fuel. Besides mentioning that levulinate esters such as butyl levulinate are important chemical feedstocks having potential applications either in flavoring and fragrance industries or as already said in biodiesel as blending component.

The aim of this work is to determine the catalytic behavior in terms of achieving total conversion of fructose, greater selectivity towards butyl levulinate and decrease the amounts in the generation of by-products (butyl formate, formic acid, etc.) by looking for the most suitable reaction conditions to be used in the industrial production of butyl levulinate.

This research work evaluates the use of thermostable ion exchange resins which low and medium amounts of divinylbenzene in the production of butyl levulinate from fructose and butyl alcohol. The present work focuses on the synthesis of n-butyl levulinate using thermostable ion exchange resins Amberlys™ 45 and Purolite® CT-484, with maximum operating temperatures of 170 °C and 190 °C respectively, to catalyze the conversion of fructose to butyl levulinate in the butanol-water medium. With these resins, the temperature will be increased up to 170 °C. To check its effect on conversion of fructose and selectivity on products, especially to butyl levulinate. Further, a study for optimizing the reaction conditions such as fructose to 1-butanol molar ratio and catalyst concentration has been described.

The effect of temperature was mainly checked in the range 120 -150 ºC at three fructose/ 1-butanol molar ratios (0.009, 0.013 and 0.0017) over three catalyst loading (1.7, 2.5 and 3.3%) with Amberlyst™ 45 and Purolite® CT 482 as catalysts. At a constant $R_{Fruct/BuOH}$ and $R_{cat(wt/wt)}$ %, an increase of temperature led to an increase of both BL mole produced and BL yield, but also secondary reactions were promoted: DBE production increased dramatically (from 130 ºC), whereas BF and FA production increase was of the same level as BL. The same behavior was observed on changing the initial molar ratio.

Consequently, the higher the temperatures, the lower fructose/ 1-Butanol molar ratios and the higher catalyst loading, the higher the fructose selectivity towards BL, but also for byproducts as BF, FA and DBE. In addition, in the opposite case for the 5-HMF and BMF, as the temperature increases the low selectivity for these by-products.

The best conditions to obtain up to 55.6 % selectivity towards butyl levulinate and 99 % fructose conversion is working with Purolite® CT-482 resin, ratio of catalyst weight to initial load weight 3.3 %, molar ratio of fructose to 1-butanol 0.013, at a working temperature of 170 °C for eight hours of reaction.

Keywords: Biomass, fructose, butyl levulinate, thermostable ion exchange resins.

2 INTRODUCTION

2.1 Bioenergy

The world energy paradigm is changing from one based on petroleum to one based on a mixture of energy platforms. This change is precipitated by a finite petroleum supply, an expanding global demand, and political instability in areas with major petroleum reserves [1].

Energy security and climate change mitigation are core elements in current European energy policy. The EU countries are mandated to meet by 2020 a target of 20 % renewable resources in the energy supply and 10% renewable resources in energy in the transport sector [2].

Among energy production sources, fossil fuels will continue to dominate largely the global market share, with an expected loss from 86 % today to 81 % by 2035. The largest gain in the market share concerning non-fossil fuels is expected to come from biofuels (from around 3 % to 8 %), overtaking nuclear power firs and hydro in the early 2030s [3].

2.2 Biomass

Biomass is a complex mixture composed primarily of more or less polymerized sugars, lipids, lignin, proteins and organic acids in varying proportions [4]. However, the emphasis is placed on the use of lignocellulosic biomass that refers more often to plants or plant materials that are not used for food or feed [5].

In addition, the biomass aims as one of the renewable energy sources with more short-term future. It is organic matter, both of plant and animal origin, which can be used for energy purposes. As a source of energy, biomass can be used directly through combustion to produce heat, or indirectly after conversion into various forms of biofuel. The conversion of biomass to biofuel can be achieved by different methods that are widely classified in thermal, chemical and biochemical methods.

2.3 Biofuel

Biofuels are fuels that are obtained from organic materials. They include but are not limited to wood, straw, sugarcane residue, animal wastes, landfill gas, biodiesel and ethanol, municipal waste, black liquor, switch grass, and a variety of synthetic gases derived from plant and animal matter. Biofuel is distinct from fossil fuels in that they are, in some sense, renewable. There are so

many biofuels, and they are derived from so many sources, that their description requires a classification scheme [6].

2.3.1 Classification according to generations

Biofuels can be classified in four generations according to their origin.

First Generation

This category includes biofuels produced from classic food crops (using seeds, grains or sugars as substrates) with cheap, well-known technologies; consequently, they are readily available and of widespread use in several countries. Nevertheless, the main drawback of first-generation biofuels is that their production can (and, in fact, do) compete with food crops, thus placing a high stress on food commodities [7].

Pros: Mature Technology, familiar feedstock, scalable production capabilities, cost competitive with fossil fuels.

Cons: Food vs fuel debate, feedstock price volatility, lowland use efficiency, geographical limitations, and modest net reduction in fossil fuel use and greenhouse gas emissions with current processing methods.

Second Generation

This category includes biofuels produced from lignocellulosic biomass. This includes either nonedible residues of food crop production (e.g. corn stalk or rice husks) or non-edible whole plant biomass (e.g. grasses or trees grown specifically for energy). These can be the product from feedstock grown on marginal arable croplands and/or using non-food crops and residues. These can be further classify based on conversion technology as biochemical and thermochemical. Ethanol is the most common product in this category but competitive production still needs research.

Pros: Surplus feedstock supply, less controversial, less dependence on geographical location, suitable for developing agrarian countries with large population.

Cons: High capital cost, technological breakthroughs needed, development of high biomass feedstock to improve land use efficiency.

Third Generation

Biofuels made using non-arable land, based on integrated technologies that produce a feedstock as well as a fuel (or fuel precursor, such as pure vegetable oil), and require the destruction of biomass. These are similar to the 2nd generation fuels but use lot fewer resources in generating feedstock. Algae is the most promising feedstock candidate in this category which cannot be matched by any other feedstock in terms of quantity or diversity. This category is under extensive research to reduce production costs and improve metabolic production of fuels.

Pros: Only inputs to get feedstock is CO_2 and water. Less controversial, versatile array of products possible.

Cons: High capital costs, early research stage. Need large amounts of nutrients such as nitrogen and phosphorus.

Fourth Generation

This category includes biofuels which can be made using non-arable land. These do not require destruction of biomass to be converted to fuel. This technology aims at directly converting available solar energy to fuel using inexhaustible, cheap and widely available resources. They (photobiological solar fuels and electrofuels) are the most advanced biofuels currently under research.

Pros: Only inputs to get feedstock is CO_2 and water. Less controversial, versatile array of products possible, least negative environmental impact

Cons: High capital costs, early research stage, long processing time. Slow yields [8].

2.4 Alkyl levulinates

Alkyl levulinates were identified already in 2004 as one of the top 10-biorefinery candidates [9] due to their specific physicochemical properties. Indeed, they could find applications as specialty chemicals and in the chemical and petrochemical industries [10]. First reports concerning alkyl levulinates date from the 19th century. However, the recent interest for biomass transformation and the discovery of new applications for bio-based products have considerably increased this literature. Consequently, most of the publications have appeared during the last five years. Levulinate esters, like methyl levulinate [ML], ethyl levulinate [EL] and butyl levulinate [BL] are kind of short-chain fatty esters with their properties similar to the biodiesel fatty acid methyl esters [FAME] [11].

These esters are suitable to be used as additives for gasoline and diesel of transportation fuels, which have manifold excellent performances, such as non-toxic, high lubricity, flashpoint stability and better flow properties under cold condition [12]. On the other hand, levulinate esters also can either be used in the flavoring and fragrance industries or as substrates for various kinds of condensation and addition reactions at the ester and keto groups in organic chemistry for the synthesis of different chemicals and drugs [13], [14], [15].

Alkyl levulinates found applications as solvents and additives as well as in the area of chemical synthesis. The development of new preparation routes and applications of alkyl levulinates are contributing to future greener and sustainable processes.

2.4.1 Synthesis of alkyl Levulinates

With the investigations carried out the levulinic acid esters have already been identified as potential fuel candidates. These are not only compatible with conventional diesel fuel but also result in significantly reduced soot formation. Additionally, ethyl levulinate has been utilizing as a bio-based diluent for biodiesel and improves cold flow properties.

2.4.1.1 Raw materials and reaction pathway of alkyl levulinates.

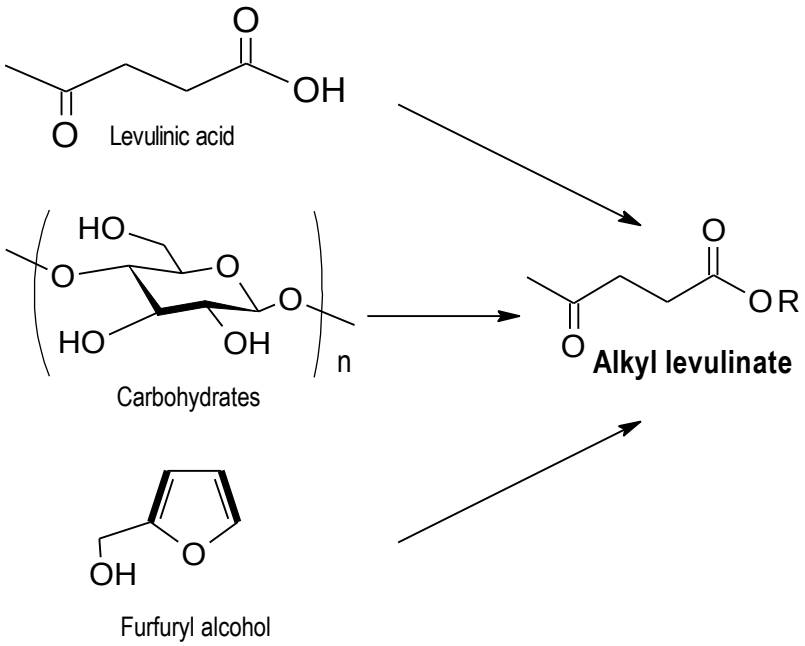

Figure 1. Raw materials for the production of alkyl levulinates.

Alkyl levulinates are obtained in high yields and selectivities from simple biomass-derived products like levulinic acid or furfuryl alcohol. They are also obtained directly from lignocellulosic resources with generally limited yields. In all cases, the transformation needs a catalyst. Interestingly, alkyl levulinates can be derived via dehydration of carbohydrates (fructose or glucose) in the presence of alcohols, this being one of the reasons that current efforts are now performed with developing efficient and recyclable catalysts [16].

Even a direct transformation of cellulose into alkyl levulinates has been demonstrating. The sequential hydrolysis and dehydration of cellulose, in the presence of alcohols, reduce the formation of by-products such as humins [17], [18]. Hu et al. have demonstrated that the synthesis of alkyl levulinates starting from dehydration of sugars proceeds via etherification of the employed carbohydrate, transformation into the corresponding ethers of 5-HMF and subsequent rehydration to yield alkyl levulinate. In this system, polymerization reactions of 5-HMF and sugars are suppressed, inhibiting the main route of humins formation. Thus, higher yields and selectivities for alkyl levulinates can be achieved than when the target product is levulinic acid.

Also, from dehydration of glucose or fructose in the presence of alcohols and acid catalysts, synthesis strategies via 5-(chloromethyl) furfural and subsequent heating in the desired alcohol or utilizing furfuryl alcohol utilizes hemicellulose as feedstock, bridging the C_5 and C_6 carbohydrate value chain [19].

Usually, all the preparations mentioned involve treatment of the reactant in alcohol and need the presence of an acid catalyst [20].

The following chain of reactions is presented in the following figure, being one of the best alternatives.

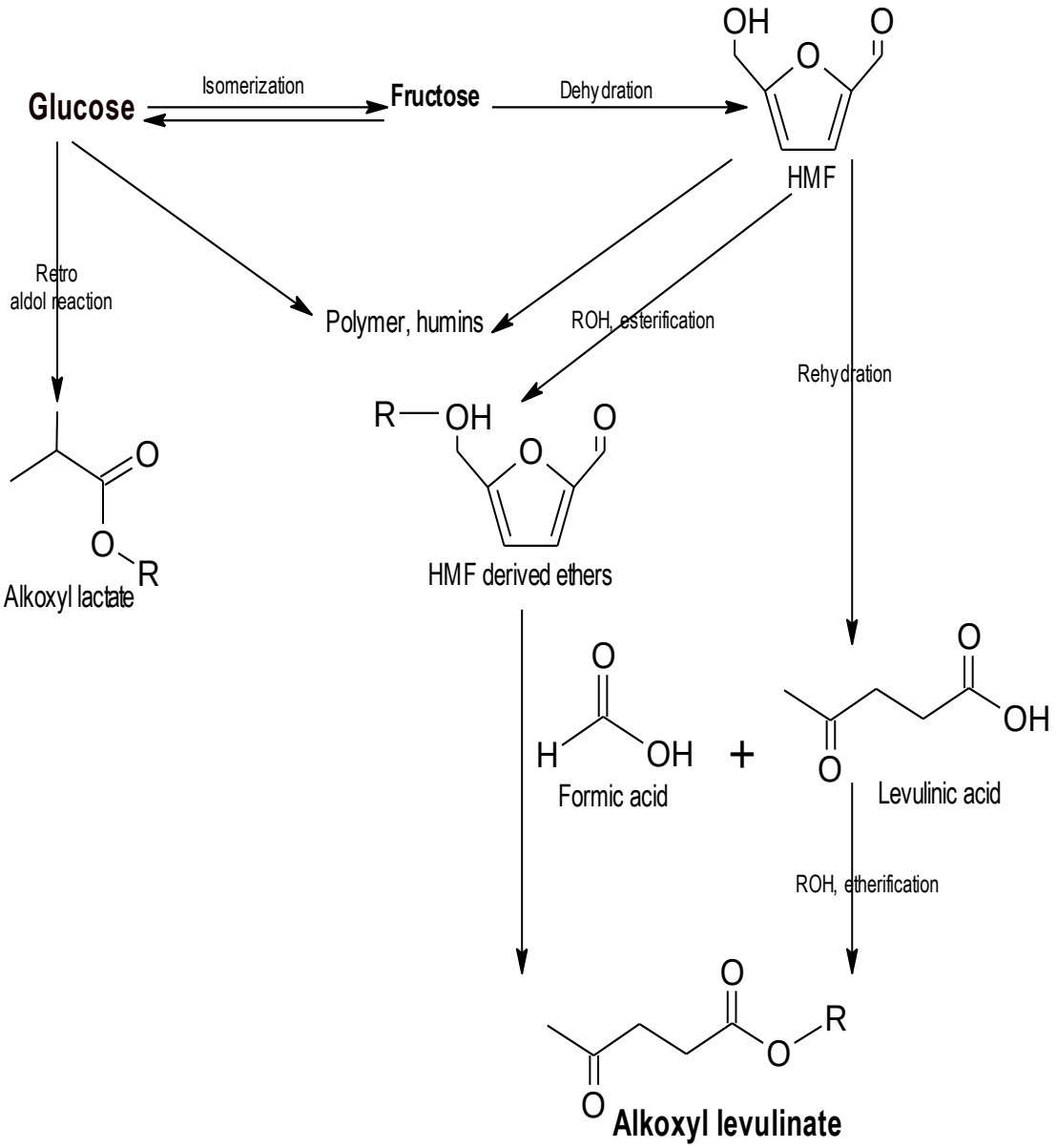

Figure 2. Reaction routes for alkyl levulinate production from glucose.

2.4.2 Catalysts used in alkyl levulinate synthesis

Due to the production reaction of alkyl levulinates is slow without the use of catalysts it has been determined to use catalysts, being substances which speed up a reaction but is chemically unchanged at the end. When the reaction has finished, you would have exactly the same mass of catalyst as you had at the beginning [19].

There are two types of catalysts, which have been used in the production of alkyl levulinates, such as homogeneous catalysts and heterogeneous catalyst.

2.4.2.1 Homogeneous Catalysts

Being the first to be used for the synthesis of alkyl levulinates. Traditionally, hydrochloric acid has been used as the first homogeneous catalyst, later developing others such as phosphoric acid H_3PO_4 and sulphuric acid H_2SO_3 [6].

But, these present several drawbacks, it is necessary a separation stage after the reaction stage in order to recover the catalyst from the final mixture, resulting in costly and generating by-products depending on the operating conditions [11]. In addition, equipment corrosion and environmental issues also arise with mineral acid [21].

2.4.2.2 Heterogeneous Catalysts

When comparing catalysts between homogeneous and heterogeneous, the heterogeneous catalyst is more environmentally friendly, less corrosive, more reusable and easy-handling. Heterogeneous catalysts are the most used nowadays, such as metal, metal salts, zeolites, ion exchange resins are employed in the production of biofuel and platform molecules from biomass [22].

2.4.2.2.1 Ion exchange resins

The ion exchange resins are solid organic materials with hydrophilic functional groups bonded to a polymer backbone with hydrophobic character. The polymeric backbone, which is a cross-linked copolymer, consists of an irregular three-dimensional matrix of hydrocarbon chains. Depending on their application, a wide variety of functional groups can be used, ranging from strongly basic systems to strongly acidic ones, including any combination of them [3].

The gel-type resins and macroreticular resins are products commercially available. Gel-type resins present a microporous collapsed structure in dry state and swell in contact with a polar solvent, exhibiting a considerable porosity. Macroreticular resins are composed by agglomerates of gel-type zones, with their respective microporous structure, that form permanent macropores between them, even in the dry state [23].

For these reasons, research on heterogeneous catalysts becomes increasingly important, of which, different types of solid catalysts have been tried, showing different results as you can see in the table 1.

Swelling is a behavior that all polymers present when interacting with solvents. This behavior is crucial to determine the ability of resins to act as catalysts [24]. The swelling capacity is understood as the variation in volume when interacting with liquid medium due to a difference in osmotic pressure between the inside and outside. Swelling takes place when dry resin comes into contact with polar substances producing an increase in surface area and porosity. The following figures show the behavior of the resins with respect to swelling.

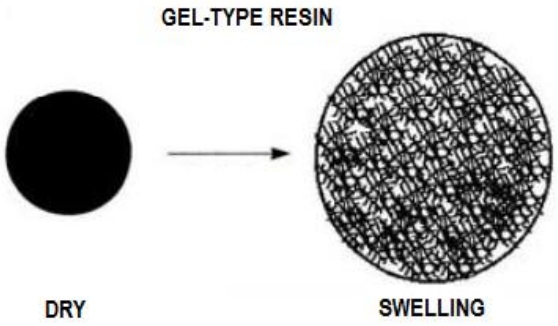

Figure 3. Morphological changes during swelling of a gel-type catalyst particle.

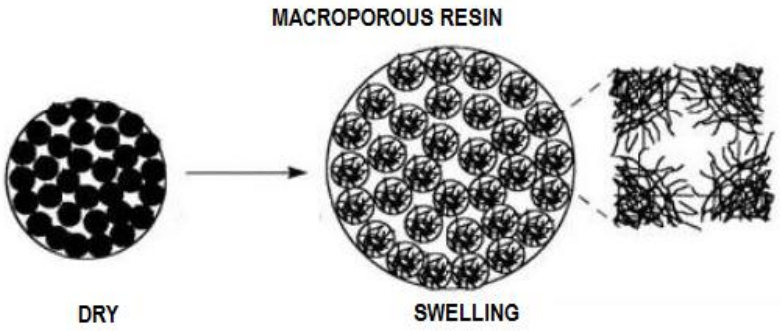

Figure 4. Morphological changes during swelling of a macroporous catalyst particle.

Furthermore, because the use of ion-exchange resins should be for extended periods, they must be chemical, thermally and mechanically stable.

Mechanical stability is defined by resistance to compression and breaking. Chemical stability is measured as the capacity for a resin to work in highly oxidizing conditions without experiencing changes in the polymeric matrix. Thermal stability allows a resin to withstand higher temperatures. This ability depends mostly on the structure of said resin. In sulfonic PS-DVB resins, thermal stability varies in relation depending on the degree of cross-linking (120-150 ºC). Given

that thermal deactivation takes place by the elimination of sulfonic groups, over sulfonated resins are slightly more stable that those that are conventionally sulfonated. A way to improve thermal stability consists in adding electron donating groups (like chlorine) to the sulfonated benzene ring, which rises the maximum operating temperature to 190 ºC [6].

2.4.3 Butyl levulinate

Levulinic acid (LA) has been recognized as a versatile building block for the synthesis of various organic chemicals as it contains ketone and carboxylic functional groups. Levulinate esters such as butyl levulinate are important chemical feed stocks having potential applications either in flavoring and fragrance industries or in biodiesel as blending component [29].

Notably, butyl levulinates could be entirely derived from cellulosic feed stocks, without the need for additional hydrogen. However, the chemical properties of this levulinate, including their capacity to act as solvent, would require modification of the materials used today's combustion systems. Furthermore, long-term road trials employing alkyl levulinate as blends or even as a pure biofuel would be necessary to assess the resulting overall engine efficiency and exhaust emissions [17].

Figure 5 presents the sequence of reactions that allows the conversion of fructose into butyl levulinate, being a series-parallel reaction scheme. Starting with the glucose isomerization to fructose, later with fructose dehydration to 5-hydroxymethyl furfural (HMF), then HMF is partially rehydrated to levulinic acid, forms ethers derived therefrom and/or polymerizes to form humins and finally levulinate is formed from the esterification of levulinic acid and/or from the decomposition of the ethers derived from HMF. Solid acids catalyze all reactions and the main problem from the industrial point of view is the loss of selectivity, mainly due to humins formed.

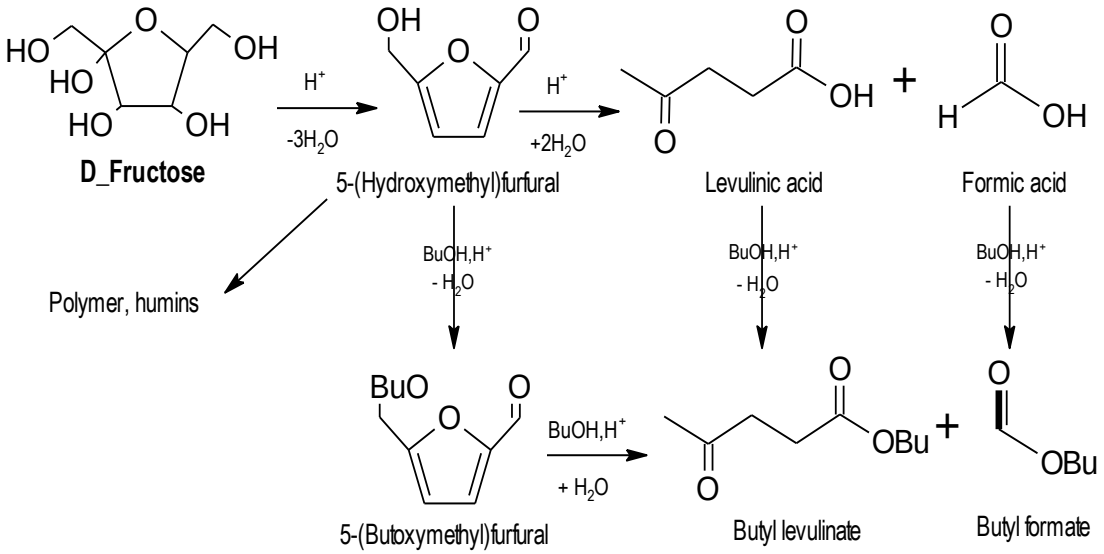

Figure 5. Reaction routes for butyl levulinate production from D-fructose [19, 20].

The research carried out to procure butyl levulinate and other levulinates, is summarizing in the following table.

Table 1. Studies on direct production of levulinate esters from biomass

Feed	$R_{MS/alc}$	T °C	Catalyst	Catalyst load [%]	Conv [%]	t [h]	S^{LE}_{SUGAR} [%]	Reference
Fruct/MeOH	0.011	200	TiO_2–SO_3H	3	59	2	---	20
Glu/MeOH	0.011	200	TiO_2–SO_3H	3	43	2	---	20
Fruct/MeOH	0.002	175	TiO_2–SO_3H	1	80	1	99	28
Fruct/MeOH	0.006	130	Fe-exch. $H_3PW_{12}O_{40}$	2	74	2	100	16
Fruct/EtOH	0.004	120	p-Styrenesulfonic acid	1	84	24	99	16
Fruct/BuOH	0.006	120	p-Styrenesulfonic acid nanotubes	1	87	24	99	11
Fruct/BuOH	0.012	120	Ion exchange resins [Amberlyst TM39]	1.5	99	8	37	25
Fruct/BuOH	0.012	120	Ion exchange resins [Dowex 50WX20]	1.5	99	8	39	25

(Alc.= Alcohol; BuOH= Butanol; EtOH= Ethanol; Fruct= Fructose; Glu= Glucose; LE= Levulinate ester; MeOH= Methanol; MS= mass of sugar)

3 OBJECTIVES

The aim of this work is to study the reaction of fructose with butyl alcohol over acidic thermostable ion exchange resins at high temperatures to produce butyl levulinate.

In particular, the following specific objectives have been set:

- Assessment of temperature, variation of feed composition (fructose/ 1-butanol molar ratios), and catalyst loading effect on catalytic activity for Amberlyst™ 45 and Purolite® CT-482 resins.

- Determination of operational condition to achieving total conversion of fructose, greater selectivity towards butyl levulinate and decrease the amounts in the generation of by-products (butyl formate, formic acid, etc).

4 EXPERIMENTAL SECTION

4.1 MATERIALS

4.1.1 Chemicals

The chemical reagents used for the production reaction of butyl levulinate was d-fructose (99 %, Labchem), water (Milli-Q ultrapure, Millipore Corp.) and butyl alcohol (99.5 %, Acros Organics).

The chemical reagents used for the system calibration of the chromatographs (gas and liquid) were butyl alcohol (99.5 %, Acros Organics), levulinic acid (98 %, Acros Organics), formic acid (98 %, Labkem), butyl formate (98 %, ACROS ORGANICS), butyl levulinate (98 %, ALDRICH), 5-HMF (98 %, Acros Organics) and di-butyl ether (99 %, Acros Organics). Moreover, for the liquid chromatograph, the mobile phase was a dilute solution of sulphuric acid elaborated by dilution of a commercial sulphuric acid solution (0.05 M, Fisher Chemical) with water (Milli-Q, Millipore Corp.).

4.1.2 Auxiliary gases

The stirred reactor was pressurized up to 20 atm by nitrogen gas (99.995 %, Abelló Linde). Moreover, for the chromatographs used helium (99.99 %, Abelló Linde) as the carrier gas.

4.1.3 Catalysts

The acidic thermostable ion exchange resins used were Amberlyst ™ 45 (A-45) and Purolite® CT-482 (C-482). Table 2 gathers a summary of the main physical properties these catalysts. For comparison purposes also Dowex 50Wx2 was used.

Table 2. Properties of acidic thermostable ion exchange resins used in this study.

Catalyst	Type	Sulfonation type [a]	Acid capacity [b] [mmol H^+/g]	%DVB	d_p [c] [mm]	Water retention [c] [%]	T_{max} [c] [°C]	d_{pore} [d] [nm]	$\sum V_{pore}$ [d] [cm^3/g]	$\sum S_{pore}$ [d] [m^2/g]	$\sum V_{sp}$ [e] [cm^3/g]
CT-482	Macro	S/Cl	3.65	Low	0.81	48-58	190	19.6	1.05	214	0.85
A- 45	Macro	S/Cl	3.65	medium	0.58-0.75	49-54	170	9.5	0.52	220.2	0.97
Dowex 50Wx2	Gel	CS	4.83	2	0.149	74-82	120	---	---	---	2.67

(a) S/Cl: sulfonated chlorinated; CS: conventionally sulfonated; (b) Titration against standard base; (c) Manufacture data; (d) Swollen state (in water); (e) Specific volume of swollen polymer in water, measured by ISEC technique.

These resins were selected due to their capacity to operate at high temperatures, Amberlyst™ 45 up to 170 °C and Purolite® CT-482 up to 190 °C. Allowing studying the direct reaction of fructose with butyl alcohol catalyzed at high temperatures. The maximum temperature reached in this study was of 170 °C.

4.2 EXPERIMENTAL SETUP

4.2.1 Reactor setup

All this study was carried out in a 100mL stainless-steel batch reactor (Autoclave Engineers) with a working overpressure of 20 atm. The reactor comprises of a stirring system, a relief valve, a pressure gauge, a thermocouple, a baffle plate and a rupture disc. The stirring system has a turbine with four paddles of the axial up disperser mounted on a model Magnedrive II Series 0.7501 rotor and a frequency converter, T-VERTER N2 SERIES, to control the stirring speed. Integrated with a turbine, a stainless steel baffle plate 316 SS that is used to minimize vortices, which can be generated by stirring. A type K (cromel-alumel) thermocouple, which is a part of proportional integral derivative (PID) temperature control system, can also be found along the turbine to measure the temperature inside the reactor. In addition to including a sintered-iron filter with a mesh size of 0.5 μm, it is used to filter the samples before taken.

The pressure values are observed in a manometer (Labon Druckmessumformer CB6020), localized between the relief valve and the reactor, this valve is used to depressurize the system whenever needed during the experiments. The relief valve is used as a security measure in case of overpressure. The rupture disc used is prepared to resist up to a maximum pressure between 50.1 and 54.8 bar with 5 % error margin.

The heating system consists of an electric heating furnace TC-22 Pro 9 controlled by the reactor's internal temperature and that of its external wall surface both measured using thermocouples. Once reached the set-point temperature the system error margin is of ±0.1 ºC.

The catalyst is injected through a stainless steel tube 316 SS. a load of the catalyst is pushed with nitrogen thanks to the pressure difference between the gas supply and the interior of the reactor. Figure 6 details the experimental set-up.

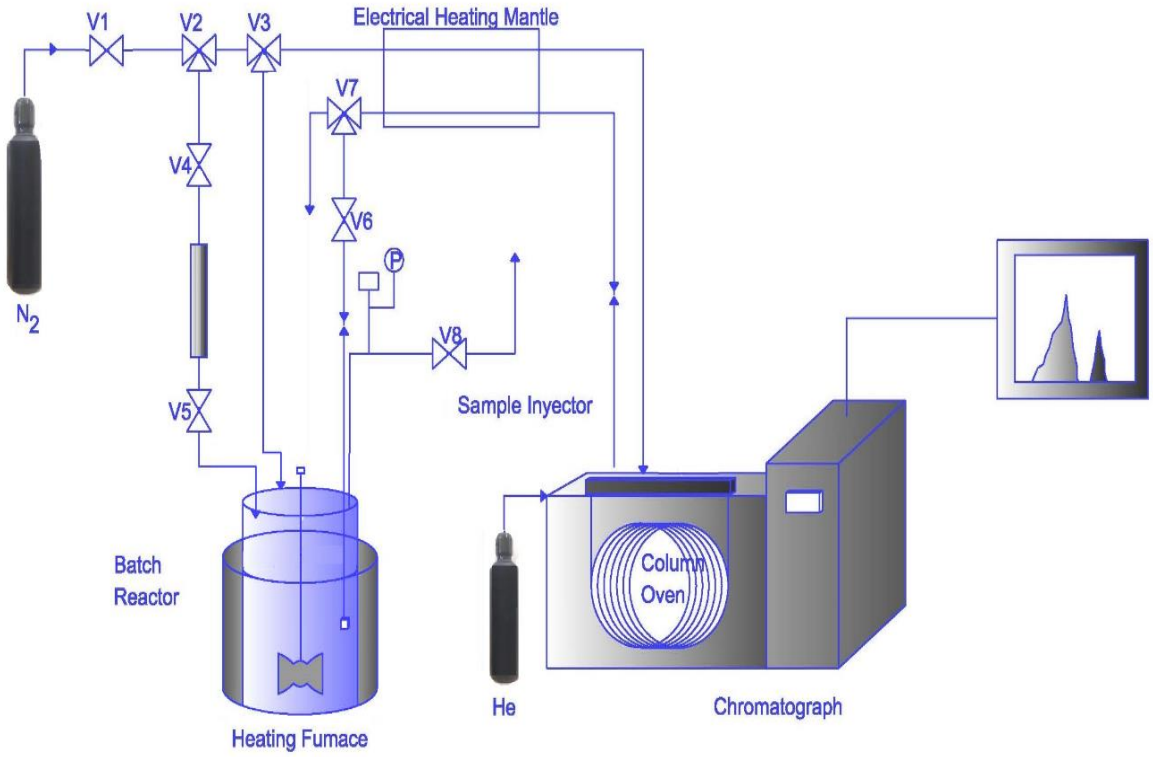

Figure 6. Scheme of the reactor setup.

4.2.2 Gas chromatography

The gas chromatograph (Hewlett Packard HP 6890 GC Series, Germany, Serial # DE00020827) is used for the analysis of the samples. The aliquots of 0.5 mL are collected manually and are injected into the gas chromatograph. The samples are introduced into the system using a 1.0 µL Agilent syringe. This is carried through the capillary column by $He_{(g)}$. The column measurements are 20 µm internal diameter, 0.5 µm stationary phase thickness and 50 m length, with Helium as carrier gas and methyl siloxane as stationary phase (HP 190915-001, HOPona Methyl Siloxane). FRUCTMAN.M analysis method is employed in the GC. Initially, the oven temperature is 60 °C, which will rise by 10 °C/min reaching 250 °C and finally remains at 250 °C for 7min. Run time is 27 min.

This procedure allowed us to detect and quantity of HMF derived esters (BMF, BF and DBE), the main product butyl levulinate, butanol and water.

4.2.3 High-performance liquid chromatography

The high-performance liquid chromatography (Agilent 1260 Infinity Quaternary) is used for the analysis of the sample. The aliquots of 0.5 mL are collected manually and are injected in the HPLC. The samples are introduced in the system using a 50µL Agilent syringe. The sample injected is carried through the column by the solvent (0.005M H_2SO_4). The column used is Aminex HPX-87H column #1250140 of 300 x 7.8 mm and pH range 1-3. GG_FRU.M analysis method is employed in the HPLC and parameters of the method for each run are flow of 0.600 ml/min of the solvent by the quaternary pump. The column compartment is maintained at 50±0.01 °C and the refractive index detector (RID) at 45±0.01 °C. Run time is of 60 min.

This procedure allowed us to detect and quantity of fructose, formic acid, 5-(Hydroxymethyl) furfural and levulinic acid.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Catalyst pretreatment

Since the resins used are highly hygroscopic, they tend to absorb water from air very easily. Consequently, this water can contribute to resin inhibition, for that reason a procedure was used to eliminate all water content. First, the resins were dried for a minimum of 2 h in an atmospheric oven at 110 °C, followed by drying in a vacuum oven at 100 °C and 10 mbar overnight.

4.3.2 Reactor loading

The loading of the reactants, which includes fructose (99 %, Labkem), 1-butanol (99.5 %, Acros Organics) and deionized water, is prepared with the corresponding quantity of each specie weighed separately and put in the stainless-steel reactor.

The volume of this mixture inside the batch reactor should not exceed 70 % of its total volume because of safety concerns. The reactor is secured with the three retaining screws and valve 1 is opened. Valve 2 is turned to position 2, and valve 3 into position 1, permitting N_2 gas to pass directly into the reactor bypassing the catalyst injector. The system is pressurized up to 20atm, and valve 1 is closed. When the manometer reading is stable, the tightness of the system can be verified. When the experiment is being performed, valve 1 is opened again. The heating furnace is placed around the reactor and fastened properly.

4.3.3 Experiment launching

The stirring is switched on for the system at 500 rpm, and the electric heating furnace is switched on. The surface temperature set point for the heating mantle is programmed 30 °C above the operating temperature in order to reach the working temperature in the reactor. The program Instrument Online by Chemstation is loaded and FRUCTMAN.M is selected as running method for GC and the program HPLC-AKC online by OpenLAB for HPLC is loaded with the running method GG_FRU.M.

Subsequently, the catalyst is injected from the topmost nut in the injection system, which is under the valve 4. In order to inject the catalyst, first the oven vacuum is broken, then the resin is weighed as quickly and accurately as possible and finally, the dry resin is introduced inside the reactor through the injection system. Once the topmost nut is screwed closed, valve 2 is turned to position 1 the valve 4 and valve 5 are opened. In this way, N_2 gas will be forced to pass through the catalyst injector and the catalyst will be added to the reactor. In addition, meanwhile the valve 4 and valve 5 are opened, a pressure drop of 10 atm is induced in the reactor by opening the relief valve 7 repeatedly and quickly, at least 5 times so that none of the catalysts is left the injector itself. The valve 2 position is reversed and valve 4 and 5 are closed. The addition of catalyst to the reactor is considered as the zero time and the system is purged by opening and closing the valve 7.

4.3.4 Sampling

For sampling the valve 3 is placed in position 2, valve 6 is opened and finally, valve 7 is opened slowly a sample of 0.2 - 0.3 ml is collected in the vial of 1.5ml. Afterwards, valve 7 and valve 6 are closed. With valve1 opened, the position of valve 3 is reversed and the relief valve 8 is opened to induce a pressure drop of 10 atm.

To recover the pressure drop, valve 8 is closed and at the same moment valve 6 is opened. In this way, the nitrogen gas $N_{2\,(g)}$ is forced to pass through the valve 6 into the reactor and the sample retained in the conduction tubes and the filter inside the reactor is returned to the system. The whole process is repeated at 1 h intervals throughout the experiment for 8 h.

4.3.5 Sample analysis

For the analysis with the gas chromatograph. The syringe was washed with the same sample collected several times. Injecting 0.1 µL to the chromatograph and pressing start for the initial analysis. After 0.5 s, the syringe was extracted from the chromatograph and cleaned several times with acetone. The analysis lasted roughly 25 min.

For the analysis with the HPLC. The aliquots of 0.5 mL are collected manually and are injected in the HPLC twice, in order to ensure that the injection loop is fully loaded with the sample. After the sample data were entered into the software, the analytical method was started and the valve turned to the position. The syringe was left inserted until the appearance of the first peaks on the chromatogram; it was then extracted and washed with acetone and water. After 50 min approximately.

4.3.6 Clean-up

At the end of the 8 hours reaction, the heating and stirring systems were switched off, valve 1 closes to cut off the nitrogen passage and valve 8 opens to depressurize the reactor. The reactor is dismantled up to reaching room temperature. Later the full reactor vessel is weighed to determine the mass loss during the reaction.

Then product mixture is filtered to recover the catalyst. Once empty, the reactor is washed with water and acetone and dried with synthetic air. The filter is unscrewed from its support, submerged in hexane in a beaker and placed in an ultrasonic bath for 25 min, then dried with synthetic air and put back in place.

4.3.7 Determination of the swelling of the thermostable ion exchange resins in water and 1-butanol.

To determine the particle diameter of resins swollen in water and 1-butanol was determined by a laser diffraction particle size analyzer (Beckman Coulter, LS 13 320). Resins samples, previously dried at 110 ºC at vacuum for 24 hours and were placed in water and 1-butanol for 48 hours to assure that resins were completely swollen. The optical model used in the analysis of the sample was the Fraunhofer diffraction pattern analysis.

4.4 EXPERIMENTAL CONDITIONS

The experiments lasted 8 hours, it was carried out at 20 atm, assuring the liquid phase in the reaction system, and mainly in the range between 120 ºC and 170 ºC. The operating temperatures were maintained constants during the experiments.

Most of the experiments were performed with a ternary mixture of water, 1-butanol and fructose. The presence of water is justified, even though it can favor the formation of undesired byproducts, because fructose is insoluble in the pure alcohol. The molar ratio between 1-butanol

and water were always $R_{BuOH/w} \approx 1.15$ [25]. The mixtures of fructose, water and 1-butanol used in the experimentation have been evaluated according to their solubility [21]. Therefore, the reaction mixture can be considered to be completely homogeneous in the conditions of the experiment.

The number of experiments carried out was 40, including replicas in the same experimental conditions in order to determine the experimental error. A list of the valid experiments and their experimental conditions can be seen in table 3.

In the experiments carried out, the effects of temperature variation of 120, 130, 140, 150 and 170 ºC, catalyst loading variation of 1.7, 2.5 and 3.3 % were analyzed. And, variation in the fructose/ 1-butanol ratio of 0.009, 0.013 and 0.017. In addition to mention two additional experiments, considering the best results.

Table 3. Description of experiments performed

Nº Experiment	CATALYST	R_{Cat} (wt/wt) %	$R_{Fruct/BuOH}$	T [ºC]
1	Without	---	0.009	120
2	DOWEX W2X	1.7	0.009	120
3-5	AMBERLYST™ 45	1.7	0.009	120
6-8	PUROLITE® CT-482	1.7	0.009	120
9	AMBERLYST™ 45	1.7	0.013	120
10	PUROLITE® CT-482	1.7	0.013	120
11	AMBERLYST™ 45	1.7	0.009	130
12	PUROLITE® CT-482	1.7	0.009	130
13	AMBERLYST™ 45	1.7	0.009	140
14	PUROLITE® CT-482	1.7	0.009	140
15	Without	---	Without butanol	150
16-18	AMBERLYST™ 45	1.7	0.009	150
19-22	PUROLITE® CT-482	1.7	0.009	150
23	AMBERLYST™ 45	1.7	0.013	150
24	PUROLITE® CT-482	1.7	0.013	150
25	AMBERLYST™ 45	1.7	0.017	150
26	PUROLITE® CT-482	1.7	0.017	150
27	AMBERLYST™ 45	2.5	0.009	150
28	PUROLITE® CT-482	2.5	0.009	150
29	AMBERLYST™ 45	2.5	0.013	150
30	PUROLITE® CT-482	2.5	0.013	150
31	AMBERLYST™ 45	2.5	0.017	150
32	PUROLITE® CT-482	2.5	0.017	150
33	AMBERLYST™ 45	3.3	0.009	150
34	PUROLITE® CT-482	3.3	0.009	150
35	AMBERLYST™ 45	3.3	0.013	150

36	PUROLITE® CT-482	3.3	0.013	150
37	AMBERLYST™ 45	3.3	0.017	150
38	PUROLITE® CT-482	3.3	0.017	150
39	AMBERLYST™ 45	3.3	0.013	170
40	PUROLITE® CT-482	3.3	0.013	170

4.5 CALCULATIONS

4.5.1 Chromatographic measurements

The data thrown by the chromatographers are given in terms of peak area percentages by HPLC and/or peak area by GC, which will be denoted by $A_{j,t}$ for a compound j at an instant t. To express in concentration the calibration equations of the form $C_{j,t} = \alpha_j * A_{j,t} + \beta_j$ are used, were α_j and β_j are the calibration coefficients for the compound j, which can be seen in the next tables.

Table 4. Coefficients for the calibration equations of GC

GC	α_j	β_j
1-Butanol	9.827E-03	-2.477E-02
Butyl formate	1.108E-02	3.916E-03
5-BMF	1.147E-02	3.234E-03
Dibutyl ether	9.422E-03	-1.018E-04
Butyl levulinate	1.147E-02	3.234E-03

Table 5. Coefficients for the calibration equations of HPLC

HPLC	α_j	β_j
D-Fructose	3.450E-06	-2.820E-03
Formic acid	9.420E-06	4.470E-03
Levulinic acid	5.120E-06	-3.400E-02
5-HMF	2.870E-06	4.720E-03

4.5.2 Contraction coefficients

The data of the chromatographic analysis can be converted directly into concentrations by means of the calibration curves previously shown and in relation to the reaction volume. Due to mass losses in the sampling process, among other causes this reaction volume is not constant. By this reason at different times, the conversion of the chromatographic data into concentrations will

be done taking different volumes. This phenomenon can be modeled using a mass contraction coefficient m_{cc}, and a volume contraction coefficient V_{cc}.

First, the density of the mixture is calculated at the end of the reaction.

$$\rho_f = \frac{m_f}{V_f} \quad \text{Eq. 1}$$

Were:

$$m_f = m_{\text{Empty reactor}} - m_{\text{catalyst}} \quad \text{Eq. 2}$$

In addition, considering a number N_s of samples is taken throughout the process with an average volume V_s, there will be a volume N_s*V_s lacking from the final reaction mixture and a volume of purge that ought to be considered. Therefore, the true total final mass will be.

$$m_T = m_f + \rho_f N_S V_S + V_{\text{Purge}} * \rho_f \quad \text{Eq. 3}$$

Then, the mass contraction coefficient will then be defined as:

$$m_{cc} = \frac{m_T - m_I}{t} \quad \text{Eq. 4}$$

For the volume contraction coefficient, the method of calculation is similar to that of mass. Assuming additive volumes, the initial total volume of the reaction mixture can be calculated as:

$$V_T = V_f + N_S V_S + V_{\text{Purge}} \quad \text{Eq. 5}$$

Then, the volume contraction coefficient will then be defined as:

$$V_{cc} = \frac{V_T - V_I}{t} \quad \text{Eq. 6}$$

So, the total mass and volume of reaction (excluding the catalyst) at the instant t are determined by:

$$m_{T,t} = m_I + m_{cc} \quad \text{Eq. 7}$$

$$V_{T,t} = V_I + V_{cc} \quad \text{Eq. 8}$$

Also, for each experiment performed, the mass balance was calculated in each experiment and only those experiments which gave less than 10 % of mass balance error has been used in this work. The results of all these operations can be seen in appendix 4 (Table 29).

4.5.3 Parameters of reaction

The important parameters such as fructose conversion, selectivity of fructose to different intermediates and products and their yield were calculated as given below:

First with the calculation of the mass fractions and mass concentrations, at the instant t are determined by:

$$n_{j\_GC,t} = \frac{C_{j,t}[\%m] * m_{T,t}}{M_i} \qquad \text{Eq. 9}$$

$$n_{j\_HPLC,t} = \frac{C_{j,t}\left[\frac{g}{L}\right] * V_{T,t}[L]}{M_j} \qquad \text{Eq. 10}$$

The conversion of fructose at an instant t is given by:

$$X_{Fruct,t} = \frac{n_{Fruct,0} - n_{Fruct,t}}{n_{Fruct,j}} \qquad \text{Eq. 11}$$

The selectivity of a substance i over fructose at an instant t can be calculated by:

$$S^{j}_{Fruct,t} = \frac{\text{mole of Fruct. forming j}}{\text{mole of Fruct consumed}} = \frac{n_{j,t}}{n_{Fruct,0} - n_{Fruct,t}} \qquad \text{Eq. 12}$$

The yield of a substance j at an instant t is given by:

$$Y^{j}_{Fruct,t} = S^{j}_{Fruct,t} * X_{Fruct,t} \qquad \text{Eq. 13}$$

Finally, as the reactions were performed in a discontinuous reactor, standardized contact time, an instant t is given by:

$$\text{standardized contact time} = CT_t = \frac{t * m_{catalyst}}{n_{Fruct,0}} \qquad \text{Eq. 14}$$

4.5.4 Experimental error

In order to verify the experimental reproduction, experimental errors were calculated. Some experiments were replicated three times each, and his experimental error was evaluated. As an example for the calculation of experimental error in the conversion of fructose.

Frist, the average is calculated by:

$$\overline{X_{Fruct,t}} = \frac{\sum_{i=1}^{3} X_{Fruct,t,i}}{3} \quad \text{Eq. 15}$$

The standard deviation of the measurement will be defined as

$$DS_{Fruct,t} = \sqrt{\frac{\sum_{i=1}^{3}\left(X_{Fruct,t,j} - \overline{X_{Fruct,t}}\right)^2}{3-1}} \quad \text{Eq. 16}$$

The standard error of mean value was calculated considering a 95 % confidence interval was chosen for its being the most commonly used.

$$EE_{\overline{X_{Fruct,t}}} = \frac{DS_{Fruct,t}}{\sqrt{3}} \quad \text{Eq. 17}$$

Because the error is evaluated only for three replicates, a very high Student's t-value would apply (only two degrees of freedom). Which would imply very high errors, invalidating the determination, whereby the following equation was applied. If three replicates were made, the 95 % confidence limits will be determined by.

$$\overline{X_{Fruct,t}} \pm EE_{\overline{X_{Fruct,t}}} \quad \text{Eq. 18}$$

5 RESULTS AND DISCUSSION

5.1 DESCRIPTION OF A MODEL EXPERIMENT

Figure 7 plots the evolution of moles of each component with regard to contact time. This figure depicts the results obtained from the experiment carried out with Purolite® CT-482 at 150 ºC, 2 g of catalyst ($R_{Cat(wt/wt)}$ = 3.3 %) and 1.5 g of fructose ($R_{Fruct/BuOH}$ = 0.013). Similar plots were obtained in the other experiments.

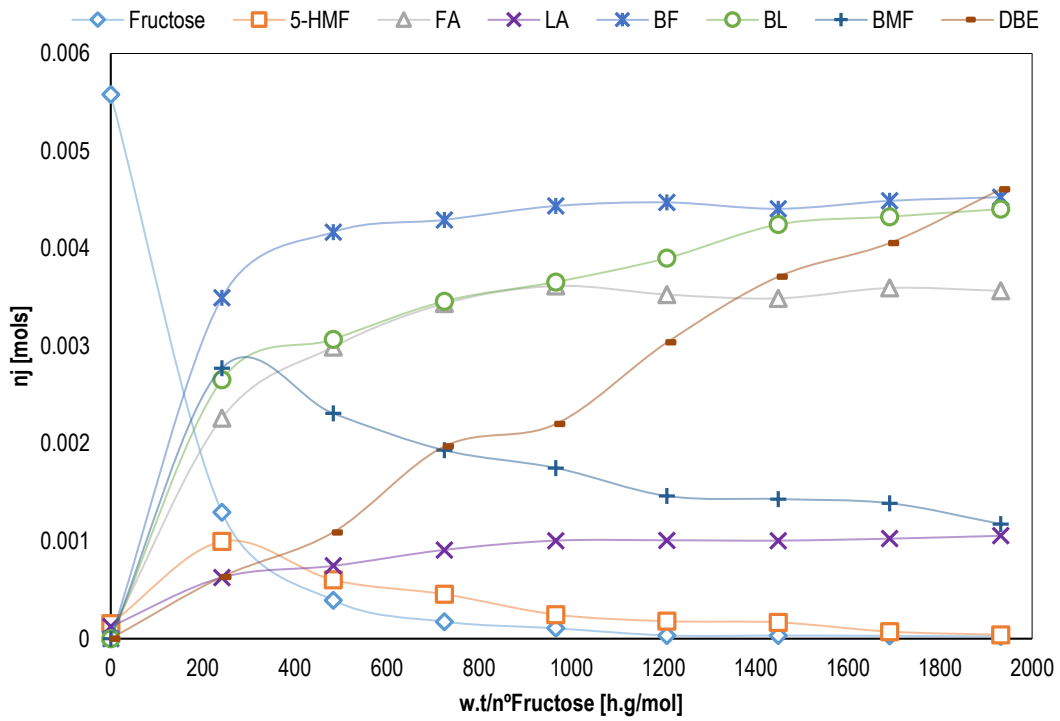

Figure 7. Mole evolution profile for substances in a batch operation. Reaction composition: Fructose, 1.5 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 2.0 g; 150 °C; 8 h.

There is an exponential decrease of fructose over time and an increase of butyl levulinate (BL), as the main product. We can see the formation of secondary products such as butyl formate (BF), formic acid (FA), levulinic acid (LA) and dibutyl ether (DBE). Also, as reaction intermediates 5-hydroximetyl furfural (5-HMF) and butyl methyl formate (BMF), peaking during the first instants of the reaction and decreasing thereafter. These tendencies confirm the reaction scheme of figure 8, where 5-HMF is the first substance produced and then decomposes rapidly into LA and FA or 5-BMF. In addition, 5-BMF can be considered an interesting compound, since it can react further to form BL. In addition, dibutyl ether can be obtained by dehydration of 1-butanol. Additionally, the production of DBE was detected from temperatures of 130 ºC.

Although, with reference to figure 8 where reaction pathway is explained, an uneven production of LA and FA and therefore of BL and BF was observed. The excess in FA and BF is due to the possible decomposition of fructose that will directly form the FA and therefore the BF. The formation of humins at higher temperatures than 150 ºC have been visibly detected. Because brown coloration is observed in the reaction mixture possibly due to the presence of soluble humins and when preparing the samples for HPLC in the filters, brown particles remain, possibly being non-soluble humins. Furthermore, the formation of BMF is observed by etherification of HMF with 1-butanol. 1-Butanol and water, which were employed in excess, have not been examined due to their interactions with the polymeric catalyst structure.

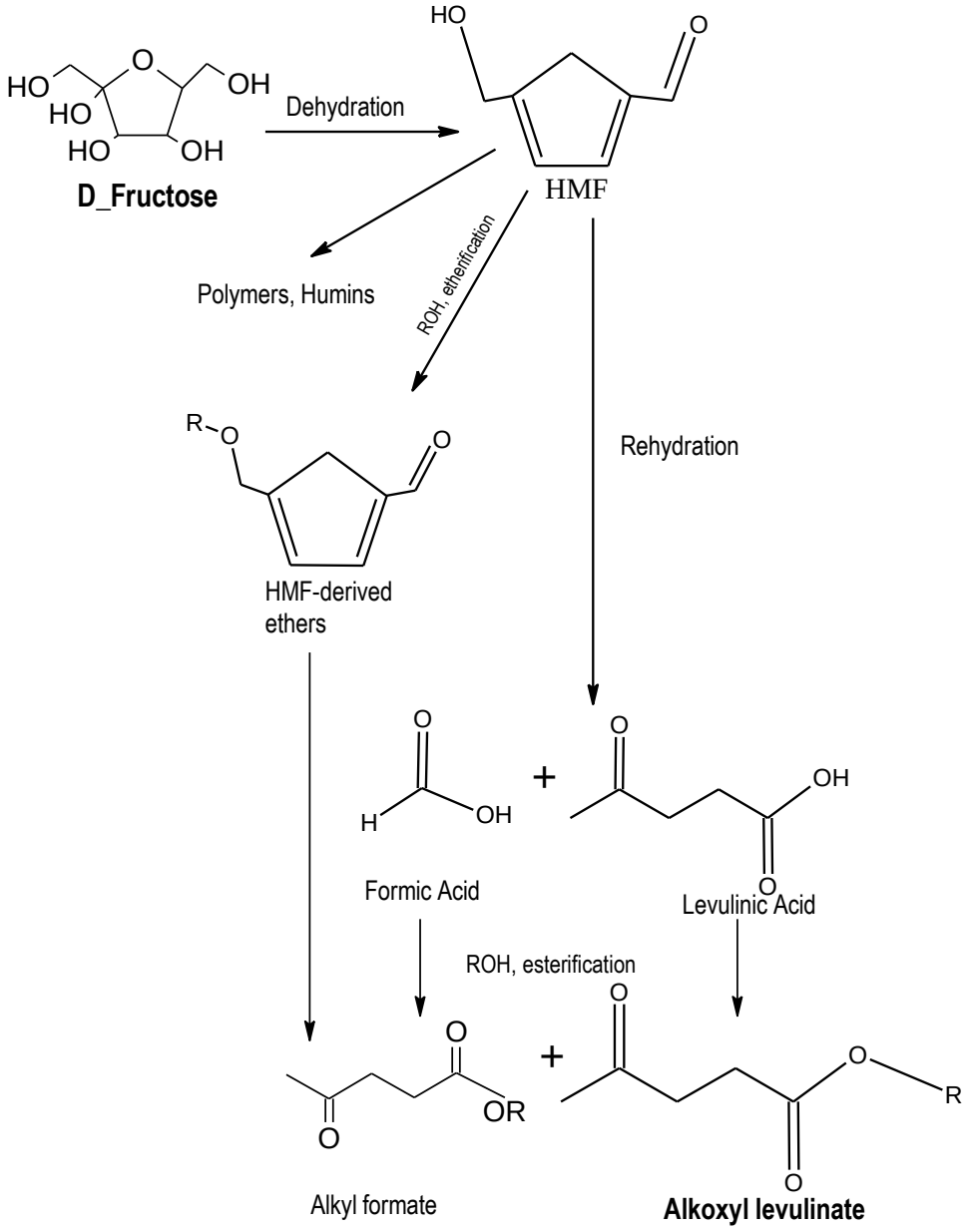

Figure 8. Proposed reaction pathway.

The selectivity and yield obtained to by-products and intermediates such as BF, FA, BMF, 5-HMF, and LA apart from the major product BL, are presented in this work with the purpose of distinguishing optimum experimental condition and catalyst. Also, to be mentioned the conversion and selectivity are only referred to fructose, as it is the raw material.

Therefore, the results of this experiment show high conversion of fructose up to 99.73 % and a selectivity of 52.95 % towards butyl levulinate (as a product of greater interest). Although a slightly higher selectivity to butyl formate compared to butyl levulinate is also shown for this experiment. The results are shown in more detail in the following table.

Table 6. Fructose conversion and selectivity to products and byproducts by a model experiment. Reaction composition: Fructose,1.5 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 1.0 g; 150 °C; 8 h.

t	w.t/n°$_{Fruct}$	X $_{Fruct}$	Selectivity [%]								
[h]	[h.g/mol]	[%]	S $^{5\text{-HMF}}_{F}$	S $^{LA}_{F}$	S $^{FA}_{F}$	S $^{BF}_{F}$	S $^{DBE}_{BuOH}$	S $^{BMF}_{F}$	S $^{BL}_{F}$	Y $^{HMF}_{F}$	Y $^{BL}_{F}$
0	0.00	33.11	5.52	4.51	1.77	0.00	0.00	0.00	0.00	1.83	0.00
1	241	84.48	14.15	8.91	32.10	49.62	1.74	39.37	37.66	11.95	31.81
2	483	95.27	7.58	9.39	37.63	52.46	2.58	29.06	38.62	7.22	36.79
3	724	97.91	5.57	11.15	42.07	52.58	3.50	23.65	42.36	5.46	41.48
4	966	98.73	3.00	12.21	43.91	53.87	3.29	21.25	44.41	2.96	43.85
5	1207	99.61	2.16	12.14	42.46	53.84	3.85	17.61	46.98	2.15	46.79
6	1449	99.62	2.01	12.10	41.99	53.04	4.34	17.22	51.11	2.00	50.91
7	1690	99.65	0.86	12.34	43.25	54.01	4.30	16.71	52.05	0.86	51.87
8	1932	**99.73**	0.48	12.68	42.88	54.41	4.46	14.13	**52.95**	0.48	**52.81**

5.2 EXPERIMENT WITHOUT CATALYST

For the purpose of evaluating and comparing the effect of the catalyst on the reaction, an experiment was carried out without the presence of any type of catalyst.

Figure 9 shows the output of this experiment. It can be seen that very little fructose reacts having a maximum conversion of 29.30 % and only a small amount of 5-HMF (0.0002 mole), FA (0.00003 mole) and LA (0.00004 mole) are generated. No other compounds are observed.

So, the dehydration of fructose occurs is spontaneously at 150 ºC but the desired product is not formed, confirming the need of a catalysts.

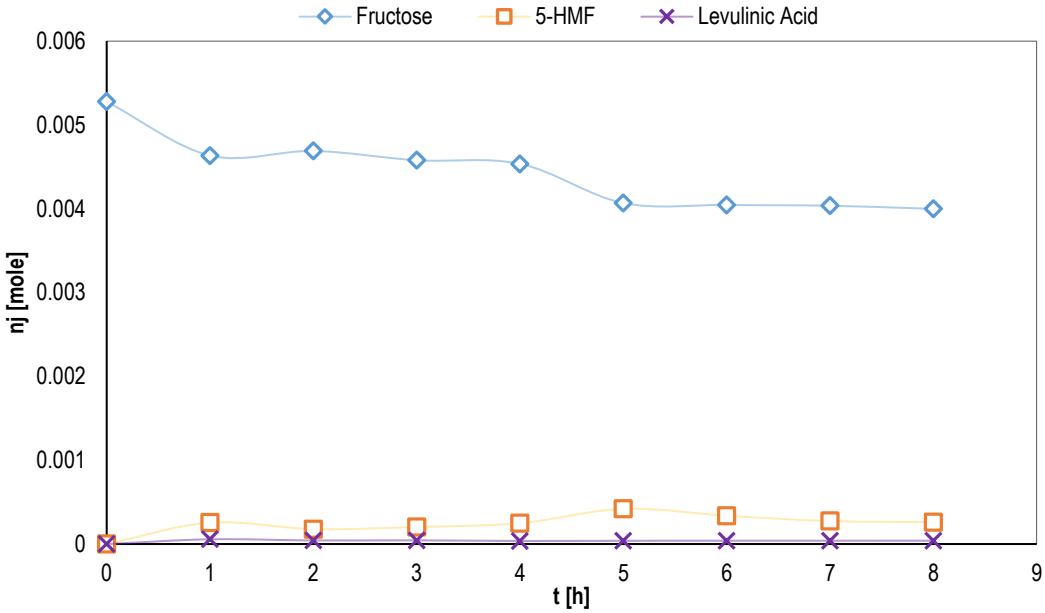

Figure 9. Mole evolution profile for fructose conversion in a batch operation. Reaction composition: Fructose, 1.5 g; BuOH, 60 mL; H_2O, 10 mL; without catalyst; 150 °C; 8 h.

5.3 FRUCTOSE-WATER EXPERIMENT

This experiment was carried out for the purpose of evaluating the influence of butanol on the production of butyl levulinate from fructose.

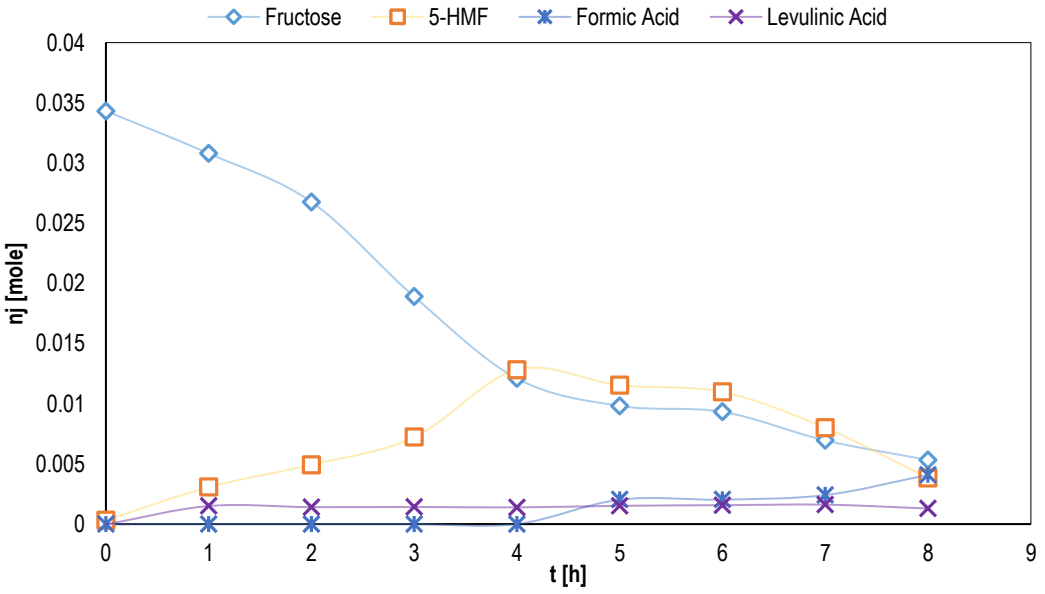

Figure 10. Mole evolution profile for fructose conversion in a batch operation. Reaction composition: $R_{Fruct/H2O}$: 0.0098; without catalyst; 150 °C; 8 h.

In the results of this experiment it is observed that little fructose reacts having a conversion of 80.0 % and quantities of 5-HMF (0.0038 mole), LA (0.0013 mole) and FA (0.0041 mole) are generated. No other compounds are observed related to the reaction scheme known. However, when analyzing the final sample by GC-MS, other compounds were detected such as methyl butane, propanol, 2, 4, 4-trimethyl and 2-pentane. These compounds are not shown in figure 10, as they were not calibrated. Also, the presence of humins and polymerization products were visually identified. Because dark brown coloration is observed in the reaction mixture possibly due to the presence of soluble humins and when preparing the samples for HPLC in the filters, dark brown particles remain, possibly being non-soluble humins. So, the need to have the presence of butanol in the reaction is moved, since we reduce the formation of humins.

5.4 EXPERIMENTAL ERROR

In order to study the experimental error, three random replicas of the same experiment were performed, for several experiments, presenting as example replicates performed at 120 °C for 8 h using the Amberlyst™ 45, 1.0 g. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL. The results obtained are shown in figure 11, figure 12 and table 7. The fructose conversion obtained was of 99.35 % ± 0.04 % and of Butyl levulinate yield was 35.71 % ± 0.03 %.

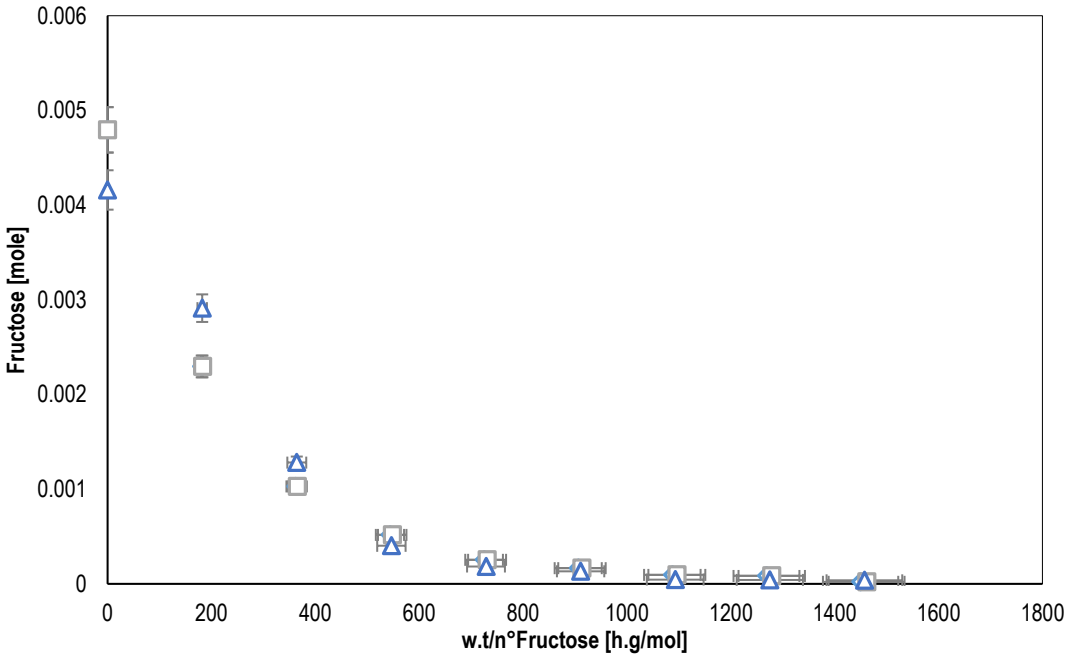

Figure 11. Study of experimental error in the evolution of fructose in the three random replicas held at 120 °C for 8 h with Amberlyst™ 45, 1.0 g. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL.

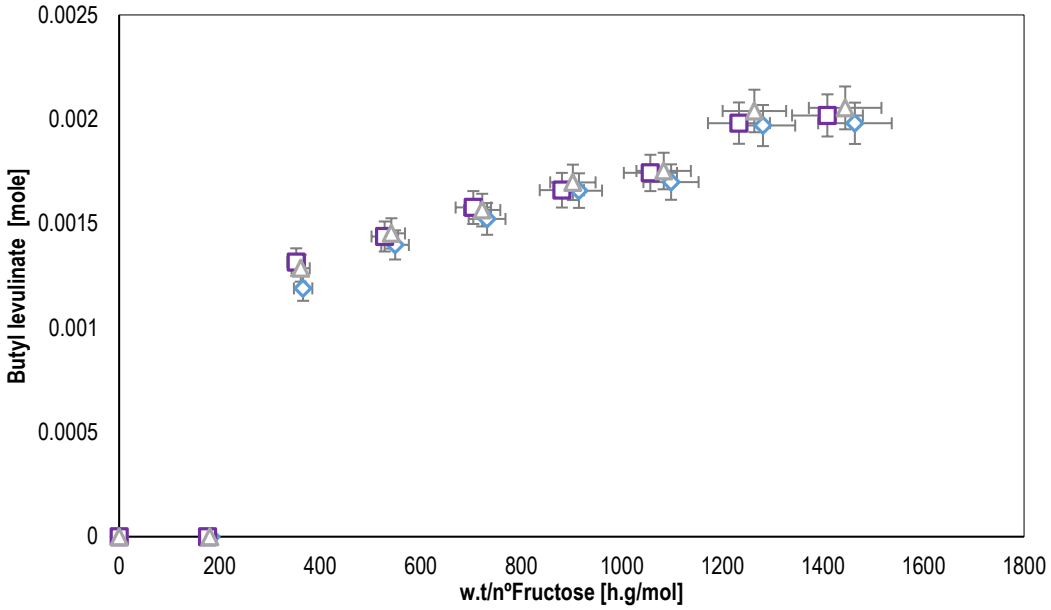

Figure 12. Study of experimental error in the evolution of butyl levulinate in the three random replicas held at 120 °C for 8 h with Amberlyst™ 45, 1.0 g. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL.

Table 7. Fructose conversion and selectivity of fructose to butyl levulinate. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst™ 45, 1.0 g; 120 °C; 8 h.

	X_{Fruct} [%]		S^{BL}_{F} [%]	
t[h]	Average	± Error	Average	± Error
0	0.00	0.00	0.00	0.00
1	38.43	0.07	0.00	0.00
2	67.23	0.06	25.22	0.05
3	88.59	0.07	26.12	0.03
4	94.70	0.04	27.85	0.01
5	96.86	0.05	29.90	0.03
6	98.43	0.04	30.90	0.03
7	98.62	0.05	35.61	0.04
8	99.35	0.04	35.71	0.03

After observing the results obtained, in figures and tables before shows, the reliability of the experiments can be proved. Also, for each experiment performed, mass balance was calculated in each experiment and only those experiments which gave less than 10 % of mass balance error has been used in this work. The said mass balance error calculation is explained in the appendix 4.

5.5 CATALYST SCREENING

For the purpose of comparing the performance of different catalysts on the production reaction of butyl levulinate from fructose and butyl alcohol, experiments were carried out at 120 °C on Dowex 50Wx2, Amberlyst ™ 45 and Purolite® CT-482 resins. The experimental conditions were: 1.0 g of fructose, 60 mL of 1-butanol, 10 mL of water, 1.0 g of catalyst and 8 h of reaction.

Figure 13 and 14 show fructose and BL mole profiles over time of reaction. As seen, a similar behavior can be observed for these three catalysts: fructose is rapidly consumed while butyl levulinate formed.

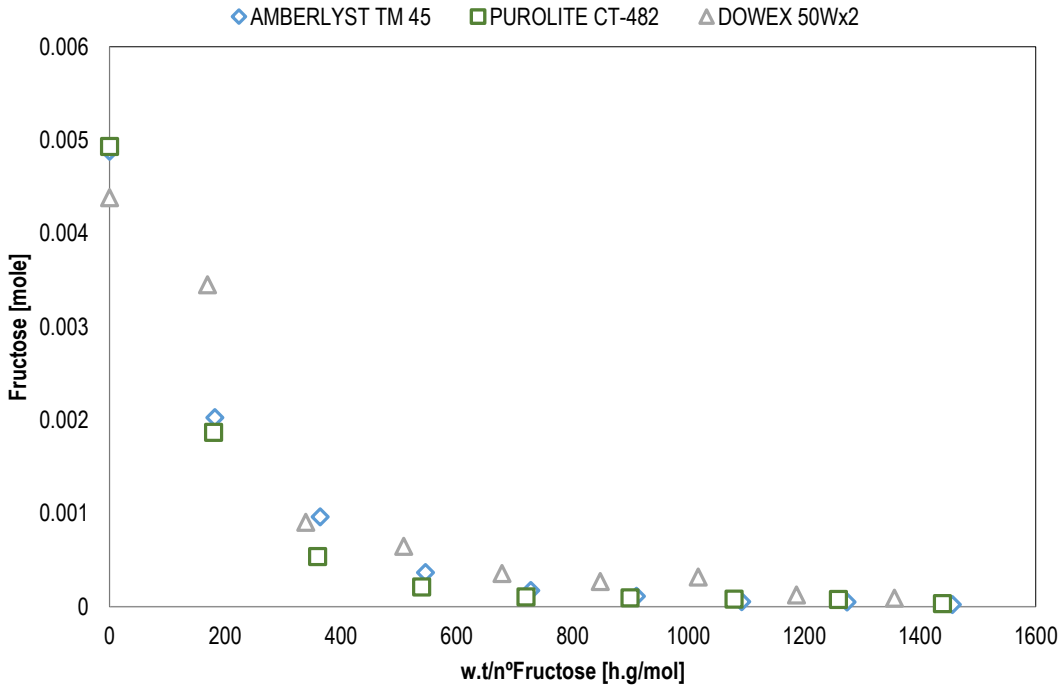

Figure 13. Mole of fructose vs contact time for synthesis of butyl levulinate for all catalysts. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Catalysts: Dowex 50Wx2, Amberlyst ™ 45 and Purolite® CT-482, 1.0 g; Temperature, 120 °C; 8 h.

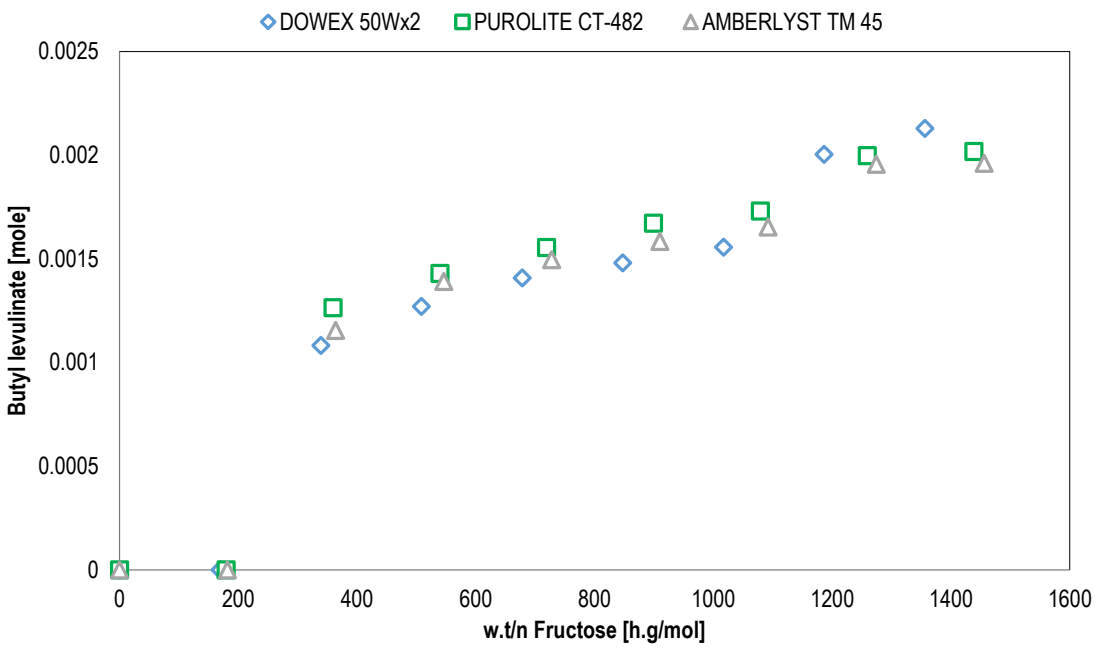

Figure 14. Mole of butyl levulinate vs standardized contact time for synthesis of butyl levulinate for all catalysts. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Catalysts: Dowex 50Wx2, Amberlyst ™ 45 and Purolite® CT-482, 1.0 g; 120 °C; 8 h.

Obtaining similar behavior among the catalysts compared, because the conversion of fructose attained high values of over 99 % in all cases.

With respect to the selectivity of fructose to butyl levulinate, with the three catalysts analyzed, their performance is very similar (see table 8). The selectivity of fructose to butyl levulinate is around 36 % for the three catalysts, resulting slightly lower over the Amberlyst™ 45.

Table 8. Selectivity of fructose to butyl levulinate. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Dowex 50Wx2, Amberlyst ™ 45 and Purolite® CT-482, 1.0 g; 120 °C; 8 h.

w.t/n° Fruct [h.g/mol]	S^{BL}_F [%]		
	Dowex 50Wx2	**Amberlyst™ 45**	**Purolite® CT-482**
0	0.00	0.00	0.00
182	0.00	0.00	0.00
364	21.65	25.22	24.55
546	24.17	26.77	26.12
728	25.37	27.74	27.85
910	26.25	29.05	29.90
1092	27.85	30.01	30.90
1274	34.68	35.45	35.61
1456	**36.63**	**35.50**	**35.71**

As a conclusion, a similar conversion of fructose (≈100 %) and selectivity to butyl levulinate (≈36 %) were obtained over the three catalysts at 120 ºC.

5.6 EFFECT OF TEMPERATURE

The direct reaction of fructose with butyl alcohol catalyzed over acidic thermostable ion exchange resins (Amberlyst ™ 45 and Purolite® CT-482) was studied at 120, 130, 140 and 150 ^{0}C. To evaluate the effect of temperature on the reaction the composition was fructose, 1.0 g, 1-butanol 60 mL, water 10 mL, catalyst 1.0 g in eight hours of reaction.

Figure 15 presents the results obtained for the thermostable ion exchange resin Amberlyst™ 45 when is increased the reaction temperature from 120 to 150 ^{0}C. The yield of 5-HMF starts at low values, which continue to grow and then decrease, but as it is observed at higher temperature this profile is less pronounced.

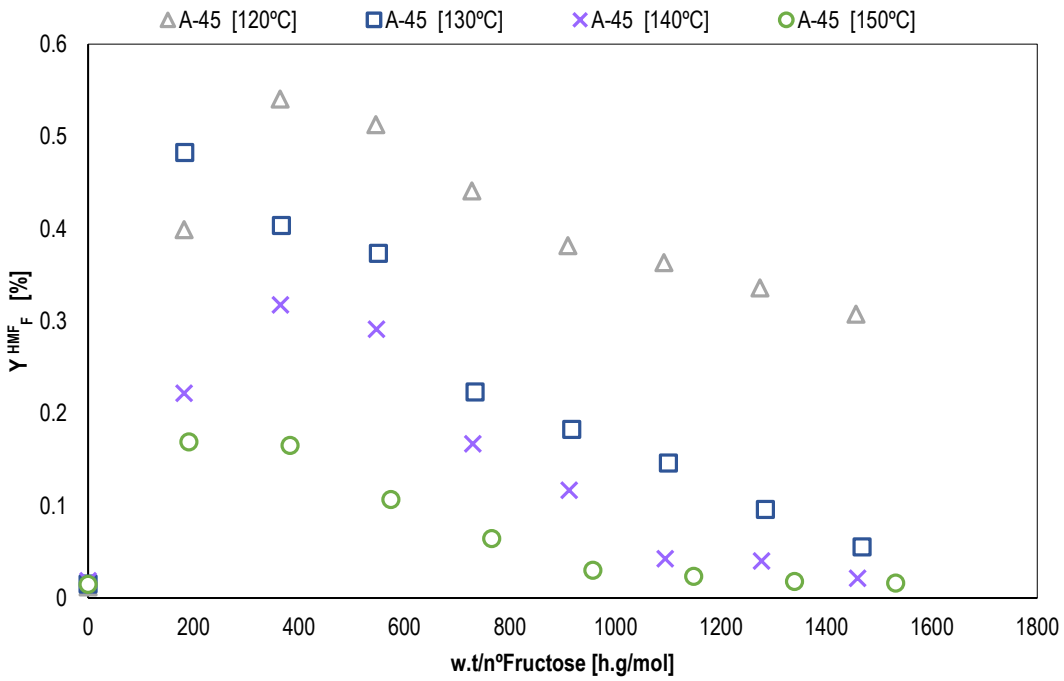

Figure 15. Effect of temperature on yield of 5-HMF for the reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst ™ 45, 1.0 g; different temperatures; 8 h.

Consequently, figure 16 shows the performance profiles for butyl levulinate, at higher temperature higher yield, for the same contact time.

These performance profiles visualized for the 5-HMF and BL is because according to the reaction path explained previously, as BL is produced, 5-HMF is consumed as a reaction intermediate besides that fructose is hydrated towards the production of 5-HMF.

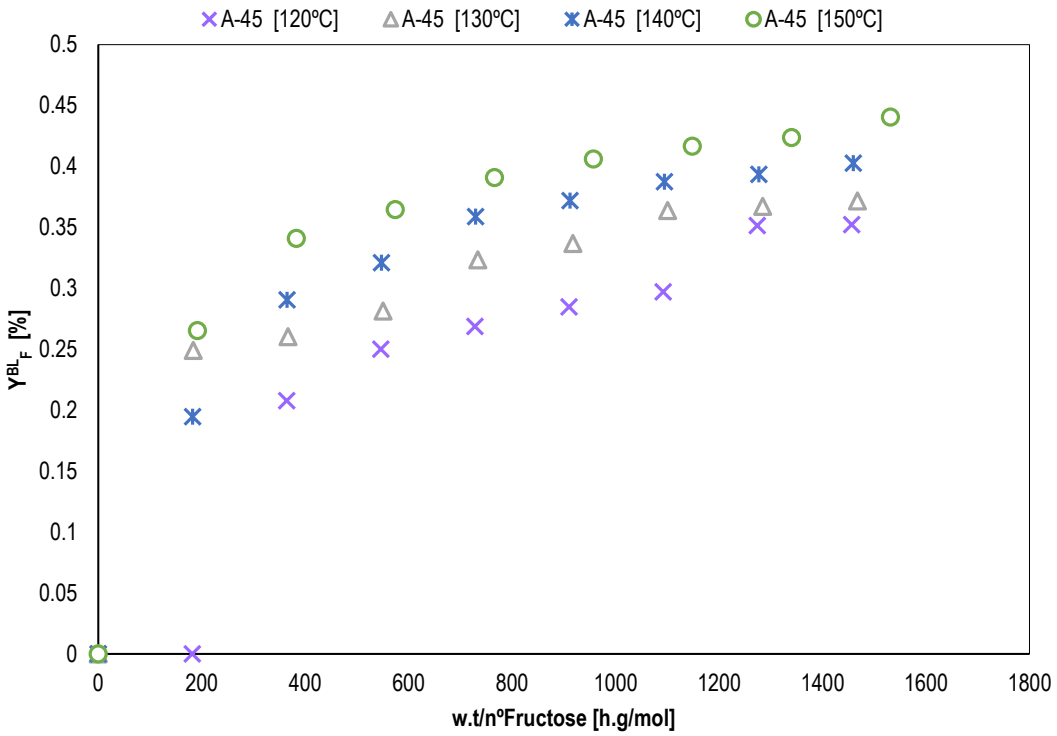

Figure 16. Effect of temperature on yield of butyl levulinate. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst ™ 45, 1.0 g; different temperatures; 8 h.

Figures 17 and 18 show the results obtained for the thermostable ion exchange resin, Purolite® CT-482. Its behavior was similar to that of the Amberlyst™ 45.

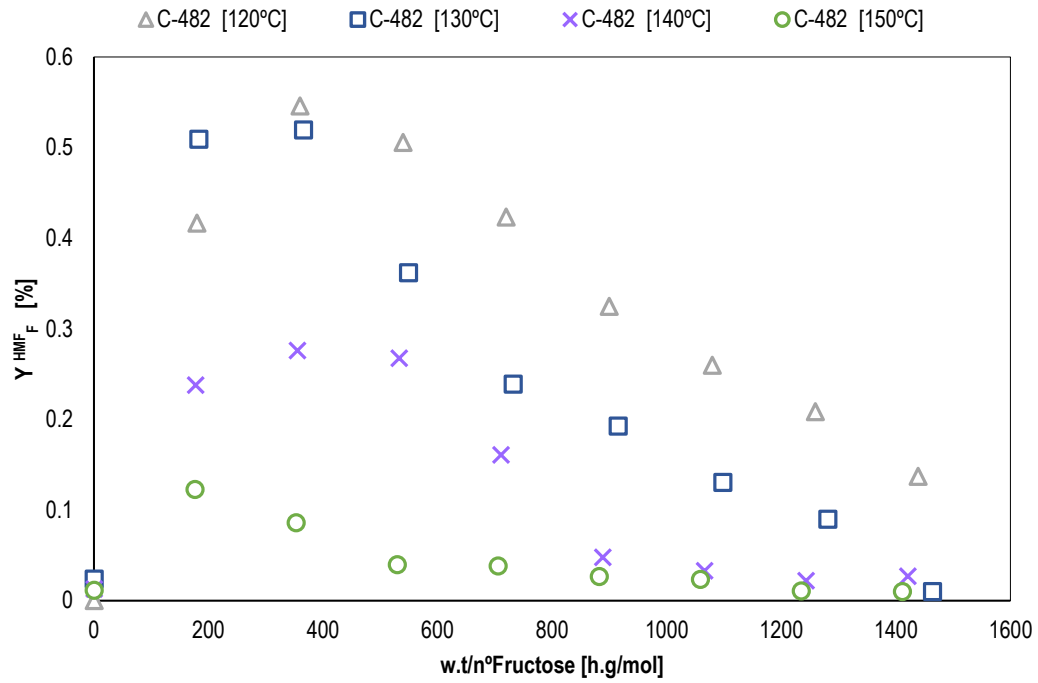

Figure 17. Effect of temperature on yield of 5-HMF. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 1.0 g; different temperatures; 8 h.

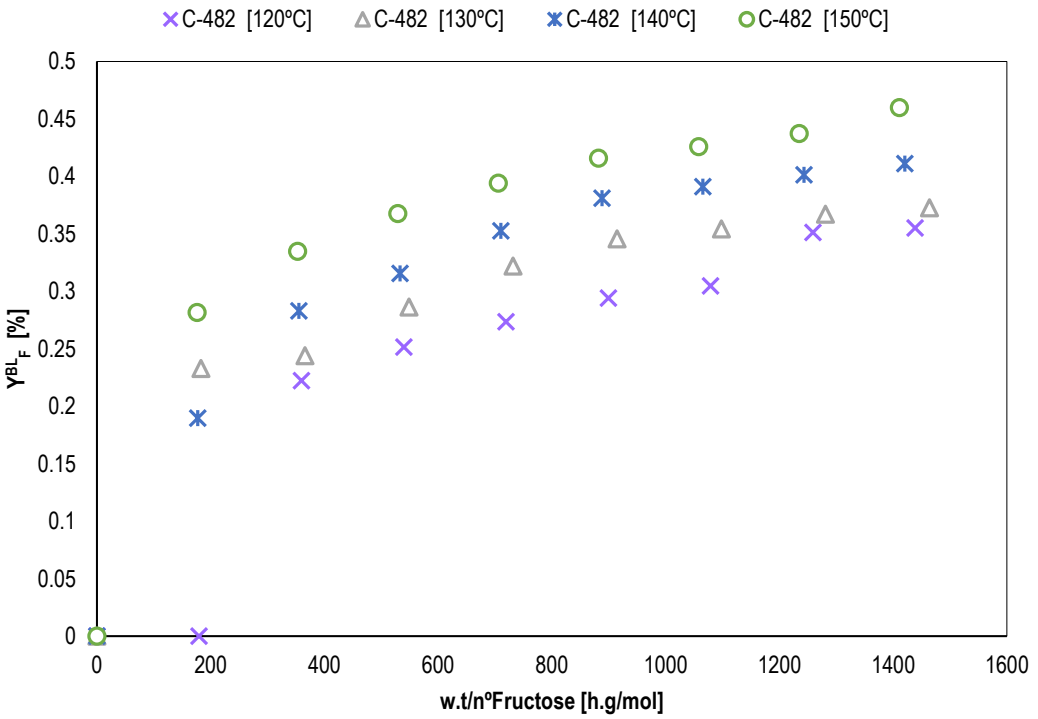

Figure 18. Effect of temperature on yield of butyl levulinate for the reaction. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 1.0 g; different temperatures; 8 h.

The effect of reaction temperature on the fructose conversion to butyl levulinate was investigated, and the experiments were carried out at 120, 130, 140 and 150 °C, respectively.

Table 9 and table 10 present the selectivity towards the products and by-products resulting from the reaction using Amberlyst™ 45 and Purolite® CT-482 catalysts after 8 hours of reaction. The higher the temperature, the higher the fructose selectivity towards BL, BF and FA. In addition, in the opposite case for the 5-HMF and BMF, as the temperature increases the low selectivity for these by-products.

Additionally, the production of DBE due to the dehydration of two butanol molecules, is observed from temperatures of 130 ºC, increasing according to the increase in temperature, although in small quantities (at 130 °C, 0.0003 mole are produced and at 150 °C, 0.003 mole are produced by the two resins used).

Table 9. Effect of temperature on conversion of fructose and selectivity of fructose to all components by reaction. Composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst ™ 45, 1.0 g; 8 h.

T [ºC]	120	130	140	150
X_F [%]	99.35	99.39	99.84	99.80
$S^{5\text{-HMF}}_F$ [%]	30.89	5.59	2.16	1.64
S^{BMF}_F [%]	33.44	35.25	27.16	22.30
S^{LA}_F [%]	10.34	9.46	10.88	10.46
S^{FA}_F [%]	34.81	31.91	40.32	38.19
S^{BF}_F [%]	47.98	51.76	55.69	57.16
S^{DBE}_{BuOH} [%]	0.00	0.46	1.11	2.36
S^{BL}_F [%]	35.38	37.41	40.32	44.14

Table 10. Effect of temperature on conversion of fructose and selectivity of fructose to all components. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 1.0 g; 8 h.

T [ºC]	120	130	140	150
X_F [%]	99.41	99.47	99.59	99.80
$S^{5\text{-HMF}}_F$ [%]	13.80	1.01	2.71	1.01
S^{BMF}_F [%]	33.71	32.49	27.63	20.94
S^{LA}_F [%]	9.81	9.60	10.28	12.27
S^{FA}_F [%]	30.19	38.28	33.95	40.03
S^{BF}_F [%]	48.26	53.25	53.25	61.02
S^{DBE}_{BuOH} [%]	0.00	0.33	0.71	2.21
S^{BL}_F [%]	35.71	37.46	41.27	46.37

Fructose reaches complete conversion at temperatures above 100 ºC, as it is presented in the literature [21, 26, 27]. Besides, it can be observed from figure 15 that temperature has a significant effect on the selectivity of fructose to all products specifically in the butyl levulinate as main product, in the two types of resins analyzed, Purolite® CT-482 and Amberlyst ™ 45.

Summing up by looking at the figures 19 and 20, the selectivity to 5-HMF began to fall sharply with the increase in temperature, as it happens with the BMF but in a moderate way. The same trend but in opposite direction was seen in the selectivity of fructose towards FA, LA, BL and BF, which increased as the temperature rose up to 150 ºC. DBE was not observed until the temperature reached 130 °C. The selectivity and the yield of BL and BF increased with the temperature and at 150 °C, maximum yield and maximum selectivity of fructose to BL (44.1 % with Amberlyst ™ 45 and 46.4 % with Purolite® CT-482) and BF (57.2 % with Amberlyst ™ 45 and 61.0 % with Purolite® CT-482) were observed. Though, the presence of intermediates at 150 ºC was higher, and also increases the rate of formation of by-products such as BF.

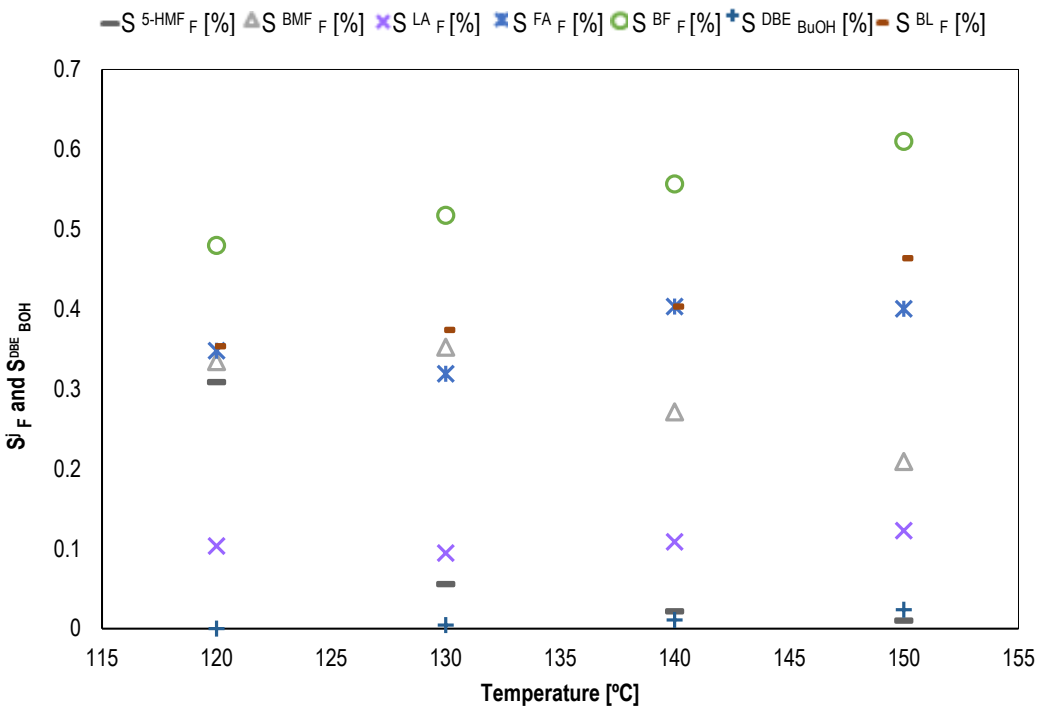

Figure 19. Effect of temperature on the synthesis of intermediates and products from fructose. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst ™ 45, 1.0 g; 8 h.

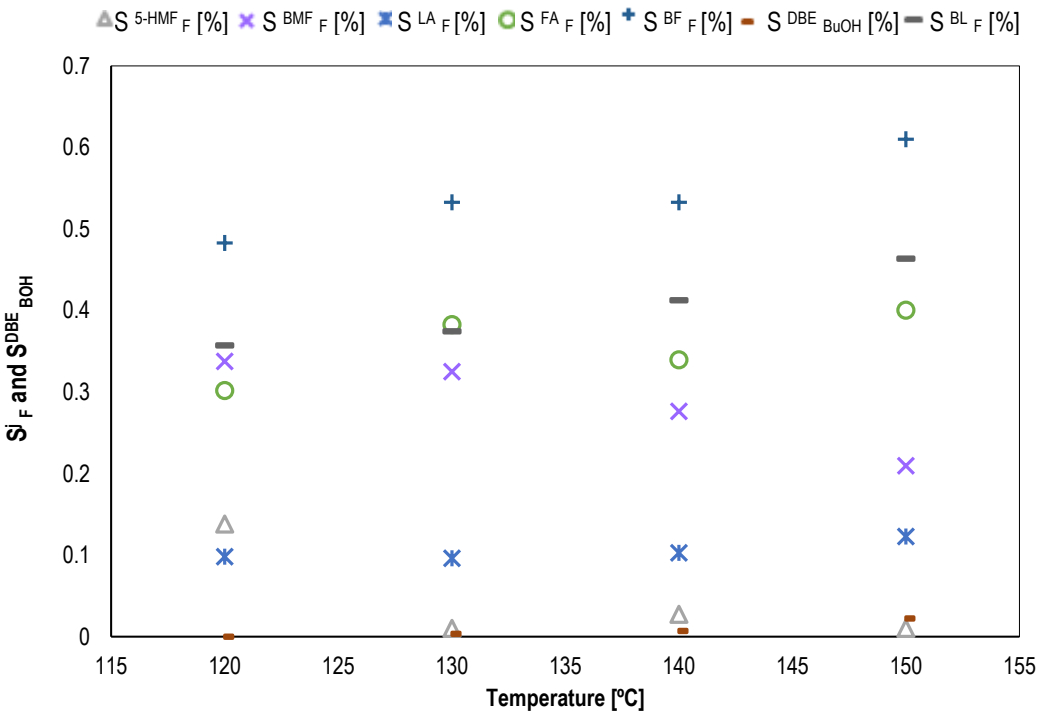

Figure 20. Effect of temperature on the synthesis of intermediates and products from fructose. Composition: Fructose, 1.0 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 1.0 g; 8 h.

5.7 EFFECT OF FEED COMPOSITION AND CATALYST LOADING

The previous experiments were performed with a feed composition of 60 mL 1-butanol, 10 mL water and 1.0 g fructose. In addition to this, new experiments have been performed varying the fructose load, such that the fructose/ 1-butanol molar ratio were 0.009, 0.013 and 0.017. Together with this variation of the molar fructose/ 1-butanol ratio, the catalyst loading (Amberlyst ™ 45 and Purolite® CT-482) of 1.7, 2.5 and 3.3 % respectively are applied.

5.7.1 $R_{Fruct/BuOH}$ 0.009 AND CATALYST LOADING $R_{Cat(wt/wt)}$ % OF 1.7, 2.5 AND 3.3.

The analysis of the experiments performed varying the catalyst load, for the molar ratio fructose/ 1-butanol 0.009, are presented in table 11 and figure 21. A the end of the eight hours of reaction, these experiments show the complete conversion of fructose to products and by-products and the selectivity towards butyl levulinate increases, as for other products such as LA, FA and BF, and decreases for 5-HMF and BMF.

Achieving a maximum yield of 52.55 % towards butyl levulinate, using Purolite® CT-482 as a catalyst. A slightly lower yield was obtained over Amberlyst ™ 45 (48.21 %).

Table 11. Experimental data for $R_{Fruct/BuOH}$ 0.009 and variation in catalyst loading $R_{Cat(wt/wt)}$ % of 1.7, 2.5 and 3.3 for 8 h of reaction.

T [ºC]	150					
$R_{Fruct/BuOH}$	**0.009**					
$R_{Cat(wt/wt)}$ %	**1.7**		**2.5**		**3.3**	
CATALYST	**A-45**	**C-482**	**A-45**	**C-482**	**A-45**	**C-482**
X_{Fruct} [%]	99.80	99.16	99.36	98.72	99.77	99.98
$S^{5\text{-}HMF}_{F}$ [%]	1.64	1.61	0.96	1.42	0.26	1.04
S^{BMF}_{F} [%]	22.30	22.78	21.93	22.68	19.53	20.94
S^{LA}_{F} [%]	10.46	12.27	12.03	12.71	12.69	12.93
S^{FA}_{F} [%]	38.19	40.03	49.81	54.69	54.17	54.97
S^{BF}_{F} [%]	57.16	61.02	62.68	68.65	65.89	70.69
S^{DBE}_{BOH} [%]	2.16	2.21	3.57	4.26	4.18	4.97
S^{BL}_{F} [%]	44.14	46.37	47.38	48.31	48.32	52.56
y^{BL}_{F} [%]	44.05	45.98	47.08	47.69	**48.21**	**52.55**

5.7.2 $R_{Fruct/BuOH}$ 0.013 AND CATALYST LOADING $R_{Cat(wt/wt)}$ % OF 1.7, 2.5 AND 3.3.

For the composition analyzed in this section, there is a complete conversion of fructose (>99%), but a very slight decrease in the selectivity of fructose to butyl levulinate. See table 13 and figure 21. A the end of the eight hours of reaction, the selectivity towards butyl levulinate increases, as for other products such as LA, FA and BF, and decreases for 5-HMF and BMF.

The selectivity towards the production of butyl levulinate is lower than the conditions when working with $R_{Fruct/BuOH}$ 0. 009.Consequently, their yields will be lower. Achieving yields towards 52.46 % butyl levulinate, using Purolite® CT-482 as a catalyst and 48.09 % using Amberlyst ™ 45 catalyst.

Table 12. Experimental data for $R_{Fruct/BuOH}$ 0.013 and variation in catalyst loading $R_{Cat(wt/wt)}$ % of 1.7, 2.5 and 3.3 for 8 h of reaction.

T [ºC]	150					
$R_{Fruct/BuOH}$	**0.013**					
$R_{Cat(wt/wt)}$ %	**1.7**		**2.5**		**3.3**	
CATALYST	**A-45**	**C-482**	**A-45**	**C-482**	**A-45**	**C-482**
X_{Fruct} [%]	99.88	99.98	99.74	99.72	99.81	99.73
$S^{5\text{-}HMF}_{F}$ [%]	1.93	2.15	1.77	1.62	0.50	0.48
S^{BMF}_{F} [%]	20.67	15.03	15.12	13.83	14.68	14.13
S^{LA}_{F} [%]	12.05	11.64	12.05	15.18	13.45	12.68
S^{FA}_{F} [%]	30.41	39.92	41.98	38.87	42.81	42.88
S^{BF}_{F} [%]	43.27	48.72	49.09	45.81	51.60	54.35
S^{DBE}_{BOH} [%]	1.56	2.85	3.56	3.67	4.02	4.46
S^{BL}_{F} [%]	43.14	44.04	44.15	46.53	48.18	52.60
y^{BL}_{F} [%]	43.09	44.03	44.04	46.40	**48.09**	**52.46**

5.7.3 $R_{Fruct/BuOH}$ 0.017 AND CATALYST LOADING $R_{Cat(wt/wt)}$ % OF 1.7, 2.5 AND 3.3.

Finally, for the molar fructose/ 1-butanol ratio of 0.017 was studied. Despite observing a conversion of fructose greater than 99 %, the selectivities towards products and by-products

decrease. Then the yield to butyl levulinate decreases to values of 46.76 % using Purolite® CT-482 as catalyst and 45.20 % using Amberlyst ™ 45 as catalyst. As seen in the table 13.

Table 13. Experimental data for $R_{Fruct/BuOH}$ 0.017 and variation in catalyst loading $R_{Cat\ (wt/wt)}$ % of 1.7, 2.5 and 3.3 for 8 h of reaction.

T [ºC]	150					
$R_{Fruct/BuOH}$	**0.017**					
$R_{Cat(wt/wt)}$ %	**1.7**		**2.5**		**3.3**	
CATALYST	**A-45**	**C-482**	**A-45**	**C-482**	**A-45**	**C-482**
X_{Fruct} [%]	99.90	99.88	99.81	99.32	99.29	99.75
$S^{5\text{-}HMF}_{F}$ [%]	2.05	0.89	0.87	0.47	0.63	0.91
S^{BMF}_{F} [%]	15.24	14.17	12.13	11.31	11.32	11.95
S^{LA}_{F} [%]	9.77	11.11	11.15	12.86	13.02	12.05
S^{FA}_{F} [%]	34.52	37.05	37.02	39.56	36.43	45.74
S^{BF}_{F} [%]	38.52	39.96	39.63	45.86	43.90	50.80
S^{DBE}_{BOH} [%]	1.75	2.71	2.88	3.97	4.38	4.90
S^{BL}_{F} [%]	36.66	37.77	41.05	43.07	45.52	46.88
y^{BL}_{F} [%]	36.62	37.72	40.97	42.78	**45.20**	**46.76**

For the conditions analyzed in this section, it is observed that fructose is completely converted and, as expected, greater amounts of fructose yield higher gross concentrations of all products. When observing the selectivity, as a function of the fructose load, increasing the fructose load decreases the selectivity.

Figure 21 shows the results obtained as a function of the variation of fructose load and catalyst load in summary form. Presenting in the abscissa molar ratios of fructose on 1-butanol, catalyst loading and type of catalyst used. In the main axis of the ordinates the selectivities to the products and by-products are presented and as a secondary axis the conversion of fructose.

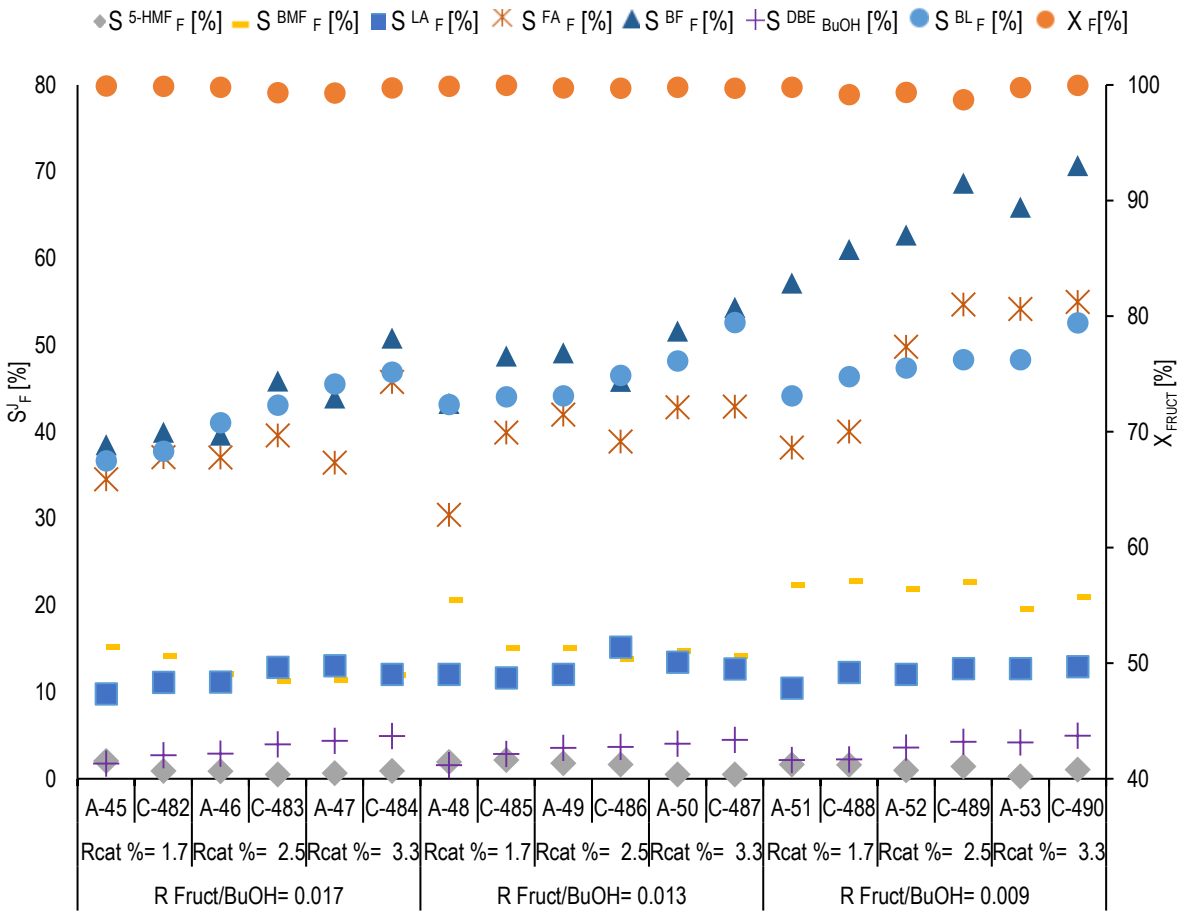

Figure 21. Representation of the results of experimentation with variation of feed compositions and catalyst loading.

The effect of feed composition and catalyst loading it is observed for all cases a complete conversion of fructose (>99 %) to products and by-products. By decreasing the $R_{Fruct/BuOH}$ and increase of $R_{cat(wt/wt)}$ consequently increases the yield and selectivity towards the BL, as for byproducts such as LA, FA, BF and DBE, and decreases for 5-HMF and BMF. The same behavior presents the two resins studied Amberlyst™ 45 and Purolite® CT-482.

Figure 22 show that at a certain standardized contact time the different catalyst loading ($R_{Cat(wt/wt)}$ of 1.7, 2.5 and 3.3 %) do not affect the yield of fructose towards the BL, the same effect was observed for both catalysts (A-45 and C-482). So similar yields to BL were obtained at same contact time.

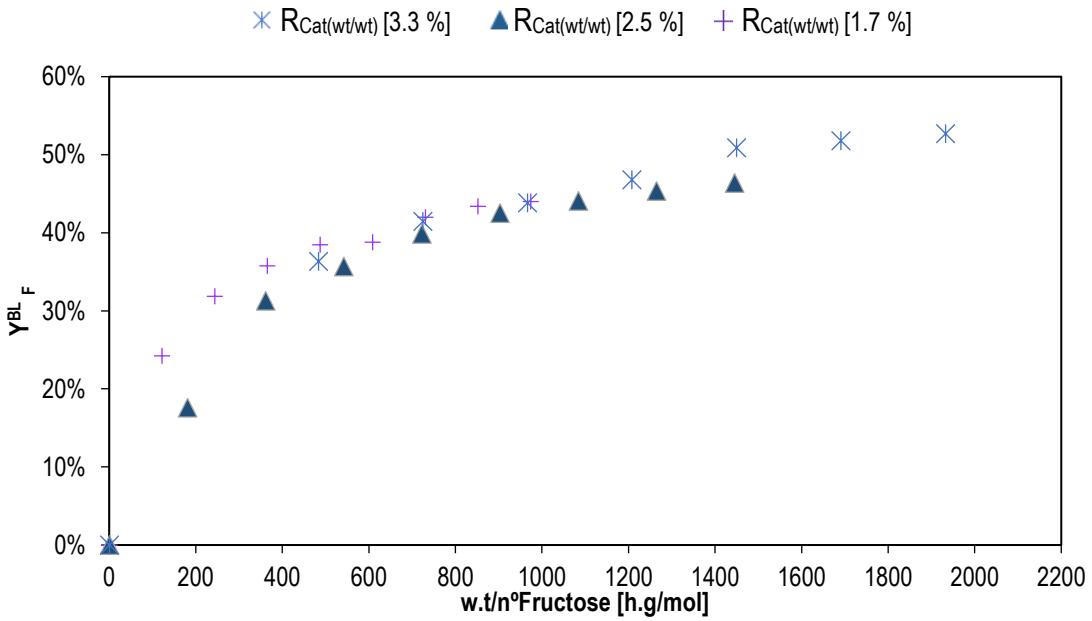

Figure 22. Yield results towards butyl levulinate with $R_{Fruct/BuOH}$ 0.013 and variation in catalyst loading $R_{Cat(wt/wt)}$ % of 1.7, 2.5 and 3.3 (Purolite® CT-482), 150 ºC and 8 h of reaction.

Table 14 shows the mole number of BL increased on increasing the initial amount of fructose and the yield to BL at the end of the run. Consequently, based on obtaining greater molar quantity of BL and higher yield to BL. The better results for BL production was getting with Purolite® CT-482, $R_{Fruct/BuOH}$: 0.013 and $R_{cat(wt/wt)}$: 3.3 % at 150 ºC of temperature and at the end of 8 hours of reaction. Because it obtains greater number of BL mole (0.004 mole) and with yield to BL up to 52.46 %.

Table 14. Experimental data for quantity of mole and yield of fructose to butyl levulinate, at 150 ºC and the end of 8 hours of reaction.

$R_{Fruct/BuOH}$	$R_{Cat(wt/wt)}$ %	BL [mole]		$y^{BL}{}_{F}$ [%]	
		A-45	C-482	A-45	C-482
0.017	1.7	0.004	0.004	36.62	37.72
	2.5	0.005	0.005	40.97	42.78
	3.3	0.005	0.005	45.2	46.76
0.013	1.7	0.004	0.004	43.09	44.04
	2.5	0.004	0.004	44.04	46.4
	3.3	**0.004**	**0.004**	**48.09**	**52.46**
0.009	1.7	0.0026	0.0026	44.05	45.98
	2.5	0.0027	0.0027	47.08	47.69
	3.3	0.0028	0.0028	48.21	52.55

5.8 COMPLEMENTARY EXPERIMENT AT 170 ºC

5.8.1 Summary of previous results

Before presenting the complementary experiments, it is necessary to analyze the results obtained with the experiments already carried out. Whose results are summarized in this section, showing the conversion of fructose, selectivity of fructose to butyl levulinate and the corresponding yield. This according to the different reaction conditions and different compositions evaluated in the present investigation, as shown in the following table ordered according to yield to BL ascending.

Table 15. Summary of results.

Nº Experiment	CATALYST	R_{Cat} (wt/wt) %	$R_{Fruct/BuOH}$	T [ºC]	X_{Fruct} [%]	S^{BL}_{F} [%]	Y^{BL}_{F} [%]
1	Without	---	0.009	120	29.00	0.00	0.00
15	Without	---	Without butanol	150	86.01	0.00	0.00
9	AMBERLYST™ 45	1.7	0.013	120	98.74	30.08	29.70
10	PUROLITE® CT-482	1.7	0.013	120	98.78	30.57	30.20
3-5	AMBERLYST™ 45	1.7	0.009	120	99.30	35.40	35.15
6-8	PUROLITE® CT-482	1.7	0.009	120	99.41	35.71	35.50
2	DOWEX W2X	1.7	0.009	120	98.50	36.60	36.05
25	AMBERLYST™ 45	1.7	0.017	150	99.90	36.66	36.62
11	AMBERLYST™ 45	1.7	0.009	130	99.30	37.40	37.14
12	PUROLITE® CT-482	1.7	0.009	130	99.50	37.50	37.31
26	PUROLITE® CT-482	1.7	0.017	150	99.88	37.77	37.72
13	AMBERLYST™ 45	1.7	0.009	140	99.80	40.30	40.22
31	AMBERLYST™ 45	2.5	0.017	150	99.81	41.05	40.97
14	PUROLITE® CT-482	1.7	0.009	140	99.60	41.30	41.13
32	PUROLITE® CT-482	2.5	0.017	150	99.32	43.07	42.78
23	AMBERLYST™ 45	1.7	0.013	150	99.88	43.14	43.09
24	PUROLITE® CT-482	1.7	0.013	150	99.98	44.04	44.03
29	AMBERLYST™ 45	2.5	0.013	150	99.74	44.15	44.04
16-18	AMBERLYST™ 45	1.7	0.009	150	99.80	44.14	44.05
37	AMBERLYST™ 45	3.3	0.017	150	99.29	45.52	45.20
19-22	PUROLITE® CT-482	1.7	0.009	150	99.16	46.37	45.98
30	PUROLITE® CT-482	2.5	0.013	150	99.72	46.53	46.40
38	PUROLITE® CT-482	3.3	0.017	150	99.75	46.88	46.76
27	AMBERLYST™ 45	2.5	0.009	150	99.36	47.38	47.08
28	PUROLITE® CT-482	2.5	0.009	150	98.72	48.31	47.69
35	AMBERLYST™ 45	3.3	0.013	150	99.81	48.18	**48.09**
33	AMBERLYST™ 45	3.3	0.009	150	99.77	48.32	**48.21**
36	PUROLITE® CT-482	3.3	0.013	150	99.73	52.60	**52.46**
34	PUROLITE® CT-482	3.3	0.009	150	99.98	52.56	**52.55**

Then with the obtained data it is observed that in all the experiments that catalysts (Dowex w2x, Purolite® CT-482 and Amberlyst™ 45) were used, the conversion of fructose is total. Analyzing the selectivity towards butyl levulinate and therefore the yield, experiments 33, 34, 35 and 36 are presented with better results. Obtaining yields between 48.09 % and 52.55 % of yield to BL, as shown in the previous table.

5.8.2 Development of the complementary experiment at 170 ºC

These complementary experiments were performed after analyzing the previous results obtained. Noting that the best results were obtained with experiments 33 and 35 for Amberlyst™ 45 catalyst, and the experiments 34, 36 with Purolite® CT-482 catalyst. Because total conversion of fructose and better selectivity of fructose to butyl levulinate were obtained. Among the experiments 33, 34, 35 and 36 that have given the best results, it was decided to carry out the complementary experiments keeping the conditions of experiments 35 and 36. Because the number of BL moles obtained in experiments 35 and 36 are more than those obtained in the experiments 33 and 34, thus presenting similar selectivities to BL. Emphasizing that these resins work at high temperatures (A-45 up to 170 ºC and C-482 up to 190 ºC).

The complementary experiments carried out were two, with 170 ºC of temperature, 0.013 fructose-butanol ratio and 3.3 % catalyst loading. As seen in table 16 the fructose is converted totally, and the selectivity to butyl levulinate reaches values of 52.98 % using Amberlyst™ 45 as catalyst and 55.61 % using Purolite® CT-482 as catalyst.

Table 16. Experimental data of additional experiments at 170 ºC.

CATALYST	A-45	C-482
X_{Fruct} [%]	99.71	99.76
$S^{5\text{-HMF}}{}_{F}$ [%]	0.15	0.29
$S^{BMF}{}_{F}$ [%]	10.76	10.95
$S^{LA}{}_{F}$ [%]	14.80	15.27
$S^{FA}{}_{F}$ [%]	33.13	36.53
$S^{BF}{}_{F}$ [%]	49.61	48.66
$S^{DBE}{}_{BuOH}$ [%]	12.98	17.90
$S^{BL}{}_{F}$ [%]	**52.98**	**55.61**
$Y^{BL}{}_{F}$ [%]	**52.82**	**55.48**

In addition, it is observed a decrease of the amounts of FA and BF in the molar reaction profile in figures 23 and 24. Similar mole evolution profiles for sustances are observed in the two resins studied. However, the reaction catalyzed with Purolite® CT-482 showed better performance.

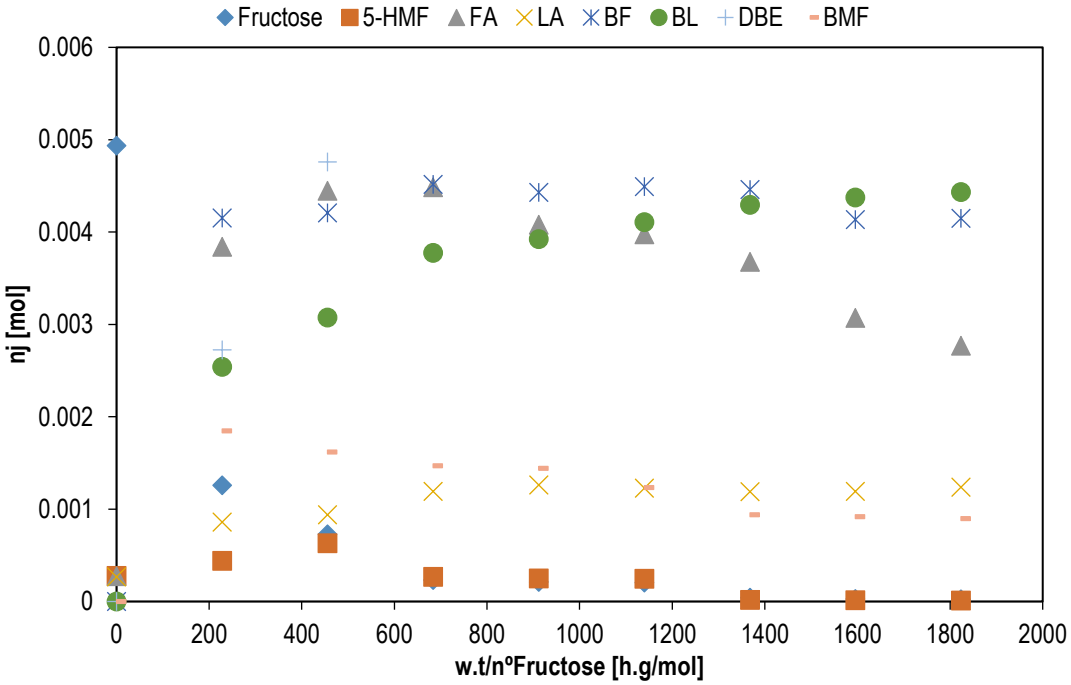

Figure 23. Mole evolution profile for substances. Reaction composition: Fructose, 1.5 g; BuOH, 60 mL; H_2O, 10 mL; Amberlyst™ 45, 2.0 g; 170 °C; 8 h.

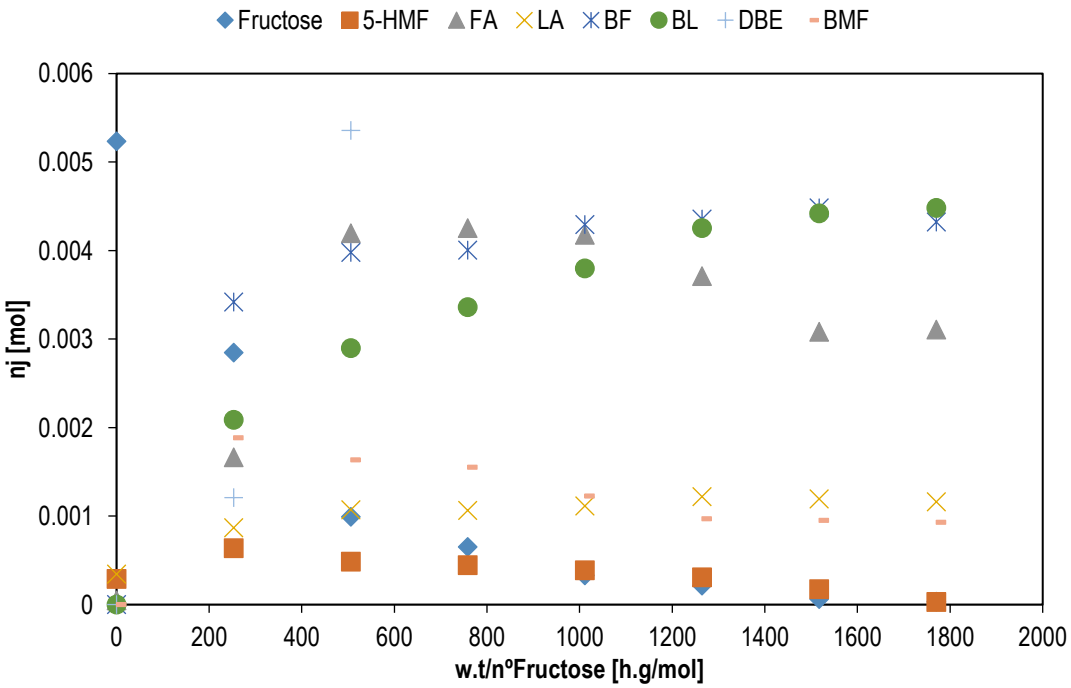

Figure 24. Mole evolution profile for substances. Reaction composition: Fructose, 1.5 g; BuOH, 60 mL; H_2O, 10 mL; Purolite® CT-482, 2.0 g; 170 °C; 8 h.

6 CONCLUSIONS

The present investigation shows the potential of thermostable resins to catalyze the synthesis of butyl levulinate from fructose in the presence of 1-butanol and water mixture at high temperatures as 120, 130, 140, 150 and 170 ºC with different composition of reaction feed and catalyst loading. As expected, the same series-parallel scheme reaction was observed as in previous works [6]: fructose dehydrates to HMF, HMF reacts with BuOH to give BMF, followed by the subsequent alcoholysis of the ether to BL and BF, and finally, HMF rehydrates to LA and FA. Subsequently both acids esterify to BL and BF, respectively. On increasing temperature, the formation of di-butyl ether (DBE) from butanol dehydration was also observed.

The experiment performed without catalyst showed that very little fructose reacts having a maximum conversion of 29.30 % and only a small amount of 5-HMF (0.0002 mole), FA (0.00003 mole) and LA (0.00004 mole) are generated, without observing the formation of other compounds. So, the dehydration of fructose occurs is spontaneously at 150 ºC but the desired product (BL) is not formed, confirming the need of a catalysts.

It was determined that when working at high temperatures the conversion of fructose is complete and the yield of fructose to BL increases. Reaching yields from 35.38 % at 120 ºC to 44.14 % at 150 ºC using Purolite® CT-482 as catalyst, and from 35.71 % at 120 ºC to 46.37 % at 150 ºC using AmberlystTM 45 as catalyst to $R_{Fruct/\ BuOH}$: 0.009 and $R_{cat(wt/wt):}$ 1.7 %. It happens in the same way for by-products such as FA, LA and BF.

By studying the effect of temperature (120 ºC-150 ºC), feed composition ($R_{Fruct/\ BuOH}$: 0.009, 0.013 and 0.017) and catalyst loading ($R_{cat(wt/wt)}$: 1.7, 2.5 and 3.3 %) it is observed for all cases a complete conversion of fructose (>99 %) to products and byproducts. By decreasing the $R_{Fruct/BuOH}$ and increase of $R_{cat(wt/wt)}$ consequently increases the yield and selectivity to BL, as for byproducts such as LA, FA, BF and DBE, and decreases for 5-HMF and BMF. The same behavior presents the two resins studied Amberlyst™ 45 and Purolite® CT-482. Getting better yield towards BL of 52.55 %, with PuroliteCT-482, $R_{Fruct/\ BuOH}$: 0.009 and $R_{cat(wt/wt)}$: 3.3 % at 150 °C of temperature and at the end of 8 hours of reaction.

The complementary experiments, which were performed at 170 °C, $R_{Fruct/\ BuOH}$: 0.013 and $R_{cat(wt/wt)}$: 3.3 % with the two types of resins, the complete conversion of fructose and selectivities to butyl levulinate is observed up to 52.98 % with AmberlystTM 45 as catalyst and 55.61 % with Purolite® CT-482 as catalyst. Showing promising results, being that at the end of the reaction there is a tend to decrease the formation of byproducts such as FA and BF.

In a general way in all the experiments carried out when comparing the catalysts used in this study, the thermostable resin Purolite® CT-482 is found to be slightly more active than the thermostable resin Amberlyst™ 45.

7 RECOMMENDATIONS AND FURTHER STUDIES

Determination of the kinetics of the reaction with the results presented in this study.

Further testing could be applied to thermostable acidic ion exchange resins to ascertain whether they are eminently suitable to catalyze this reaction in an industrial setting. Follow-up studies of the lifespan and reusability of these catalysts would be necessary. Nonetheless, thermostable ion exchange resins are cheaper and readily commercially available and thus more readily applicable to existent and new industrial processes.

According to experimental results obtained on thermostable ion exchange resins show a promising future for these catalysts on butyl levulinate production from lignocellulose derived fructose and butanol. So that it is recommended to continue researching with higher temperatures and other types of thermostable catalysts, to improve the results obtained so far.

8 NOTATION

DVB	Divinylbenzene
BL	Butyl levulinate
ML	Methyl levulinate
EL	Ethyl levulinate
FAME	Fatty acid methyl esters
LA	Levulinic acid
5-HMF	5-(Hydroxymethyl)furfural.
A-45	Amberlyst ™ 45
C-482	Purolite® CT-482
BF	Butyl formate
BL	Butyl Levulinate
BMF	5-(Butoxymethyl)-2-furaldehyde
DBE	Dibutyl ether
FA	Formic acid
BuOH	1-butanol
Fruct/F	D-Fructose
HPLC	High-performance liquid chromatography
GC	Gas chromatography
ISEC	Inverse size exclusion chromatography
MeOH	Methanol
Glu	Glucose
EtOH	Ethanol
LE	Levulinic ester
µL	Microliters
mL	Milliliters
min	Minutes
h	Hour
°C	Celsius degree
$R_{BuOH/w}$	Molar ratio between 1-butanol and water
g	Grams
M	Molecular weight

ρ	Density
Eq	Mathematical equation
R_{Cat} (wt/wt)	Catalyst loading
$R_{Fruct/BuOH}$	Molar ratio between fructose and 1-butanol
$R_{BuOH/H2O}$	Molar ratio between 1- butanol and water
$R_{Fruct/H2O}$	Molar ratio between fructose and water
Mol	Mole
wt%	Percentage of weight
M	Mass
N	Mole
$A_{j,t}$	Compound j at an instant t
C	Concentration
A	Calibration coefficients
B	Calibration coefficients
V	Volume
N	Number
T	Time
X	Conversion
S	Selectivity
CT	Standardized contact time
DS	Standard deviation
EE	Standard error
d_p	Particle diameter
d_{pore}	Pore diameter
CT-482	Purolite CT-482
A-45	Amberlyst ™ 45
S/Cl	Sulfonated chlorinated
CS	Conventionally sulfonated
T	Temperature
Vsp	Specific volume of swollen polymer

Subscripts

MS	Mass of sugar

Alc	Alcohol
G	Gas face
j	Substance
0	Initial
F	Final
Cc	Contraction coefficient
T	Total final
I	Total initial
T	Time
HPLC	High-performance liquid chromatography
GC	Gas chromatography
Cat	Catalyst
s	Samples
i	Generic replicate identifier

Superscripts

a	Sulfonation type
b	Titration against standard base
c	Manufacture data
d	Swollen state (in water)
e	Specific volume of swollen polymer in water, measured by ISEC technique.
j	Substance

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10 APPENDICES

APPENDIX 1: Gas chromatography calibration

Gas chromatography involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.

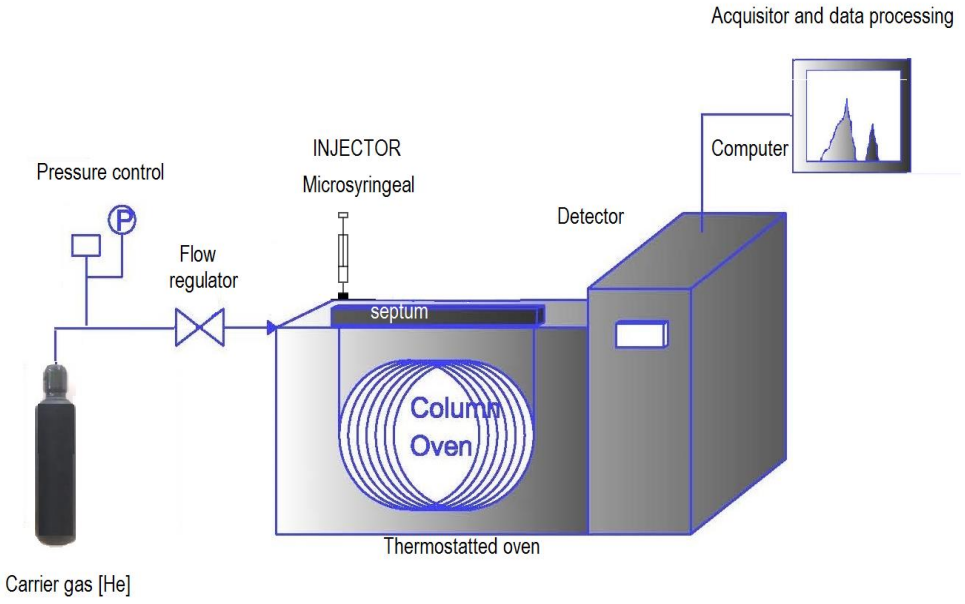

Figure 25. Scheme of gas chromatography.

The sample solution injected into the GC enters a gas (He) stream, which transports the sample into a separation tube known as the "column." The various components are separated inside the column. The detector measures the quantity of the components that exit the column. To measure a sample with an unknown concentration, a standard sample with known concentration is injected into the instrument. The standard sample peak retention time (appearance time) and area are compared to the test sample to calculate the concentration.

The retention times for the substances that were analyzed in this study are presented in the following table:

Table 17. Retention time of components in the production of BL from fructose in GC.

Substance	Retention Time [min]
Water	3.98
Formic Acid	4.57
1-Butanol	6.42
Butyl Formate	7.45
DBE	10.54
Levulinic Acid	13.17
HMF	14.68
Butil Levulinate	15.22
BMF	16.85

The calibration was necessary to correlate mathematically the percentage of area with the percentage in mass. A calibrate the system was made with standards of known composition. To study the direct conversion of fructose to BL, vials with known percentage of mass was prepared. Three replicates were performed of each analysis of each vial to evaluate the dispersion statistically. Below is an example type of calibration.

Table 18. Example of linear regression for the calibration of butyl levulinate through GC.

	Area [%]	m [%]
1	0.00	0.00
2	3.74	4.91
3	5.85	7.43
4	10.76	13.53
5	11.94	14.43
6	12.56	15.06
7	15.02	17.79
8	16.39	18.13
9	17.25	20.97
10	19.29	23.73
11	20.01	23.33
12	20.44	23.01
13	25.88	31.26
14	30.15	34.59
15	33.02	38.32
16	37.37	42.66
17	40.5	46.08
18	52.19	57.43
19	55.16	62.35

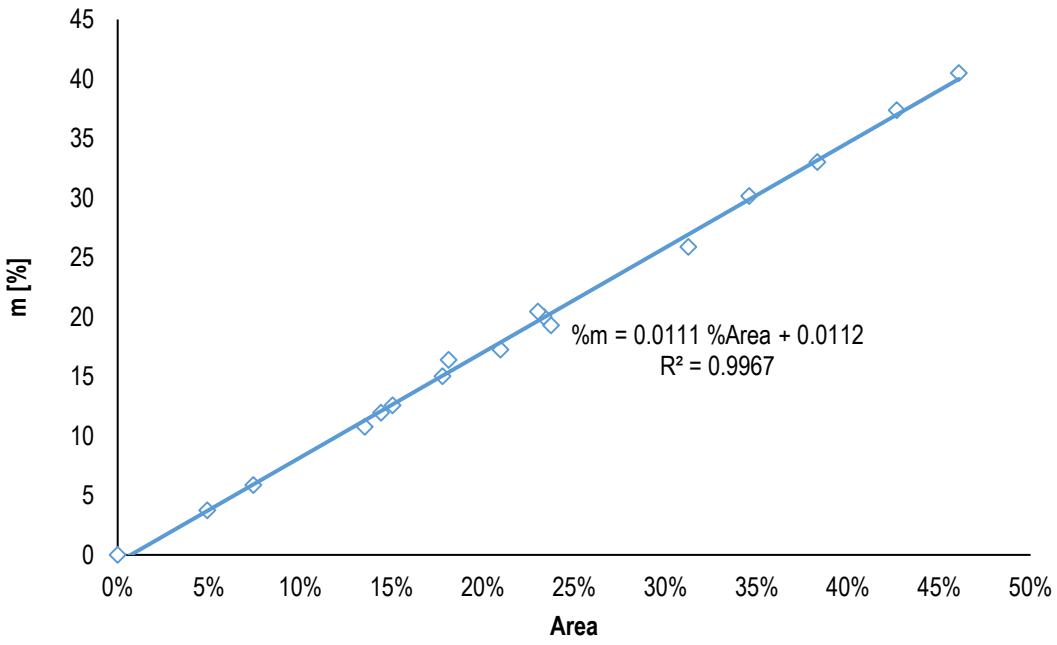

Figure 26. Example of linear regression for the calibration of butyl levulinate through GC.

APPENDIX 2: High-performance liquid chromatography calibration

Similar to the Gas chromatography the High-performance liquid chromatography is a technique used to separate, identify, and quantify each component in a mixture. It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out the column.

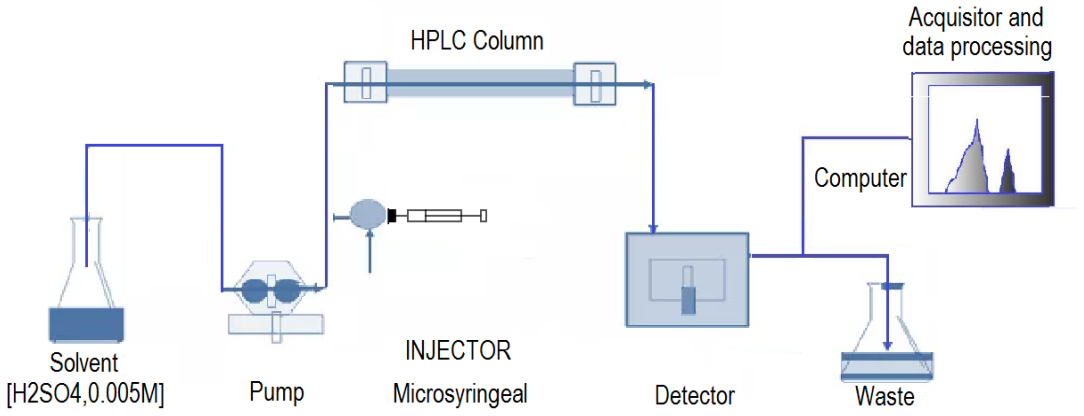

Figure 27. Scheme of high-performance liquid chromatography.

Retention times for components of the system for the production of BL with fructose and 1-butanol are specified in the next table.

Table 19. Retention time of components in the production of BL from fructose in HPLC.

Substance	Retention Time [min]
D-Fructose	10.88
Formic Acid	14.82
Levulinic Acid	17.35
5-HMF	34.93
Glucose	9.82

In addition, it is subject to a calibration to relate area values towards mass-volume percentage. A calibrate the system was made with standards of known composition. Three replicates were performed of each analysis of each vial in order to evaluate the dispersion statistically. Below is an example type of calibration.

Table 20. Example of linear regression for the calibration of D-Fructose through HPLC.

	C [mg/ mL]	Area
1	0.000	0.0
2	0.036	10404.3
3	0.051	15637.9
4	0.064	19093.6
5	0.064	18915.1
6	0.081	24412.5
7	0.102	30309.2
8	0.121	36776.8
9	0.128	38057.2
10	0.148	41245.7
11	0.161	48236.9
12	0.193	57517.6
13	0.227	65098.5
14	0.242	74221.6
15	0.255	76437.0
16	0.255	75342.8
17	0.340	100417.4
18	0.453	130464.3
19	0.510	147836.1
20	0.680	197714.4
21	2.500	742330.1
22	4.505	1359844.3

23	6.424	1882367.5
24	10.610	3059000.0
25	12.157	3552340.0
26	14.030	4043500.0
27	16.016	4748879.0
28	17.818	5240220.0
29	20.000	5930000.0

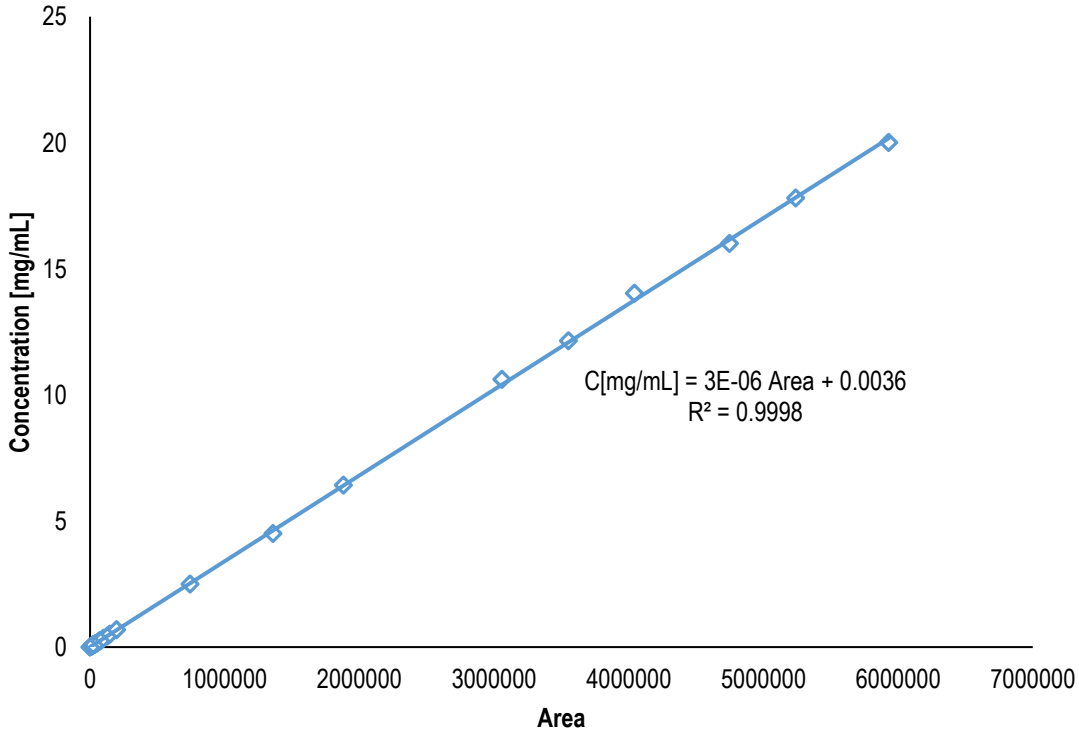

Figure 28. Example of linear regression for the calibration of D-Fructose through HPLC.

APPENDIX 3: Catalytic swelling tests

Ion exchange resins swell in polar media and, as a result, morphology changes and non-permanent pores appear. Table 21 and 22 show the morphological parameters of tested resins both in dry state and swollen in water.

To determine the particle diameter of resins swollen in water and 1-butanol shown in the next table was determined by a laser diffraction particle size analyzer (Beckman Coulter, LS 13 320).

Table 21. Mean to in different media.

	Mean dp [µm]		
Resin	**Air**	**Water**	**1-butanol**
Amberlyst™ 45	660.2	1078.0	898.9
Purolite® CT-482	471.1	584.2	482.8

Table 22. Volume increase with respect to air.

	Volume increase [%]	
Resin	**Water**	**1-butanol**
Amberlyst™ 45	335	152
Purolite® CT-482	91	8

Table 21 and 22 show the particle size and the volume increase with respect to air for Amberlyst™ 45 and Purolite® CT-482 resins swollen in water and 1-butanol. As it can be seen in water and 1-butanol is higher than in air as a consequence of swelling. For all the tested resins the volume increase in 1-butanol is slightly lower than in water. Thus, Amberlyst™ 45 present the highest swelling whereas Purolite® CT-482 show the lowest swelling.

APPENDIX 4: Experimental data and calculation

- **Identification of experiment and work conditions**

All the experiments have been identified as shown in table 4 taking experiment 32 as an example.

Table 23. Experimental data.

Experiment:	Nº 32
Date:	14/11/2017
T [ºC]:	150
P [bar]:	20
t reaction [h]:	8

- **Initial load data**

Load of raw materials

Table 24. Load of raw materials.

Raw materials [i]	m_i [g]
Fructose [g]=[1.5g]	1.50
1-Butanol 60ml=48.6 [g]	48.8
H_2O [g]	10.01
Purolite® CT-482 [g]	2.01

Properties

Table 25. Properties of substances.

	M_i [g/mol]	Density ρ_i [g/ml]
D-Fructose	180.16	1.69
FA	46.02	1.22
LA	116.11	1.14
HMF	126.11	1.29
BF	102.13	0.892
BL	172.22	0.974
1-Butanol	74.12	0.81
H_2O	18.01	1
DBE	130.2	0.769
BMF (5-(Butoxymethyl)-2-furaldehyde)	182.21	1.1

The results of all these operations can be seen in next tables.

Table 26. Initial calculations.

Raw materials [i]	m_i [g]	n_i [mol]	wt_i [%]	mol_i [%]
D-Fructose [g]	1.50	0.01	2.49	0.68
1-Butanol (99.5%) [g]	48.80	0.66	80.51	53.14
H_2O [g]	10.01	0.57	17.00	46.18

Table 27. Initial ratios.

R_{Cat} (wt/wt) %	3.34%
$R_{Fruct/BuOH}$	0.013
$R_{BuOH/H2O}$	1.15
$R_{Fruct/H2O}$	0.01

Also, for each experiment performed, the mass balance was calculated in each experiment and only those experiments which gave less than 10 % of mass balance error has been used in this work.

The results of all these operations can be seen in next tables.

Table 28. Experimental download data.

Empty Reactor [g]	754.92
Produc + R.empty [g]	801.83
Final Volume [ml]	50
Final mass [g]	44.89
Number of samples	9
Purge [ml]	1.20

Table 29. Calculations for coefficient of contraction and mass error.

	Recovered	Sample	Purge	Total Experimental	Mass error
Volume [ml]	50.0	4.50	1.20	55.7	
Mass [g]	44.8	4.04	1.08	50.0	9.0%
Density [g/ml]	0.90			0.90	

Table 30. Contraction coefficients.

Volume [ml/h]	1.71
Mass [g/h]	1.14

Assuming that the volume varies linearly with time, the number of moles for each substance in the reaction system is calculated, fructose conversion, selectivities towards products and by-products and yields.

Table 31. Results of experiment 32.

t (h)	w.t/nºFruct [h.g/mol]	n_i [mol]									X_{Fruct} (%)	Selectivity [%]							Y_{HMF}	Y_{BL}
		Fruct	5-HMF	FA	LA	BUOH	BF	DBE	BMF	BL		$S^{5\text{-HMF}}_{F}$	S^{LA}_{F}	S^{FA}_{F}	S^{BF}_{F}	S^{DBE}_{BuOH}	S^{BMF}_{F}	S^{BL}_{F}		
0	0	0.0056	0.0002	0.0000	0.0001	0.6508	0.0000	0.0000	0.0000	0.0000	33.1	5.5	4.5	1.8	0.00	0.00	0.00	0.00	1.8	0.00
1	242	0.0013	0.0010	0.0027	0.0006	0.6186	0.0040	0.0006	0.0028	0.0027	84.5	14.1	8.9	38.2	56.2	1.7	39.4	37.6	12.0	31.8
2	483	0.0004	0.0006	0.0030	0.0007	0.6128	0.0041	0.0011	0.0023	0.0030	95.3	7.6	9.4	37.6	51.5	2.6	29.1	38.1	7.2	36.3
3	725	0.0002	0.0005	0.0034	0.0009	0.5987	0.0045	0.0020	0.0019	0.0035	97.9	5.6	11.1	42.1	55.6	3.5	23.6	42.4	5.5	41.5
4	966	0.0001	0.0002	0.0036	0.0010	0.5881	0.0044	0.0022	0.0018	0.0037	98.7	3.0	12.2	43.9	53.9	3.3	21.3	44.4	3.0	43.8
5	1208	0.0000	0.0002	0.0035	0.0010	0.5761	0.0045	0.0030	0.0015	0.0039	99.6	2.2	12.1	42.5	53.8	3.8	17.6	47.0	2.1	46.8
6	1449	0.0000	0.0002	0.0035	0.0010	0.5637	0.0044	0.0040	0.0014	0.0042	99.6	2.0	12.1	42.0	53.0	4.3	17.2	51.1	2.0	50.9
7	1691	0.0000	0.0001	0.0036	0.0010	0.5485	0.0045	0.0046	0.0014	0.0043	99.7	0.9	12.3	43.3	54.0	4.3	16.7	52.0	0.9	51.8
8	1932	0.0000	0.0000	0.0036	0.0011	0.5339	0.0045	0.0054	0.0012	0.0044	99.7	0.5	12.7	42.9	54.3	4.5	14.1	52.9	0.5	52.7