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A contribution to the study of acidic ion-exchange resins to produce butyl levulinate from fructose and butyl alcohol.

Contribución al estudio de resinas ácidas de intercambio iónico en la producción de butil levulinato a partir de fructosa y alcohol butílico.

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Science is a differential equation. Religion is a boundary condition.

Alan Turing

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1. SUMMARY

Biomass is the only renewable resource on the earth that can derive liquid fuel and fine chemicals to replace the petroleum-based chemicals. In recent years, the development of bioenergy concerning the synthesis of levulinate esters from biomass via chemical/catalytic process has attracted more and more interests, and extensive research is being carried out worldwide. Levulinate esters, like methyl levulinate, ethyl levulinate, and butyl levulinate, are a kind of important intermediates and energy chemicals having high reactivity and widespread application in many fields.

Alkyl levulinates are proposed as oxygenates of potential interest as diesel fuel components. In blends with commercial gasoil it has been shown that cold flow properties of blends are substantially upgraded and particulate emissions greatly decrease. These green diesel fuel enhancers can be synthesized by the acid catalysed reaction of levulinic acid with alcohol[32].

Direct conversion of carbohydrates to levulinate esters using solid acids such as NaY, SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, are described in the literature, but direct conversion of fructose to esters of levulinic acid using ion-exchange resins has never been attempted to the best of our knowledge.

In this study, the catalytic performances of ion-exchange resins (Dowex 50Wx2, Dowex 50Wx4, Amberlyst 39, Amberlyst 16, Amberlyst 15) in the direct conversion of carbohydrates such as fructose to butyl levulinate in butanol-water media were investigated. With temperature above 100ºC, almost 100% of fructose conversion was obtained irrespective of the catalyst employed. However, different catalysts showed different activity and selectivity towards the production of butyl levulinate.

Among these catalysts employed, gel-type resins (especially Dowex 50Wx2) were found to be a type of potential catalysts for prospective utilization, which showed the highest selectivity and yield to butyl levulinate. The catalyst range assayed showed spurious effect on the reaction rates. The higher temperatures led to higher reaction rates but also presented higher formation of by-products such as butyl formate and BMF. Although, no humins were detected during the investigation.

Catalysts with less degree of cross-linking present higher selectivity towards levulinate esters. The reuse of Dowex 50Wx2, after reconditioning them with deionised water and methanol, showed lesser catalytic activity after each use due to the loss of acid sites above the surface of catalyst, providing less catalytic activity for the reaction.

Overall, this study indicated that acidic ion-exchange resins are promising catalysts for the direct production of levulinate esters from fructose and can be employed for the large-scale synthesis of butyl levulinate from renewable carbohydrates in the future.

Keywords: fructose; 5-HMF, levulinic acid, butyl levulinate, acidic ion-exchange resins.

2. RESUM

La biomasa es el única fuente de energía renovable en el planeta de la puede obtenerse petróleo líquido y productos de química fina, capaces de reemplazar los productos químicos tradicionales basados en petróleo. En los últimos años, el desarrollo de la bioenergía relativa a la síntesis de esteres de levulinato a partir de biomasa, por medio de procesos químicos/catalíticos, ha despertado un creciente interés y se está investigando ampliamente a nivel mundial. Los ésteres de levulinato, como el metil levulinato, el etil levulinato y el butil levulinato, son una clase de importantes intermediarios y químicos energéticos de gran reactividad y con múltiples aplicaciones en diversos campos.

Los levulinatos de alquilo se han propuesto como oxigenados de interés potencial como componentes de petróleo diésel. En mezclas con gasoil comercial, se ha observado que las propiedades del flujo en frío de las mezclas son sustancialmente mejoradas, y que las emisiones particulares decrecen de forma importante. Estos potenciadores de diéseles ecológicos pueden ser sintetizados a partir de la reacción catalizada por ácido levulínico con alcohol butílico, tal y como recoge la literatura[32] .

La conversión directa de carbohidratos a esteres de levulinato, utilizando ácidos sólidos como NaY, SO^{2-}_4/ZrO_2, SO^{2-}_4/TiO_2, se ha descrito en la literatura, pero no así la conversión directa de fructosa a ésteres de ácido levulínico mediante resinas iónicas la cual, según nuestras fuentes, no ha sido intentada hasta la fecha.

En este estudio se ha investigado el comportamiento catalítico de las resinas ácidas de intercambio iónico (Dowex 50Wx2, Dowex 50Wx4, Amberlyst 39, Amberlyst 16, Amberlyst 15) en la conversión directa de fructosa a butil levulinato, en un medio de butanol-agua. Cuando la temperatura superó los 100ºC, se dio prácticamente la totalidad de la conversión de la fructosa, independientemente del tipo de catalizador utilizado. Sin embargo, distintos catalizadores mostraron una selectividad distintiva hacia la producción del butil levulinato.

Entre los catalizadores empleados, las resinas de tipo gel (especialmente la Dowex 50Wx2) resultaron ser el tipo de catalizador potencial para uso prospectivo que mostró mayor actividad

y selectividad hacia la producción de butil levulinato. La cantidad del catalizador no tuvo ningún efecto sobre la velocidad de la reacción. A medida que se aumentó la temperatura también lo hizo la cinética de la reacción, pero aumentó también la formación de productos secundarios, como butil formate y BMF, aunque, no se detectaron humins.

Los catalizadores con un menor grado de reticulación presentaron mayor selectividad hacia los ésteres de levulinato. La reutilización de las Dowex 50Wx2, después de reacondicionarse con agua desionizada y metanol, dio lugar a un decremento en la actividad catalítica que fue mayor después de cada uso, debido a la perdida de sitios ácidos sobre la superficie del catalizador que dejó menos sitios activos disponibles para la reacción.

En conclusión, los resultados de este estudio indican que las resinas de intercambio iónico son catalizadores prometedores para la producción directa de ésteres de levulinato a partir de fructosa y que pueden ser empleadas para la síntesis de butil levulinato a gran escala a partir de carbohidratos en un futuro.

Palabras clave: Fructosa, 5-HMF, Ácido Levulínico, Butil levulinato, resinas acidas de intercambio iónico.

3. INTRODUCTION

3.1. FROM BIOMASS TO BIOFUELS

Over the last few decades due to the gradual depletion of fossil fuel resources and the progressive decline in the environment condition, considerable effort has been devoted to the development of chemical or biological means for converting the abundant renewable biomass into transportation fuels and industrial chemicals that can serve as replacements for petroleum-based products.

Biofuels, liquids fuels obtained from biomass, has attracted increasing interest as an alternative to the fossils fuels. In addition, they provide a single solution to three important challenges of modern life, which are: concerns over energy security; need to moderate climate change and achieve lower greenhouse gas emissions; and economic development by creating o sustaining jobs in agriculture. These challenges and the attempts of policy makers and stockholders have contributed an increase in the biofuels technology interests. Human beings have been using bioenergy and biofuels for domestic purposes since pre-recorded history. A brief history of biofuels is explained in Table 1[1].

Table 1: A brief history of Biofuels[1]

From 3000 B.C	Charcoal have been used for cooking, heating and metallurgy purpose.
Before 19th century	Firewood was primary fuel for cooking and heating.
In 1826	1st spark-ignition piston engine using alcohol invented by Samuel Morey
In 1860	Nikolaus Otto develops Otto-cycle engine to run on ethanol.
In 1900	Rudolf Diesel designed diesel engine to run on peanut oil.
In 1925	H. Ford designed Model T car, designed to use hemp derived biofuel.

Biofuels are mostly classified as primary and secondary biofuels. Meanwhile, the primary biofuels are used in an unprocessed form, the secondary biofuels are obtained through the processing of biomass. Based on the source of biomass, and their technological process the secondary biofuels are classified as 1st, 2nd and 3rd generation as shown in the Figure 1[2].

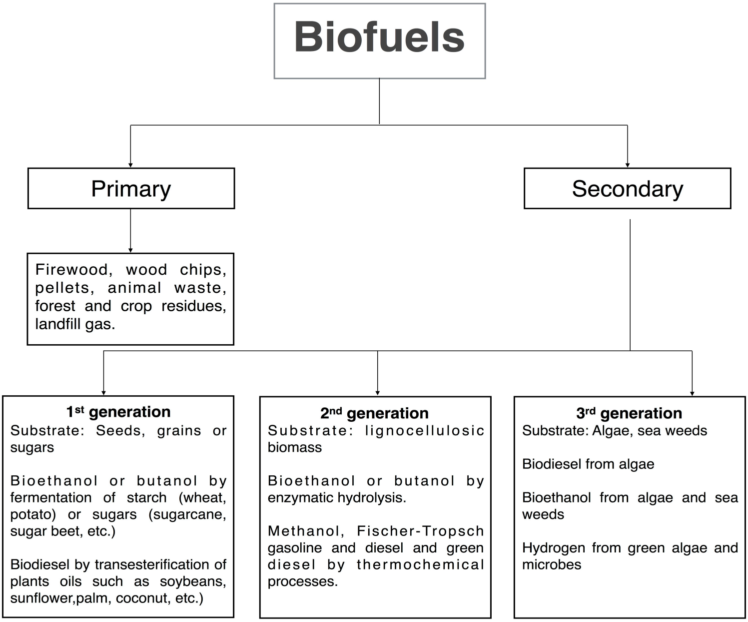


Figure 1: Classification of biofuels[2].

Biofuels offer numerous benefits such as energy security, economic stability and environmental gains. But at the same time several challenges must be overcome for the production and utilization of the biofuels. The main advantages and challenges related to biomass conversion to biofuels are highlighted in the Table 2. First generation biofuels can help to improve domestic energy security. But there are concerns about the effects on the environment, on food security and prices, and on the human rights of workers and communities in countries where biofuels crops are grown.

The second generation biofuels, which are produced from lignocellulosic feedstocks instead of food crops, has a critical factor in the production process. It is obtaining sugars from the lignocellulosic matrix economically and in high yields. The sugars are polymerised in the cell walls into chains and embedded with a component called lignin, making lignocellulose. Due to the complex nature of lignocellulose, obtaining sugars by pre-treatment and hydrolysis is quite challenging and can add up to 45% to the total biofuel cost. And further conversion of this sugar into biofuels, in an economical way and in high yields, is equally difficult.

Table 2: Advantages and Disadvantages of Biofuels[3].

Advantages	**Disadvantages**
First-generation Biofuels	
- Familiar feedstocks. - Well-established production. - Compatibility with fossil fuels. - Commercial production and use in several countries.	- Competition with food crops. - High-cost feedstocks lead to high production costs. - Modest reductions of fossil fuel use and greenhouse gas emissions.
Second-generation fuels	
- Similar processes to the petroleum /chemical /bio industry. - No competition issues with food. - Reduction of the amount of waste that needs to be treated/disposed of (if any used as feedstocks).	- Unfamiliar feedstock and availability uncertain/fluctuating. - High capital and energy costs. - Processing not optimized for the new feedstocks (e.g. tar formation, syngas clean up). - Competition for land and water for some energy crops. - For anaerobic digestion of waste, only a fraction of waste can be used.
Third-generation fuels (microalgae)	
- High oil content. - Can be cultivated in a range of systems. - A wide spectrum of processing routes and biofuels.	- Not commercially available yet. - High initial costs. - High water content. - If cultivated artificially, could require large areas. - If exploited from oceans, could impact on the marine life.

According to the litreature[5], these biofuels (in particularly second-generation biofuels) are truly carbon neutral and in future, they are expected to reduce net greenhouse gas emissions, improve energy security and aid development. But some crucial concerns circle the commercial scaling up of these biofuels, like uncertain availability of the feedstocks. Apart from the research and technology, solutions are required in order to design a market and policy structure that can inspire the production of second-generation fuels.

On commercial level, the production of biofuels is promising in the future[4].

- In Germany, the Cutec Institute is investigating the thermochemical conversion of different types of biomass to synthesis gas
- And Fraunhofer institute has developed Greasoline technology that can convert oily and fatty raw and waste material to products, which can later be used as fuels and fuel components.
- Another project named “BioTfuel” has been launched in France to produce biodiesel and biokerosene based on biomass gasification.
- And in Louisiana (USA), a commercial facility named Cool Planet is using a thermo-mechanical fractionation system to convert, via catalyst, wood waste and energy crops into high-octane, renewable gasoline blendstocks.

Nowadays, the three main catalytic routes to transform biomass into fuels and chemicals are *gasification*, *pyrolysis* and *hydrolysis*. While gasification and pyrolysis treats with the whole biomass leading it to syn-gas and bio-oil, hydrolysis is more complicated process that requires lignocellulose to be broken into its constituent parts.

Lignocellulose, which is composed of lignin (15-20%), cellulose (40-50%) and hemicellulose (25-35%), delivers stability to the plant and acts against microbial and enzymatic degradation. This firmness of the cell wall has to be overcome to release the sugars. Several studies[5] have been made towards releasing cellulose from its lignin rigid structure support so it can be hydrolysed into glucose monomers. These sugars, obtained through hydrolysis, can be transformed into bio-based platform molecules, which further, through catalytic transformations such as reduction, esterification, etherification, and acetalization reactions, can be converted into a variety of fuel additives in facilities like bio-refineries.

3.2. PLATFORM MOLECULES FROM BIOMASS

A bio-based platform molecule is a chemical compound whose constituent elements originate wholly from biomass and that can be utilised as a building block for production of other chemicals[6]. In other words, they serve as intermediates for the production of carbon-based fuels and chemicals. 5-hydroxymethyl furfural (5-HMF) and levulinic acid (LA) are two examples of such molecules.

Levulinic Acid, which can be considered as one of the top bio-based chemical of the future, has been well known since 1870. However, it has never reached a commercial use in a significant volume. This failure, despite its great potential as an industrial chemical, can be attributed to the fact that in 20th century the corresponding raw materials were expensive, conversions yields were low and equipment for its purification and separation was not available. Also, the yield is significantly low due to the formation of soluble polymeric by- products and undesired black solids, called humins, which can cause clogging of the reactor[7].

Industrially, levulinic acid (LA) is produced by the Biofine process (Figure 2), which is one of the most advanced and commercially viable lignocellulosic-fractionating technology currently available and converts polysaccharides like cellulose into valuable platform chemicals like levulinic acid and 5-HMF. This process consists of two distinct acid-catalysed stages that are operated to give optimal yields with a minimum of degradation products and tar formation[8]. In a complete Biofine plant, additional processing may occur depending on the final product target such as levulinate esters. Furthermore, the production of levulinic acid esters from LA formed in the Biofine Process has the added advantage over conventional bio-esters that there is no co-production of glycerol.

As mentioned by the *“ResearchandMarkets”* reports about Global LA market[4], major industry participants like DuPont, Segetis and Biofine with other prominent vendors like Avantium, Le Calorie, Sigma-Aldrich have already developed patented technologies for commercializing LA through renewable sources. Currently LA costs between 5 to 8 USD per kilo, but in the future prices are expected to drop under 1 USD per kilo.

The full potential of levulinic acid promises exciting developments, new application and markets:

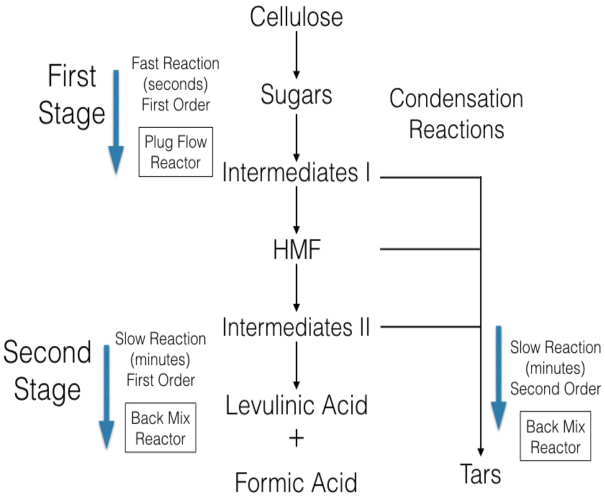


Figure 2: The Biofine Process[8]

- LA and its derivatives can be used in polyester coating resins, powder coatings for protective and decorative finishes.
- In food applications, levulinic acid is used for multiple functions like pH regulator for ingredients, disinfectants and the derivative levulinate ester as flavouring agent.
- Levulinic acid-derived ketal esters can replace major phthalate-based plasticizers.
- Fuel additives based on levulinic acid such as alkyl levulinates can replace current octane and cetane improvers for diesel.
- Levulinic acid offers a sustainable solution for chemical and biofuels with a new range of pricing compared to existing processes.

3.3. APPLICATION OF LEVULINATE ESTERS AS BIODIESEL BLENDERS

Through various investigations[13], it has been revealed that levulinates esters such as methyl, ethyl, n-butyl, octyl levulinates, etc., are very attractive candidates with wide applications such as solvents, plasticizers, as gasoline and diesel additives.

But, before being used as blending agents for diesel or gasoline, the esters of LA should meet the minimum requirements such as:

- They should not deteriorate the emission control devices.
- They must produce low atmospheric emissions (SO_2 in exhaust gases and combustion fumes).
- And they must provide an acceptable combustion rate inside the engine i.e. neither too fast (which can cause overheating of the injector) nor too slow (to assure complete combustion of fuel).

According to the EN 590[15] standard, all automotive diesel fuel must meet the diesel fuel specifications, provided in the Table 4, if it has to be sold in the European Union and other European countries.

Table 3: EN 590: 2014 Diesel Fuel Specification

Fuel Property	**Unit**	**Specification**		**Test**
		Lower limit	Upper limit	
Cetane index		46,0	-	EN ISO 4264
Cetane number		51,0	-	EN ISO 5165
Density (15ºC)	kg/m^3	820	845	EN ISO 3675
Poly aromatics		-	8	EN ISO 12185
Sulphur	mg/kg	-	10	ASTM D-5453
Flash Point	ºC	55	-	EN ISO 2719
Carbon residue (10% btms)	% (wt.)	-	0.30[a]	EN ISO 10370
Ash	% (wt.)	-	0.01	EN 26245
Water content	mg/kg	-	200	ASTM D1744
Copper strip corrosion	rating	Class 1	Class 1	EN ISO 2160
Oxygen stability	g/m^3	-	25	ASTM D2247
Viscosity (40ºC)	mm^2/s	2.00	4.50	EN ISO 3104
Distillation (vol% recovered)	ºC			EN ISO 3405
10% point	ºC	report	-	
50% point	ºC	report	-	
65% point	ºC	250	-	
85% point	ºC	-	350	
95% point	ºC	-	370	
FAME content	% (wt.)	-	7	

(a) Limit does not apply if ignition improper additives are used). (b) 3h at 50ºC.

Nowadays, the main potential application of levulinate esters is as fuel additive. They exhibit characteristics that make it suitable as cold flow improvers in biodiesel and as oxygenate additives for gasoline and diesel fuels[16]. The properties like low toxicity, high lubricity, flash point stability and moderate flow properties under low temperature conditions make them acceptable diluent for biodiesel fuels with high-saturated fatty acid content.

There are various advantages of introducing alkyl levulinates in transportation fuel such as[13]:

- The substitution of conventional additives such as ethanol, methyl-tert-butylether by biomass-derived products.
- Presence of these oxygenated compounds leads to cleaner combustion processes with fewer smoke or NOx (nitrogen oxides) emissions.
- And levulinate esters such as, butyl levulinate, cause lower degradations to some elastomeric constituents of the engine than other additives.

Table 4: Alkyl levulinates as possible blending components of fuel.

Alkyl Levulinate	Positive aspect of blending	Drawbacks
Methyl levulinate[17]	- It presents cetane number of 106.5, which is suitable for blending.	- It is fully miscible with water and can be separated from gasoline at cold temperatures.
Ethyl levulinate[18]	- A possible diesel-blending component due to the high boiling point (> 200 °C) and a flash point of 91 °C. - It also improves lubricity and conductivity of diesel fuel.	- EL separates from diesel fuel at temperatures below 0 °C. - It forms a separate liquid phase, with low aromatic diesel, at temperature above the cloud point of the diesel fuel. - Low cetane number limits the amount that can be blended into diesel fuel.

Various esters of levulinic acid have been studied recently such as methyl levulinate, ethyl levulinate, n-butyl levulinate, etc. Table 5 highlights positive aspects and possible drawbacks of using alkyl levulinates such as methyl levulinate (ML), ethyl levulinate (EL) as promising blending component of gasoline and diesel. Meanwhile, ML and EL have been studied as possible candidates as fuel additive, butyl levulinate (BL) has been left unexploited. Few studies have been presented on butyl levulinate effects on diesel. According to Christensen et al.[18] BL is completely miscible with the diesel fuel (up to -10 ºC) and a blend of 20% BL in diesel fuel had the same cloud point.

BL exhibits lower cetane number than EL, however, it improves the lubricity and conductivity of diesel fuel, just like EL. Furthermore, both esters present acceptable properties for diesel fuel such as a very low freezing point (below -60 ºC), high boiling point (> 200 ºC), low solubility of water in ester and low sulphur content i.e., below 1 ppm. So meanwhile EL has been recommended as gasoline additive, BL appears to be more adequate for diesel blending. However, despite being a potential diesel-blending component, a quiet little attention has been paid to the BL synthesis[17].

Traditionally, in the synthesis of n-butyl levulinate homogenous catalysts such as mineral acids (H_2SO_4, HCl) were employed. In 1994, Bart et al. presented a kinetic model for the esterification of LA with butanol using homogenous catalysts[19]. They described the reaction mechanism in two steps: protonation of LA by sulphuric acid and later reversible reaction of protonated acid with n-butanol forming n-butyl levulinate, water and the regenerated catalyst. The reaction was described as reversible and of first order with respect to each component. Studies have also been made for the direct preparation of butyl levulinate by a single solvolysis process of cellulose[19].

Recently, direct conversion of mono- and disaccharides to alkyl levulinates have been studied using heterogeneous catalysts such as H-USY zeolites[20], $H_4SiW_{12}O_{40}$ /K10[21], TiO_2-SO_3H[22] and p-styrenesulfonic acid grafted on nanotubes[23]. In 2011, Hu et al. presented study on direct conversion of glucose using Amberlyst-70 in the presence of methanol. Other well-known examples of acidic ion-exchange resins as heterogeneous catalysts are alumina, immobilized lipases, ion exchange resins and heteropolyacid (HPA).

3.4. SYNTHESIS OF ALKYL LEVULINATES

One of the LA-derived product which has gained a lot of interest recently are the alkyl levulinates. Alkyl levulinates or levulinate esters have been identified as potential fuel candidates as they are not only compatible with conventional diesel fuels but also reduce soot formation[9].

About 150 years ago[13], a series of studies described the formation of methyl to propyl levulinate from purified levulinic acid. And later on Sah[10] and Schuette[11] published the formation of several alkyl levulinates in the corresponding alcohol in the presence of HCl. In these studies, low yields were reported (35-75%), employing relatively high temperatures (up-to 162ºC). Alcohol was used in high molar ratio from 5 to 10 to favour the ester formation, as esterification is a reversible reaction.

Nowadays, there are up to four potential pathways for the synthesis of levulinates esters from cellulosic biomass (Fig. 3)[12].

- Direct acid-catalysed alcoholysis of sugars derived from biomass.
- Direct esterification of levulinic acid with alcohols in the presence of acid catalysts[13].
- Alcoholysis of 5-(chloro-methyl) furfural.
- Alcoholysis of furfuryl alcohol obtained from hydrogenation of biomass-derived furfural.

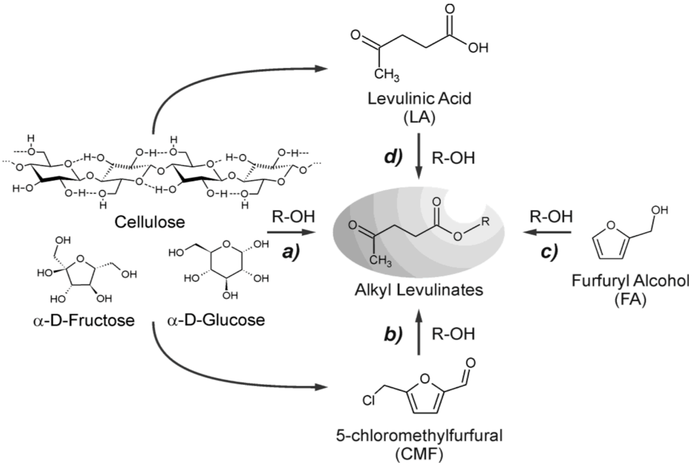


Figure 3: Potential pathways for synthesis of Alkyl levulinates from cellulosic biomass[12]

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

Due to the economical attraction, direct conversion of biomass to alkyl levulinates is of great interest. Moreover, the sequential hydrolysis and dehydration of sugars, in the presence of alcohols, reduces the formation of by-products such as humins.[14]

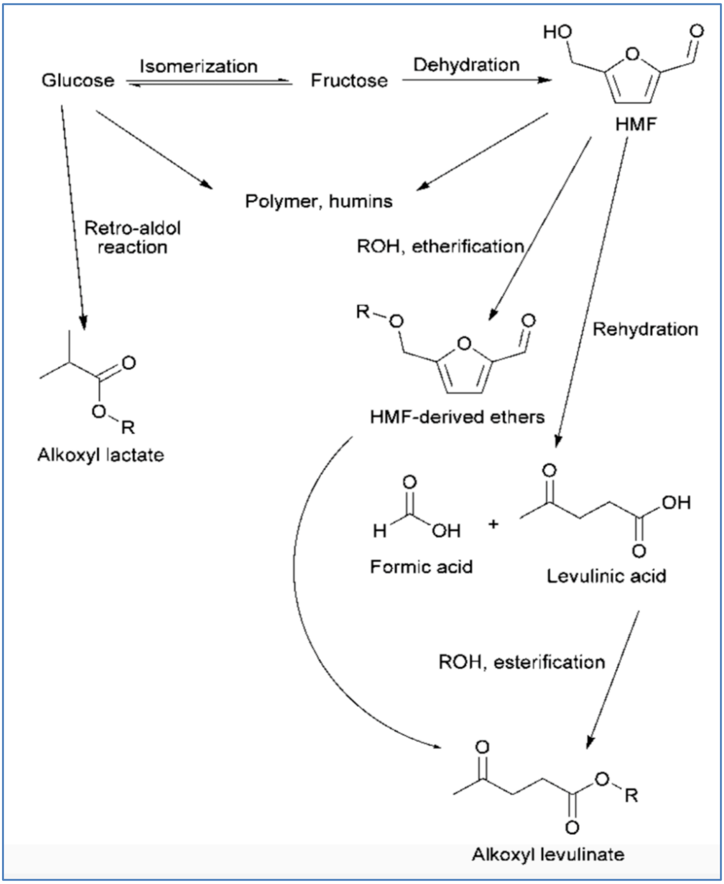


Figure 4: Proposed reaction pathway for the transformation of hydrolysed sugar to platform molecules[5].

In Figure 4 a possible reaction pathway is proposed, according to which monosaccharides (like glucose, fructose) can be transformed into these platform molecules via thermal dehydration followed by rehydration and esterification in acid media.

Industrially, levulinate esters were obtained through esterification of levulinic acid with alkyl alcohols in the presence of sulphuric acid. However, some problems were reported such as the presence of H_2SO_4 as catalyst leads to equipment corrosion, special processing is needed to neutralize the spent H_2SO_4 and side reactions leading to ether were also reported[14]. Moreover, levulinic acid as a raw material is quite expensive.

Due to which, as shown in Table 3, direct production of levulinate esters from biomass-based sugars has been proposed by several authors using heterogeneous catalysts. These catalysts present several advantage such as easy handling, lack of corrosion, environmental friendly, etc. And, the esters of levulinic acid obtained present various applications such as in the food industry as flavouring agent or in the automobile industry as octane booster for gasoline and fuel extender for diesel.

Table 5: Summary of studies on direct production of levulinate esters from biomass.

Sugar/Alc	$R_{MS/Alc}$	T (ºC)	Catalyst	% cat (g/g)	Conv Alc. (%)	$S_{Sugar}^{L.E.}$	t (h)	Ref
Fr/ Met	0.011	200	TiO_2-SO_3H	3%	59	---	2	12
Glu/ Met	0.011	200		3%	43	---	2	12
Fr/ Met	0.002	175	TiO_2-SO_3H nanoparticles	1%	80	99	1	14
Fr/ Met	0.006	130	Fe-exch $H_3PW_{12}O_{40}$	2%	74	100	2	17
Fr/Eth	0.004	120	p-styrenesulfonic acid (nanotubes)	1%	84	99	24	13
Fr /But	0.006	120		1%	87	99	24	13

(Alc. =Alcohol; But =Butanol; Eth =Ethanol; Fr =Fructose; Glu = Glucose; L.E. =Levulinate ester; Met =Methanol; MS= mass of sugar)

3.5. ACIDIC ION-EXCHANGE RESINS AS HETEROGENEOUS CATALYSTS

Today, heterogeneous catalysis has gained a good reputation in the chemical industry, generally because they present numerous benefits such high reactivity, lack of corrosion, easy handling, low cost, easy recovery and reuse. Nowadays, more than 85% of all chemical products are manufactured with the help of catalysts due to which they are referred as backbone of the industrial chemistry[24]. About 20% of the economic activities in industrialized countries depend directly on catalysis.

However, they do present limitations as well. One limitation of heterogeneous catalysis has to do with the available surface area of the catalyst. Once the surface is saturated completely with reactant molecules, the reaction cannot proceed until products leave the surface. For this reason, adsorption step is often the rate-limiting step. Moreover, at least one of the reactants must be adsorbed over the solid's surface. Due to these reasons, large and extensive surface is essential.

Generally heterogeneous catalysts are porous solids providing a large surface area in a small volume and consist of several components and phases. There are different families of existing catalysts such as: (1) unsupported (bulk) catalysts; (2) supported catalysts; (3) confined catalysts; (4) hybrid catalysts; (5) polymerization catalysts. The catalytic activity and selectivity critically depend on the morphology and texture, surface chemical composition, phase composition, and structure of solid catalysts.

A heterogeneous catalyst usually consists of promoters and a support material. The basic chemical principle of heterogeneous catalysis consists in the coordination of reactant molecule to neighbouring atoms at the surface of the solid matrix (support material). The necessary elementary steps in a heterogeneous catalytic reaction are Adsorption, Desorption, and Surface Reaction. These different chemical stages take place in specific places on the catalyst surface called active sites. However, they do not have infinite life and are assessed in terms of activity (measured in conversion), selectivity, lifespan and reusability. Typical heterogeneous catalysts are inorganic solids such as metals, oxides, sulphides, metal salts and organic materials such as organic hydroperoxides, ion exchangers, and enzymes[25].

Ion-exchange resins (IERs) are organic polymers in which active sites are supported on the polymer backbone (insoluble matrix). The insolubility of the matrix is obtained through cross-linking, which improves the robustness of the resin, but decreases ion-exchange capacity of the resin and prolongs the time needed to accomplish the ion exchange processes. Physically, ion exchange beads have either a dense internal structure with no or minimal discrete pores, that is, gel (microporous) (0.5-20 nm) resins or macroporous (macroreticular) (20-200nm) resins with multichannel structure. In Table 6 some of the important features of these resins are described.

Table 6: Physical Classification of Ion-exchange resins (IERs)

Macroreticular resins	Gel type IERs
- Macroporous resins, with their tri-dimensional matrix, has a permanent pore structure. - This type of resin has two phase structure: microspheres and macrospheres. - Macropores between aggregated microporous beads give reactants access to the inside of resin particles providing rigidity but, avoid resin swelling.	- Gel type resins has no distinctive pore structure - It has non-permanent pores established when its polymeric matrix swells after contacting a good solvent - These porous spaces of cross-linked gel-type resins can increase significantly upon swelling.

The type of internal structure of the resins beads dictates the selection of the ion exchange for a particular application. In Figure 5[26] the effects of swelling on the morphology of ion-exchange resins is shown.

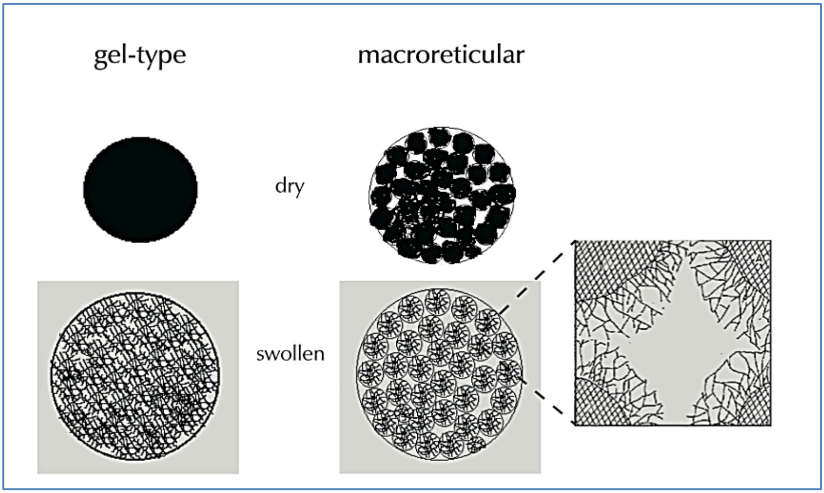


Figure 5: Dry and Swollen-state morphology of Gel and Macroreticular ion exchange resins[26].

The performance of ion exchange resins in terms of kinetics and sorption equilibrium depends on the physical and chemical properties that get influenced by the cross-linking. The main physical properties include colour, density, mechanical resistance, particle size and porosity. In Table 7[27], a brief view on these properties is provided.

Table 7: A brief view on the physical properties of IERs

Physical properties of IERs

Colour	- Depends on degree of cross-linking in the resin network - Strong acidic ion exchange resins are brown whereas, acrylic acid polymers are white.
Density	- There are two types: dry resin density and water-swollen resin density. - Depends on resin type, structure, ionic form, degree of cross-linking.
Mechanical strength	- The solidity of resin increases with degree of cross-linking, and reduces after regeneration. - Mechanical strength is influenced by structure, ionic equilibria and kinetics properties.
Particle size	- It ranges in between 0.04-0.12 mm. - Small particle size has favourable effect on kinetics and provide physical and osmotic stability but also increases hydrostatic resistance which could cause serious pressure drop and lower liquid flow. - The particle size selected would be the result of an appropriate compromise between the reaction kinetics and hydrodynamics.
Porosity	- It is the ratio of volume of voids to total volume of the resin. - The shape and size distribution of pores can vary significantly and depends on the manufacturing process. - To have large surface area, large number of smaller pores should be incorporated.

And the chemical properties of ion exchangers that determine performance include active groups, capacity, selectivity, degree of cross-linking and swelling. According to the chemical strength between the exchangeable ions and the functional groups (active groups) in the resins, ion-exchange resins can be classified as:

- Cation exchangers: strong and weak-acidic cation resins.
- Anion exchangers: strong and weak-base anion resins.

Ion-exchange resins are formed with a cross-linked polymer matrix as a backbone and then numerous charged functional groups are attached to this. The four functional groups commonly found in the four categories of resins are strongly acidic groups, sulfonated group ($-SO_3^-$);

weakly acidic groups, carboxylate group ($-COO^-$); strongly basis groups, quaternary amine group [-N+(CH3)3]; and weakly basic groups, tertiary amine group [-N+(CH3)3]. Table 8[27] exhibits some of the important chemical properties.

Table 8: A brief view on the chemical properties of resin catalysts.

Chemical properties of IERs.

Exchange capacity	- It is defined as the quantity of positively or negatively charged ions that an IER can accommodate on its charged surfaces. - This capacity can be expressed as milliequivalents (meq) per g IER.
Selectivity	- Ion exchange resins are selective for ions. - Multivalent ions normally are more strongly absorbed from dilute solutions than ions of lower valence
Degree of cross-linking	- Cross-linking provides rigidity to the matrix and reduces the number of larger pores. - A resin with high degree of cross-linking swells in aqueous solution and has a smaller loss of volume during drying.
Swelling	- It can be reversible or irreversible. - The degree of swelling is very much dependent on the chemical and physical properties of the resin matrix and on the degree of cross-linking. - The more cross-linked the resin is, the smaller is the degree of the swelling. - The charge capacity and swelling capacity increase with an increase in the amount of active groups on resin.

One of the most common macroreticular resins used today are those with styrene-divinylbenzene (PS-DVB) matrixes (Figure 6)[28]. These are addition-type polymer resins, in which styrene monomers are combined by a free-radical mechanism forming a linear polymer. The polystyrene is cross-linked with divinylbenzene, which regulates the porosity of the particle. Moreover, the amount of crosslinking, which defines the physical and chemical properties of the resin, is controlled by the ratios of styrene to DVB. Resins with low DVB content are soft and gelatinous and swell strongly, while those with higher DVB content are mechanically stable and swell very little. However, diffusion in such materials is slow causing reduction of the rate of all processes. Practical ranges of cross-linking are in the range of 0.5 to 25 wt%.

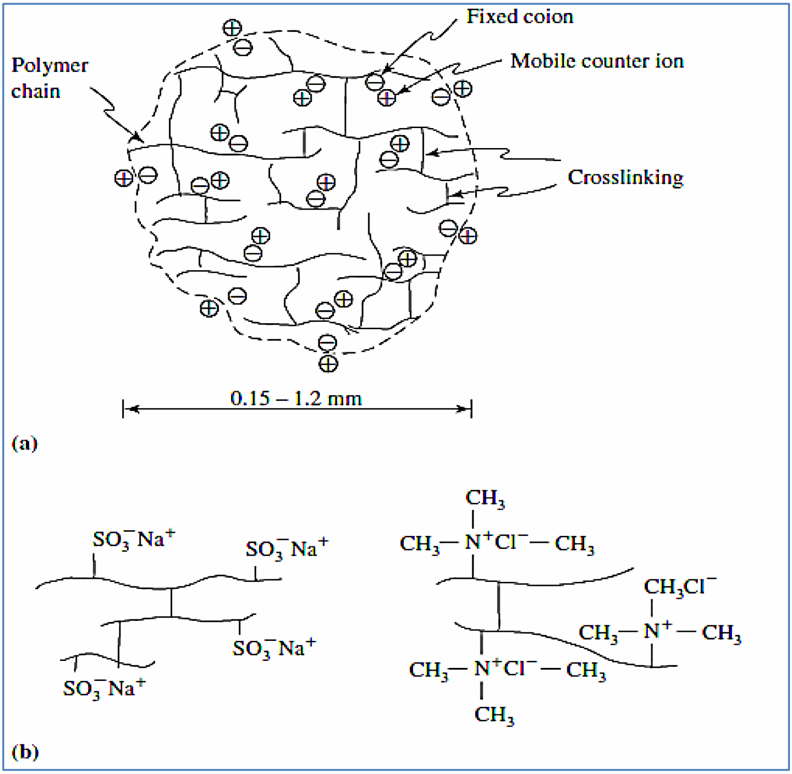


Figure 6: Schematic of organic cation-exchanged bead: a) Polystrene polymer cross-linked with divinylbenzene (DVB); b) Strong cation Exchange resin on left (Na+ form) and strong base on right (Cl-form)[28].

Sulfonated PS-DVB resins are widely used as acid catalysts in liquid phase reactions. They do not exhibit a catalytically active surface in the conventional sense; their activity is dependent on reactants diffusing into the solvated-polymer gel to access acid sites. They offer advantages over many inorganic solid acids in terms of ease of handling, structural uniformity and high abundance of acid sites, but their application is limited because of their intolerance to temperatures greater than 140-150ºC, and their acid sites are generally weaker than those found on zeolitic and similar solid acid catalysts[29-31].

In the industry all applications, which implicates ion exchange resins as catalyst, are performed under solid-liquid conditions, i.e., in circumstances under which the resin polymer backbone may undergo swelling in the liquid medium. And because of the intimate relation between the structure and catalytic activity of a resin, mentioned above, description of resin morphology is necessary to understand resin effects during the reaction in the liquid media. This refers to physical parameters such as surface area, pore volume, average pore size and pore size distribution and where possible an understanding of how these change in the working state of the polymer, i.e., when wetted by a solvent.

Some of the important techniques that are widely employed in the evaluation of the above parameters are: Solvent Imbibition, Nitrogen Sorption at 77K, and Mercury Intrusion Porosimetry. Meanwhile, solvent imbibition or uptake indicates the porous nature of a polymer support, both nitrogen sorption and mercury intrusion measure pore volume in the function of pressure. (MA, 55). Although the morphological data obtained through the instrumental techniques such as N_2 sorption and Hg intrusion are invaluable, but they present severe limitation in the dry state of resin. Due to which, interpretation of such data requires the assumption that the morphology is not changed significantly when the resin is wetted with solvent. This assumption might not be valid in many cases, as structures are affected by swelling both in macroporous and gel-type resins.

Recently the technique of inverse size exclusion chromatography (ISEC) has attracted attention for examining morphology in the wet state. The inverse application of the size-exclusion chromatography utilizes a set of molecular probes with defined sizes to determine pore dimensions. The porous structure of a resin is evaluated quantitatively in the solvent wetted state by packing the resin as the stationary phase in a chromatographic column and then recording the elution volume of a series of solutes of known molecular weights[32]. The morphological information given by ISEC technique has been employed successfully with catalytic activity of ion-exchangers in polar environments[33-37], in which, the accessibility of the reactant to acid centres was described as a key factor.

4. OBJECTIVES

Given the scarcity of bibliographical studies found on obtaining alkyl levulinates from sugars on acidic ion-exchange resins, the aim of this work is to study the direct reaction of fructose with butyl alcohol catalysed over s set of ion exchange resins to obtain the butyl levulinate, using a discontinuous reactor.

In particular, the following specific objectives have been set to study:

1. Selection of suitable acidic ion-exchange resin(s) for the process on the basis of catalytic activity: conversion and selectivity towards the ester.
2. Assessment of effect of catalytic mass and temperature on catalytic activity for optimum resins.
3. Evaluation of reusability of the best catalyst(s).

5. EXPERIMENTAL SECTION

5.1. MATERIALS: REACTANTS, AUXILIARTS AND CATALYSTS

Experiments for the synthesis of Butyl levulinate were carried out using fructose (99%, labkem), 1-butanol (99.5%, ACROS ORGANICS) and Water (Milli-Q, Millipore) without further purification. In the chromatographic calibrations the reagents used were 1-butanol, levulinic acid (98%, Acros Organics), formic acid (98%, labkem), butyl formate (98%, ACROS ORGANICS), butyl levulinate (98%, ALDRICH), 5-HMF (98%, Acros Organics), di-butyl ether (99%, Acros Organics).

The stirred reactor used was pressurized up to 21 atm by nitrogen gas of 99.99% purity. And in case of gas chromatograph (GC), helium of 99.99% purity was used as the carrier gas. Both were supplied by Abelló Linde (Barcelona, Spain).

Ion-exchange polystyrene-divinylbenzene (PS-DVB) sulfonated resins were used as catalysts throughout the experiments. The acidic resins used were Amberlyst 15 (A15), Amberlyst 16 (A16), Amberlyst 39 (A39), Dowex 50 Wx4, Dowex 50Wx2 (Dow Chemicals). Important resin properties are specified in the Table 9 below.

The resins used in this study have two type of morphology: macroreticular (all Amberlyst) and gel-type (Dowex resins). The ion-exchange resins were selected with wide range of %DVB, i.e. from 2% up to 20%. This property, the percentage of cross-linking agent (%DVB), is related to the stiffness of the polymeric structure of the resins. All the resins selected were conventionally sulfonated and the maximum temperature employed in this study was of 120°C.

Table 9: Properties of acidic resin catalysts used in this study

	A 15	**A 16**	**A 39**	**Dowex 50 Wx4**	**Dowex 50Wx2**
Type	Macro	Macro	Macro	Gel	Gel
Sulfonation type [a]	CS	CS	CS	CS	CS
Acid capacity (mmol H^+/g) [b]	4.81	4.80	5.00	4.95	4.83
%DVB	20	12	8	4	2
d_p[c] **(mm)**	0.74	0.70	0.71	0.149	0.149
Water retention (%)[c]	52-57	52-58	60-66	64-72	74-82
T_{max}(°C) [c]	120	130	130	150	150
d_{pore} (nm) [d]	12.4	15.5	15	-	-
$\sum V_{pore}$ (cm^3/g) [d]	0.616	0.188	0.155	-	-
$\sum S_{pore}$ (m^2/g) [d]	192.00	46.00	56.00	-	-
$\sum V_{sp}$[e] **(cm^3/g)**	0.622	1.136	1.643	1.920	2.677

(a) 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.

5.2. EXPERIMENTAL SETUP

As shown in the Figure 7, the experimental set-up consists of a 100mL stainless steel batch reactor (316 SS 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 includes 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. Beside the turbine, a stainless steel baffle plate 316 SS is placed to cut through the vortex, 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.

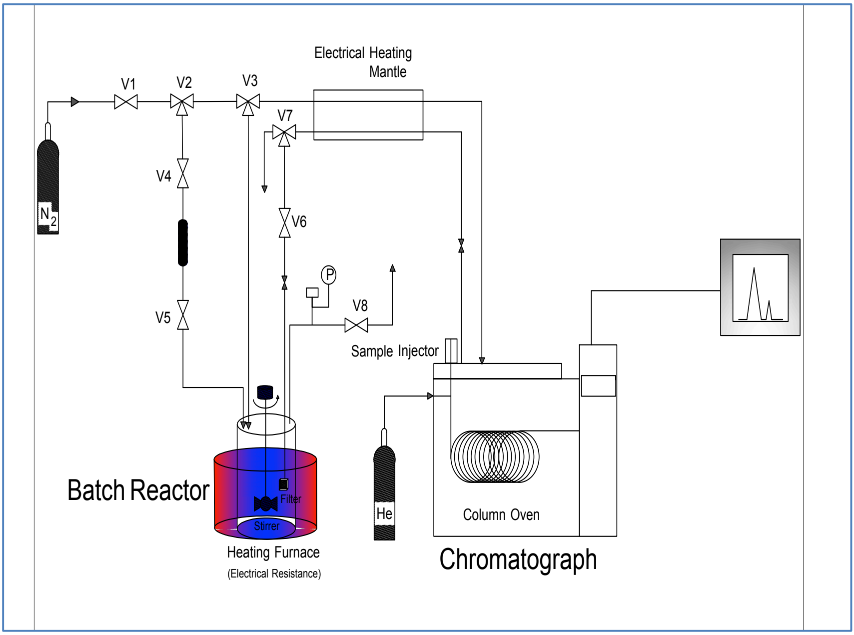


Figure 7: Scheme of Experimental Set-up.

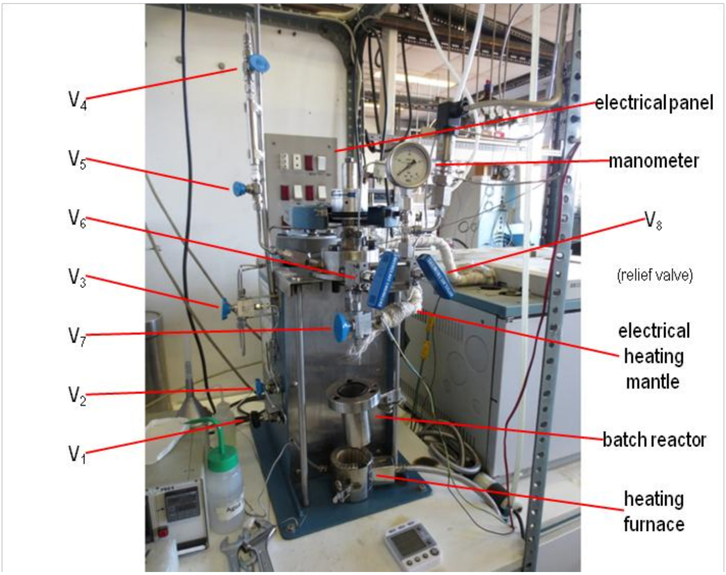


Figure 8: Disassembled experimental set-up[32].

Between the relief valve and the reactor, pressure measurements are taken through a manometer (Labon Druckmessumformer CB6020) and 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 bars with 5% error margin. The heating system comprises of an electric heating furnace TC-22 Pro 9 and is controlled by measuring the temperature inside the reactor and that of external wall through thermocouples. The error margin of the system is of ±0.1°C.

The catalyst injector is a stainless steel tube 316 SS through which, with the help of N_2 gas, the desired amount of catalyst is pushed inside the reactor. A sintered iron filter of 0.5 µm mesh size is used to filter the samples before taken. The composition of system is determined by means of a gas chromatograph (Hewlett Packard HP 6890 GC Series, Germany, Serial # DE00020827) and a high performance liquid chromatograph (HPLC AGILENT 1260 INFINITY Quaternary LC VL). Sample aliquots (0.1-0.2 ml) are collected manually and are injected in the gas chromatograph (GC) and high performance liquid chromatograph (HPLC).

In GC the sample injected is carried through the capillary column by He gas. The column measurements are: 20 µm internal diameter, 0.5 µm stationary phase thickness and 50 m length, with He as carrier gas and methyl siloxane as stationary phase (HP 190915-001, HO-Pona Methyl Siloxane). FRUCTMAN.M analysis method is used in the GC. Initially the oven temperature is of 60°C, which will rise by 10°C/min reaching 250°C and finally remains at 250°C for 7min. Run time is of 27 min, with an additional 15 min cool-down.

In HPLC the sample injected is carried through the column by the solvent i.e., dissolution of 0.005M H_2SO_4. The column specifications are: Aminex HPX-87H column #1250140 of 300 x 7.8mm and pH range 1-3. DEF_LC.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, which was used as isocratic pump throughout the analysis, through the column. 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, which includes the additional time for stabilization of the signal.

5.3. EXPERIMENTAL PROCEDURE

5.3.1. RESIN PRE-TREATMENT

All acidic resins have been washed with deionized water, before being used, and dried at room temperature for 10-12 h. Due to the highly hygroscopic nature of the PS-DVB resins a specified 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. In case of gel type resins such as Dowex 50Wx2, Dowex 50 Wx4, the commercial sample of 100-200 mesh size (0.074 - 0.149 mm) was used. And in the case of macro type resins such as A15, A16 and A39, the commercial sample was sieved and size of 0.08-0.1 mm was used.

5.3.2. REACTOR LOADING

The feed mixture, 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 introduced in the reactor. The volume of this mixture inside the batch reactor should not exceed 70% (70mL) of its total volume because of safety concerns. The reactor is secured with the three retaining screws and valve 1 (V1, Figure 7) is opened. Valve 2 (V2) is turned to position 2, and V3 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 V1 is closed. When the manometer reading is stable, the tightness of the system can be verified. When the experiment is being performed, V1 is opened again. The heating furnace is placed around the reactor and fastened properly.

5.3.3. EXPERIMENT LAUNCHING

The electrical panel is switched on and the stirring system (500rpm) is turned on together with the computer terminal, where 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 running method DEF_LC.M. The operating temperature inside the reactor and that of the electric heating mantle is programmed manually in the heating mantel (PRO 9) i.e., the electrical oven. 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.

Once the operating conditions are stationary, the catalyst is injected from the topmost nut in the injection system, which is under the V4 (Figure 7), through a funnel inside. 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, V2 is turned to position 1and V4 and V5 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. Also, meanwhile the V4 and V5 are opened, a pressure drop of 10atm is induced in the reactor by opening the relief valve (V7) repeatedly and quickly, at least 5 times, so that none of the catalyst is left the injector itself. The valve V2 position is reversed and valve 4 and 5 are closed. The addition of catalyst to the reactor is considered as the zero time (t_0) and the system is purged by opening and closing the valve V7.

5.3.4. SAMPLING

As mentioned before, the addition of catalyst to the system is considered as the zero time and, at this moment the first sample is collected. For this task, valve V3 is placed in position 2, V6 is opened and finally valve V7 is opened slowly a sample of 0.2 - 0.3 ml is collected in the vial of 1.5ml. Afterwards, valve V7 and V6 are closed. With valve V1 opened, the position of valve V3 is reversed and the relief valve, V8, is opened to induce a pressure drop of 10atm. To recover the pressure drop, valve V8 is closed and at the same moment valve V6 is opened. In this way the N_2 gas is forced to pass through the the valve V6 into the reactor and the sample retained in the conduction tubes and the filter inside the reactor is returned to the system. In order to assure the emptiness of the conduction tubes and filter, the pressure drop is induced at least 5 times, recovering the pressure each time as explained above. Also, during this process, a temperature drop of 1°C is observed. The whole process is repeated at 1 h intervals throughout the experiment for 8 h.

5.3.5. SAMPLE ANALYSIS

The sample collected is analysed in gas chromatograph and in high liquid performance chromatograph simultaneously. Meanwhile, in GC 0.1 μL of the sample is needed, in HPLC 100μL of the sample is injected to analyse. The corresponding methods loaded in each chromatograph, during the experiment launch, examine the samples and results obtained from each chromatograph will be recorded and mole composition was calculated by the calibration curves obtained previously. For more information regarding calibration curves see annex I. In some runs both analysis i.e., the GC and HPLC analysis, were repeated three times. Also, GC-MS analysis was used as well to identify all the components presented in the sample after 8 h of reaction.

5.3.6. CLEAN UP

After the last sample is collected, the heating system is shut off from the electrical panel and at the same time the stirring is turned off as well. the heating mantle is removed carefully and the system is left to cool down to ambient temperature. Once the reactor reached the ambient temperature, the three retaining screws are removed and the contents are weighed and filtered to recover the catalyst. The reactor is washed with the deionized water and later with ethanol and is dried through synthetic air. The filter is unscrewed carefully from its support and placed in the beaker with hexane in ultrasonic bath for 25 minutes, and later is dried as well with the synthetic air and placed back in the reactor.

The catalyst injector is cleaned by turning the valve V2 to position 2 and opening the valve V4 and V5 quickly. For security measures, a moistened beaker of 1L with water is placed under the catalyst injector so that the catalyst residue can be collected. At the same time, the filter support is also cleaned in the same way. For this purpose, the position of valve V2 is reversed, V3 is turned to position 1 and finally V6 is opened. A few drops of sample were collected while this process was performed. The other accessories of the reactor are washed with the deionized water and dried with synthetic air.

5.3.7. RESIN POSTTREATMENT

The recovered catalyst was weighed and was washed in a column with deionized water to remove materials. The following steps are used to downwash the resin catalyst:

- Add resin catalyst water slurry to a column containing some water.
- Occasionally drain excess water through the bottom of the column.
- Do not permit the liquid level to fall below the resin catalyst level.
- Continue adding in this manner until all resin is transferred.
- Do not load column to more than half of its height.
- Add 2 bed volumes (BV) of deionised water at 4BV/h and drain water through the bottom of the column at the same speed. Always keep the liquid level 1 or 2 cm above the rein catalyst level.
- Sample the water after 2nd BV and check that the water is colourless. If not continue the washing until the rinse water is colourless.
- After finishing, the catalyst is downwash with methanol three times.
- And before using the catalyst for an experiment, the pre-treatment mentioned previously in 5.4.1. is done again to eliminate all water content.

5.3.8. DETERMINATION OF ACID CAPACITY OF THE RESIN

Before determining the acid capacity, all catalysts should be pre-treated to eliminate all water content. Afterwards, at least 1.0 g of catalyst is introduced in conical flask of 250mL. 150 mL of NaOH 0.1N (standardized previously with potassium hydrogen phthalate) with 50mL of 2.5wt% of NaCl solution is added to the conical flask. The conical flask is put on agitation for at least 8h. After 8h of agitation, 25 mL of the solution is titrated with HCl 0.1N (standardised previously with NaOH 0.1N) using methyl orange as indicator. The titration is repeated at least three times.The acid capacity of the resin is calculated as follows:

$$Acid\ capacity\ (meq/g) = \frac{\mathrm{V_{NaOH}} \times \mathrm{N_{NaOH}} - \left\{(\mathrm{V_{HCl}} \times \mathrm{N_{HCL}}) \times {}^{\mathrm{V_{liquid}}}\!/_{\mathrm{V_{titrated}}}\right\}}{\text{catalyst mass}}$$

5.4. EXPERIMENTAL CONDITIONS

Experiments of 8 h duration were carried out at 21 atm, assuring the liquid phase in the reaction system, and in the range of 80 - 120 °C. The operating temperatures were maintained constants during the experiments.

As the nominal capacity of reactor is 100 mL, the loading volume should not exceed 70 mL, because of safety concerns. And the composition of initial load, which is marked by the limited solubility[41,42] in between fructose, butanol and water, is shown in the Table 10. Preliminary experiments were performed to obtain a one fase reaction system composed of these three reactants, i.e., fructose, water and 1-butanol at the desired temperature. These experiments were performed after revising the literature mentioned previously in Table 3.

To the best of our knowledge, no studies have been performed until now with the composition of initial load shown in the Table 10. This composition was remained constant in all the experiments performed in this study.

Table 10: Composition of initial load.

Reactants	**Weight %**
Fructose	**2.5**
Water	**16**
1-Butanol	**81.5**

For mostly all the experiments performed in this study, the mass of catalyst used was 1.0 g (1.7 wt%), however two experiments were performed, one with 0.5 g (0.8 wt%) and other with 2.0 g (3.3 wt%) in order to study the effect of catalyst mass on the reaction rates.

Stirring speed of 500 rpm was employed as recommended by the literature[32,43], because no resistance of external mass transfer was found. Moreover, study of the possible effects of this variable on the external mass transfer is not inside the bounds of this study. Due to which, the assumption of reaction rates is not affected by the resistance of external mass transfer is made.

5.5. CALCULATIONS

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

$$X_{Fructose}(t) = \frac{mols\ of\ fructose\ reacted}{initial\ mols\ of\ fructose} = \frac{n^{o}_{Fructose} - n_{Fructose}(t)}{n^{o}_{Fructose}} \quad \left[\frac{mol}{mol}\right]$$

$$S^{k}_{Fructose} = \frac{mols\ of\ k\ produced}{mols\ of\ fructose\ reacted} = \frac{n_k(t)}{n^{o}_{Fructose} - n_{Fructose}(t)} \quad \left[\frac{mol}{mol}\right]$$

$$Y^{k}_{fructose} = X_{Fructose} \times S^{k}_{Fructose} = \frac{n_k(t)}{n^{o}_{Fructose}} \quad \left[\frac{mol}{mol}\right]$$

where k refers to intermediates or product such as 5-HMF, levulinic acid (LA), formic acid (FA), 5-tert-butoxymethyl furfural (BMF), butyl formate (BF) and butyl levulinate (BL).

As the reactions were performed in a discontinuous reactor, standardised time variable is used:

$$Standardised\ time,\ \frac{w.t}{n^{o} fructose} = \frac{t\ (h) \times catalyst\ mass\ (g)}{initial\ mols\ of\ fructose\ (mol)}$$

6. RESULTS AND DISCUSSION

6.1. DESCRIPTION OF A TYPICAL EXPERIMENT

The monitoring of the composition, made through the time allows to evaluate the evolution of moles of each component with regard to standardised time. The Figure 9 depicts the results obtained from the experiment, carried out with Dowex 50Wx2 at 120 ºC.

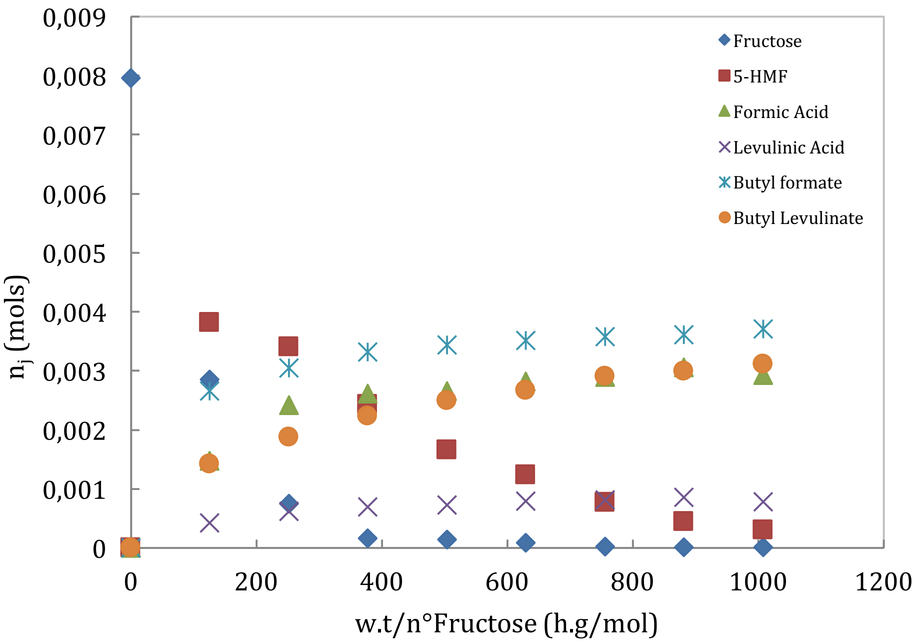


Figure 9: Mole evolution profile for fructose conversion in a batch operation. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: Dowex 50Wx2, 1.0 g; Temperature, 120 °C; 8 h.

As mentioned earlier, the synthesis of butyl levulinate from fructose involves a series of consecutive and parallel reactions starting from dehydration of fructose to 5-HMF in the presence of an acid catalyst. The intermediate product, 5-HMF, react further to form BMF through etherification, and LA and FA by rehydration, which in the presence of alcohol, i.e., BuOH, undergoes esterification to yield butyl levulinate and butyl formate. Accordingly, as can be seen in Figure 9, an exponential decrease of fructose composition and simultaneous increase of butyl levulinate can be observed. As expected, immediate production and consumption of intermediate products, i.e., 5-HMF, BMF, LA, FA was observed as well.

Although, with reference to Figure 4, where reaction pathway is explained, uneven mol production of LA and FA and therefore of BL and BF was observed. No explanation has been found for these unexpected results. Also, mol production of BMF has not been shown in the Figure 9 as it was not calibrated though detected through GC-MS. Although in literature[22, 23], the presence of humins has been informed, no visual identification of humins, in this work, has been detected. 1-Butanol and water, which were employed in excess, have not been examined due to their interactions with the polymeric catalyst structure.

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

6.1.1. EVALUATION OF THE EXPERIMENTAL ERROR

Before considering the effects of temperature, catalyst mass or any other parameter, it is important to study the experimental error which can be made during the experiments. In order to study this parameter, three random replicas of the same experiment were performed at 100°C using Dowex50x2 as the catalyst. As seen in the Figure 9, the mol production and immediate consumption of intermediates was quite hurried. So in order to study in a better way, the synthesis route, so that all the intermediates could be detected, the random replicas for the evaluation of experimental error were carried at 100 ºC.

The results obtained are shown in Figure 10 and Figure 11. The fructose conversion obtained was of 98.9% ± 0.03% and of Butyl levulinate yield was 22.9% ± 0.5%. after observing the results obtained, shown in Figure 8, 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 annex II.

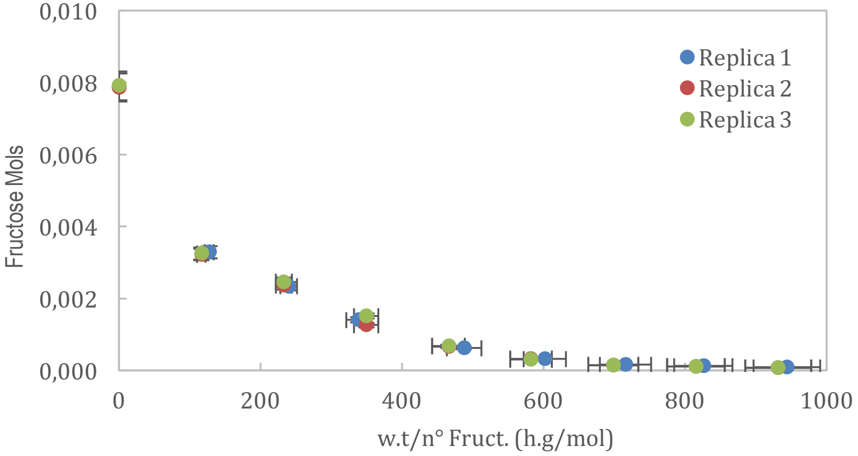


Figure 10: Study of experimental error in the evolution of fructose and butyl levulinate in the three random replicas held at 100 °C for 8 h with Dowex 50Wx2. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g.

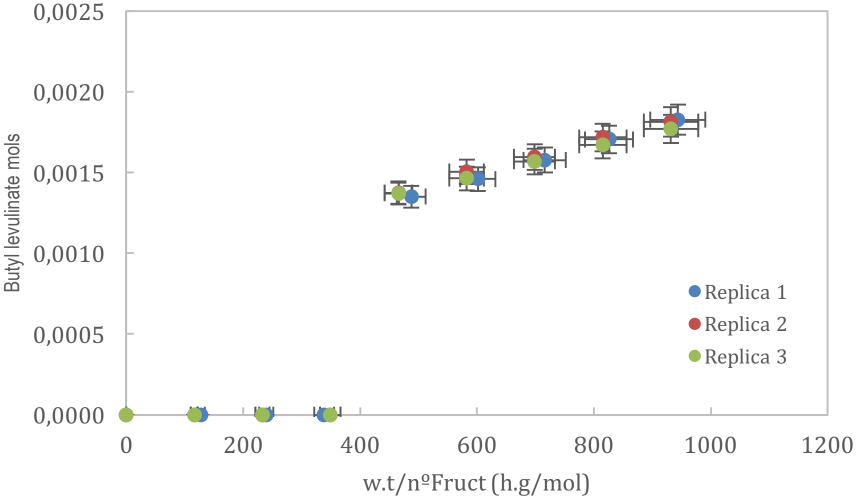


Figure 11: Study of experimental error in the evolution of fructose and butyl levulinate in the three random replicas held at 100 °C for 8 h with Dowex 50Wx2. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g.

6.1.2. EFFECT OF CATALYST MASS

To evaluate the effect of catalyst loading, experiments were held at 120 ºC with different mass of catalyst, i.e., 0.5 g, 1.0 g, 2.0 g, employed in each experiment. The results illustrated in Figure 12 reveals that BL yield improved as catalyst loading was increased from 0.5 g to 2.0 g.

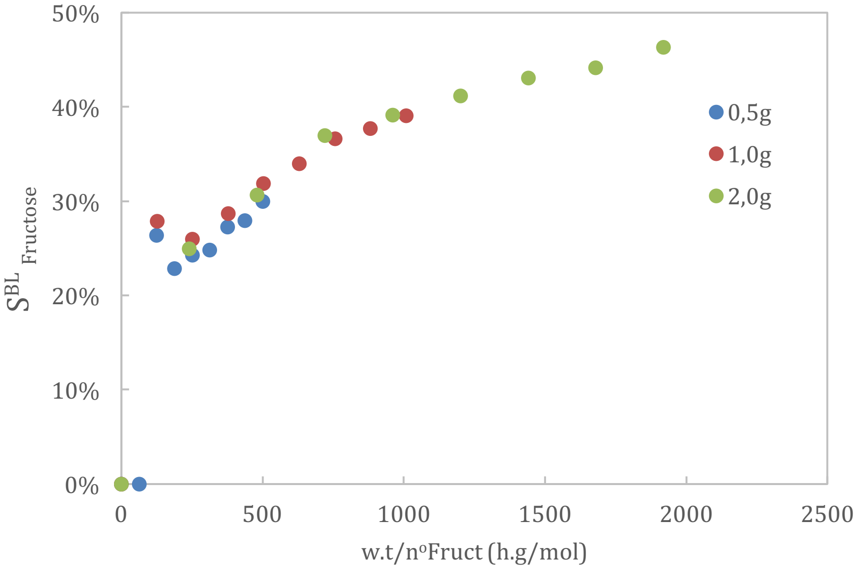


Figure 12: Effect of catalyst mass on the selectivity to butyl levulinate. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: Dowex 50Wx2; T: 120 °C; 8 h.

In each case of different catalyst loading, around 99% of fructose conversion was obtained as shown in Table 11, but selectivity of fructose to butyl levulinate was quite different. But, focusing on the same reaction point, BL yield was quite similar. Taking the standardised time (w.t/nº Fructose) at 500, as an example, BL yield was 29.5% when 0.5g of catalyst was loaded and was 31.3% and 30.1%, when 1.0g and 2.0g of catalyst was used respectively.

Within the experimental error, it can be concluded that same BL yield was obtained employing different catalyst loading or in other words, the catalyst loading in between 0.5-2.0g does not affect the reaction rate.

Table 11: Results obtained varying catalyst mass in the synthesis of BL, with Dowex 50Wx2 as catalyst at 120°C after 8h.

Catalyst mass (g)	0.5	1.0	2.0
$X_{Fructose}$	98,4%	99,9%	100%
$S_{Fructose}^{5-HMF}$	20,8%	3,9%	1,6%
$S_{Fructose}^{LA}$	8,8%	9,8%	13,2%
$S_{Fructose}^{FA}$	32,6%	37,6%	46,4%
$S_{Fructose}^{BF}$	41,0%	46,6%	50,8%
$S_{Fructose}^{BL}$	30,0%	39,1%	46,3%

6.2. COMPARISON OF VARIOUS ACIDIC ION-EXCHANGE RESINS BEHAVIOUR.

The catalytic behaviour of each catalyst tested, i.e., Dowex 50Wx2 (Dow 2), Dowex 50Wx4 (Dow 4), Amberlyst 39 (A39), Amberlyst 16 (A16), and Amberlyst 15 (A15), was determined by the activity and selectivity showed after 8 h in an experiment carried at 120 ºC. Table 12 presents the results obtained after 8h of experiments from different catalysts employed in the synthesis of Butyl levulinate at 120°C. The reaction temperature of 120°C was chosen based on the maximum temperature at which the mentioned set of catalysts can be used.

Table 12: Results of experiments performed with different catalysts at 120°C after 8h.

Catalyst	Dow 2	Dow 4	A 39	A16	A15
$X_{Fructose}$	99,9%	99,9%	99,9%	99,9%	99,9%
$S_{Fructose}^{5-HMF}$	3,9%	19,8%	9,6%	21,0%	36,6%
$S_{Fructose}^{LA}$	9,8%	12,3%	11,1%	12,7%	10,8%
$S_{Fructose}^{FA}$	36,9%	33,2%	37,6%	35,4%	37,6%
$S_{Fructose}^{BF}$	46,6%	42,7%	44,7%	42,9%	36,4%
$S_{Fructose}^{BL}$	39,1%	31,2%	37,7%	30,6%	23,9%

Although, almost 100% conversion of fructose was obtained with each catalysts (Table 12), the consumption of fructose does not occur in the same way. This can be seen in the Figure 13. In case of A16, the fructose reacted slightly slowly as compared to rest of the catalyst but, no clear conclusion over the most suitable catalyst can be taken by comparing fructose conversion only.

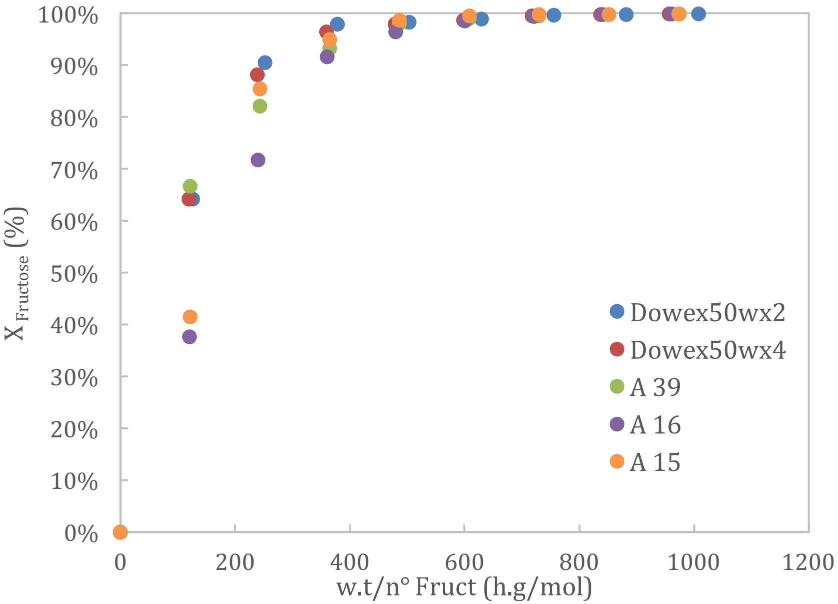


Figure 13: Conversion vs adimensional time for synthesis of butyl levulinate for all of the solid catalysts. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g; Temperature, 120 °C; 8 h.

Due to which main attention will be paid on selectivity of fructose towards the intermediates and product in this report. As shown in Figure 14, beside high conversion of fructose, the selectivity of fructose to intermediates (5-HMF, LA, FA) and products (BL and BF) was different with each catalyst. It can be observed that, with Dowex 50Wx2 and A39, selectivity of fructose to butyl levulinate and butyl formate was enhanced significantly. Meanwhile A15 present more affinity towards the intermediate product, 5-HMF. The selectivity towards FA and LA does not show any particular trend however, the yield of FA was observed higher than that of LA in all the cases studied. Same trend was seen while observing BF and BL.

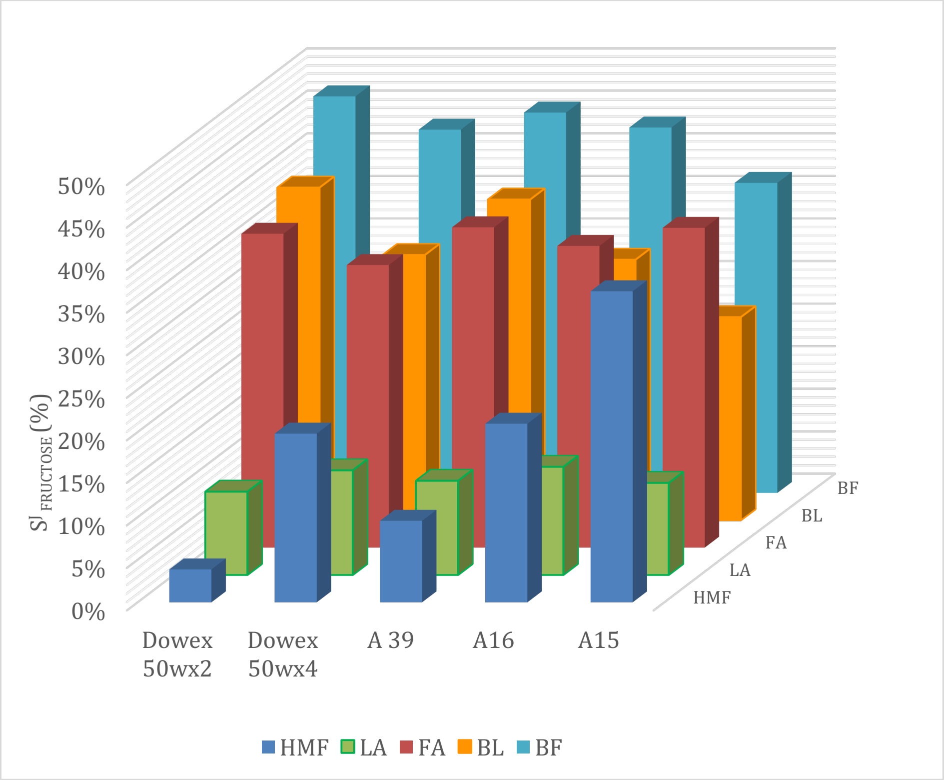


Figure 14: Selectivity of fructose to different intermediates and product for all of the catalysts after 8 h of reaction at T = 120 °C. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g.

Comparing the two gel type catalyst employed in this study, Dowex 50Wx2 and Dowex 50Wx4, the yield of BL hike from 31% to almost 40% when Dowex 50Wx2 was employed. And, only 4% of 5-HMF was detected after 8h with Dowex 50Wx2 in comparison to almost 20% with Dowex 50Wx4. However, LA and FA yield does not show the same progress. With Dowex 50Wx2, almost 10% and with Dowex 50Wx4, 12% of LA was found, meanwhile, around 33% of FA was observed with Dowex 50Wx4 and almost 37% with Dowex 50Wx2. By comparing the results of 5-HMF and BL, it suggests that higher cross-linking, which allows partial swelling, does not favours the esterification of intermediates to BL or the reaction is more confined to dehydration of fructose with higher cross-linking.

In case of macro type catalyst used, i.e., A39, A16 and A15, A39 presented the highest yield of BL, up to 37% within the macro-type catalyst. Whereas, with A15 similar yields of 5-HMF, 37%, was obtained. To resume the effect of cross-linking agent on the selectivity of intermediate products and major product, Figure 15 is presented. This Figure suggests that the esterification of intermediates to BL is more favourable when less cross-linking agents are presented, or in other words, resins with lesser degree of cross-linking (%DVB) present higher reaction rates. This result is in agreement with the results of esterification of LA to BL performed by M.A. Tejero[32] (2015).

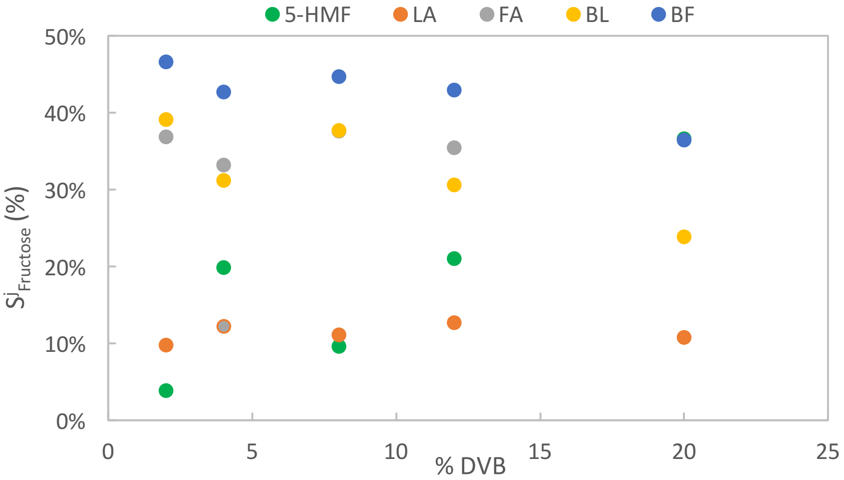


Figure 15: Effect of degree of cross-linking (%DVB) over selectivity towards intermediate and major product. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g; T: 120 °C; 8 h.

Comparing the results between gel-type and macro-type catalysts, as mentioned earlier, both Dowex 50Wx2 and A39 presented quite similar yields and selectivity towards butyl levulinate. However, the different yields and selectivity were obtained from rest of the catalyst employed. Though A39 presents higher degree of cross-linking and less acid sites, more BL yield was reported than Dowex 50wx4. And by comparing the number of acid sites of rest of the catalyst employed with the selectivity of fructose towards different intermediates and products, BL and BF, no marked correlation was found.

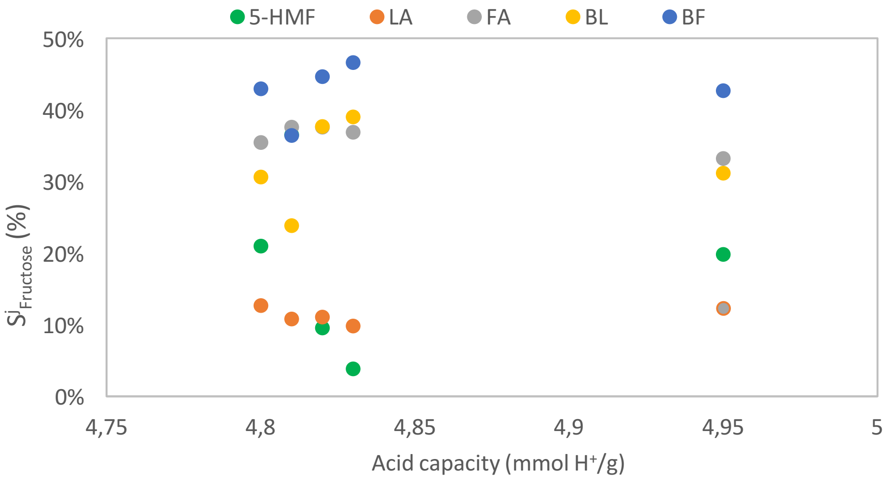


Figure 16: Effect of acid capacity over selectivity towards intermediate and major product. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g; T: 120 °C; 8 h.

As depicts Figure 16, many resins with similar acid capacity display different selectivity. This suggests that other structural parameters such as diameter, global surface and volume should be of greater importance in resin catalyst efficiency. But these parameters mentioned above are only important in case of macroporous resins. Nevertheless, these factors can give us a hint regarding accessibility. In Table 13, results comparing these parameters are presented along with the selectivity of fructose towards BL.

Table 13: Comparison of butyl levulinate selectivity with different catalyst parameters. a: Swollen state.

Catalyst	**%DVB**	**Acid Capacity**	d_{pore}(nm)^a	$\sum S_{pore}$ (m^2/g)^a	$\sum V_{pore}$ (cm^3/g)^a	$\sum V_{sp}$ (cm^3/g)	$S^{BL}_{Fructose}$
Dow 2	2	4,83				2,7	39,1%
Dow 4	4	4,95				1,9	31,2%
A39	8	4,81	15,0	56,0	0,155	1,643	37,7%
A16	12	4,80	15,5	46,0	0,188	1,136	30,6%
A15	20	4,81	12,4	192,0	0,616	0,622	23,9%

By comparing A39 with A15, it can be suggested that a larger macropores present higher reaction rates, yielding greater amount of BL. Moreover, it appears that larger global macropore surface and volume does not promote the reaction towards the synthesis of BL. These results can easily be explained as larger macropore surface and volume correspond to highly cross-linked and thus, stiferf resins.

However, to understand more efficiently the catalyst performance it is better to study molecule access to the catalyst pore rather than studying pore size. When immersed in a polar solvent the polymeric catalysts tend to swell, due to the interaction of medium with the catalyst molecule. And in the swollen state, a large number of accessible active sites appears on the top of macropore surface. The formation of these macropores is determined by the amount of cross-linking used in the catalysis synthesis. Both types of resins used in this study: Gel-type and Macroporous, undergoes swelling. Although gel-type resins swell a lot more than macroporous due to their polymeric structure.

One parameter which gives an accurate idea of this magnitude of polymer swelling in polar medium is volume of swollen polymer, V_{sp}. V_{sp} gives an accurate idea of the magnitude of polymer swelling in polar medium. Figure 17 shows the effect of polymer swelling on the selectivity of fructose towards the intermediates and the major product and their yields. It can be observed that as the V_{sp} increases, the selectivity and yield of BL increases and that of 5-HMF decreases except in case of A39 and Dowex 50Wx4, where beside having slight less V_{sp}, A39 present better yield and selectivity.

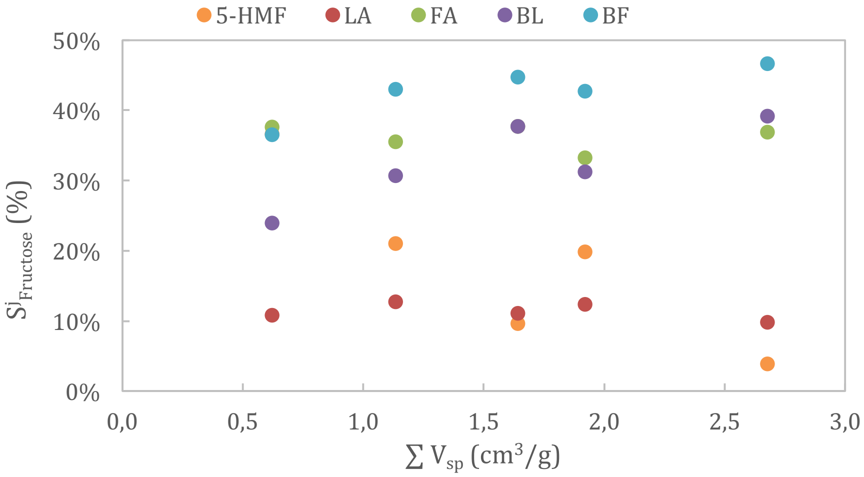


Figure 17: Effect of polymer swelling over selectivity towards intermediate and major product. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: 1.0 g; T: 120 °C; 8 h.

Apart from the pore size after swelling, the molecule access also depends on the size of molecule. As shown in the Figure 18, the 5-HMF molecule presents greater surface area than butyl levulinate and this may create impediment for the second reaction step, i.e., rehydration of HMF to LA. Moreover, in the same step water is consumed and this may not have let Dowex 50Wx4 swell completely. Due to which, less active sites were present in Dowex 50Wx4 and this has led to less BL yield. Meanwhile, A39 does not get affected that much by the consumption of water as it has permanent porous and this has resulted in slightly higher BL yield. Both reasons are quite valid to explain why less yield of butyl levulinate was obtained by employing Dowex 50Wx4 as catalyst despite of having less cross-linking agent than A39.

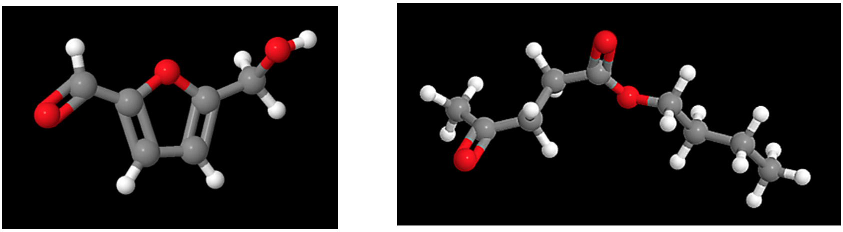


Figure 18: 3-D model of 5-HMF and Butyl levulinate molecules[38].

To summarize, it can be concluded that Dowex 50Wx2 was clearly the most suitable catalyst providing the highest Butyl levulinate yield (nearly 40%) and selectivity as well (around 40%).

6.3. EFFECT OF REACTION TEMPERATURE

The effect of reaction temperature on the fructose conversion to butyl levulinate was investigated, and the experiments were carried out at 80, 90, 100, 110 and 120°C, respectively. It can be observed from Figure 19 that temperature played a significant effect on the fructose conversion. Almost 100% of fructose conversion was obtained after 8h, when the reaction temperature was above 100°C. Although the results shown in the Figure 20 illustrates that the selectivity of fructose to intermediates and products was different at different temperature.

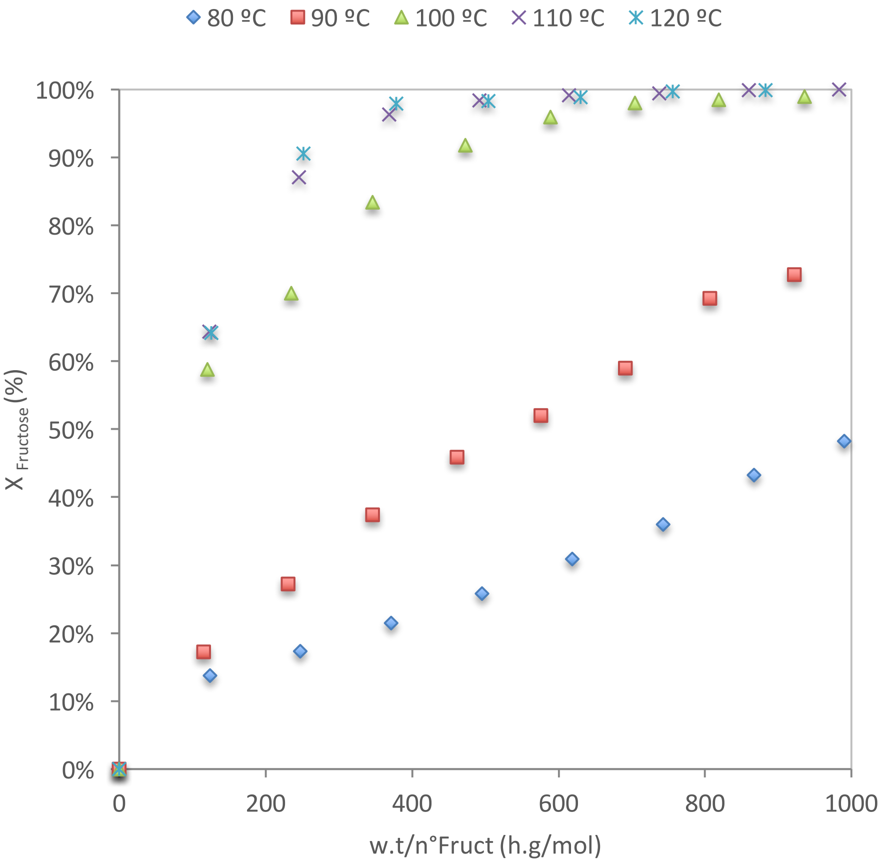


Figure 19: Effect of temperature on conversion of fructose. Reaction composition: Fructose, 1.0 g; BuOH, 60 mL, H_2O, 10 mL; Catalyst: Dowex 50Wx2, 1.0 g.

As evidenced in Figure 20, the selectivity to 5-HMF began to fall intensely with the increase in temperature. 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 120ºC. BL and BF were not observed until the temperature reached 100°C. The selectivity and the yield of BL and BF augmented with the temperature and at 120°C, maximum yield and maximum selectivity of fructose towards BL and BF was observed. Though, the BL yield obtained at 110ºC and 120ºC was quite similar, the presence of intermediates at 110ºC was higher.

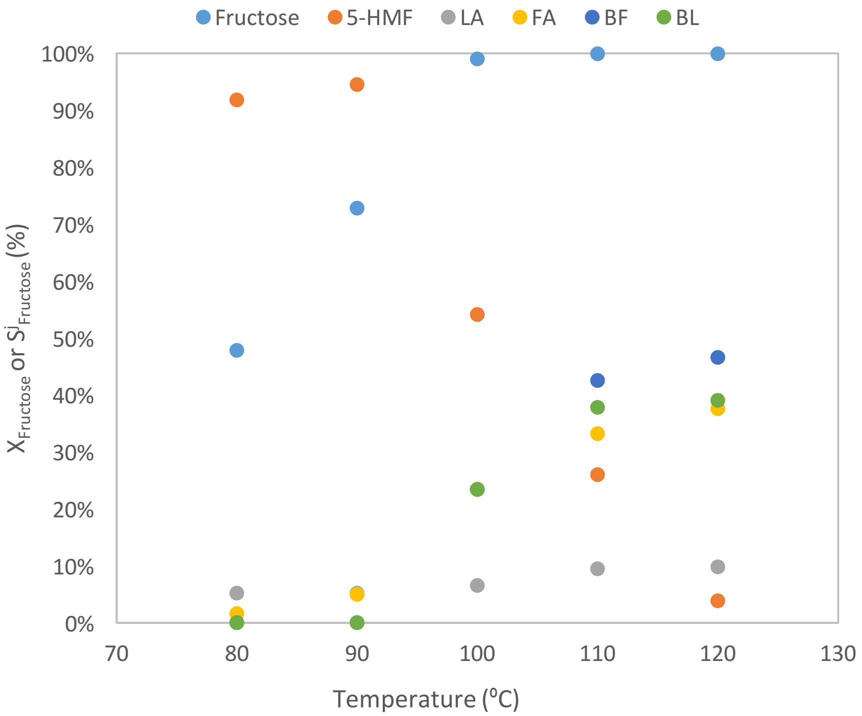


Figure 20: Effect of temperature on the synthesis of intermediates and products from fructose. Reaction composition: Fructose, 1.0g; BuOH, 60mL, H_2O, 10mL; Catalyst: Dowex 50Wx2, 1.0g.

By observing these results, it can be concluded that higher temperature accelerates the reaction rate and favours the synthesis of butyl levulinate, but also increases the rate of formation of by-products such as BF.

6.4. CATALYST REUSE EXPERIMENTS

Long-term stability of heterogeneous catalyst is an extremely important characteristic for practical usage to reduce production cost. After completing 8h of reaction, the spent Dowex 50Wx2 was separated from the liquid products. It was found that the colour of the catalyst surface became dark grey. It may be resulted from the adsorbed humins which were formed during the experiment. The used catalyst was post-treated as mentioned in 5.4.7 and was reused in a new experiment. And to study the possible deactivation of the catalyst, same experimental conditions were employed. The results of selectivity to BL and fructose conversion as a function of time of Dowex 50Wx2 catalyst reuse cycle are presented in Figure 21.

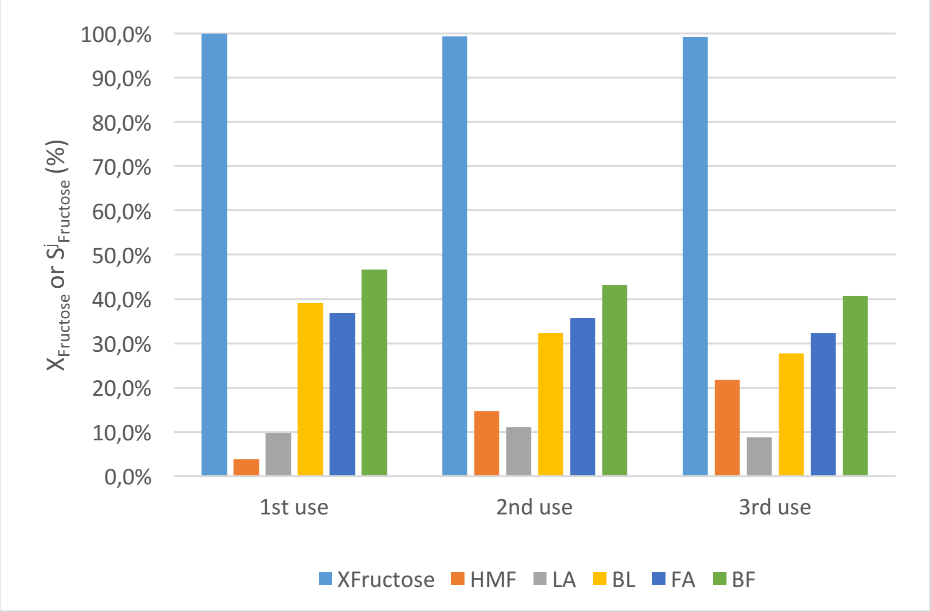
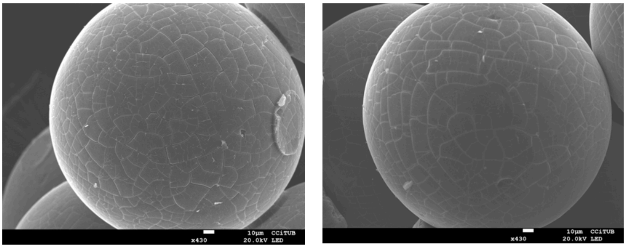


Figure 21: Fructose conversion and Selectivity to intermediates and products as a function of catalyst reuse cycle with post-treatment of catalyst with deionised water and methanol between each experiment. Reaction composition: Fructose, 1.0g; BuOH, 60mL, H_2O, 10mL; Catalyst: Dowex 50Wx2, 1.0g; T: 120°C; 8h.

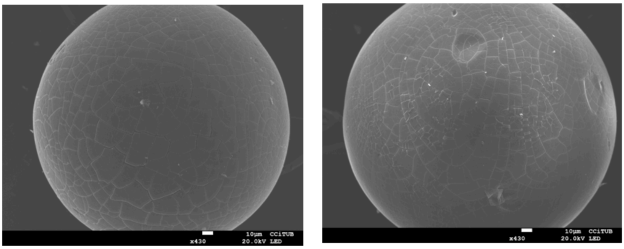
It can be seen that conversion of fructose does not seem to be affected by the recycling of catalysts however, the selectivity of fructose towards different intermediates and products do get affected. After three uses, the yield of BL decreased from 39% to 28% and that of BF from 47%

to 41%. In case of intermediates, LA and FA does not show any particular trend. But 5-HMF yield reached 22% after the 3rd use.

The gradual decrease in the selectivity may be caused by the deterioration suffered by the resins after each use, possible loss of sulphur during the reaction and/or due to less accessibility of acid sites. To confirm the presence of fewer availability of acid sites, the acid capacity of the resin after each use was calculated by titration and to study the deterioration suffered by the resins and loss of sulphur groups, after and before the reaction, a brief morphological study was done by SEM/EDS. The results obtained through the SEM are shown in Figure 22.



Fresh resin After 1st use



After 2nd use After 3rd use

Figure 22: Scanning electronic microscopy images of Dowex 50Wx2. Courtesy of Department of Chemical Engineering, UB.

By observing the Figure 22, it can be concluded that after three uses of the catalyst Dowex 50Wx2, no damage has been noted on the surface image of resin bead. The deactivation of resin should not be caused due to the deterioration of the catalysts beads.

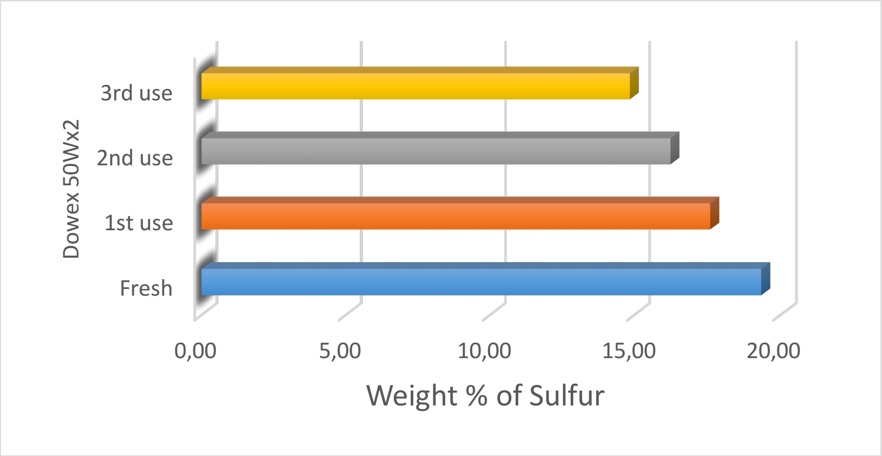


Figure 23: Weight of sulphur measured for fresh and used catalysts resin.

By observing the Figure 23, it can be noted that the weight of sulphur decreases gradually after each use, which can explain the gradual decrease in the catalytic activity of Dowex 50Wx2 upon reusing.

6.4.1. ACID CAPACITY OF CATALYST REUSED.

Acid capacity of an ion-exchange resin is the number of active sites available for the reaction. As shown in the Figure 24, the acid capacity of Dowex 50Wx2 declines after each use for the synthesis of butyl levulinate, providing only half of the active sites compared to the fresh catalyst after its third use.

Thus, by observing Figure 23 and 24, it can be concluded that the gradual decrease in the catalytic activity is because of loss of acidic group $SO_3^- H^+$ after each use and this cause the decrease in the yield of butyl levulinate. Though it seemed to be a rational reason, more investigation is recommended in order to understand the deactivation of catalyst, during the direct conversion of fructose to butyl levulinate in the presence of butanol and water, in a better way.

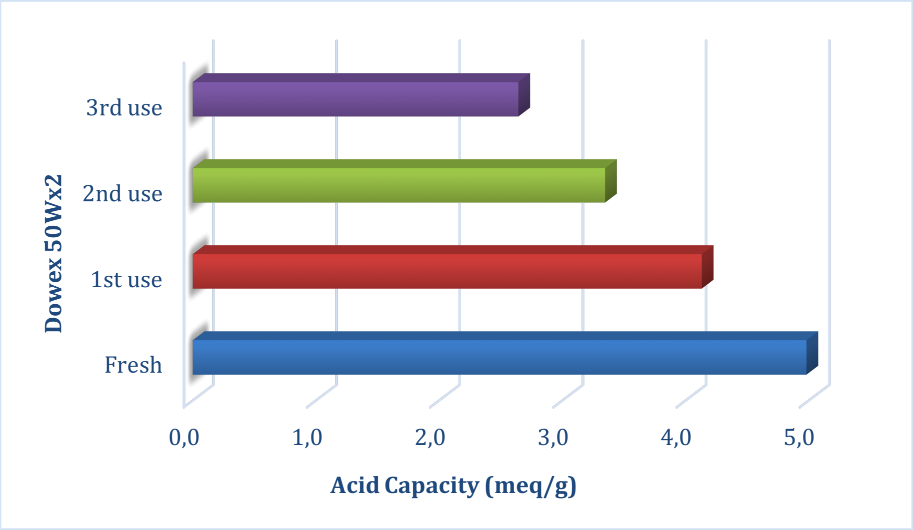


Figure 24: Acid capacity of Dowex 50Wx2, calculated by titration, after using for the synthesis of BL. Reaction composition: Fructose, 1.0g; BuOH, 60mL, H_2O, 10mL; Catalyst: Dowex 50Wx2, 1.0g; T: 120°C; 8h.

7. CONCLUSIONS

This study has shown that direct synthesis of butyl levulinate from fructose can take place in the presence of butanol employing ion exchange resins at higher temperatures such as 100°C or above.

Higher temperature can accelerate the rate of chemical reaction providing considerable yields of BL, but by-products such as BF also occur at the same time. Although, the presence of humins is mentioned in the literature, no humins were detected in this investigation. Apart from the reaction condition such as temperature, the choice of catalyst has significant effect on the yield of BL obtained from fructose in butanol media.

Between two types of catalysts employed in this study, gel-type resins with low degree of cross-linking showed better activity as a whole. Of the catalysts employed in this study, Dowex 50Wx2 was found to be the most active. However, the catalyst loading of Dowex 50Wx2 in between 0.5-2.0g does not affect the reaction rate.

The high selectivity and yield of BL were attributed to the low degree of cross-linking agent (%DVB) and high swelling capacity in polar medium ($\sum V_{sp}$ (cm^3/g)) of the catalyst. The degree of cross-linking agent, which also affects the swelling capacity of resins can be termed as the catalyst property with most control over catalyst efficiency in this work. The reaction rates increase significantly as the degree of cross-linking diminished. But other catalyst properties such as acid capacity does not have an important effect on the catalyst activity.

The reuse of catalyst showed slow decrease in the catalytic activity, which may be caused by the loss of acid sites on the surface of catalyst. Although, broaden analyses will be required to understand in a better way the deactivation of the catalyst after every cycle.

Overall, it can be concluded that ion-exchange resins are quite efficient for the synthesis of butyl levulinate directly from fructose in the presence of butanol and water. And as they are cheaper and more readily available commercially, they can be applied to existent and new industrial processes. However, further studies will be required in order to determine whether or not they are highly suitable for industrial use.

As recommendation, a possible study on deactivation of reused acidic ion-exchange resins is suggested. Although, it has been seen that the resins lose the acid sites after each use, a study of deactivation in a continuous stirred reactor is highly recommended.

Another recommendation is direct conversion of glucose to butyl levulinate and in this way compare and deduce which form of sugar is recommendable for the synthesis of levulinate esters and why it is so.

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9. ACRONYMS

5-HMF 5-(Hydroxymethyl)furfural.

A-39 Amberlyst 39

BF Butyl formate.

BL Butyl levulinate.

BuOH 1-butanol.

CS Conventionally sulfonated.

Dow 2 Dowex 50Wx2.

d_p Particle diameter, mm.

d_{pore} (macro)pore diameter, mm.

DVB Divinylbenzene.

ETBE Ethyl *tert*-butyl ether.

FA Formic acid

ISEC Inverse size exclusion chromatography.

LA Levulinic acid.

m_{cat} Catalyst mass.

n_j Mol of species j.

$N_{dis(NaOH)}$ Normality of NaOH dissolution standardized previously.

N_{HCl} Normality of HCl dissolution standardized previously.

$R_{BuOH/LA}$ Molar ratio of butanol versus levulinic acid.

S^E_j Selectivity of reagent j towards product E.

SS Surface sulfonated.

t time.

T Temperature, ^{o}C, K.

T_{max} Maximum work temperature, ^oC, K.

$V_{dis(NaOH)}$ Initial volume of NaOH dissolution (150 mL).

V_{HCl} Volume of HCl usedin titration.

V_{liquid} Volume of total dissolution. (200 mL).

$V_{titrated}$ Volume of NaOH used for titration. (25 mL).

V_{sp} Specific volume of swollen polymer, cm^3/g.

X_j Conversion of reagent j.

ΣS_{pore} Global (macro)pore surface, m^2/g.

ΣV_{pore} Global (macro)pore volume, cm^3/g.

APPENDICES

APPENDIX 1: CALIBRATION

GC calibration

Chromatography is used to separate mixtures of substances into their components. All forms of chromatography work on the same principle.

They all have a stationary phase (a solid, or a liquid supported on a solid) and a mobile phase (a liquid or a gas). The mobile phase flows through the stationary phase and carries the components of the mixture with it. Different components travel at different rates.

In gas-liquid chromatography, the mobile phase is a gas such as helium and the stationary phase is a high boiling point liquid adsorbed onto a solid. Very small quantities of the sample are injected into the machine using a small syringe. The syringe needle passes through a thick rubber disc (known as a septum) which reseals itself again when the syringe is pulled out.

The injector is contained in an oven whose temperature can be controlled. It is hot enough so that all the sample boils and is carried into the column as a gas by the helium (or other carrier gas). The vaporized compounds analysed interact with the walls of the column, each of them elute at different times known as the retention time of the compound. Different compounds have different retention times. For a particular compound, the retention time will vary depending on: the boiling point of the compound, the solubility in the liquid phase and the temperature of the column. A detector is used to monitor the output stream of the column and makes it possible to determine both retention times and the relative amount of the components (signal intensity). The output will be recorded as a series of peaks - each one representing a compound in the mixture passing through the detector. The areas under the peaks are proportional to the amount of each compound which has passed the detector. In identical conditions, elution time will remain same in the same chromatograph, which is why GC is a viable method of analysis. Retention time for components in the direct conversion of fructose to BL in the presence of BuOH and water measured through GC are specified in Table 14.

Compound	Retention time (min.)
Water, H_2O	4,484
1-Butanol, BuOH	6,498
Butyl formate, BF	7,523
Butyl levulinate, BL	15,214

Table 14: Retention time of components in the production of BL from fructose in GC.

In order to relate the percentage of area with the percentage in mass in any given sample it is necessary to first calibrate the system with standards of known composition. To study the direct conversion of fructose to BL with BuOH, vials with known percentage of mass was prepared. And three replicates were performed of each analysis of each vial in order to evaluate the dispersion statistically. Fisher's test was applied to linear fit in order to ascertain statistical significance. An example of such calibration is shown in the Figure 25 below.

Butanol	m %	Area %
1	0,00%	0
2	9,05%	11,12±0,029
3	16,38%	19,22±0,039
4	24,83%	29,57±0,029
5	27,10%	30,64±0,16
6	36,23%	40,55±0,13
7	49,21%	53,92±0,07
8	51,13%	55,25±0,12
9	58,02%	61,88±0,11
10	60,34%	63,18±0,08
11	79,59%	82,49±0,015
12	86,50%	88,30±0,07
13	64,64%	69,63±0,11
14	77,18%	81,04±0,09

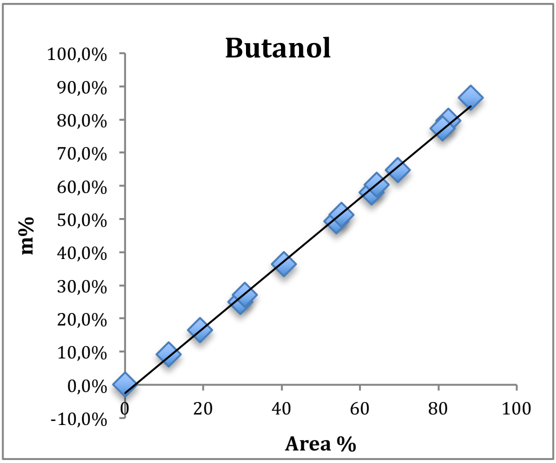

Figure 25: Calibration data and linear fit for Butanol.

Component	*%Mass = f(%area)*	*R^2*
1-BuOH	% mass =(0,0098±0,0001) *%area + (-0,0247±0,0076)	0,9973
BF	% mass =(0,0111±0,0001) *%area + (0,0032±0,0029)	0,9981
DBE	% mass =(0,0095±0,0001) *%area + (0,0012±0,0030)	0,9978
BL	% mass =(0,0111±0,0001) *%area + (0,0112±0,0046)	0,9967

Table 15: Calibration curves for the components measured by GC

And the linear equations obtained through the calibration for each component measured by GC are shown in Table 15.

HPLC calibration

High performance liquid chromatography is basically a highly improved form of column chromatography. Instead of a solvent being allowed to drip through a column under gravity, it is forced through under high pressures. This technique is used for separating and analysing compounds based on differences in their interaction with a stationary phase. In the food industry, HPLC technique is well established for the analysis of invert sugars. In Table 16 below, retention time of the components in the production of BL from fructose are shown and in Table 17, the calibration curves obtained from HPLC:

Compound	**Retention time (min.)**
Fructose	10,888
Formic acid	14,828
Levulinic acid	17,854
5-HMF	34,934

Table 16: Retention time of components in HPLC.

Component	Mass = f(area)	R^2
Fructose	*mass =(3,456E-6±1,968E-7) *area +(-0,004±0,0016)*	*0,9995*
FA	*mass =(9,602E-6±9,486E-8) *area +(-0,0017±0,0062)*	*0,9984*
LA	*mass =(5,253E-6±8,621E-8) *area +(-0,0423±0,0291)*	*0,9960*
BL	*mass =(2,902E-6±5,315E-8) *area +(0,0031±0,0070)*	*0,9947*

Table 17: Calibration curve for components measured through HPLC.

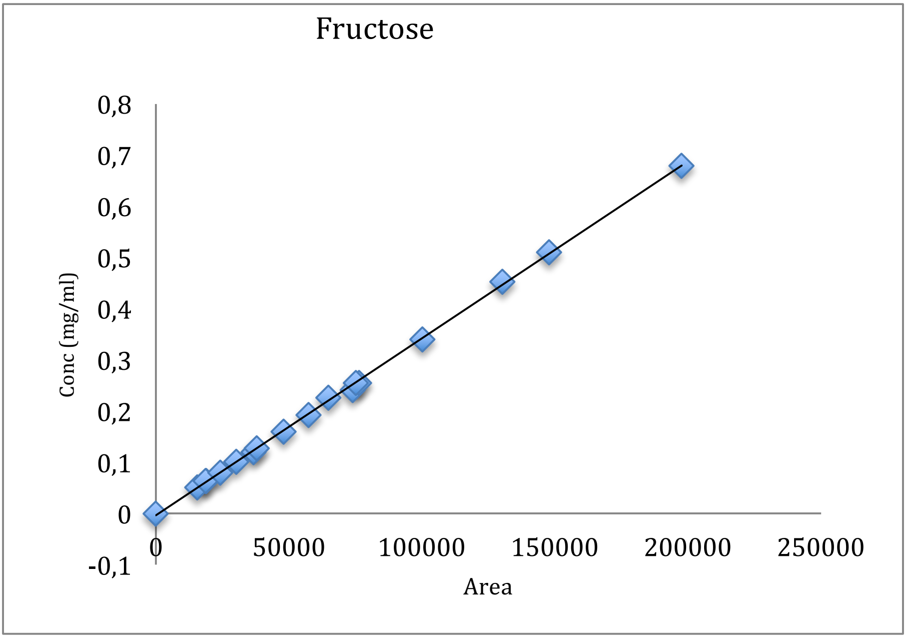

Figure 26: Example of linear regression for the calibration of fructose through HPLC.

APPENDIX 2: EXPERIMENTAL DATA AND CALCULATION

Initials Conditions

Component	**Initial mass (g)**	T (ºC)	110
Fructose	1,494	$R_{Fruct/BuOH}$	0,0127
1-Butanol	48,35	m_{cat} (g)	1,019
H2O	9,65	Catalyst	Dowex 50x2

w.t/nºFruct	**Fructose**	**5-HMF**	**FA**	**LA**	**BF**	**BL**	**Butanol**	**H_2O**	**X Fructose (%)**
0,00	0,0074	0,0006	0,0001	0,0001	0,0000	0,0000	0,653	0,518	0,00%
122,88	0,0026	0,0045	0,0011	0,0004	0,0000	0,0000	0,644	0,505	64,34%
245,76	0,0010	0,0053	0,0012	0,0006	0,0000	0,0014	0,627	0,526	87,08%
368,64	0,0003	0,0046	0,0018	0,0006	0,0028	0,0016	0,614	0,531	96,30%
491,52	0,0001	0,0041	0,0021	0,0006	0,0029	0,0018	0,609	0,513	98,40%
614,40	0,0001	0,0033	0,0021	0,0006	0,0030	0,0020	0,603	0,501	99,13%
737,28	0,00004	0,0027	0,0026	0,0007	0,0030	0,0021	0,594	0,500	99,44%
860,16	0,00001	0,0023	0,0023	0,0006	0,0032	0,0024	0,588	0,482	99,84%
983,04	0,000005	0,0019	0,0025	0,0007	0,0032	0,0028	0,583	0,463	99,94%

			Error
Masa (g)	59,5	53,79	9,58%
Mol	1,195	1,057	11,60%

Table 18: Data corresponding to a typical experiment performed.

Another example of data collected from a different experiement.

	Initial Mass	**wt%**
Fructose (g)	1,481	2,52%
BuOH (g)	47,6	80,91%
H_2O (g)	9,75	16,57%

Dowex 50Wx2	
T (ºC)	120
$R_{Fruct/BuOH}$	0,0128
m_{cat} (g)	1,036

	n_j (mols)								
w.t/nºFruct	Fructose	5-HMF	FA	LA	BF	BL	Butanol	H_2O	$X_{Fructose}$
0,0	0,0080	0,0000	0,0000	0,0000	0,0000	0,0000	0,632	0,567	0,00%
126,0	0,0029	0,0038	0,0015	0,0004	0,0027	0,0014	0,625	0,545	64,17%
252,1	0,0008	0,0034	0,0024	0,0006	0,0030	0,0019	0,619	0,531	90,54%
378,1	0,0002	0,0024	0,0026	0,0007	0,0033	0,0022	0,612	0,523	97,93%
504,1	0,0001	0,0017	0,0027	0,0007	0,0034	0,0025	0,608	0,507	98,27%
630,1	0,0001	0,0012	0,0028	0,0008	0,0035	0,0027	0,603	0,494	98,87%
756,2	3E-05	0,0008	0,0029	0,0008	0,0036	0,0029	0,600	0,477	99,68%
882,2	3E-05	0,0004	0,0031	0,0009	0,0036	0,0030	0,592	0,478	99,83%
1008,2	5E-07	0,0003	0,0029	0,0008	0,0037	0,0031	0,585	0,476	99,94%

	Initial	**Final**	**Error**
Masa (g)	58,8	54,21	7,86%
Mols	1,21	1,07	11,57%

Table 19: Data corresponding to a typical experiment performed.

Although, in the Table 19 and 20 the error calculated by the mol balance is more than that of calculated by mass balance. This is because of the fact that the intermediate BMF formed was not calibrated and because of this reason, mols of BMF present during the reaction could not be calculated and are not present in the mol balance. The presence of BMF was confirmed by analysing the samples in GC-MS. In the Figure 27 results obtained from GC-MS are shown.

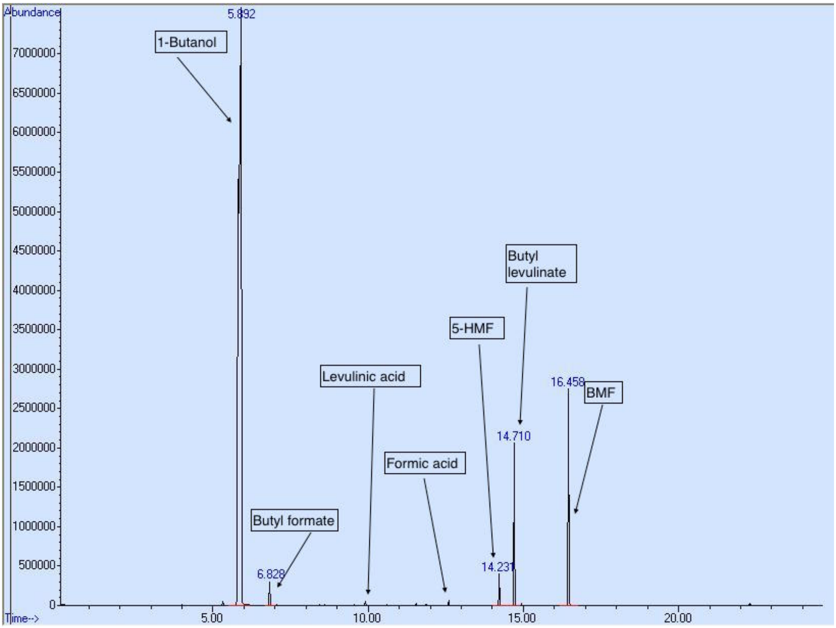

Figure 27: GC-MS spectrum of a typical sample of the experiment.

Experimental error of the three random experiments performed at 100 ºC, with Dowex 50Wx2.

Table 20: Results from three random experiments performed at 100 ºC with Dowex 50Wx2

	X Fructose (%)		$S^{5-HMF}_{Fructose}$		$S^{BL}_{Fructose}$	
w.t/nºFruct	Mean	Error	Mean	Error	Mean	Error
0,0	0,0%	0,00%	0,00%	0,00%	0,00%	0,00%
120,2	58,8%	0,49%	52,87%	1,80%	0,00%	0,00%
235,2	70,0%	0,19%	88,12%	10,28%	0,00%	0,00%
345,6	83,4%	1,04%	86,90%	4,41%	0,00%	0,00%
473,0	91,8%	0,31%	79,84%	4,31%	18,92%	0,26%
588,7	95,9%	0,09%	71,95%	1,55%	19,75%	0,37%
704,3	98,0%	0,05%	66,82%	1,77%	20,61%	0,14%
818,6	98,5%	0,04%	61,81%	0,25%	22,10%	0,08%
935,6	99,0%	0,03%	54,11%	1,15%	23,35%	0,10%

APPENDIX 3: ACID CAPACITY OF REUSED RESINS

Using the formula explained in 5.3.8. acid capacity of resins was calculated. By using Fischer-Kunill method.

Table 21: Data and results obtained from titration of fresh and re-used resins by Fischer-Kunill Method.

N NaOH	**0,13**
N HCl	**0,1**
Vt NaOH	**150**
Vt Nacl	**50**
Vt	**200**
V valorada	**25**

Dowex 50Wx2 Fresh	Mass	0,501
V_{HCl} spent		CA
20,47		4,90
20,42		4,98
20,38		5,04
20,41		5,00
	Mean CA	4,98
	Error CA	0,06

Dowex 50Wx2 1st use	Mass	0,462
V_{HCl} spent		CA
21,19		4,07
21,15		4,14
21,12		4,19
	Mean CA	4,13

	Error CA	0,06

Dowex 50Wx2 (2nd use)	Mass	0,111
V_{HCl} spent		CA
9,25		2,99
9,22		3,53
9,22		3,53
	Mean CA	3,35
	Error CA	0,31

Dowex 50Wx2 (3rd use)	Mass	1,021
V_{HCl} spent		CA
20,00		2,77
20,3		2,54
20,2		2,62
	Mean CA	2,64
	Error CA	0,12