

1 **ROLE OF ION-EXCHANGE RESINS AS CATALYST IN THE REACTION-NET-**  
2 **WORK OF TRANSFORMATION OF BIOMASS INTO BIOFUELS<sup>†</sup>**

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9 **ABSTRACT**

10 The use of acidic ion exchange resins on the transformation of biomass into biofuels is  
11 revised and their potential application is presented. Relationships between morphology and  
12 structure of resins and their catalytic activity for some existing reactions of the transfor-  
13 mation net from sugars to biofuels are observed. In the synthesis of 5-hydroxymethyl fur-  
14 fural and levulinic acid, catalytic activity of resins increases when the crosslinking content  
15 decreased for both macroreticular and gel-type resins. Gel-type resins with low crosslink-  
16 ing were found as the most suitable resins to direct esterification of levulinic acid with  
17 linear alcohols. However, for the alcoholysis of furfuryl alcohol macroreticular resins are  
18 better than gel-type ones. Deactivation due to probably humins formation is the main draw-  
19 back for industrial application.

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21 **Keywords:** Biofuels; Furfural; 5-hydroxymethyl furfural, levulinic acid and levulinate

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## 1 INTRODUCTION

2 In recent times, the substitution of non-renewable fossil resources by renewable biomass as  
3 sustainable feedstocks has been extensively investigated for the manufacture of high value-  
4 added products such as biofuels, commodity chemicals, and new bio-based materials includ-  
5 ing bioplastics. Since the European Union has scheduled the introduction of up to 20% bio-  
6 fuels by 2020<sup>1</sup>, it is timely to think about the routes for obtaining such compounds from  
7 green non-edible sources. Lignocellulose, composed by hemicellulose, cellulose, and lignin,  
8 is an inexpensive non-edible biomass that could be an excellent source of fuels and chemi-  
9 cals without affecting food supplies. These new fuels are called second generation biofuels  
10 or advanced biofuels.

11 Despite the advantages of homogeneous catalysis, namely, accessibility to active sites, ac-  
12 tivity and selectivity, the drawbacks of separation and reusability have reduced to a 10-15<sup>2</sup>  
13 its application in the industrial processes share. In this context, the development of easily  
14 recoverable and recyclable solid catalysts has received particular interest for environmen-  
15 t friendly syntheses of building blocks chemicals and the derivate biofuels. All type of solid  
16 catalysts<sup>3</sup>, namely, micro-mesoporous materials, metal oxides, supported metal catalysts,  
17 and sulfonated polymers have been used to obtain biofuels from biomass through different  
18 reaction routes. Whereas there are a lot of published works where the first three types of  
19 quoted solid catalysts are used, there are comparatively only a few with sulfonated polymers,  
20 particularly acidic ion-exchange resins.

21 The main routes to produce second generation biofuels from lignocellulose are presented in  
22 Fig. 1. These reaction routes highlight the formation of interesting platform (building block)  
23 chemicals such as furfural, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), which  
24 are in the US Department of Energy (2010) list of top 10 platform chemicals that can be

1 produced from biomass<sup>4,5</sup>. Besides, the  $\gamma$ -valerolactone (GVA) is considered a possible fu-  
2 ture chemical platform. Second generation biofuels are not yet produced commercially, be-  
3 cause they are not currently cost competitive compared to first generation biofuels obtained  
4 from edible sources such as bioethanol and biodiesel, and fossil fuels. This fact is due to that  
5 releasing the sugars from lignocellulose is difficult and because platform molecules are  
6 highly oxygenated their conversion into liquid fuels requires partial oxygen removal.

### 7 **FIGURE 1**

8 In this paper, the use of ion-exchange resins is re-examined to check their applicability as  
9 catalysts in transformations of Figure 1 and in others more specific quoted below. Acid ion  
10 exchange resins are composed of copolymers of styrene, divinylbenzene, and sulfonic acid  
11 groups grafted on benzene rings of styrene. Acid ion exchange resins are produced in two  
12 basic morphological types: Gel-type (microporous) and macroreticular (macroporous) res-  
13 ins<sup>6</sup>. Both are spherical beads with a diameter usually in the range 0.3- 1.2 mm. Both types  
14 can be conventional sulfonated when there is one sulfonic group per styrenic ring as a max-  
15 imum or oversulfonated when there is more than one sulfonic group per styrenic ring  
16 Gel-type resins are rigid transparent beads and on microscopic scale its polymeric matrix is  
17 a homogeneous structure with no discontinuities. In dry state, the polymeric matrix is col-  
18 lapsed and the chains are as close as atomic forces will allow. In this condition, the matrix  
19 is completely impervious and there is no catalytic activity because only the relatively few  
20 catalytic sites on the surface of the beads would be available to the reactant. The internal  
21 surface area determined by conventional methods (BET area) is almost nil (see Table 1).  
22 Therefore, catalysis by gel-type resins requires the use of a swelling medium capable of  
23 expanding the polymeric matrix. In swollen state, gel-type resins contain two types of pores:  
24 micropores for inaccessible part of matrix and new accessible mesoporous formed on swell-  
25 ing which disappear on deswelling.

1 Macroporous resins are rigid opaque beads and present porosity independent of swelling  
2 of the polymer matrix. They are obtained by copolymerization of styrene and divinylbenzene  
3 in presence of a solvent called “porogen”. When the solvent is taken out of polymer perma-  
4 nent pores appear. On the contrary, in absence of a solvent, gel-type resins are obtained with  
5 no permanent pores in dry state. Then, macroporous resins consist of large agglomerates  
6 of gel microspheres, which, in turn, show smaller nodules that are more or less fused to-  
7 gether<sup>7</sup>. BET surface area is in the range 20-50 m<sup>2</sup>/g (see Table 1). In swollen state, macro-  
8 reticular resins show three types of pores: micropores of non-swelling inaccessible part of  
9 polymer matrix, new mesoporous, and macroporous coming from permanent porosity. So,  
10 catalytic activity of macroporous resins is effective catalysts in both swelling and non-  
11 swelling medium.

12 On the other hand, anion exchange resins are effective catalyst for a variety of reactions  
13 involving low catalyst concentrations and relatively low temperatures (293-333K), and em-  
14 ploying reagents which are not readily hydrolyzed to acids capable of inactivating the basic  
15 catalyst<sup>8</sup>. Thus, by considering that temperatures to be used in the reaction net of Figure 1  
16 (> 100 °C), acidic ion exchange resins are the preferred resins respect to anion resins, due  
17 their thermal stability are higher enough.

18  
19  
20

## TABLA 1

### 21 PREPARATION OF FURFURAL

22 Currently, the furfural market size is estimated to be over 250,000 tone/year<sup>9</sup>, and its price  
23 is in the range of commodity petrochemicals, such as benzene and toluene<sup>10</sup>. As can be seen  
24 in Figure 1 and 2, acidic degradation of xylose is the conventional path for furfural produc-  
25 tion. Industrially, furfural is obtained in an energy intensive process (443-458 K) using batch

1 or continuous reactors catalysed by mineral acids (sulfuric, hydrochloric and phosphoric ac-  
2 ids). Other materials (zeolites, heteropolyacids, and sulfonic acid functionalized-MCM and  
3 ion-exchange resins) that exhibit activities and selectivities comparable to homogeneous cat-  
4 alysts for aqueous phase dehydration<sup>11</sup> have been tried as alternatives for the homogeneous  
5 catalysts used in furfural production. However, up to now, all of them present some draw-  
6 backs mainly derived from insoluble-polymers formation (humins).

## 7 **FIGURE 2**

8 Besides, the water presence can accelerate some of the undesired side reactions that decrease  
9 the yield of furfural. Thus, polar aprotic solvents have been used to counter this effect.

10 Table 2 presents results quoted in literature to obtain furfural using ion-exchange resins. It  
11 can be observed that generally solvents are used to extract the furfural. With dimethyl sul-  
12 foxide (DMSO) as solvent and Amberlyst-15 as catalyst, a xylose conversion of 87% with a  
13 selectivity to furfural of 68% was obtained<sup>12</sup>. With dimethylformamide (DMF) and Amber-  
14 lyst-15, a conversion of xylose of 51% can be obtained<sup>13</sup> and a low selectivity (<1%) at low  
15 temperature (373 K), but high conversion (74%) and moderate selectivity (52%) at higher  
16 temperatures (403 K). However, this relatively high temperature produced a significant  
17 drawback for reusing the ion-exchange resin. The same authors obtained better results using  
18 a combination of solid acid (Amberlyst-15) and base catalyst (Hydrotalcite) in one-pot under  
19 moderate conditions<sup>13,14</sup>. Hydrotalcite promotes xylose isomerization to xylulose, while Am-  
20 berlyst-15 dehydrates xylulose to furfural.

## 21 **TABLE 2**

22 The option of introducing an extractant agent to separate the furfural produced has been used  
23 for many years with interesting results. Thus, stripping the mixture water-furfural with ni-  
24 trogen combined with ion exchange resin Amberlyst-70, proved to recover a 65% of the

1 produced furfural<sup>15</sup>. However, after 4 hours of reaction at 448 K a 50% resin deactivation  
2 was observed.

3 More recently, the combination of a cosolvent and two catalysts, has given excellent results.  
4 In this sense, the multi-step conversion of xylan and xylose to furfural was investigated in a  
5 continuous-flow biphasic fixed-bed reactor over a catalytic bed. This reactor was formed by  
6 a physical mixture of a Lewis acid gallium containing USY zeolite for xylose isomerisation  
7 and a Brønsted acid ion-exchanged resin, Amberlyst-36, for hemicellulose hydrolysis and  
8 xylulose dehydration system<sup>16</sup>. A furfural yield of 72% from xylose was obtained, which is  
9 one of the highest yield levels reported in the literature for hemicellulose processing over a  
10 heterogeneous catalyst. Thus, there remains a need for a selective catalyst in the dehydration  
11 of xylose to furfural.

12

### 13 **Biofuels from furfural**

14 Furfural and its hydrogenated derivatives, furfuryl alcohol and 2-methyl furfural (sylvan) (Fig-  
15 ure 1), are considered excellent platform molecules which can be converted mainly into fuel  
16 additives such as 2-methyltetrahydrofuran, sylvan trimers, esters and ethers. Esters for-  
17 mation will be considered later.

18 Sylvan can be catalytically trimerized or condensed with aldehydes or ketones under acidic  
19 conditions to form oxygen-containing diesel precursors, which after hydrogenation can pro-  
20 duce an alkane mixture within the diesel range<sup>17</sup>. The good results achieved for the reaction  
21 of sylvan with butanal in the presence of *para*-toluensulfonic acid envisage promising results  
22 also with acidic resins. However, only a few evidences of such potential application have  
23 been reported. As for the hydroalkylation/alkylation of sylvan with butanal a product (2,2'-

1 butilenebis(5-methylfurfural)) yield of 90% was achieved by using Amberlyst-15 and of  
2 80% for Dowex 50Wx2-100 at 323 K after 480 min of reaction<sup>17</sup>.

3 The etherification of furfuryl alcohol with ethanol catalyzed by acids produces ethylfurfuryl  
4 ether (EFE), which has been proposed as a gasoline component. Heterogeneous catalysts  
5 such as zeolites, specifically ZSM-5, have been reported for this reaction at 125 °C, where  
6 yields between 50-80% were achieved<sup>18</sup>. No reference has been found in open literature  
7 concerning acid resins. Notwithstanding, taking into account the activity of ion-exchange  
8 resins in etherification reactions, it is expected that acidic resins could also give interesting  
9 results for this etherification<sup>19,20</sup>.

10

## 11 **PREPARATION OF 5-(HYDROXYMETHYL) FURFURAL**

12 5-(hydroxymethyl) furfural, the long-known dehydration product obtained from hexose car-  
13 bohydrates (Figure 2), has become an important nexus to access to liquid biofuels (Figure  
14 1), polymers and chemicals. Fructose is a source more effective, but is more expensive, than  
15 glucose for making HMF in terms of conversion and selectivity<sup>21</sup>. Some side reactions can  
16 take place during the HMF synthesis. The most harmful for the catalyst is the intermolecular  
17 reaction between the reaction intermediates which lead to condensation products, such as  
18 soluble polymers and insoluble humins. Others byproducts can be formed by the rehydration  
19 of HMF to form levulinic acid and formic acid.

20 HMF is a more multifunctional molecule than furfural because its aldehyde and alcohol  
21 functional groups and its furan ring system. As said, HMF is listed among the top value-  
22 added bio-based chemicals by the US Department of Energy. Besides, it is called a “sleeping  
23 giant”, as is considered as the key intermediate to bridge the gap between biomass and bio-  
24 fuels and biochemicals. A great deal of works have been published in the last years about its

1 preparation and transformation in others products. Several reviews on HMF preparation, re-  
2 action mechanisms, derivates, and process design have been published recently<sup>21-24</sup>. Herein,  
3 only those works using ion-exchange resins as catalyst are considered.

4 Table 2 shows the progress in the catalytic synthesis of HMF using ion exchange resins. In  
5 1980, the first HMF synthesis in DMSO as solvent using the macroreticular solid resin Di-  
6 aion PK-216 was reported by Nakamura and Morikawa<sup>25</sup> with a 90% of HMF yield. The  
7 effect of the divinylbenzene (DVB) content in three macroreticular [Diaion PK-208 (4%,  
8 DVB), Diaion PK-216 (8%) and Diaion PK-228 (14%)] and three gel-type resins [Amberlite  
9 IR-118 (4%), Amberlite IR-120 (8%) and Lewatit SC-108 (8%)] was also studied. The low  
10 crosslinking of Diaion PK-208 (4%) should be considered unusual and exceptional for  
11 macroreticular resins whose usual content of crosslinking is higher than 8%. The activity of  
12 the resin increased when the DVB content decreased for both types of resins. For the same  
13 content of DVB, macroreticular resins were more effective than the gel-type ones. Both facts  
14 can be explained by a greater accessibility to acid sites the swelling and the diffusion-per-  
15 meation inside the polymeric matrix is greater. The stability of the catalytic activity of Am-  
16 berlyst IR-118 was checked at 333 K; no decrease in the HMF conversion was found after  
17 900 hours in continuous mode. One year later (Table 3), it was found that strong acid ion  
18 exchange resins allowed the dehydration of D-fructose into 5-hydroxymethyl-2-furancar-  
19 boxyaldehyde at mild temperatures and pressures<sup>26</sup>. The use of MIBK (methyl isobutyl ke-  
20 tone) as a solvent improved the yield of this reaction.

21 In 2006, Lansalo-Matras and Moreau<sup>27</sup> carried out the fructose dehydration in ionic liquids  
22 with and without DMSO as co-solvent and Amberlyst-15 as catalyst. HMF yields of 80% at  
23 353 K in 24 h with DMSO and 52% without DMSO in 3h were achieved. Dumesic and  
24 coworkers<sup>28,29</sup> in 2006-2007 introduced a biphasic system to separate HMF from the aqueous  
25 phase obtaining interesting yields to this product. Afterwards, Qi et al.<sup>30</sup> investigated the



1 dehydration of fructose with Dowex 50Wx8 using a mixture of acetone and DMSO by mi-  
2 crowave heating. HMF yield as high as 88% was achieved for a 20-min reaction time for the  
3 70:30 (w/w) acetone/DMSO solvent mixture at 423 K. The solvent mixture can effectively  
4 suppress the HMF rehydration to form levulinic acid. With ionic liquid and Amberlyst-15,  
5 high conversions of fructose and selectivity to HMF in only 10 min at 353 K (Table 3) were  
6 obtained<sup>31</sup>. In order to facilitate the separation process and or recovery of the solvent, the  
7 same group investigated the effects of different cosolvents (acetone, DMSO, methanol, eth-  
8 anol, ethyl acetate, and supercritical CO<sub>2</sub>)<sup>32</sup>. HMF yields were 78-82%, and there were no  
9 important differences when using different cosolvents.

### 10 **TABLE 3**

11 The majority of the commented studies were focused on the comparison between resins and  
12 other acidic catalysts, and on using different solvents. In 2009, HMF was directly produced  
13 from monosaccharides (fructose and glucose) and disaccharides (sucrose and cellobiose) by  
14 a simple one-pot reaction including hydrolysis, isomerization and dehydration using solid  
15 acid and base catalysts under mild conditions<sup>33</sup>. Shimizu et al.<sup>34</sup> reported high yields (>95%)  
16 for fructose dehydration in DMSO with Amberlyst-15 with and without water removal. The  
17 resin could be recycled at least three times keeping 100% yield after washing with water and  
18 drying at 60 C. Soon after, Ohara et al.<sup>14</sup> achieved a selective formation of 5-hydroxymethyl-  
19 furfural by using a combination of solid acid and base catalysts. Hydrotalcite was used as  
20 the base catalyst for isomerization of glucose to fructose, and Amberlyst-15 was used as the  
21 acid catalyst for dehydration of fructose to 5-hydroxymethylfurfural. That system gave (Ta-  
22 ble 3) a moderate HMF yield and selectivity under mild conditions (below 373 K)<sup>33</sup>. Zhu et  
23 al.<sup>35</sup> used THF (tetrahydrofuran) as the extracting agent, which is a good solvent for HMF  
24 and other by-products. With Amberlyst-15 high fructose conversion was obtained at 393 K  
25 but the selectivity was rather low. However, HMF yields in average were about 50%. It is to

1 be highlighted that the resin catalyst could be reused eleven times without losing its catalytic  
2 ability, which is in line with the stability of resins at temperatures below the maximum op-  
3 erating ones. Although the HMF yield obtained in this way was much lower than that in  
4 DMSO or ionic liquids, it provides a new approach to synthesise HMF from fructose, which  
5 facilitated the separation of products from solvent. Ordonsky et al.<sup>36</sup> in 2012 confirmed  
6 again that Brønsted acid sites (ion-exchange resin) led to high selectivity in the dehydration  
7 of fructose with an increase with the addition of an organic phase.

8 In 2012, Aellig and Hermans<sup>37</sup> studied the dehydration of D-fructose to 5-hydroxymethyl-  
9 furfural under single-phase conditions in the low boiling solvent 1,4-dioxane at moderate  
10 temperatures in the presence of Amberlyst-15. The reaction was first examined and opti-  
11 mized under batch conditions, where yield could be increased up to 75% by adding small  
12 amounts of DMSO. Under continuous conditions, HMF yield could be further increased until  
13 92%. As already showed, continuous operation can increase the selectivity towards the de-  
14 sired product. A long-term stability test (96 h), including solvent regeneration, proved that  
15 catalyst was stable over time. Jeong et al.<sup>38</sup> developed a process for the dehydration of high  
16 fructose corn syrup in dioxane with Amberlyst-15 and 80% HMF yield was achieved at 373  
17 K in 2 h. Both solvent and resin could be recycled.

18 Separation and purification of HMF from the reaction mixture has been a challenging issue  
19 up to date. High boiling solvents not only require lots of energy to evaporate but also HMF  
20 can be seriously decomposed under the conditions to remove such solvents. In particular, the  
21 use of a readily evaporable solvent and a heterogeneous catalyst would allow highly practical  
22 purification of HMF, which still remains as a major obstacle to its commercialization.

23 In 2013 Tucker et al.<sup>39</sup> showed that the use of HMF-derived 2,5-(dihydroxymethyl)tetrahy-  
24 drofuran (DHMTHF) or low-boiling tetrahydrofuran (THF) as co-solvents results in in-  
25 creased selectivity (>60%) to HMF at fructose conversions of 70%. Also in that year, Li et

1 al.<sup>40</sup> used six different ion-exchange resins to catalyze the dehydration of fructose to HMF,  
2 including macroreticular strong-acid and weak-acid ion exchange resins, and gel strong-acid  
3 ones. They found that macroreticular strong-acid resins showed a higher activity than the  
4 other resins because, with good agreement with what have been explained on page 3 and 4,  
5 they present a greater accessibility to acid centres in non-aqueous medium and because a  
6 higher acid strength favors the dehydration reactions. They also concluded that for gel-type  
7 resins the catalytic activity decreased with the increasing value of the cross-linking degree.

8 Sampath and Kannan<sup>41</sup> showed that DMSO is a better solvent than N,N-dimethylformamide  
9 (DMF). Dehydration of fructose to HMF using Amberlyst-15 catalyst showed a significant  
10 loss in activity upon reuse in DMF, while no activity loss was observed in DMSO even up  
11 to seven cycles. The loss in activity was attributed to the neutralization of amine groups of  
12 DMF. Gallo et al.<sup>42</sup> obtained high yields at 403 K for the production of HMF from glucose  
13 using a combination of Amberlyst-70 and Sn- $\beta$  as solid acid catalysts: 59%, 55%, 60% and  
14 63% using GVL, GHL( $\gamma$ -hexalactona), THF : MTHF (methyltetrahydrofuran) (1:1), and  
15 THF as solvents, respectively.

16 A recent work on the effect of the structure of acidic ion exchange resins on the fructose  
17 conversion to HMF is that of Richter et al.<sup>43</sup> in 2013. Several resins with different acid ca-  
18 pacities and DVB content were tested. In accordance with previous works, they also found  
19 that crosslinking degree has an important effect in this reaction. The dehydration of fructose  
20 in the aqueous phase is ideally catalysed by highly acidic resins with low cross-linker content  
21 (<8%), which allows a better swelling and, as result, a better accessibility of the active cen-  
22 tres.

23 It is worthwhile to indicate the efforts that have being made to obtain HMF directly from  
24 sucrose<sup>44</sup>, in a four-steps sequence using acid (Amberlyst IR-120) and basic (Amberlyst

1 IRA-400) resins. After glucose/fructose isomerization, and fructose dehydration a 50% HMF  
2 yield can be obtained.

3 Research with DMSO as a solvent goes on nowadays. In 2014 Morales et al.<sup>45</sup> reported a  
4 93% yield to HMF from fructose and 100% fructose conversion in such solvent with sulfonic  
5 acid resin, Amberlyst-70. However, for glucose the reaction is much more difficult requiring  
6 longer reaction time, which promotes the occurrence of undesired side-reaction of glucose  
7 degradation. Without regeneration, resins deactivates progressively.

8 Recently, our research group has studied HMF production starting from fructose using di-  
9 oxane as solvent in the temperature range 363-383 K<sup>46</sup>. Two sets of resins were used during  
10 the study in the catalysts screening: a set of macroreticular resins (Amberlyst-15 and Am-  
11 berlyst- 39) and another set of gel-type (Dowex 50Wx8, Dowex 50Wx4 and Dowex 50Wx2).  
12 From the results, it was concluded that a lower content of cross-linker agent leads to a higher  
13 yield, which is better at the lower temperatures. Humins formation was the cause of the  
14 noticeable reduction of the global reaction yield. The highest yield reached for HMF was  
15 72.4% at 363 K, the catalyst being Dowex 50Wx4.

16

### 17 **HMF as precursor of fuel components**

18 Like furfural, HMF is considered an excellent platform molecule that can be converted into  
19 fuel additives such as dimethylfuran (DMF), derived products from alkoxyethyl furfural<sup>47</sup>,  
20 valeric esters, *etc.* Products selectivities in HMF etherification strongly depends on the type  
21 and strength of acid solid employed. For instance, in the etherification of HMF with ethanol  
22 at 413 K strong Brønsted acid sites, as Amberlyst-15, produced ethyl 4-oxopentanoate  
23 (EOP), while in the presence of strong Lewis acid sites 5-(ethoxymethyl)furan-2-carbalde-

1 hyde (EMF) was formed preferentially<sup>48</sup>. The results indicate that EMF or EOP can be ob-  
2 tained selectively by direct reaction of HMF with bioethanol by tuning the acid strength of  
3 the catalyst. EMF is a valuable biodiesel component, but also EOP which can produce va-  
4 leric-based biofuels by subsequent selective hydrogenation.  
5 HMF ethers can also be obtained by reacting carbohydrates (hexose, fructose) with alcohols  
6 in presence of solid acid catalysts. In case of starting from fructose and using Amberlyst-15  
7 or Dowex 2030 at 393 K the main formed ether is EMF, with a yield range of 55-71% after  
8 1800 min<sup>49</sup>. Amberlite IR120 and Dowex 50Wx8 were less active because they are gel-type  
9 resins while the two first are macroporous ones.

10

## 11 **PRODUCTION OF LEVULINIC ACID**

12 Levulinic acid (LA), also named 4-oxopentanoic acid or gamma ketovaleric acid has been  
13 described as one of the most promising platform chemicals from lignocellulosic biomass for  
14 fuels (Fig. 1) and chemicals. The production of LA from biomass starts with acid hydrolysis  
15 of hexoses and pentoses (Figure 2).

16 Already in 1956 ion exchange resins were used in LA synthesis<sup>50</sup>. However, yields of LA  
17 were typically lower than expected due to occurrence of side reactions specifically that of  
18 insoluble-polymers formation with undefined structures of humins, whose amount increased  
19 with temperature and time. Later in 1975 a comparative study on LA synthesis by using four  
20 commercial ion-exchange resins (Dowex MSC-1H, Amberlyst-15, Amberlyst XN-1010 and  
21 Amberlyst XN-1005) showed that HMF formation was favored by resins with larger pores  
22 and LA formation by resins with the smaller ones<sup>51</sup>.

23 The low yields and selectivities, and consequently high cost, had led over several decades to  
24 search for the heterogeneous and homogeneous acidic catalysts that produce a cost-effective

1 LA. Homogeneous catalysis produced high yields, but the humins formation drove to heter-  
2 ogeneous catalysts. In the last two decades, many solid acid catalysts have been tested and  
3 many papers published. Recent reviews present the obtained progress<sup>52-54</sup>. However, works  
4 using ion exchange resins as catalyst are rather scarce. Some of them are commented below  
5 and presented in Table 4. In 2000, in an intermediate step of the synthesis of 2,5-furandicar-  
6 boxylic acid, a yield as high as 79 % in LA was obtained starting from fructose and using  
7 Lewatite SPC 108<sup>55</sup>.

8 Cellulose was directly converted with high yield (69%) to levulinic acid (LA) using Amber-  
9 lyst-70 as catalyst and using a solution of 90 wt% GVL and 10 wt% water as solvent, com-  
10 pared to the low yield of 20% obtained only in water<sup>56</sup>. The convenient behaviour of Am-  
11 berlyst-70 in the GVL solvent is likely due to the GVL capacity of solubilizing cellulose,  
12 which increases the accessibility of the sugar oligomers to the acid sites where the dehydra-  
13 tion reactions take place. In addition, GVL swells the Amberlyst-70, thereby improving the  
14 diffusivity through the pores and increasing the catalytic activity of Amberlyst-70. This resin  
15 undergoes deactivation due to deposition of coke, but catalytic activity can be recovered.  
16 Amberlyst-70 gives also good results with high LA yield into the transformation of wood  
17 pulp in LA under relatively mild condition<sup>57</sup>.

#### 18 **TABLE 4**

19 Currently, the semi-commercial LA production is obtained by the Biofine process due to the  
20 yield obtained, around 70-80 mol%, using dilute sulfuric acid as catalyst<sup>58</sup>. The principal  
21 drawback of this process lies in its inefficient separation and recovery of the levulinic acid.  
22 In addition, humins produced can clog the piping system and reactor.

23 Our research group has studied recently the LA production starting from fructose using di-  
24 oxane as solvent in the temperature range between 363 °C and 383 K<sup>46</sup>. Two sets of resins

1 were used in the catalysts screening study: a set of macroreticular resins (Amberlyst-15 and  
2 Amberlyst-39) and a set gel-type resins (Dowex 50Wx8, Dowex 50Wx4 and Dowex  
3 50Wx2). From the results it was concluded that a lower content of cross-linker agent leads  
4 to a higher LA yield. LA yield increased at higher temperatures. Humins formation is the  
5 cause of the noticeable reduction of the global reaction yield. The highest yield for LA was  
6 34.4% at 373 K with Dowex 50Wx2 after 8 hours of reaction.

7

## 8 **Transformation of levulinic acid to biofuels**

9 Derivatives such as MTHF, angelica lactone (AL), GVL and alkyl levulinates are used as  
10 fuel extenders. Angelica lactone can be derived easily by vacuum distilling LA at about 433  
11 K in presence of acids. However, this production has the drawback of the polymerization of  
12 angelica lactone and formation of coke<sup>59</sup>. All these reactions could be a chance for ion ex-  
13 change resins since there is no information about their application in such reactions. GVL  
14 produced by reduction of angelica lactone is a promising biofuel, since it has very similar  
15 properties to ethanol as a fuel additive and that its production is affordable<sup>60</sup>. But its high  
16 water solubility, its corrosive potential in storage and its lower energy density, compared  
17 with oil-based fuels, could limit its practical application. These limitations introduced the  
18 reduction of GVL to MTHF, which can be blended up to 30% by volume in gasoline with  
19 no adverse effects on engine performance, being a more promising biofuel.

20 Figure 3 presents some of the alternatives for converting GVL to C<sub>9</sub> - C<sub>18</sub> liquid fuels in  
21 which ion exchange resins could participate as a bifunctional catalyst for one-pot hydrogena-  
22 tion/dehydration and oligomerization. In this case, resins should be doped with the appropri-  
23 ated metal nanoparticle<sup>61-63</sup>. For the steps dehydration/oligomerization steps, thermostable

1 resins can catalyse simultaneously the two reactions. This way, the resin Amberlyst-70 has  
2 been tested with good results by the group of Dumesic<sup>64</sup>.

3 Alkyl esters of levulinic acid are the most notable of LA derivatives with a good number of  
4 commercial uses. They have the potential to substitute compounds currently derived from  
5 petrochemical routes for blending to conventional diesel or gasoline because of their low  
6 toxicity and physicochemical properties; exhibiting characteristics that make them appropri-  
7 ate for use as cold-flow improvers in biodiesel or oxygenate additives for gasoline and diesel  
8 fuel.

9 **FIGURE 3**

10 **FIGURE 4**

11 Alkyl levulinates can be synthesized from acid levulinic (Figure 4) and furfuryl alcohol (Fig  
12 5). Direct esterification of levulinic acid with alcohols is typically acid catalyzed. The alco-  
13 hol itself acts always as a solvent and therefore it is always in excess. The molar ratio of  
14 alcohol to LA falls often in the 5-10 range. On one hand, this ratio is low enough for the  
15 alcohol dehydration what prevents somewhat the formation of symmetrical ethers. On the  
16 other hand, as esterification is a reversible reaction, alcohol excess favors the ester for-  
17 mation. Temperatures typically range between 338 K and 433 K, depending on the alcohol  
18 used for esterification and on the catalyst employed in the levulinate synthesis.

19 **FIGURE 5**

20 Early studies used mostly homogeneous catalysis, but more recently a variety of heteroge-  
21 neous catalysts have been tested, mainly solid Brønsted acids. The most studied of the LA  
22 esters is a low-smoke diesel formulation developed by Biofine and Texaco that uses ethyl  
23 levulinate (EL) as an oxygenate additive<sup>65</sup>. Traditionally, EL is synthesized by esterification  
24 of LA with ethanol in presence of mineral acids. Recently, the reaction has been re-examined



1 to introduce solid acid catalysts and other alcohols produced in biomass fermentation such  
2 as biobutanol. It should be noted that the synthesis of butyl levulinate (BL) has been mostly  
3 overlooked, despite BL is potentially better as a diesel fuel additive than EL<sup>66,67</sup>. Surpris-  
4 ingly, only a few papers can be found in open literature on the synthesis of those esters  
5 catalyzed by ion exchange resins. Table 5 presents part of the results available. A very recent  
6 paper of our group<sup>68</sup> was devoted to the study of the synthesis of BL over sulfonated resins.  
7 A resins screening among several macroreticular and gel-type resins with different cross-  
8 linking degree and sulfonation procedure (Amberlyst-15, -16, -35, -36, -39, -46, -70, Purolite  
9 CT-224, Dowex 50Wx2, x4, x8) was carried out in order to select suitable catalyst for ob-  
10 taining BL and to find a possible effect of resins morphology on the catalytic activity. At  
11 353 K and 2.5 MPa with a slight alcohol excess, BL was successfully obtained with selec-  
12 tivity higher than 99.5% for all the resins<sup>68</sup>. By comparing the catalytic behaviour, it was  
13 seen that resins morphology plays a very important role in BL synthesis. From the catalytic  
14 results it was concluded that accessibility of LA and 1-butanol to the acid centers was high  
15 over highly swollen and low polymer density resins. Thus, gel-type resins with low divi-  
16 nylbenzene (DVB) content were found to be the most suitable to produce BL, e.g. Dowex  
17 50Wx2, Dowex 50Wx4 and Purolite<sup>®</sup> CT224. Among them, Dowex 50Wx2 gave the highest  
18 conversion of 94% after 8 hours. It is noticeable that no humins were detected under the  
19 operation conditions at all.

#### 20 **TABLE 5**

21 Levulinic esters can be also directly obtained from the acid-catalyzed reactions of sugars and  
22 alcohols. The advantage of this procedure is that humins acids formation is suppressed enor-  
23 mously because the alcohol protects the reactive functional groups of sugars and reaction  
24 intermediates and prevents unwanted polymerization reactions, what remarkably enhances  
25 the production of levulinic esters<sup>69,70</sup>. The possible formation of the dialkyl ether from lighter

1 alcohols at such temperature seems unavoidable what could lead to a complex process to  
2 separate and eliminate or recycle the formed ether at industrial scale. Table 5 gathers the few  
3 results quoted in open literature that use Amberlyst-35 and Amberlyst-70<sup>71-73</sup> and some ob-  
4 tained by our research group<sup>74</sup>. In the last, three macroreticular resins (Amberlyst-15,  
5 20%DVB, -16, 12%DVB, and -39, 8%DVB) and two gel-type resins (Dowex 50Wx2,  
6 2%DVB, and Dowex 50Wx4, 4%DVB) were tested for fructose transformation to 5-HMF  
7 and butyl levulinate. Both for macroreticular and gel-type resins, it was found that lower  
8 crosslinking favours butyl levulinate formation; meanwhile high crosslinking enhanced the  
9 intermediate product, 5-HMF. In others words, as the volume of swollen polymer increased,  
10 the selectivity and yield of BL increased and those of 5-HMF decreased. After 3 runs a light  
11 decrease in the catalytic activity was detected.

12 Levulinate esters can be also obtained by alcoholysis of furfuryl alcohol under acid catalysis.  
13 As quoted for others aforementioned reactions, literature for this reaction using ion exchange  
14 resins is very scarce and has appeared only recently. Table 6 presents the results published  
15 in the scientific literature. Van de Graaf et al.<sup>75</sup> studied the efficiency of macroreticular and  
16 gel-type resins. They conclude that the main factor is the accessibility of furfuryl alcohol to  
17 acid centres. They obtained high conversion and selectivity with Amberlyst-35. Later, the  
18 same group evaluated a variety of commercial ion exchange resins at 398 K in a semibatch  
19 mode<sup>76</sup>. The main byproduct was diethyl ether. Gel-type resins (Dowex 50Wx4 and Dowex  
20 50Wx8) produce little ethyl levulinate but comparatively much diethyl ether. The authors  
21 explain this fact by assuming the higher affinity of those resins for the more polar ethanol  
22 and the lack of sufficient swelling. In contrast, the macroreticular Amberlyst-15, -35, -36  
23 and -46 and Purolite MN500 allowed for a higher formation of EL (Table 5) and a lower  
24 diethyl ether production, because of a better accessibility of furfuryl alcohol to acid sites.

1 Neves et al.<sup>77</sup> reported that acid site density, acid strength and porosity also had also some  
2 effect on the resin activity in this reaction, and affirmed that accessibility was the main fac-  
3 tor. In order to go deeper into such aspects our group has tested four macroreticular resins  
4 of different crosslinking degree (Amberlyst-15, (20%), Amberlyst-35, (20%), Amberlyst-  
5 39, (8%), and Amberlyst-46, (25%)) and one gel-type resin (Amberlyst-121 with 2% cross-  
6 linking)<sup>78</sup>. Full conversion was achieved after 6 hour for all the resins at 373 K, Amberlyst-  
7 15 and -35 being the most active. Even though Amberlyst-39 gave the best selectivity (67%)  
8 to butyl levulinate, it was the catalyst that took more time to achieve complete conversion of  
9 furfuryl alcohol. The combination of both parameters, number of acid sites and accessibility,  
10 seemed to be the most relevant properties that determine the catalytic activity. It should be  
11 noted that a significant amount of polymeric substances were detected.

12

#### TABLE 6

13 Alkyl esters can be also obtained from a reaction of  $\alpha$ -angelica lactone (Figure 4) with ole-  
14 fins<sup>79</sup> in the presence of water and an acid catalyst at 373-423 K and 5.5 MPa. LA was  
15 formed as byproduct. Table 7 presents some results obtained in presence of ion exchange  
16 resins. It can be seen that Amberlyst-36 is the most active and that hexyl levulinates yield  
17 depends on temperature with a maximum at 393 K. The yield decreased with shorter and  
18 branched olefins, compared with the corresponding linear ones. The different behavior of  
19 the three tested catalysts opens the door for tailoring the effect of structural properties of ion-  
20 exchange resins on these reactions

21

#### TABLA 7

22

23 **CONCLUSIONS AND OVERLOOK**

1 As can be seen throughout the paper, acidic ion-exchange resins have a great field of poten-  
2 tial application to catalyze many of the transformation reactions from biomass to biofuels.  
3 The following correlations between morphology and structure of resins and catalytic activity  
4 for some of the transformation presented were observed. Firstly, the fructose dehydration in  
5 aqueous phase is ideally catalysed by high acid capacity resins with low cross-linker content.  
6 Secondly, the same can be said for fructose dehydration to levulinic acid. Thirdly, gel-type  
7 resins with low divinylbenzene content were found as the most suitable to direct esterifica-  
8 tion of levulinic acid with alcohols. Finally, number of acid sites and accessibility are the  
9 main factors that affect ester yields for alcoholysis of furfuryl alcohol.

10 Some of transformations above presented seem to have a consolidated character, at least at  
11 laboratory scale, for instance, the esterification of levulinic acid with alcohols with very high  
12 yield without humins and the alcoholysis of furfuryl alcohol. Others, such as 5-HMF prepa-  
13 ration still needs further work despite the great work made devoted to this product prepara-  
14 tion. Other reactions are even virgin from a resins point of view, such as all simultaneous  
15 hydrogenation-dehydration reactions where ion exchange resins doped with Pd, Pt, Co or Ni  
16 could have an important role. It is to be noted that there already exist resins doped with Pd  
17 used in the methyl isobutyl ketone synthesis with good results. Besides the hydrogenation-  
18 dehydration reactions explained in the text and presented in Figure 1, Figure 6 shows  
19 additional reactions for the last step to obtain biofuels from biomass in which bifunctional  
20 ion-exchange resins could also work.

21 Nonetheless, much remains to be done to use ion-exchange resins at industrial scale. Deac-  
22 tivation and reusing of acid resins have to be explored for each reaction and its operation  
23 conditions. Thus, the two biggest issues with the catalytic transformation of biomass to bio-  
24 fuels are the high amount of humins and coke produced which needs additional research and

1 efforts. It is also necessary to research the structure-activity relationship between ion-ex-  
2 change resins and dehydration of carbohydrates in order to tailor the optimum resin. Related  
3 studies are very scarce and practically all of them are done in batch mode. Continuous runs  
4 of long duration are needed to assess the long live resins for industrial applications. There is  
5 something else to be considered to improve the influence of the polymer support on the  
6 interaction substrate-acid site. Beads is the common form in which resins are used but an-  
7 other forms such as monoliths, nanotubes and ways of anchoring the sulfonic groups will  
8 also need much to do to minimize mass transfer effects and leaching.

## 9 **FIGURE 6**

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1 **Table 1. Main characteristics and structural parameters of resins in dry state**  
 2 **considered in this paper**

Catalyst	Type <sup>a</sup>	Character <sup>b</sup>	T <sub>max</sub> (K)	[H <sup>+</sup> ] <sup>c</sup> (mol/kg)	DVB%	Dry state
						Surface area <sup>d</sup>
Amberlyst-15	M	A	393	4.81	20	42
A-16	M	A	393	4.80	12	1.7
A-35	M	A	423	5.32	20	34
A-36	M	A	423	5.40	12	21
A-39	M	A	403	4.81	7-8	0.09
A-46	M	A	423	0.87	25	57
A-70	M	A	463	2.65	7-8	0.018
A-70 <sup>e</sup>	M	A	463	2.65	7-8	30
Amberlyst 121	G	A	403	4.8	2	--
Purolite CT-224	G	A	423	5.34	4	0.95
Purolite MN500	M	A	403	2.70	Hyper	900
CT-276	M	A	408	5.3	16-18	23.5
DOW50Wx4	G	A	423	4.95	4	0.011
DIAION PK-208	M	A	393	4.3	4	
DIAION PK-216	M	A	393		8	
DIAION PK-228	M	A	393		14	
Amberlite IR-118	G	A	393		4	-
Amberlite IR-120	G	A	393	4.4		0.78
Lewatit SC-108	G	A	393	~5	8	-
Dowex 50Wx8	G	A	423	4.8	8	-
Dowex 50Wx2	G	A	423	4.95	2	-
Dowex MSC-1H	M	A	423			35
Dowex 2030	M	A	423	4.7		30
Amberlyst XN-1005	M	A	423	3.5		125
	M	A	393	3.3	70-75	540
Amberlyst XN-1010	G	B	333	2.6-3	8	0.64
Ambelyst IRA-400						

3 <sup>a</sup> Macroreticular (M) or gel-type (G)

- 1 <sup>b</sup> Acid (A), basic (B)
- 2 <sup>c</sup> Acid capacity. Titration against standard base
- 3 <sup>d</sup> By adsorption-desorption of N<sub>2</sub> at 77 K (N<sub>2</sub> for S<sub>g</sub> ≥ 1 m<sup>2</sup>/g; Kr for S<sub>g</sub> < 1 m<sup>2</sup>/g). BET method
- 4 <sup>e</sup> Rinsed with methanol, after with toluene and finally with isooctane
- 5

**Table 2. Dehydration of xylose into furfural using ion-exchange resins**

<b>Solvent</b>	<b>Catalyst /Resin</b>	<b>T / K</b>	<b>t /min</b>	<b>Conv. /%</b>	<b>Sel. /%</b>	<b>Yield /%</b>	<b>Deactivation</b>	<b>Humins</b>	<b>Ref</b>
DMSO	Amberlyst-15	413	240	87	68	59	Yes	Yes	12
DMF	Amberlyst-15	403	180	74	52	39	Yes	Yes	13
DMF	Amberlyst-15/ Hydrotalcite	403	180	83	50	42	Yes	Yes	14
H <sub>2</sub> O/ toluene	Amberlyst-70	448	240	94	44	42	N/A	Yes	15
H <sub>2</sub> O/ MIBK	GaUSY/ Amberlyst-36	393- 413	Contin- uous	N/A	N/A	72	N/A	N/A	16

1



**Table 3. Dehydration of carbohydrates (fructose) into HMF using ion-exchange resins**

Solvent	Catalyst /Resin	T /K	t /min	Conv. /%	Sel. /%	Yield /%	Cata. reuse	Ref.
DMSO	DIAION PK-216	353	500	N/A	N/A	90	N/A	25
DMSO	Amberlite IR-118	333	900 TOS	90	N/A	N/A	No after 900h TOS	25
MIBK	Lewatit SPC 108	369	300	N/A	N/A	80	N/A	26
Ionic liquid/ DMSO	Amberlyst-15	353	1440	N/A	N/A	80	N/A	27
Ionic liquid	Amberlyst-15	353	180	N/A	N/A	52	N/A	27
H <sub>2</sub> O-DMSO MIBK-butanol	N/A	363	480-960	83	65	54	N/A	28
H <sub>2</sub> O-DMSO /MIBK	DIAION PK-216	363	240	87	84	73	N/A	29
Acetone/DMSO	Dowex 50wx8-100	423	20	98	87	88	5 runs	30
Ionic liquid	Amberlyst-15	353	10	99	84	83	7 runs	31
Ionic liquid /acetone	Amberlyst 15	298	360	90	87	78	N/A	32
DMF	Amberlyst-15/ hydrotalcite	373	180	>99	73	73	N/A	33
DMSO	Amberlyst-15	393	120	100	100	100	3 runs	34
DMF*	Amberlyst-15/ hydrotalcite	353	540	73	58	42	N/A	34
H <sub>2</sub> O /THF	Amberlyst-15	393	120	98	49	48	11 runs	35
H <sub>2</sub> O	Amberlyst-15	408	400	31	54	17	N/A	36
H <sub>2</sub> O-dioxane /DMSO	Amberlyst-15	383	3	98	90	88	96 h	37
Dioxane	Amberlyst- 15	373	180	98	82	8	5 runs	38
H <sub>2</sub> O-DHMTF	Amberlyst-70	403	29	87	60	61	N/A	39
Ionic liquid	Macroporous	348	20	N/A	N/A	93	7 runs	40
Ionic liquid	Gel	348	20	N/A	N/A	48	N/A	40
DMSO	Amberlyst-15	393	60	100	82	82	7runs	41
THF	Amberlyst-70	403	10	91	85	77	N/A	42
H <sub>2</sub> O-MTHF	Several	403	60	84	60	50	N/A	43
DMF	Amberlyst IR-120(H <sup>+</sup> )	373	600	70	N/A	N/A	4 runs	44
DMSO	Amberlyst-70	413	60	100	93	93	3 runs	45
Dioxane	Dowex 50Wx4	363	120	N/A	N/A	34	N/A	46

\*Glucose as source; TOS, time on stream

1 **Table 4. Production of levulinic acid using ion-exchange resins**

Substrate	Solvent	Resin	T /K	t /min	Con. /%	Sel. /%	Yield /%	Cata. reuse/ Humins	Ref.
Glucose	H <sub>2</sub> O	Amberlite IR-120	397	N/A	N/A	N/A	5.8	N/A	50
Fructose	H <sub>2</sub> O	Amberlite IR-120	Room temperature	1620	N/A	N/A	23.5	N/A	50
Sucrose	H <sub>2</sub> O	Dowex MSC-1H	373	1440	N/A	N/A	24	N/A	51
Fructose	H <sub>2</sub> O+ MIBK	Lewatit SPC 108	353	30	N/A	N/A	79	Humins presence	55
Cellulose	GVL and H <sub>2</sub> O	Ambelyst-70	433	960	N/A	N/A	69	Coke formation	56
Fructose	Dioxane	Dowex 50Wx2	383	480	N/A	N/A	34	Humins presence	46

2

**Table 5. Synthesis of alkyl levulinates by direct esterification of levulinic acid and from reaction of sugars and alcohols**

Alcohol/ Solvent	Acid/ Substrate	Resin	T /K	t /min	Conv /%	Sel. /%	Alkyl ester yield %	Cata. reuse/ Humins	Ref.
Butanol	LA	Dowex 50Wx2	353	480	94	99.9	94	No humins	68
Ethanol	LA	Amberlyst-15	343	300	55	N/A	N/A	4 runs	69
Ethanol	LA	Amberlyst-15	348	180	7	N/A	N/A	N/A	70
Methanol /H <sub>2</sub> O	Levogluco- san	Amberlyst-70	443	200	100	>90	>90	N/A	71
Ethanol	Dextrose	Amberlyst-35 /microwave	403	30	N/A	N/A	49	N/A	72
Ethanol	Xylose	Amberlyst-70 /Pd/Al <sub>2</sub> O <sub>3</sub>	428	120	N/A	N/A	22.8	N/A	73
1-butanol /H <sub>2</sub> O	Fructose	Dowex 50Wx2	393	480	99.9	39.1	39	No humins	74
1-butanol /H <sub>2</sub> O	Fructose	Amberlyst-39	393	480	99.9	37.7	37.6	No humins	74
1-butanol /H <sub>2</sub> O	Fructose	Amberlyst-15	393	480	99.9	23.9	23.9	No humins	74

1

**Table 6. Alcoholysis of furfuryl alcohol catalyzed by ion exchange resins**

<b>Alcohol/Solvent</b>	<b>Resin</b>	<b>T / K</b>	<b>t /min</b>	<b>Conv. /%</b>	<b>Sel. /%</b>	<b>Yields /%</b>	<b>Reuse/ Humins</b>	<b>Ref.</b>
Ethanol	Amberlyst-35	398	Continuous	99.5	91	91	N/A	75
Ethanol	Amberlyst-35	398	Semi batch	>90	>90	90	Diethyl ether formation	76
Ethanol	Amberlyst-15	383	1440	100	72	72	N/A	77
Butanol	Amberlyst-39	373	360	100	67	67	Yes	78

1

**Table 7. Synthesis of alkyl esters from  $\alpha$ -angelica lactone and olefins catalyzed by acidic resins**

Olefin	Solvent	Resin	T /K	t /min	Conv./ %	Sel. / %	Alkyl ester yield/%	Ref.
1-hexene	H <sub>2</sub> O	Amberlyst-15	423	120	99.6	54.1	54	79
1-hexene	H <sub>2</sub> O	Amberlyst-15	393	120	99.1	62.7	63	79
1-hexene	--	Amberlyst-36	393	120	98.3	83.1	82	79
1-hexene	---	Amberlite IR-120	393	120	99.2	36.9	37	79
1-hexene	H <sub>2</sub> O	Amberlyst-15	363	120	99.7	4.8	4.8	79
2,3-dimethyl-butene	H <sub>2</sub> O	Amberlyst-36	393	120	100	9.7	9.7	79
cyclohexene	--	Amberlyst-36	393	120	99.2	78.2	78	79
propylene	H <sub>2</sub> O	Amberlyst-36	120	120	99.1	12.7	12.6	79

1

## FIGURE CAPTIONS

**Figure 1. Main molecular transformations from biomass to biofuels and potential use of acidic ion-exchange resins**

**Figure 2. Biomass-derived platform molecules from dehydration of monosaccharides.**

**Figure 3. Catalytic routes for the conversion of levulinic acid and gamma-valerolactone into liquid hydrocarbon transportation fuels. Potential participation of ion exchange resins as bifunctional catalyst to dehydrate/oligomerize and hydrogenate simultaneously.**

**Figure 4. Pathways to obtain ester levulinates from levulinic acid.**

**Figure 5. Several pathways to obtain alkyl levulinates**

**Figure 6. Potential application of bifunctional resins for hydrogenation/dehydration reactions. Adapted from reference 29**

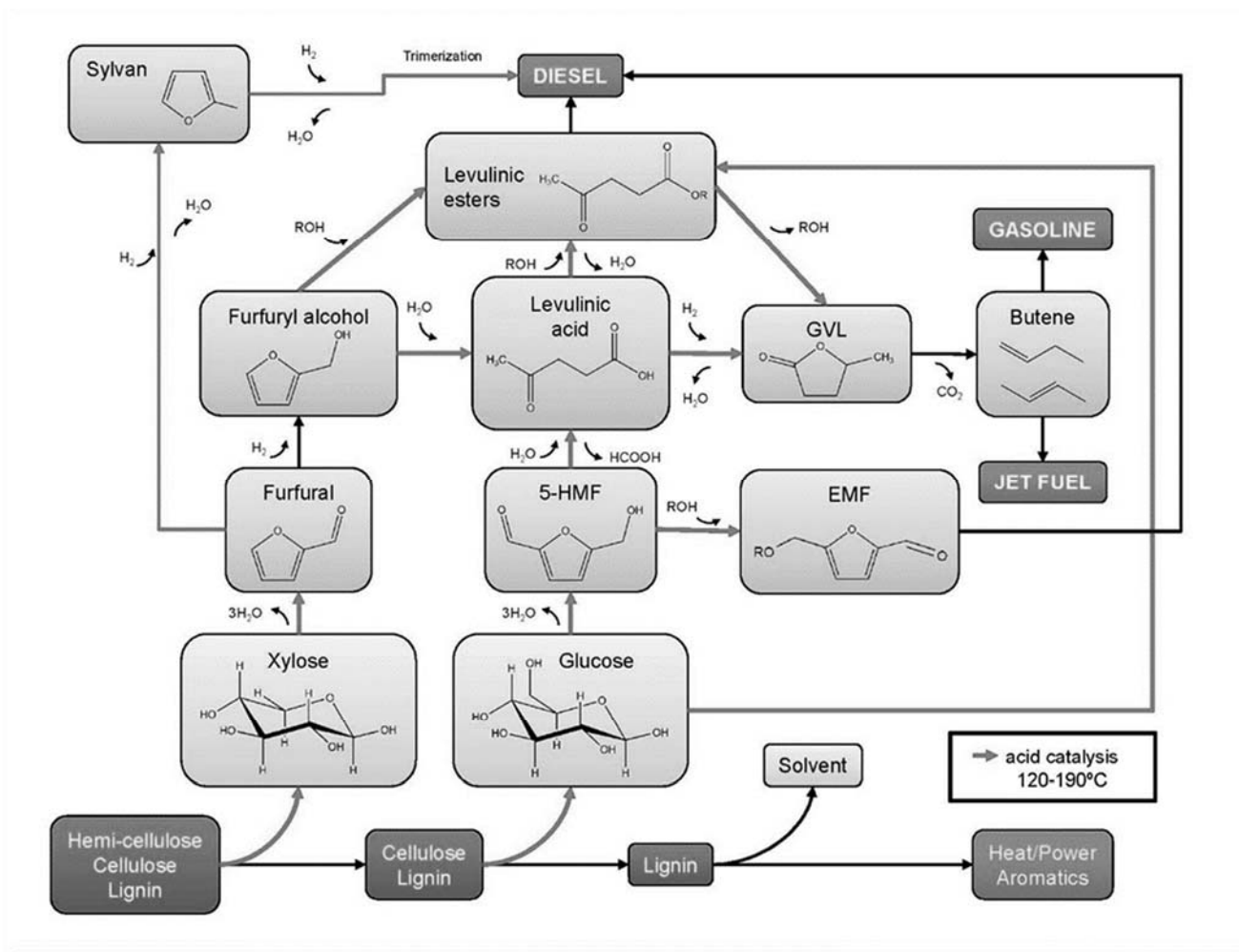
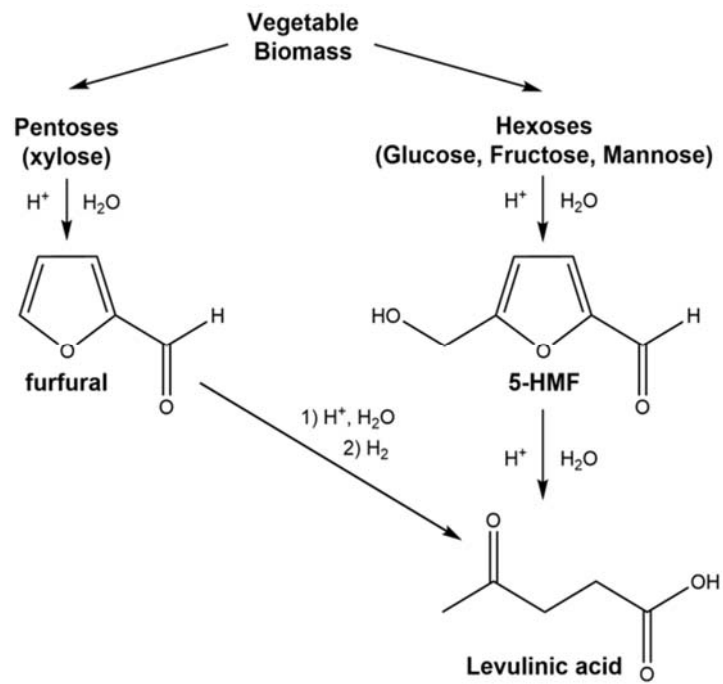


FIGURE 1



**FIGURE 2**



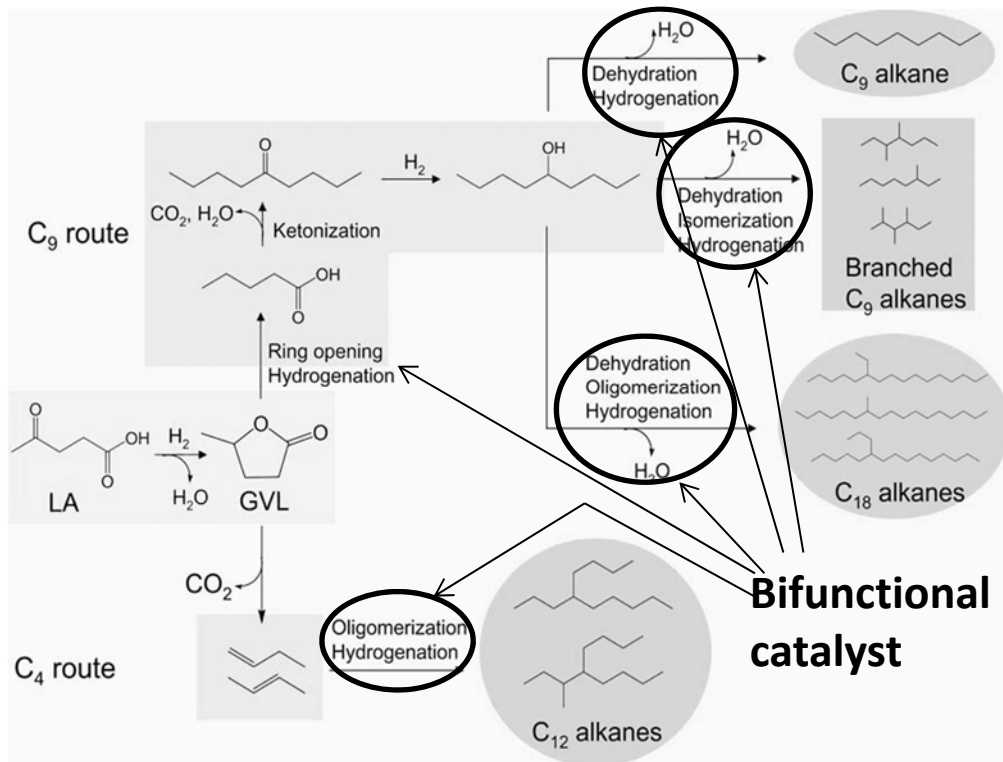


FIGURE 3

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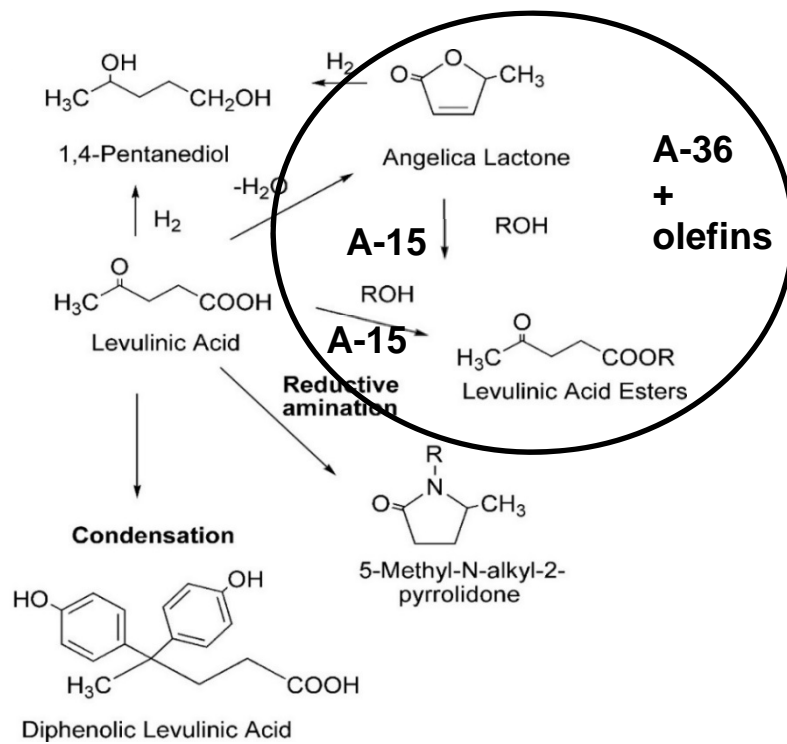
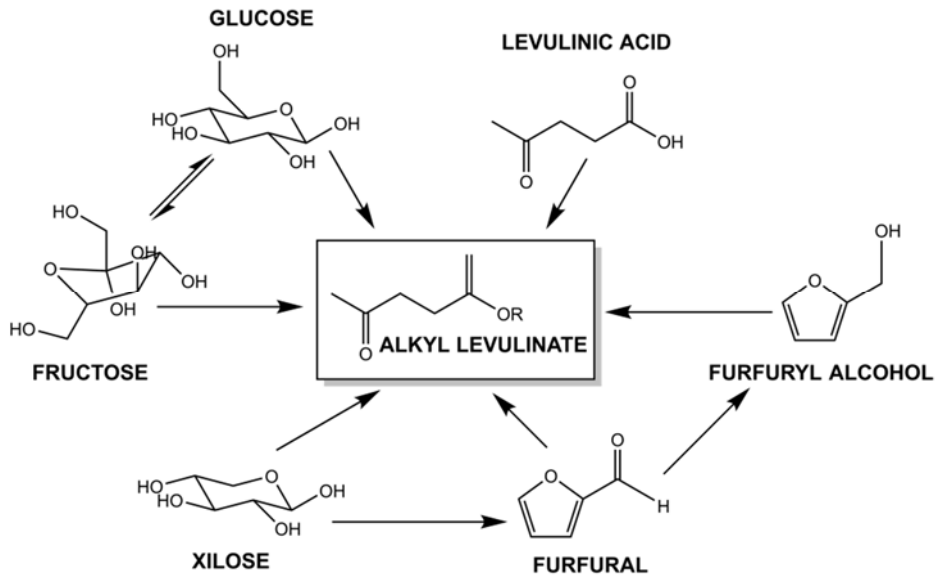


FIGURE 4



**FIGURE 5**

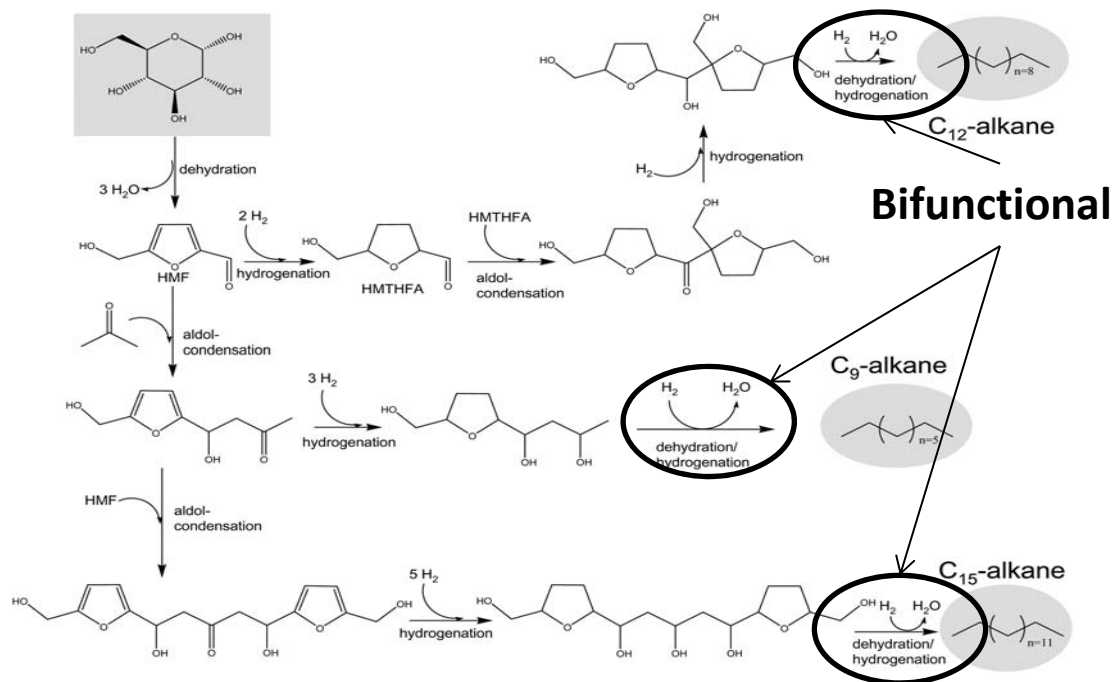


FIGURE 6