

Aqueous phase transformation of glucose into HMF and levulinic acid combining homogeneous and heterogeneous catalysis

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Abstract: Homogeneous (HCl) and heterogeneous catalysis (different kinds of zeolites) were combined for enhancing the glucose upgrading into two different platform molecules: 5-hydroxymethylfurfural (HMF) and levulinic acid (LA). β -zeolite was the most active material for the glucose isomerization to fructose, improving also the activity of HCl for the subsequent steps. Reaction time, temperature and pH were then modified, identifying 140°C, 200 ppm of HCl and 5 h as the optimum conditions for HMF formation (41 % selectivity; 0.06 mol·L⁻¹) and 140°C, 400 ppm of HCl and 24 h for the levulinic acid (34 % selectivity; 0.12 mol·L⁻¹). This new approach is also relevant because of the significant changes on the mechanism of humins formation. All results are successfully fitted to a kinetic model simultaneously considering both catalytic mechanisms.

Introduction

In the frame of the circular economy, renewable carbon sources are of key interests. At this point, the transformation of sugars derived from cellulose and hemicellulose into valuable platform molecules, such as 5-hydroxymethylfurfural (HMF) or levulinic acid (LA), is a required step to go forward in the development of new biodegradable polymers, drop-in biofuels and commodity chemicals.^[1] HMF and LA are precursors of many different pharmaceuticals, personal care products, fragrances, resins, coatings, flavours, agro-chemical compounds, fuel additives, monomers and plasticizers.^[2] Both platform molecules are included in the top 10 list of the most valuable bio-based products from the carbohydrate biorefinery, according to the US Department of Energy.^[3] Their industrial value is also revealed in economic terms, with prices around 2500 €/ton and 5500 €/ton for HMF and LA, respectively,^[4] which also justifies the need of developing new strategies for their production in a cheaper and more sustainable way.

For manufacturing these platform molecules, a common first step, based on the hydrolysis of the stable and strong β -(1→4)-glycosidic bonds of cellulose is required, obtaining the corresponding glucose molecules.^[5] Once the monomers are available, glucose can be transformed into LA or HMF by an acid-catalysed hydrolysis. Typically, these hydrolyses are carried out using homogeneous acids (HCl, H₂SO₄, etc.) in a multi-step reaction.^[6,7] Considering the reaction pathway

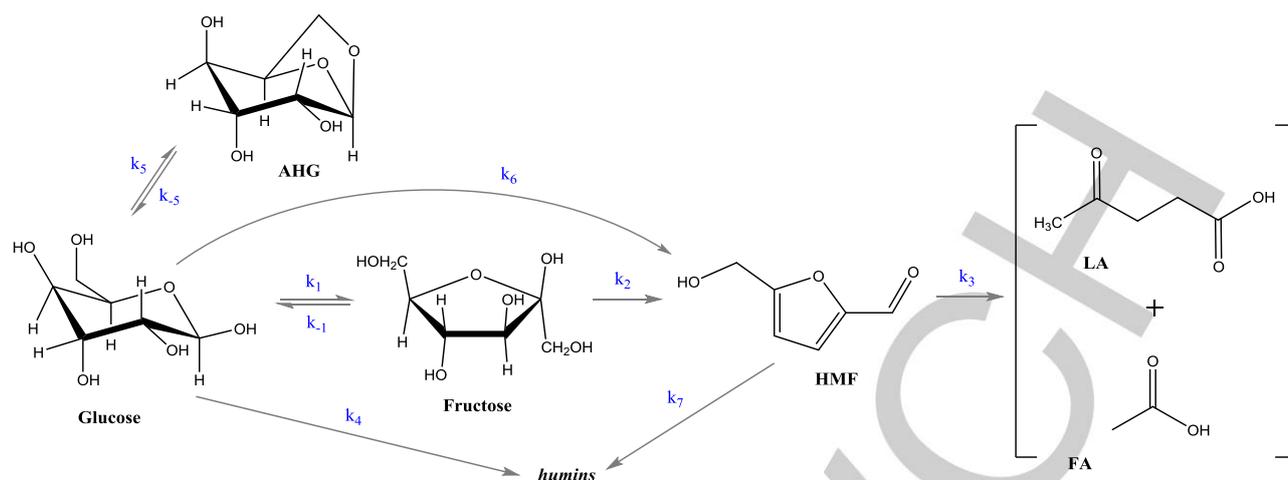
summarized in **Scheme 1**, levulinic acid (in equimolar quantities as formic acid) is produced by the rehydration and subsequent oxidation of HMF molecules, previously generated in the fructose dehydration. Fructose is obtained by isomerization of glucose molecules, being this step considered as a limiting step. According to these assumptions, reaction is limited by an inefficient isomerization (transformation of glucose into fructose) and the product selectivity is conditioned by the co-existence of aldehydes and acids in the medium, as well as undesired products obtained by lateral condensations of products and unreacted glucose (producing the generally known as humins).^[8] In particular, typical yields of 5-HMF reported in the literature are lower than 25 %, highlighting the low reaction rate and the large amount of anhydroglucose and glucose dimers, due to the presence of Brønsted acid catalysts.^[9,10] The direct dehydration of fructose to 5-HMF was also reported.^[11] However, the relevance of this direct route is conditioned by the relative low-quantity available of this sugar. Glucose is the ideal raw material for the production of HMF since it is the most abundant and cheapest hexose. So, most of the current studies are focused on the development of new alternatives to make this reaction more attractive from the industrial point of view.

Higher selectivities to HMF have been reported using ionic liquid and organic solvents, such as DMA, MIBK, DMSO, DMF and γ -valerolactone.^[12,13] Under these conditions, a common drawback related to the high affinity between HMF and those solvents was observed, requiring difficult purification steps that are not needed if the reaction is carried out in water. Solubility was taken into account in those studies proposing the use of two immiscible solvents, in such a way that the transference of HMF to the organic phase prevents its degradation into levulinic acid, reaction that only takes place in an aqueous medium.^[14-16] However, the optimum approach should use water as solvent, that could be adapted for the productivity of one or other platform molecule as needed. Concerning the LA, more severe conditions are required (long reaction times, higher temperatures, lower pH), being the selectivities typically conditioned by the large amount of humins produced at these conditions.^[7,8] With this premise, the main limiting factor is the good disposition of acid sites: Brønsted acid catalysts, such as HCl, are required to promote dehydration and rehydration steps, whereas Lewis acids are needed to catalyse the isomerization from glucose to fructose.^[17] These sites are present in heterogeneous catalysts (zeolites, silico-aluminiophosphate, Al-MCM-41 and Al-MSU-F mesoporous materials and zirconia). The activity of these type of materials was previously reported in the literature obtaining promising productivities to HMF and levulinic acid.^[18,19] At these point, some authors have focused their efforts introducing different metals in the previously mentioned solid catalyst to improve their isomerization activity, obtaining relevant results combining tin in the large-pore beta (Sn-Beta).^[18b,20] The isomerization is clearly improved, but the activity for the other steps of the whole process decreases in comparison to the results previously reported with homogeneous catalysts.

In this work, a combination of homogeneous and heterogeneous catalysis for the glucose dehydration to HMF and levulinic acid is proposed, with the aim to optimize the kinetic of the process and to tune the reaction to the desired products, avoiding oligomers

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Scheme 1. Reaction pathway for the glucose valorization in aqueous media, as well as the kinetic constants identification

that can be produced by non-isomerized glucose. HCl was chosen as homogeneous catalyst, based on the well-known activity of this acid, its wide availability and the low cost of this chemical, being considered nowadays as a typical waste in many different industrial processes.^[6] Concerning the heterogeneous material, zeolites were considered because of their acid character (with important contribution of Lewis acidity), high hydrothermal stability and the easiness of regeneration.^[15]

Results and Discussion

The effect of combining homogeneous and heterogeneous catalysis is analysed in **Figure 1**, comparing the temporal evolution of glucose conversion as function of the solid catalyst (ZSM-5, beta zeolite and Y zeolite), working in presence of an acid solution (HCl). Reaction conditions (313 K, 0.185 M of glucose, 200 ppm of HCl) were optimized in our previous work for the homogeneous reaction,^[21] whereas 2.66 g/L of solid catalyst was added to each reaction. The presence of these heterogeneous catalysts does not affect to the global pH, being constant at 2.03. This fact is justified by the strong acid character of HCl that prevails over the effect of any other weak acid introduced in the medium. Keeping constant the pH, differences in terms of conversion and selectivities can be directly related to the influence of each solid catalyst. Concerning the glucose conversion, no effect of adding ZSM-5 was observed, obtaining a similar behaviour than using only the homogeneous catalyst: a fast conversion in the first two hours

(around 20%) and a softer increase in the following 22 h to reach a final conversion of 48.8 and 51.2%, with and without ZSM-5, respectively. On the other hand, a clear improvement is observed in presence of beta zeolite, reaching almost complete conversion after 24 h (94.3%). This conversion is considerably higher than typical data reported for this reaction using heterogeneous materials, even at higher temperatures,^[19] corroborating the synergistic effect of combining homogeneous and heterogeneous catalysis. Y-zeolite presents an intermediate behaviour, with a parallel evolution to that of the ZSM-5 during the first 12 hours, but without reaching the stationary state, extended the reaction to a final conversion of 67.2% after 24 h.

In order to determine the role of the heterogeneous catalyst in the reaction products distribution, the selectivities of main compounds involved the reaction (fructose, anhydroglucose (AHG), 5-HMF and levulinic acid) as function of the glucose conversion are plotted in **Figure 2**. Formic acid was observed in equimolecular amount as levulinic acid, so its profiles are not included. Similar behaviour was obtained with only mineral acid, and combining HCl with ZSM-5 and β -zeolite. Fructose follows a typical profile of an initial reactive intermediate, with initial selectivities of 100% at differential conversion and a continuous decrease at increasing conversions. AHG and HMF show profiles congruent with primary products produced by parallel routes. The decreasing trend of HMF is congruent with its degradation into the corresponding acids (behaviour mainly observed with the beta zeolite) whereas AHG seems to reach a constant value, typical of a side product not undergoing further reactions. Finally, levulinic acid is a final product, with a continuous increase trend and a clear induction time.

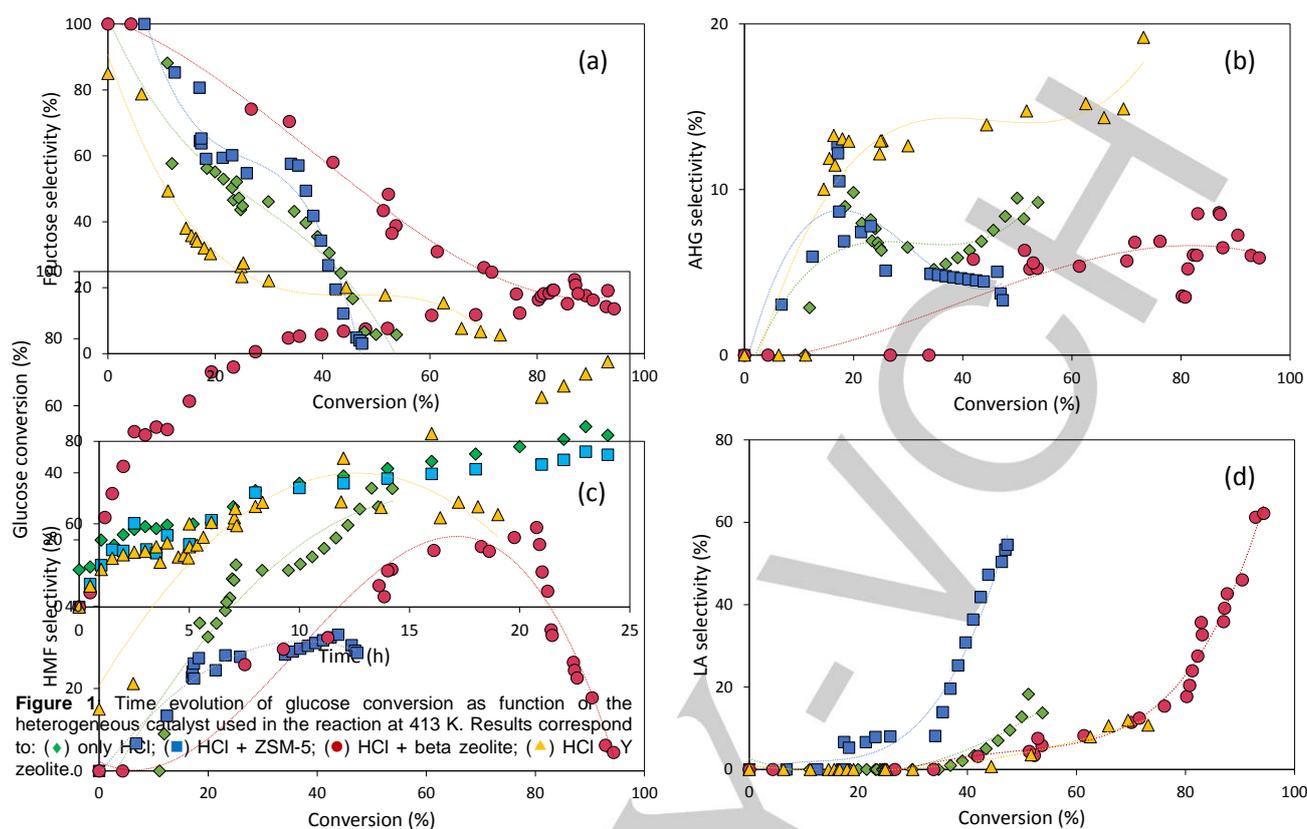


Figure 2. Selectivity evolution of main compounds involved glucose valorization at 413 K: (a) fructose; (b) AHG; (c) HMF; (d) Levulinic acid. Results as function of the catalyst: (♦) only HCl; (■) HCl + ZSM-5; (●) HCl + beta zeolite; (▲) HCl + Y zeolite.

Results obtained in absence of heterogeneous catalyst are conditioned by the low glucose conversion and the low levulinic acid production (final selectivity lower than 14 %), observing a continuous increase of HMF selectivity, reaching values higher than 68 %. Similar profiles were observed with ZSM-5 and beta zeolites, with higher selectivities to final acids, highlighting the results obtained with the second one (final selectivity higher than 62 % for levulinic acid with almost total conversion of glucose). With ZSM-5, this selectivity is close to 54 %, but the lower conversion restricts its productivity. The high selectivities for HMF formation at high reactant conversions are also remarkable (70 % of selectivity at 80 % of conversion, whereas in absence of heterogeneous catalysts, this value of the selectivity is obtained at a 40 % of conversion).

A different evolution is observed with the Y-zeolite. With this material, total selectivity to fructose formation is not observed at the lowest reaction time. This is congruent with the profiles observed for the HMF, with initial selectivity of 18 %. According to these results, a relevant direct dehydration of glucose is proposed when Y-zeolite is used, without requiring the previous isomerization. This phenomenon has been previously reported in the literature when using other homogeneous catalysts,^[8,10] concluding that this dehydration is usually negligible in comparison to the dehydration of fructose. Despite this advantage, this material was discarded because of its low levulinic acid and the high AHG selectivity.

Humins were not quantified in the previous analysis because of the huge amount of different polymers that could be obtained from these compounds, both soluble and insoluble ones. Thus,

this formation will be analysed in terms of decrease in the carbon balance, assuming that all the compounds of the main pathway were identified and all the lack of carbon is due to the formation of these oligomers. The carbon balance evolution is analysed in **Figure 3**. A parallel behaviour is observed for reaction catalysed by HCl and the combination of this mineral acid with Y-zeolite, with a continuous slight decrease, reaching final values close to 60 %. On the other hand, the carbon balance obtained with ZSM-5 (always higher than 74 %) suggests a lower humins productivity with this material, whereas a more relevant decrease is observed with the beta zeolite, obtaining a stable value at 42 %. The lack of correspondence between this profile and the levulinic acid one discards the degradation of acids and suggests that humins are produced by different oligomerizations of previous intermediates. If the carbon balance closure is analysed in detail for the reaction performed in presence of zeolite beta, it is observed that carbon balance is close to 100 % at the initial reaction times, when fructose is the main reaction product, and HMF concentration is still low. When HMF selectivity increases, carbon mass balance closure starts to decrease, suggesting that HMF is the main humin precursor. On the contrary, glucose is considered as the main humins precursor in the case of homogeneous acid catalysed reactions,^[8,10,22]

The low conversion obtained with only HCl and the Y-zeolite is congruent then with the continuous decrease in their carbon balance profiles, suggesting humins production as a competitive reaction with the main pathway. However, this explanation is not congruent with the stable carbon balance profile obtained with ZSM-5, despite having final conversion lower than 50 %. The ZSM-5 profile must be explained according to the morphological

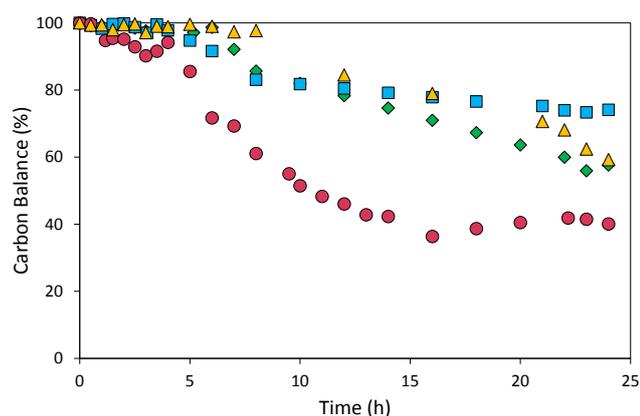


Figure 3: Evolution of carbon balance as function of the heterogeneous catalyst used in the reaction at 413 K. Results correspond to: (♦) only HCl; (■) HCl + ZSM-5; (●) HCl + beta zeolite; (▲) HCl + Y zeolite.

and chemical surface properties, summarized in **Table 1**. The low pore diameters of all these zeolites structures discard the oligomerization inside their structures, suggesting that these reactions are produced in the external surface or in the aqueous phase. The lower concentration of Lewis acid sites of ZSM-5 in comparison to the other solids is then proposed as the main cause of the low humins production observed with this material.

The expected improvement obtained by combining homogeneous and heterogeneous catalysis is better observed in terms of reaction kinetics. According to the literature, Lewis acidity from solid catalysts is required to promote the glucose isomerization to fructose.^[17] However, the subsequent reactions from fructose are catalysed by Brønsted acids.^[17] The presence of a mineral acid promotes them, displacing the first equilibrium, as well as the Brønsted acid of these zeolites. As consequence, all the steps are affected by the presence of heterogeneous materials and the reaction must be analysed globally without being possible to isolate the role of zeolites in this reaction.

This reaction involves both, liquid and solid phases. Thus, mass transfer processes must be considered for a complete kinetic analysis. A negligible effect of both, external and internal, mass transfer limitation is assumed since the fast stirring (turbulent flow regime) and the small catalytic particle size (50 – 80 μm). These hypotheses were checked as function of two common criteria: the Wheeler-Weisz criteria and the Carberry number, for internal and external mass transferes, respectively.^[25] According to these methodologies, values higher than 0.1 and 0.05 are related to internal and external mass transfer limitations, whereas their effect can be considered as negligible for lower values. As it was expected, experimental values are several orders of magnitude lower than these maximums: $1.2 \cdot 10^{-7}$ and $3 \cdot 10^{-5}$, respectively.

Despite a Langmuir-Hinshelwood model based on adsorption equilibria could be considered (assuming a kinetic control based on the compounds adsorbed on the catalytic surface), power law

kinetic models are more commonly used for aqueous-phase reactions.^[10] This approach also allow determine the homogeneous and heterogeneous contribution to the global kinetic. According to the most accepted pathway (**Scheme 1**), individual kinetic expressions must be considered since different kinetic orders are reported for each individual step. Thus, the glucose isomerization to fructose is a reversible reaction, with a first order dependence.^[10] Dehydration of fructose to HMF is considered as an irreversible reaction, kinetically conditioned by the enol formation, and with subsequent first order dependence.^[10,26] Different researchers conclude that direct dehydration of glucose into HMF is also possible, but the typical kinetics is significantly slower than the corresponding to dehydration via previous isomerization.^[27,28] The levu-linic and formic acids are stoichiometrically obtained by the HMF through a first-kinetic order.^[29]

Finally, two side reactions must be considered. On the one hand, glucose undergoes intramolecular dehydration in acid medium, yielding anhydroglucose. This reaction is considered in the literature as a first-order reversible one.^[30] On the other hand, there is not a good agreement about the humins production, being their formation reported from glucose and polymerization reactions, but also from HMF or by reaction intermediates, such as the formic acid.^[6,11,31,32] As the ratio formic acid to levulinic acid keeps almost constant and equimolecular during all the experiments, and according to the carbon balance obtained with the beta zeolite, this last option has been discarded. So, the formation from both glucose and HMF is considered as routes for humins formation. In this case, a first order dependence can be discarded because of the polymerization character, involving more than one molecule. According to the previous results reported in the literature, and because of the best fitting with experimental results, a second kinetic order was considered.^[4,10] All these theoretical premises were experimentally confirmed analysing the profiles obtained when using different intermediates as reactants. Temporal profiles are included in **Figure 4**. It is observed that when fructose is used as a reactant, significant amounts of glucose were produced, suggesting the reversibility of the glucose-fructose reaction, whereas glucose is also observed when using anhydroglucose as reactant. Concerning to the two main reaction products, LA was observed to be a stable final product, whereas HMF reaction leads to LA and humins.

According to these considerations, proposed kinetic model is summarized in the following equations, where “G” indicates glucose; “F”, fructose; “A” anhydroglucose; “H”, humins; “LA”, levulinic acid; and “FA”, formic acid.

$$\frac{dG}{dt} = -k_1 \cdot G - k_4 \cdot G^2 - k_5 \cdot G - k_6 \cdot G + k_{-1} \cdot F + k_{-5} \cdot A$$

$$\frac{dA}{dt} = k_5 \cdot G - k_{-5} \cdot A$$

Table 1. Morphological and chemical properties of heterogeneous catalysts used in this work^[23,24]

Catalyst	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$)	d_p (Å)	Lewis acidity ($\mu\text{mol} \cdot \text{g}^{-1}$)			Brønsted acidity ($\mu\text{mol} \cdot \text{g}^{-1}$)		
				Weak	Medium	Strong	Weak	Medium	Strong
ZSM-5	443	0.301	5.1	36	8	3	416	395	285
Beta	589	0.409	6.7	82	43	25	219	187	125
Y	884	0.47	7.4	123	75	58	255	205	129

$$\frac{dF}{dt} = k_1 \cdot G - k_{-1} \cdot F - k_2 \cdot F$$

$$\frac{dH}{dt} = k_2 \cdot F + k_6 \cdot G - k_3 \cdot H - k_7 \cdot H^2$$

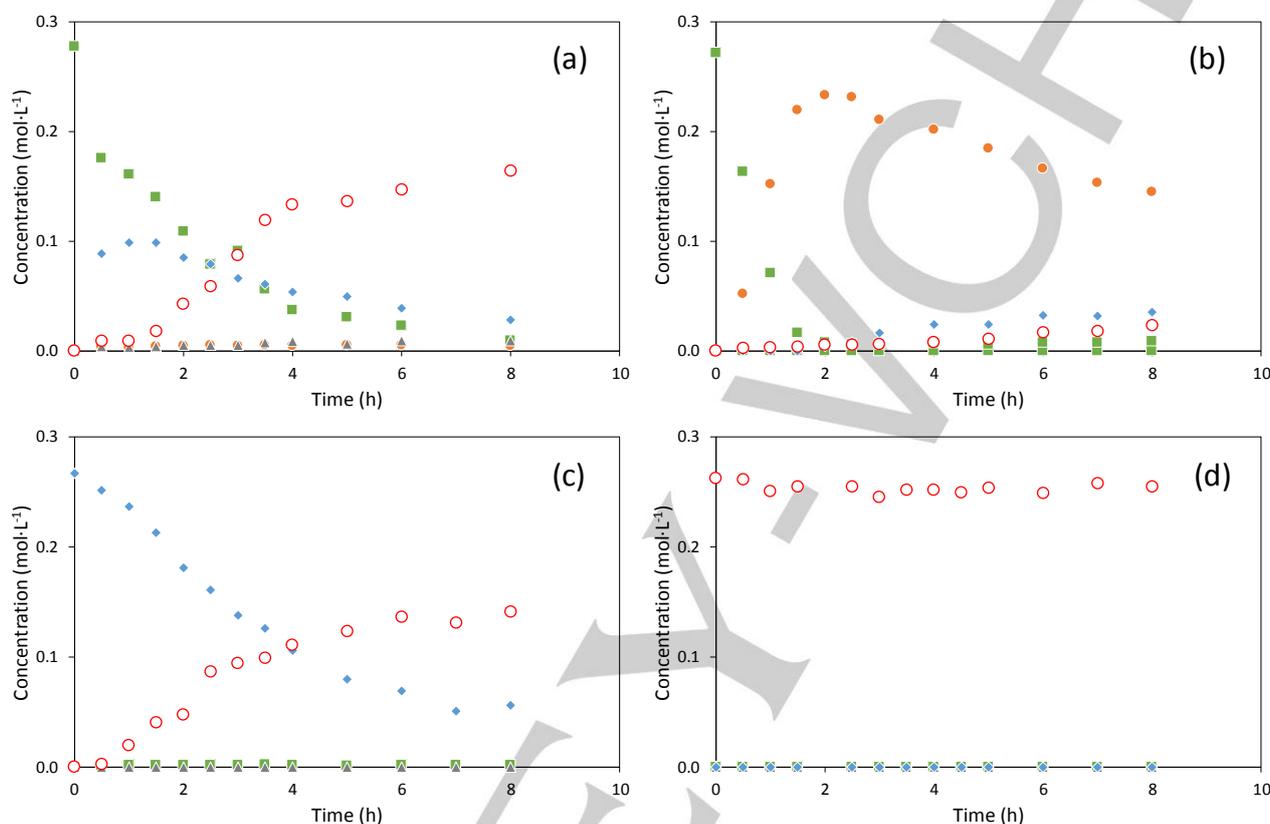


Figure 4. Temporal profiles obtained when (a) fructose; (b) AHG; (c) HMF and (d) LA as reactants in the reaction catalyzed by beta zeolite and 200 ppm of HCl at 413 K. Symbols: (●) glucose; (■) fructose; (◆) HMF; (▲) AHG; (○) LA.

$$\frac{dLA}{dt} = \frac{dFA}{dt} = k_3 \cdot H$$

It must be highlighted that all these constants are apparent constants, in which the role of HCl in the kinetic model is also included. Taking into account that all these experiments were carried out with the same HCl concentration, this assumption can be done. The correspondence among experimental and model prediction for the reactions performed in absence of heterogeneous catalyst and in presence of the three zeolites proposed in this work is observed in the lines of **Figure 5**, whereas the kinetic constants are summarized in **Table 2**.

The goodness of this model is clearly observed, with correlation

factors higher than 0.96 in all the cases. It must be highlighted that, in good agreement with the initial hypothesis, all these coefficients are higher than the previously reported ones considering a kinetic model based on adsorption equilibria.^[33] Concerning the analysis step-by-step, the positive effect of combining heterogeneous and homogeneous catalysts is in

agreement with the increase in all the direct reactions, with main effect observed when using the beta zeolite. With this material, the fructose reverse isomerization is also reduced, with the corresponding effect in the global results. The levulinic acid production step is also promoted with this zeolite, but experimental results are mainly conditioned by the second step of the process: the fructose dehydration to obtain HMF. This step is strongly improved when using the β -zeolite, but is almost prevented with the other two zeolites. Considering that same amount of HCl is presented in all the experiments, an improvement was expected when a second acid material is added to the system. However, same type of acidity is responsible of undesired reactions, such as the humins production and the glucose stabilization. In addition, zeolites

Table 2. Kinetic constants obtained after fitting the experimental results to the model proposed. Results corresponding to the different catalytic systems studied in this work

HCl (ppm)	Heter. Catalyst	T (K)	Kinetic constants (units in h^{-1} except k_4 and k_7 that are in $\text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)									r^2
			k_1	k_{-1}	k_2	k_3	k_4	k_5	k_{-5}	k_6	k_7	
200	-	413	0.19 ± 0.03	1.55 ± 0.47	0.19 ± 0.03	0.01 ± 0.01	0.40 ± 0.07	0.002 ± 0.001	0.10 ± 0.04	0.02 ± 0.01	10.81 ± 1.41	0.994
200	ZSM-5	413	0.28 ± 0.14	3.01 ± 1.26	$0.04 \pm 6 \cdot 10^{-9}$	0.02 ± 0.02	$0.56 \pm 3 \cdot 10^{-7}$	$0.01 \pm 8 \cdot 10^{-16}$	0.10 ± 0.02	$0.03 \pm 2 \cdot 10^{-7}$	21.31 ± 1.12	0.992
200	Y zeolite	413	0.17 ± 0.10	2.65 ± 0.83	0.02 ± 0.01	0.02 ± 0.01	0.53 ± 0.13	0.002 ± 0.001	0.07 ± 0.05	0.09 ± 0.03	19.97 ± 2.19	0.994
200	β zeolite	413	0.43 ± 0.01	0.14 ± 0.10	0.69 ± 0.10	0.08 ± 0.02	1.13 ± 0.08	0.01 ± 0.01	0.19 ± 0.14	0	10.27 ± 0.41	0.97

have different behaviours as function of their internal structure, and this acidity cannot be entirely active for molecules as big as these sugar derivatives. Moreover, it is known that Y-zeolite is not entirely stable in aqueous phase, and surface modifications can affect to the exposed acidity. As conclusion of the first experiments, β -zeolite is chosen as the best heterogeneous catalyst, despite the lower carbon balance obtained with this material (kinetically explained by the promotion of humins

obtained at softer temperatures (lower than 45 % in both cases). Similar behaviour is obtained for the levulinic acid. In this case, this component is promoted at longer reaction times, in such a way that the selectivity after 24 h increases, for values around 37 – 40 % at 393 and 403 K to more than 62 % at 413 K.

As function of these results, the initial temperature (413 K) is chosen as the optimum one for both components, setting the time to the desired product. These results can be explained with evolution of the kinetic constants (the correspondence among

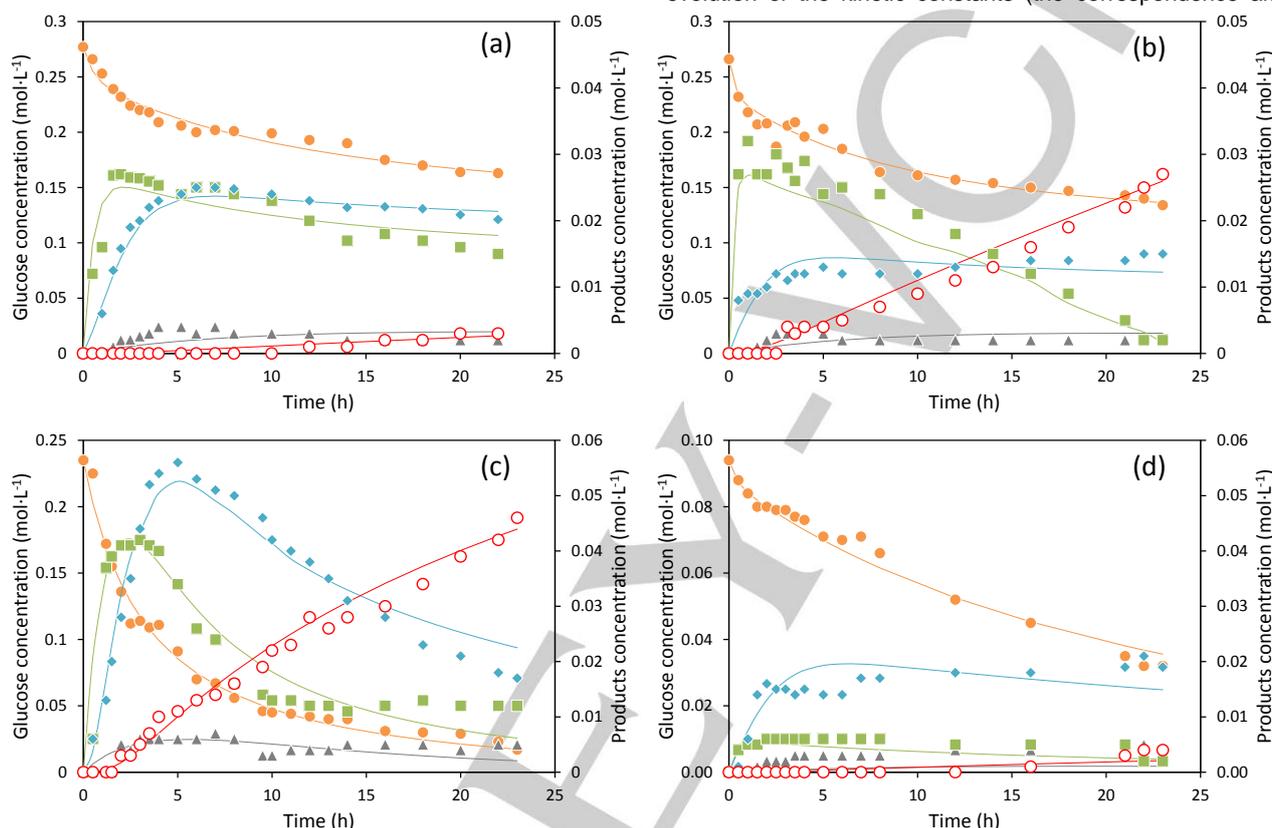


Figure 5: Experimental (points) and fitted values (lines) obtained according to the kinetic model proposed for the glucose conversion at 413 K catalyzed by (a) HCl; (b) HCl + ZSM-5; (c) HCl + β -zeolite; (d) HCl + Y-zeolite. Symbols: (●) glucose; (■) fructose; (◆) HMF; (▲) AHG; (○) LA.

production, mainly from HMF).

Trying to reduce this degradation, the effect of temperature was analysed, carrying out same experiments at softer conditions. Main results can be observed in **Figure 6**, whereas the detailed profiles are included in the Supporting Information (Fig. S1 – S3). Concerning the glucose conversion, a clear decrease is observed at lower temperatures, obtained an almost parallel evolution for reactions at 393 and 403 K. In all the cases, apparent irreversible first-order kinetics was observed. After 24 h reaction time, more than 54 and 71 % of glucose disappearance was obtained at 393 and 403 K, respectively. This decrease in the glucose conversion, however, does not correspond to an improvement in the final carbon balance, obtaining same decreasing trend and similar final values between 47 and 51 %. According to these results, the humins formation cannot be prevented by decreasing the temperature.

Concerning the most relevant products, both are preferentially obtained at the highest temperature tested. The maximum HMF productivity is reached after 5 h, with a selectivity higher than 54 %. This value is significantly higher than the maximum ones

experimental and fitted data is plotted in Fig. S1-S3 of supporting information).

According to results shown in **Table 3**, the expected improvement in the kinetic constants at increasing temperature is clearly observed, being this enhancement more evident in the case of the first step: the glucose isomerization. The reaction rate for this step sharply increases with the temperature, boosting the production of both desired platform molecules. An Arrhenius dependence was observed for the main reaction steps, obtaining the activation energies also included in **Table 3**. The good fit of these constants and the Arrhenius model is included in the Supporting Information (Fig. S4). The important improvement obtained by combining homogeneous and heterogeneous catalysis is clearly observed by comparing these values with the previous ones reported in the literature. Almost all the activation energies are around 40 to 50 % lower than values included in studies using only homogeneous catalysis, where the typical values are in the range 120 – 160 kJ/mol.^[1c,8,10,34,35] In fact, these values are 30 % than values corresponding to using acetone as solvent, one of the best alternatives for maximizing the 5-HMF under mineral acid

conditions.^[36] The only exception is the k_6 activation energy. This kinetic constant corresponds to the AHG production and the value obtained is quite similar to the proposed one using only HCl (138 kJ/mol in the literature,^[8] 132.6 kJ/mol in our results). Considering the negative role of this compound in the proposed aim, the lack of influence in this reaction is also an advantage that must be highlighted.

In order to determine the effect of the mineral acid on the reaction performance, experiments at different HCl concentration were carried out: 50, 200 and 400 ppm. An additional reaction was performed in absence of mineral acid (only beta zeolite, pH=4.92) in order to compare the results obtained. In general terms, each kinetic constant (previously labelled as " k_i ") corresponds to the intrinsic " k_i^* ", and a power-law

expression:

$$k_i = k_i^* \cdot [HCl]_i^{m_i}$$

This dependence has been previously proposed for kinetic studies controlled by homogeneous catalysis.^[21,37] Experimental data obtained with 0, 50, 200 and 400 ppm were fitted to the proposed model, being these profiles included in the Supporting Information (Fig. S5-S7, except in the case of 200 ppm, previously plotted in Fig. 6c). **Table 4** summarizes the main results obtained, whereas the goodness of the proposed dependence of the kinetic constants on the pH is depicted in the supporting information (Fig. S8). The lowest value of the intrinsic constant is obtained for the first step, in good agreement with

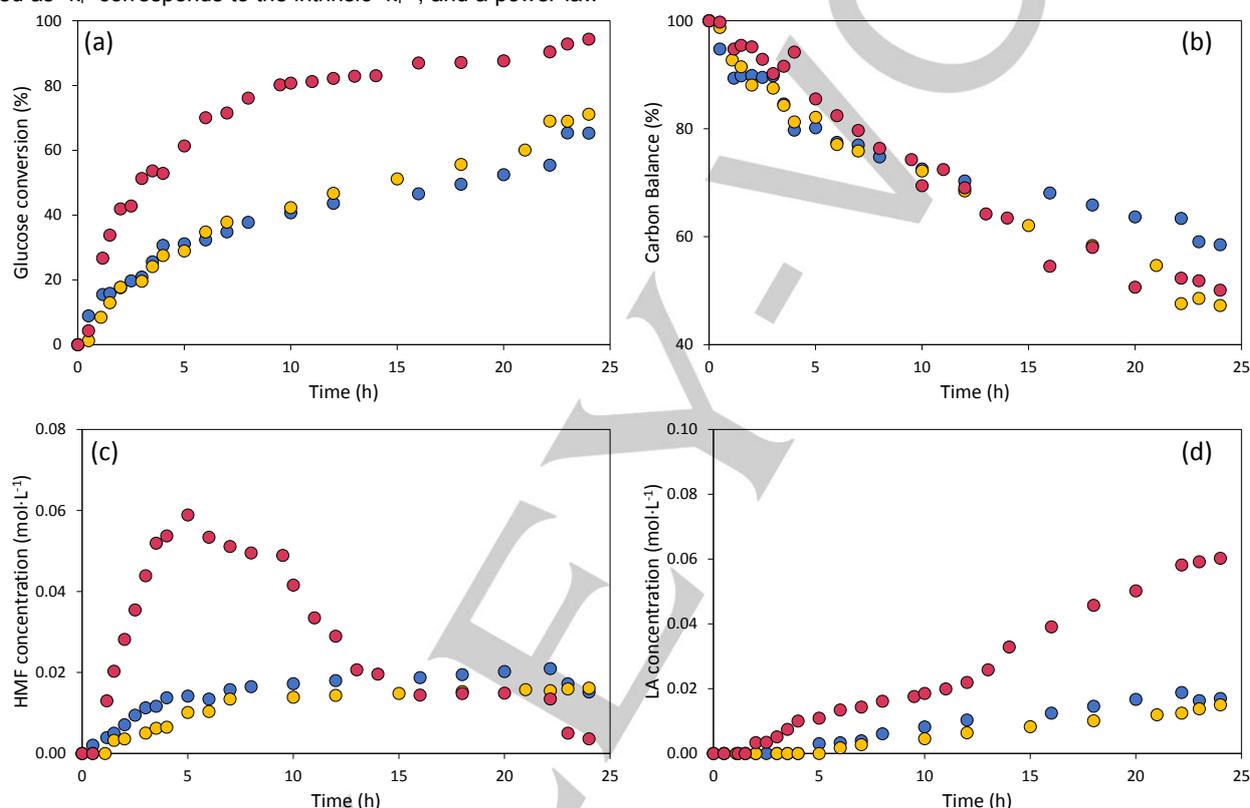


Figure 6: Effect of reaction temperature in the glucose valorization catalyzed by HCl + β -zeolite when reaction is carried out at 393 K (blue); 403 K (yellow); and 413 K (red). Results analyzed in terms of: (a) glucose conversion; (b) carbon balance; (c) HMF concentration; (d) levulinic acid.

function of the HCl concentration, according to the following the previous hypothesis that this step is mainly catalysed by

Table 3. Kinetic constants obtained after fitting the experimental results at different temperatures to the model proposed and constants obtained applying an Arrhenius model

HCl (ppm)	Heter. Catalyst	T (K)	Kinetic constants (units in h ⁻¹ except k_4 and k_7 that are in L·mol ⁻¹ ·h ⁻¹)								r^2
			k_1	k_{-1}	k_2	k_3	k_4	k_5	k_{-5}	k_7	
200	β zeolite	413	0.43 ± 0.01	0.14 ± 0.10	0.69 ± 0.10	0.08 ± 0.02	1.13 ± 0.08	0.01 ± 0.01	0.19 ± 0.14	10.27 ± 0.41	0.97
200	β zeolite	403	0.29 ± 0.07	0.56 ± 0.12	0.43 ± 0.13	0.08 ± 0.03	0.74 ± 0.01	0.02 ± 0.001	0.12 ± 0.05	5.41 ± 0.52	0.98
200	β zeolite	393	0.17 ± 0.02	2.74 ± 0.08	0.28 ± 0.21	0.05 ± 0.01	0.38 ± 0.01	0.002 ± 0.001	0.05 ± 0.02	3.97 ± 0.34	0.96
Pre-exponential factor			$3.6 \cdot 10^7$	-	$2.7 \cdot 10^7$	$1.3 \cdot 10^3$	$1.8 \cdot 10^9$	$1.2 \cdot 10^{15}$	-	$1.2 \cdot 10^9$	-
Activation Energy (kJ/mol)			62	-	60	33	72	132	-	64	-
r^2			0.992	-	0.997	0.999	0.98	0.68	-	0.95	-

Lewis acid sites. According to results obtained, the kinetic order of HCl is close to one in most of the individual steps (considering as first order those exponents from 0.5 to 1.1, being these discrepancies justified by experimental errors), except in the case of the HMF oxidation to levulinic and formic acids, in which the power coefficient is higher. This unexpected value could indicate a stronger proton dependence for the HMF degradation, probably justified by the breakdown required (one HMF molecule will be divided into two acids) as well as the strong oxidation required). Hypothesis proposed is that this step is not really an elementary step but a set of experimental ones. This global sense is congruent with a higher kinetic order. In fact, values higher than 1 were previously obtained in kinetic studies about

$$CSF = \log(R_0) - pH$$

$$R_0 = t \cdot \exp\left(\frac{T - T_{ref}}{14.75}\right)$$

Where "T" is the reaction temperature in Celsius degrees; "T_{ref}" is 100°C; "t" is the reaction time in minutes; and 14.75 is the fitted value of an arbitrary constant. pH is measured before the reaction, at room temperature, having values of 4.92, 2.76, 2.03 and 1.76 for reaction using 0, 50, 200 and 400 ppm of HCl, respectively. The most relevant results are summarized in **Figure 7**. As it can be observed, the maximum HMF productivity is obtained when CSF factor has a value close to 1.6-1.7. In order to obtain the maximum HMF concentration, this CSF factor

Table 4. Apparent and real kinetic constants obtained after fitting the experimental results to the model proposed. Results corresponding to reactions at 413 K with different mineral acid concentrations and using β -zeolite as heterogeneous catalyst.

$k_i = k_i^* \cdot [HCl]_i^{m_i}$	HCl (ppm)	k_1	k_{-1}	k_2	k_3	k_4	k_5	k_6	k_7	r^2
Apparent kinetic constants*	0	0.01 ± 0.01	0	0.42 ± 0.13	0.001 ± 0.001	0.53 ± 0.11	0.006 ± 0.002	0.07 ± 0.01		0.993
	50	0.12 ± 0.04	0.02 ± 0.05	0.17 ± 0.03	0.001 ± 0.01	0.49 ± 0.04	0.004 ± 0.003	0.04 ± 0.02	1.42 ± 0.50	0.92
	200	0.43 ± 0.01	0.14 ± 0.10	0.69 ± 0.10	0.08 ± 0.02	1.13 ± 0.08	0.01 ± 0.01	0.19 ± 0.14	10.27 ± 0.41	0.97
	400	0.53 ± 0.03	0.02 ± 0.01	1.15 ± 0.17	0.23 ± 0.05	1.33 ± 0.09	0.02 ± 0.02	0.22 ± 0.04	11.24 ± 1.80	0.92
Real kinetic constants**		0.007	2.253	83.797	1.10 ⁵	13.162	0.435	11.288	1.7·10 ³	-
"m" exponential		0.7	1.1	0.9	2.8	0.5	0.7	0.8	1.1	-
r^2		0.96	0.94	0.994	0.98	0.96	0.94	0.93	0.91	-

* (units in h⁻¹ except k_4 and k_7 that are in L·mol⁻¹·h⁻¹)

** (units in h⁻¹·(L·mol⁻¹)^m except k_4 and k_7 that are in L·mol⁻¹·h⁻¹·(L·mol⁻¹)^m)

the decomposition of HMF into acids.^[37,38]

According to the previous results, the relevance of HCl concentration is unquestionable, but its effect in the HMF and levulinic acid productivity can be partially masked by the role of temperature. In order to identify which parameter is more relevant and the best conditions to maximize the productivity of each platform molecule, results obtained for temperature and HCl concentration influence are analysed together as function of the combined severity factor (CSF), parameter defined in 1987 by Overend and Chornet.^[39] to quantify the green character by a global analysis of all reaction conditions involved in any process. This parameter has been introduced in the last years to analyse processes as different as the ethanol production from cotton stalk,^[40] the hydrothermal carbonization of wastes,^[41] the enzymatic hydrolysis of cellulose,^[42] or the conversion of glucose into levulinic and formic acid.^[43] The CSF parameter used in this work, considers pH, time and temperature as the main reaction parameters (some similar expressions are also reported in the literature for other key conditions). It is defined according to the following expression:

must be reached at the maximum temperature studied (140°C). In fact, results obtained at lowest temperatures are, in all the cases, lower than those values obtained when using only homogenous catalysis (absence of zeolite, black asterisks in the figure). At 140°C, the optimum situation can be obtained at large times (around 24 h) if reaction is carried out with only 50 ppm of HCl, whereas this times strongly decreases if the mineral acid concentration increases to 200 ppm. In fact, the maximum HMF concentration is obtained at this conditions, after 5 h (0.06 mol·L⁻¹). Similar maximum concentration is obtained working with 400 ppm of HCl, but after only 3 h (0.063 mol·L⁻¹). Considering that, in both cases, these values correspond to 41 % of selectivity, 200 ppm of HCl and 5 h of reaction are chosen as the best reaction conditions in order to enhance the HMF production (differences are too low to justify the increase to 400 ppm of HCl). Concerning the LA, CSF higher than 2 are required to obtain a significant amount of this compound. In this case, the relevance of HCl concentration is more marked than for the HMF, obtaining double amount of LA if results at 200 and 400 ppm of HCl are compared. In summary, more than 0.11 mol·L⁻¹ of LA are obtained after 24 h of reaction, with a global selectivity of 34 %. These conditions are chosen as the optimum ones to maximize the productivity of this platform molecule. In both

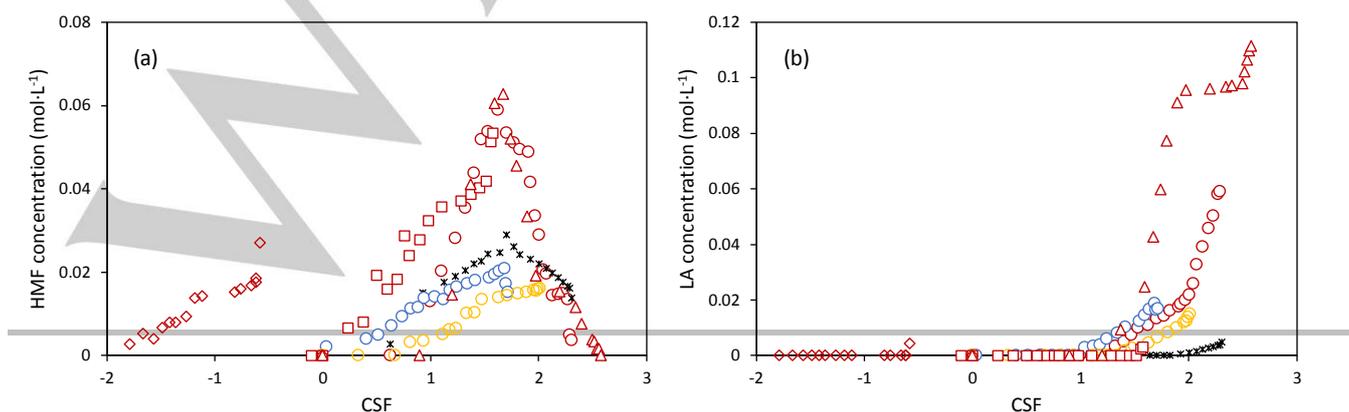


Figure 7: Analysis of (a) HMF and (b) LA productivity as function of the CSF factor. Data correspond to different concentration of HCl: 0 ppm (diamonds); 50 ppm (squares); 200 ppm (circles); 400 ppm (triangles). Results as function of the temperature: 393 K (blue); 403 K (yellow); 413 K (red). In order to make easier the comparison, results using only homogeneous catalysis (200 ppm of HCl) at 140°C are also included (*).

cases, these results are significantly higher than those previously reported at similar severity factors when using only homogenous or heterogeneous catalysis.^[7-10]

Conclusions

A clear improvement in the glucose valorisation to HMF and levulinic acid is obtained when heterogeneous and homogeneous catalysis are combined, obtaining promising results in aqueous medium. Beta zeolite is identified as the best material tested, with main effect in the improvement of glucose to fructose isomerization. A minimum temperature of 140°C is required to obtain significant amount of both platform molecules. After 24 h almost complete conversion (94 %) is obtained, with a significant decrease in the humins and AHG production (main undesired reactions). Reaction time and HCl concentration can be modified to maximize HMF or LA, as required. Thus, maximum amount of HMF is obtained after 5 h with 200 ppm of HCl, whereas more severe conditions are required to enhance the LA (24 h, 400 ppm of HCl). Under these conditions, both platform molecules are the main product obtained. A complete kinetic model is proposed, combining the effect of both catalysis. A clear decrease in the activation energy of main steps is obtained, with values 30-40 % lower than those previously proposed when using only mineral acid.

Experimental Section

Materials

D-(+)-glucose (≥99.5%) and sodium hydrogen carbonate (≥99.7%) were purchased from Panreac Applichem. 5-(Hydroxymethyl)furfural (≥99%), formic acid (98%) and levulinic acid (98%) for HPLC calibration were acquired from Sigma-Aldrich, and hydrochloric acid (37%) was purchased from Fisher Chemical. β-zeolite CP814E (SiO₂/Al₂O₃=25), ZSM-5 CBV2314 (SiO₂/Al₂O₃=23) and Y-zeolite CBV712 (SiO₂/Al₂O₃=12), were purchased from Zeolyst International. Zeolites were activated by a heat treatment at 823 K for removing the NH₄⁺ functional groups of the commercial zeolites, obtaining the proton forms that are active for this reaction. This treatment has been previously reported in the literature.^[44]

Reaction system

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) with a backpressure regulator and a PID temperature controller. In a typical experiment, 0.175 L of an aqueous solution of 5.83 g of D-(+)-glucose and 0.466 g of β-zeolite were used. Four different HCl concentrations were studied (0-400 ppm, corresponding to feed pH between 4.92 and 1.76) and the influence of reaction temperature was also analysed (from 393 to 413 K). Once reached the desired temperature, 25 mL of a solution of hydrochloric acid was added resulting the acid concentration corresponding to each experiment. Air was purged with N₂ and dehydration was carried out with 10 bar of N₂ with a stirring of 600 rpm for 24 hours.

Analysis

Samples were taken from the sampling port, filtered using 0.45 μm Nylon syringe filters and diluted in a 1:20 ratio. The reactants were quantified by HPLC (1200 Series, Agilent) using a refraction index detector (G1362A RI). A Hi-Plex H Column (Agilent) was used as stationary phase, whereas 0.6 mL/min of a 5 mM H₂SO₄ solution was chosen as the mobile

phase. With these data, selectivities are calculated according to the following equation:

$$S_i = n_i \cdot \text{mol}_i / \sum (n_i \cdot \text{mol}_i)$$

where "n_i" correspond to the number of carbon of the component "i"; and the denominator.

Kinetic modelling

The kinetic model is based on the assumption that the system can be described as an ideal stirred batch reactor (BR). Mass balance for a given compound follows a differential equation considering both, homogeneous and heterogeneous kinetic contributions. By combining the reactor model and the power-law rate expressions, the complete model is obtained. Equations obtained were implemented and solved in Scientist® 3.0 Software (MicroMath) and experimental results were fitted to model proposed considering the least squares methodology.

$$dC_i/dt = \sum_{j=1}^M -\alpha_{ij} r_j$$

being "C_i", concentration of "i" component (mol L⁻¹); α_{ij}, stoichiometric coefficient of component "i" on the reaction "j"; "r_j", reaction rate for the reaction "j" (mol L⁻¹ s⁻¹).

$$r_j = k_{jHo} \prod_{k=1}^N C_k^{n_{kHo}} + k_{jHe} \prod_{k=1}^N C_k^{n_{kHe}}$$

being "k_{jHo}", rate constant of "j" reaction corresponding to homogeneous reaction; "C_k", concentration of "k" component (mol L⁻¹); "n_{kHo}", reaction order of "k" component corresponding to homogeneous reaction; "k_{jHe}", rate constant of "j" reaction corresponding to heterogeneous reaction; "n_{kHe}", reaction order of "k" component corresponding to heterogeneous reaction.

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Keywords: kinetics • biomass • zeolites • bio-platform molecules • biorefinery

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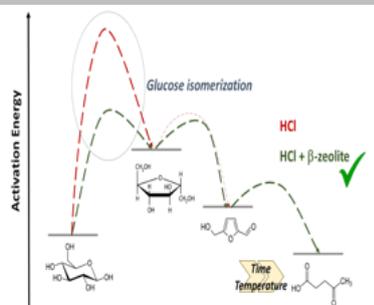
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Entry for the Table of Contents (Please choose one layout)

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FULL PAPER

Cooperation in catalysis: The presence of a heterogeneous acid catalyst, as zeolite beta, promotes the transformation of glucose into hydroxymethylfurfural or levulinic acid (depending on reaction conditions). Specifically, the presence of Lewis acid sites increases the reaction rate of the glucose isomerization into fructose, a more reactive hexose.



Diego Garcés, Laura Faba, Eva Díaz
and Salvador Ordóñez*

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**Aqueous phase transformation of
glucose into HMF and levulinic acid
combining homogeneous and
heterogeneous catalysis**