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Zeolite-assisted acid hydrolysis of cellulose: Optimization of reaction conditions and chemical pretreatments for enhancing HMF yields

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ABSTRACT

This study explores the hydrolysis of microcrystalline cellulose under soft conditions using a combination of both homogeneous (HCl) and heterogeneous catalysts (β-zeolite). The impact of temperature and HCl concentration is studied, revealing that the most favorable results (highest HMF yield) are achieved at 140°C with 0.02 %w/w of HCl (19% of selectivity, 23.5% of conversion). Nevertheless, the inherent recalcitrance of cellulose limits the conversion and the HMF concentration. Three chemical pretreatments (HCl, H_2O_2, HNO_3) are considered, assessing the effect of concentration. Except when using 69% of HNO_3, the bulk structure of cellulose remains largely unaffected (low effect on conversions). However, the surface of cellulose undergoes chemical alteration due to the acidic and predominantly oxidizing pretreatment, leading to the detection of C5 compounds. These modifications have a positive influence on the reaction, significantly enhancing the selectivity towards HMF up to 50% (34% of conversion).

1. Introduction

Recently, the production of renewable fuels and chemicals from biomass has focused the attention of the scientific community. There is total agreement on the essential role of lignocellulosic biomass (industrial crops or wastes) in boosting this industrial transition based on biorefineries and the circular economy as fundamental pillars (Velvizhi et al., 2022; Rathour et al., 2023).

In all the possible biorefinery schemes, the breakdown of biomass into sugars and other platform molecules for subsequent conversion into bioproducts is always the first step. However, one of the main challenges in using this bioresource is its complex structure and recalcitrant nature, mainly due to the hydrophobicity of lignin that forms a physical barrier around cellulose and hemicellulose (Zoghlami and Paës, 2019; Takkellapati et al., 2018; Gong et al., 2023) and the high crystallinity of cellulose (Schwarz, 2001). Hence, the depolymerization of cellulose, hemicellulose, or lignin fractions typically requires the application of cost-effective chemical or thermochemical methodologies, such as pyrolysis, gasification, or liquefaction. It is noteworthy that, in certain instances, the long-term sustainability of these processes may become questionable (Wang et al., 2014; Mika et al., 2018; Wu et al., 2023).

Hydrolysis is a liquid-phase alternative that requires softer conditions (100–250°C), allowing tighter control of the final products (Zhou et al., 2023). This option is more recommended when the scope is obtaining chemical platform molecules for their subsequent valorization to chemicals. There are two types of hydrolysis: a) enzymatic and b) acid hydrolysis. Notwithstanding the merits inherent in the enzymatic approach, characterized by its high product yield, cost-effectiveness, and reduced toxicity (Vaidya et al., 2022), the remarkable specificity of enzymes hinders its universal applicability. Factors such as reaction duration, enzyme loading, and substrate concentration, alongside other pertinent parameters, require complex optimization steps (Bhatia et al., 2020). The studies on acid hydrolysis have emerged as a focal point, mainly to produce 5-hydroxymethylfurfural (HMF) and levulinic acid (Wang et al., 2014; Pileidis and Titirici, 2016). Both compounds are considered in the top ten of biomass-derived platform molecules, being interesting intermediates for liquid fuel production, and precursors of resins, solvents, polymers, and other fine chemicals (Bohre et al., 2015; Yan et al., 2015; Rout et al., 2016).

The reaction pathways for HMF and levulinic acid production are fairly similar, HMF is a key intermediate for levulinic acid formation, see Scheme 1. This reaction involves four consecutive steps: (1) hydrolysis of cellulose into glucose, (2) isomerization of glucose to fructose, (3) dehydration of glucose and, mainly, fructose into HMF, and (4) rehydration of HMF to levulinic acid (Mukherjee et al., 2015; Faba et al., 2019). Different catalysts have been proposed for this reaction,

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including organic and inorganic acids, salts, Lewis acids, and ion-exchange resins (Kang et al., 2018), concluding that the glucose to fructose isomerization (catalyzed by Lewis acids) is the rate-limiting step. Besides metal chlorides (homogeneous catalysis), zeolites such as metal-modified ZSM-5, zeolite Y, or mordenite have been tested to obtain a good isomerization activity (Moreau et al., 2000; Choudhary et al., 2013; Galadima et al., 2022). At this point, the combined use of zeolites and mineral acids has shown very good results for transforming glucose into HMF (Garcés et. al., 2019), but its effect on those reactions combining hydrolysis and dehydration (as obtaining the HMF from the polymer) has not been studied yet, being one of the main novelties of this work.

However, the selective conversion of cellulose into HMF in aqueous medium is still not optimized, and very low yields are reported because of the low stability of this compound in aqueous medium. Different techniques are suggested to increase the HMF yield, including adjusting the process parameters (pH, temperature, pressure, reaction time, cellulose dosage), and conducting *in situ* extraction (Zhang et al., 2022; Shi et al., 2022). To sum up, temperatures in the range of 180–240ºC, short reaction times, low acidity or acid concentration are preferred for HMF production (no HMF detected when $pH>4$), whereas opposite conditions promote the levulinic acid one, being favored by $pH<3$ (Kuster and Temmink, 1977; Takeuchi et al., 2008; Weingarten et al., 2012).

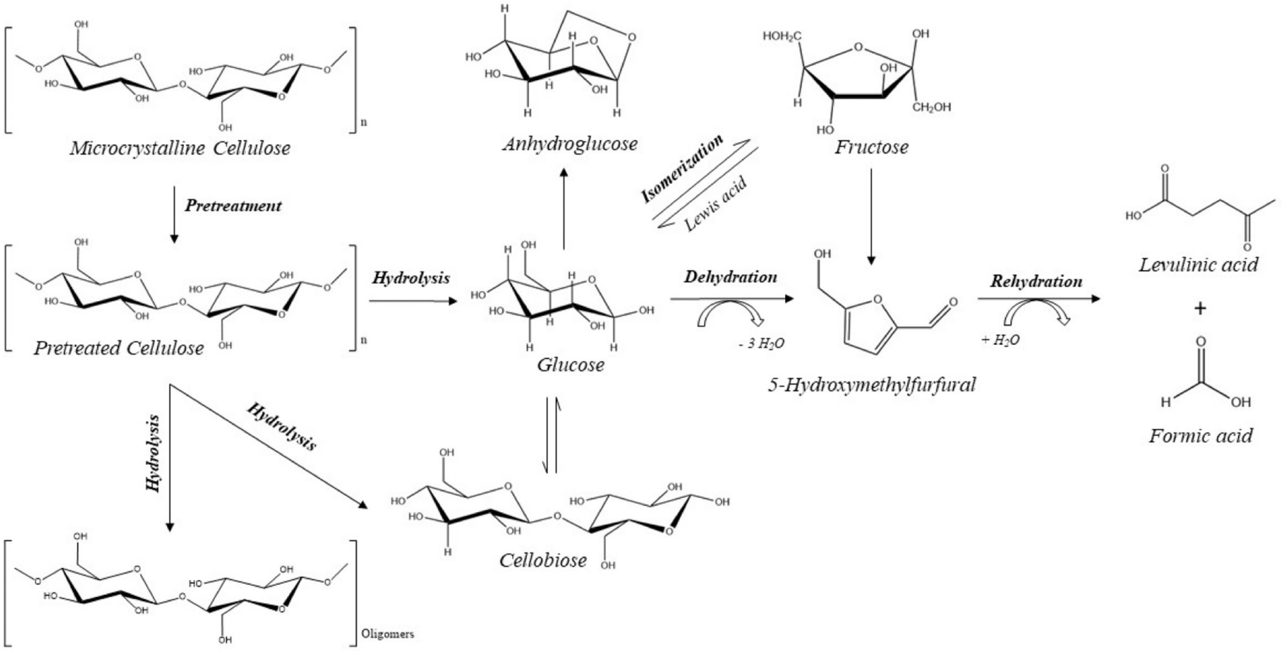
Regarding the kinetic, the high crystallinity of cellulose restricts the accessibility of the β-1,4-glycosidic bonds, which results in a slow hydrolysis rate (Meng et al., 2017; Liao et al., 2020). Biomass pretreatments reduce the polymerization degree of the cellulose. Several physical and chemical alternatives are proposed in the literature, highlighting milling, microwaves, ultrasounds, and acidic and alkali pretreatments, among others (Ni et al., 2015; Shimizu et al., 2018; Li et al., 2020; Tsalagkas et al., 2020; Lan et al., 2022). Most of these methods are designed to maximize the yields of sugars or acids, rather than aldehydes (i.e., HMF), due to their intermediate character and low stability. Thus, despite the existence of some studies (Steinbach et al., 2017; Rezayan et al., 2023), no conclusive results regarding the optimum pretreatment conditions are presented. In general, physical methods usually require long processing times (from 12 to 16 h) to obtain good results, whereas chemical ones use high concentrations of alkalies/acids, casting doubt on their sustainability. Thus, most of the references in the literature consider the pretreatment conditions optimized for the first step of sugar production and the use of organic solvents (against the principles of Green Chemistry) to maximize the HMF yield in the second step (Widsten et al., 2018).

Based on the conclusions of the previous literature, this work evaluates the cellulose hydrolysis using a bi-catalytic system, HCl and β-zeolite, to guarantee the Lewis and Bronsted acidity required to maximize the HMF productivity reducing the severity of the process. This zeolite has been chosen based on a previous work where the activity of different zeolites for glucose dehydration has been studied (Garcés et al., 2019). Three chemical pretreatments are considered: HCl, which introduces acidity; H_2O_2, with oxidizing activity; and HNO_3, which combines both effects. The influence on conversion and product distribution was studied as a function of the chemical dosage.

2. Materials and methods

2.1. *Chemicals*

Microcrystalline cellulose (CAS: 9004–34–6, Sigma Aldrich) is used as a reactant in this work. According to the supplier's specifications, this reagent is a cotton cellulose with high crystallinity (>80%) and a polymerization degree lower than 400. 5-Hydroxymethylfurfural (≥99%), furfural (≥99%), levulinic acid (98%), and hydrogen peroxide (30%) were also supplied by Sigma-Aldrich. D-glucose (≥99.5%) and cellobiose (98%) for HPLC calibration were purchased from Panreac Applichem. Nitric acid (69%) was acquired from Van Waters and Rogers (VWR) and hydrochloric acid (37%) was purchased from Fisher Chemical. β-Zeolite CP814E ($SiO_2/Al_2O_3=25$) was acquired from Zeolyst International. Commercial β-Zeolite was activated to remove NH_4^+ functional groups by a heat treatment at 550ºC according to methods applied by Patet et al. (2017). A deep characterization of this catalysts is provided in (Gancedo et al., 2022), highlighting its high acidity (10.1 mmol $NH_3·g^{-1}$) and its 6.1 Å of crystallographic pore diameter. The reactants were used without any further purification. Solutions were prepared using distilled water.



Scheme 1. Reaction pathway for cellulose conversion into HMF and levulinic acid by hydrolysis (Faba et al., 2019).

2.2. Pretreatments

Pretreatments were carried out at room temperature. 10 g of cellulose was added in solutions of 250 mL of HCl, HNO_3, and H_2O_2 at different concentrations (1%, 5%, 10% and, in case of HNO_3, also 69%). After 6 h under stirring, the pretreated cellulose samples were filtered and washed with distilled water until neutral pH. Finally, the samples were dried in an oven at 105ºC for 24 h.

2.3. Characterization of cellulose samples

The morphology of the different celluloses (fresh and pretreated ones) was investigated by using a scanning electron microscope (SEM, JEOL-6610LV). The change of crystalline structure was evaluated by X-ray diffraction on a Philips X'Pert Pro diffractometer, using Cu-Kα radiation. The scanning degree ranged from 5 to 50°, with a rate of 2°/s at 45 kV and 40 mA. The crystalline index (CrI) was calculated by the Segal equation that evaluates the crystalline portion (I_{200}-I_{AM}) over the total intensity of the crystalline peak portion (I_{200}). The Segal equation applied to cellulose type I is evaluated at 22–23° and 18–19° for the crystalline peak and the amorphous area, respectively.

The amount of amorphous cellulose was determined by gravimetry. The sample of cellulose was suspended in a NaOH solution (20 g/L) and brought to a boil for 3.5 h, using a cooling coil to ensure a constant volume. After cooling, the sample was filtered using a Büchner funnel and a nitrocellulose filter (0.45 µm), washed and dried. The content of amorphous cellulose is evaluated as the difference in weight between the initial mass and the treated one. This procedure has been originally developed for determining the hemicellulosic fraction of biomass-derived materials, characterized by lower crystallinity and higher reactivity.

2.4. Reactions

The hydrolysis was performed in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) with a back pressure regulator and a PID temperature controller. In each experiment, 0.175 L of an aqueous suspension of 5.83 g of cellulose (untreated or pretreated cellulose as a function of the experiments, as detailed in each section) was loaded in the reactor. Air was purged with N_2 and hydrolysis was carried out with 10 bar of N_2. Once the mixture reaches the desired temperature, 50 mL of a hydrochloric acid solution and β- zeolite (0.467 g) is added. The acid concentration as well as the temperature depends on the experiment, and it is specified in the results and discussion section.

The reaction is carried out for 8 h under continuous stirring (700 rpm). Samples were taken from the sampling port, filtered by using 0.22 µm nylon syringe filters and diluted in water to a final 1:20 ratio, and analyzed by HPLC (1200 Series, Agilent) using a refraction index detector and 0.5 mL/min of a 5 mM H_2SO_4 solution as the mobile phase. The column (Hi-Plex H, 300 × 7.7 mm, Agilent) and detector operate at 50ºC. Cellobiose is identified as the majority dimer (>95%), but the presence of other isomers, such as maltose, cannot be discarded. However, the low resolution of the analytic method to isolate both compounds (differences in the retention times lower than 0.2 min) discourage the distinction. Thus, the term "dimer" is used in all the manuscript for the simultaneous consideration of both compounds.

Results were described in terms of conversion, carbon balance closure and selectivity. The cellulose conversion is calculated in terms of liquid-phase carbon yield, i.e., the theoretical cellulose required to obtain all compounds detected in the liquid phase (cellobiose and maltose, glucose, HMF, formic and levulinic acid), according to Eq. (1):

$$x_C = \frac{\left[V \cdot \Sigma \quad (n_i \cdot C_i)\right]_{aq}}{0.4421 \cdot \frac{m_{cellulose}}{M_{cellulose}}} \tag{1}$$

where x_C is the liquid-phase carbon conversion, V is the total reaction volume, C_i the molar concentration of each compound detected in liquid phase, n_i the number of carbons in the molecule of compound i, $m_{cellulose}$ the mass of cellulose introduced in the reactor (5.83 g), $M_{cellulose}$ the molar mass of cellulose (162 g/mol), and 0.4421 corresponds to the atomic percentage of carbon in this cellulose, according to results obtained by ICP analysis of the raw material (44.21% C, 6.2% H, 49.59% O).

Carbon balance closure (C.B.) and selectivity were calculated as follows:

$$C.B. \quad (\%) = \frac{\sum_{i=1}^{n} m_{C_i} + m_{C_t}}{m_{C_{t=0}}} \cdot 100 \tag{2}$$

where $\sum_{i=1}^{n} m_{C_i}$ is the sum of the carbon mass present in all the reaction products; $m_{C_{t=0}}$ is the mass of carbon present in the cellulose initially introduced into the reactor; and m_{C_t} is the carbon mass of the cellulose collected by filtering and drying after the reaction.

$$S_i \quad (\%) = \frac{n_i}{\sum_{j=1\ldots i}^{n} n_i} \cdot 100 \tag{3}$$

where n_i is the moles of carbon that contains the reaction product i and $\sum_{j=1\ldots i}^{n} n_i$ is the sum of the moles of carbon corresponding to reaction products.

3. Results and discussion

3.1. Hydrolysis of the non-pretreated cellulose

The initial experiments evaluate the influence of HCl on cellulose hydrolysis in the presence of β-zeolite to identify the optimum concentration of this homogeneous catalyst considering the equilibrium between activity, selectivity, and process sustainability. By sustainability criteria, a maximum value of 0.4% w/w (400 mg/L) was established to prevent corrosive effects in the equipment and to guarantee that the wastewater produced could be assimilated to a municipal wastewater stream, being far from the maximum allowed by the normative (2000 mg/L in the Spanish laws). It is expected that these low concentrations also minimize levulinic acid production (promoted by strong acidity). All reactions were performed in the presence of β-zeolite to promote the HMF formation by the glucose isomerization route, this study is the first one reporting the co-utilization of homogeneous and heterogeneous acids for treating polymeric biomaterials. Results are analyzed in Fig. 1.

Results shown in Fig. 1 are in good agreement with the general hydrolytic mechanism. Thus, dimers (mainly cellobiose but traces of maltose are also detected) are the first products obtained in the reaction, with very high selectivities at low cellulose conversion. The presence of heavier oligomers cannot be discarded but they cannot be analyzed because of their insoluble character (only the liquid phase is analyzed). For those reactions with low acidity, the initial selectivity of dimers is not 100% (close to 80%) because of the presence of glucose, even at very low conversions. This fact suggests the existence of terminal anhydroglucose units weakly linked to the general polymeric structure. These terminal units are easily hydrolyzed, resulting in an initial mixture containing oligomers but also glucose, as previously reported in the literature (Faba et al., 2019). When using 0.02 and, mainly, 0.04%w/w, the high acidity increases the hydrolytic rate, and the relative weight of this glucose decreases because of the higher concentration of cellobiose.

As the reaction progresses, the decreasing selectivity of these dimers observed (more pronounced at higher acidity) is compatible with their hydrolysis into monomeric units. This behavior suggests that the hydrolysis at these diluted acidic conditions is limited, making total conversion not possible to reach. In fact, cellulose conversion never exceeds 50%, although results with 0.04% demonstrate the advance of the

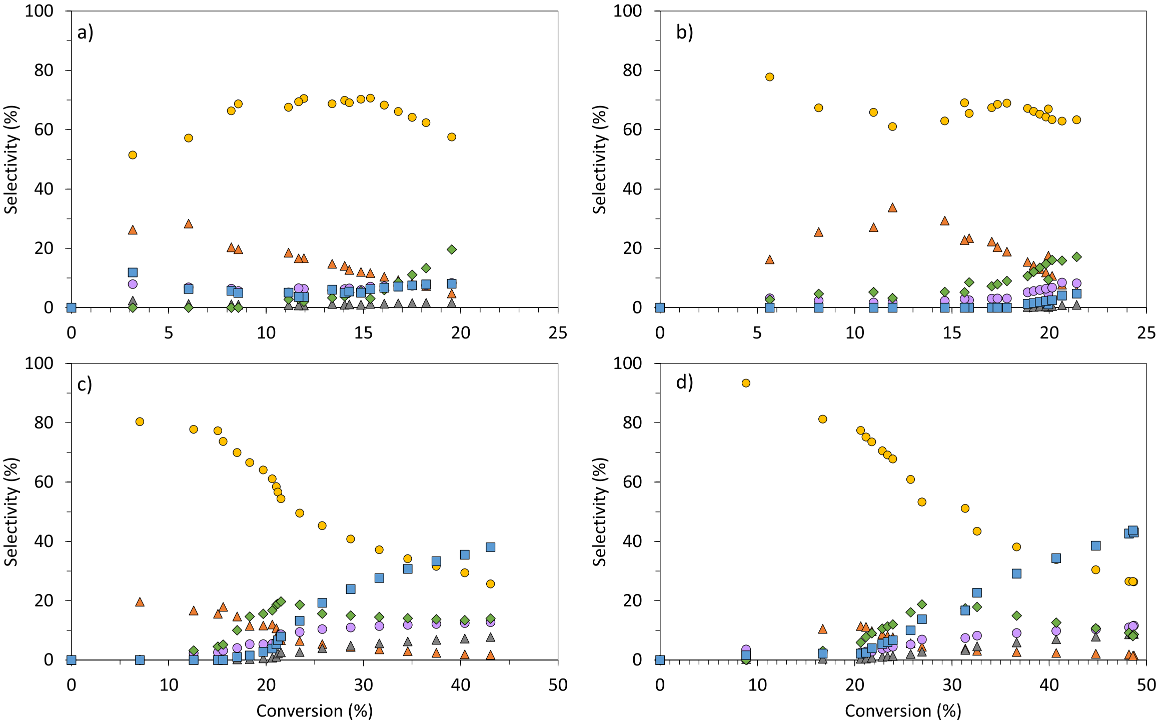


Fig. 1. Selectivity *vs.* conversion plots obtained for the cellulose hydrolysis at 140ºC using 8% β-zeolite as a function of the HCl concentration: (a) absence of HCl; (b) 0.005%; (c) 0.02%; (d) 0.04%. Symbols: (●) dimers; (▲) glucose; (◆) HMF; (●) AHG; (■) levulinic acid.

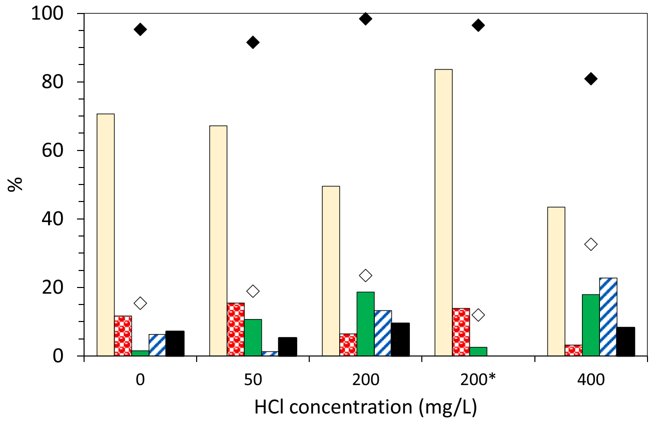


Fig. 2. Cellulose conversion (◇), carbon balance (◆) and products selectivity obtained in the cellulose hydrolysis at 140ºC using 8% of zeolite as a function of the amount of HCl. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black). (*) Experiment in the absence of zeolite.

reaction to subsequent steps once reached this threshold. According to the literature, glucose suffers dimerization in an acidic medium, establishing an equilibrium with cellobiose (Pedersen et al., 2015; Garcés et al., 2017). Analyzing the results in concentration units (see Fig. S1), this contribution cannot be discarded.

Glucose selectivity decreases with the advance of the reaction because of the simultaneous appearance of two different compounds: HMF and anhydroglucose (AHG). Both compounds are obtained by glucose dehydration, being catalyzed by the same acidic sites. In the presence of β-zeolite, HMF prevails over AHG because the Lewis acidity of the zeolite promotes the previous glucose isomerization into fructose, a requirement to promote the pathway to HMF, according to the literature (Ohara et al., 2010; Choudhary et al., 2012). However, fructose is not included in Fig. 1 since its selectivity is always lower than 1% (it dehydrates rapidly).

AHG is a final product, with a soft but continuous increasing trend. On the other hand, HMF can suffer rehydration, mainly under strong acidity, obtaining levulinic and formic acids. Both compounds are equimolar produced, their differences in selectivity being explained by the equation used (in carbon basis). These compounds are very relevant when cellulose conversion exceeds 30%.

This analysis was done considering the theoretical cellulose conversion since its solid character makes impossible its sampling with the actual reaction system. To evaluate the carbon balance and determine the representativeness of these results, the reactions were repeated, reducing the time to 8 h (time that is expected to be the optimum one to maximize the HMF selectivity). The temporal profiles of all the products are included in the Supplementary Information (Fig. S1), observing a discrepancy lower than 5% between both repetitions. Fig. 2 compares the results obtained after 8 h, in this case considering the conversion as the difference in weight between the solid initially introduced and the one recovered after the reaction. The recovered solids maintain their white color, discarding the presence of adsorbed humins, polymers obtained from glucose derivatives under high temperature and/or acidity (Girisuta et al., 2007; Fan et al., 2013).

The reaction performed in the absence of HCl mainly produces the dimer (9 mM), the compound that represents 70.6% of the products detected. Glucose is also obtained, being an 11.7% selectivity. In the absence of any catalyst, the dehydration is almost negligible, HMF being less than 3% of the total products. The high carbon balance (95.3%) indicates the representativeness of these data, suggesting that the production of soluble humins or other undetected liquid compounds is not very relevant.

The positive action of HCl is observed, leading to a linear dependence of cellulose conversion on acid concentration, from 15.4% in the absence of HCl to 32.6% when working with 0.04% of this acid (results after 8 h). The concentration of glucose dimer (cellobiose) remains almost constant despite the amount of HCl present, reaching final values (9–10 mM). These values are far from the maximum solubility of this compound (1 g/8 mL) discarding the saturation of the sample. Acidity also promotes the HMF formation and the selectivity toward this compound rises to 10.7, 16.4, and 17.9%, with 0.005, 0.02, and 0.04% of HCl, respectively. At 0.02, and 0.04% of HCl, the rehydration of this compound is significantly promoted, levulinic and formic acid being the majority compounds detected (31.3 and 40.6 mM, selectivities of 13.6 and 22.7%, respectively). The good carbon balances obtained when working at 0.005 and 0.02% of HCl (91.5 and 98.4%) demonstrate a high control of the reaction. On the contrary, the significant depletion observed at 0.04% (80.9%) suggests that a relevant amount of cellulose is transformed into soluble humins. In global terms, 0.02% of HCl (pH 2.03) is suggested as the optimum acidity to enhance the HMF production.

As introduced before, fructose is only detected in traces. To identify if this fact is due to a null activity of the zeolite (i.e., all the HMF is produced directly by glucose dehydration) or if the fructose dehydration is so fast that fructose instantaneously disappears, a particular experiment with 0.02% of HCl but in the absence of zeolite is performed (see Fig. 2). Results after 8 h demonstrate the relevance of these Lewis sites. When no zeolite is included, the HMF selectivity decreases by more than 84% (from 16.4% to 2.5%). Moreover, conversion is reduced by half in absence of zeolite, and the final mixture is enriched in dimers (83.6%), indicating the greater difficulty of breaking these structures and allowing the reaction to progress toward the final products. These effects are assumed to be due to the presence of Bronsted sites in the zeolite (proton form). Thus, solid cellulose particles migrate to the surface of the zeolite, which donates protons. The solid protonated cellulose on the surface of cellulose particles can degrade since part of it can dissolve and react with water. The corresponding chemisorption of oligomers justifies the improvement in glucose production, whereas the increase in 5-HMF is justified by the previously mentioned role of Lewis sites. This experiment also corroborates the dimerization equilibrium between glucose and cellobiose since comparing the results at the same cellulose conversion, the total yield to products obtained without the zeolite is significantly lower than with it. As dehydration steps consume glucose, this equilibrium is shifted.

To sum up, both catalysts (HCl and zeolite) contribute to all the steps of the hydrolysis of cellulose. Increasing the acidity is discarded as a valid option to promote HMF production since the impact on the levulinic acid formation is more relevant, with the subsequent decrease in the HMF selectivity. Thus, increasing the HMF concentration and selectivity requires evaluating other options, such as modifying the temperature, considering cellulose pretreatments to increase the hydrolysis capacity, or working with biphasic systems that could selectively extract the HMF to prevent its decomposition into levulinic and formic acid.

3.2. Influence of the severity of the reaction conditions

According to the literature, temperatures lower than 200–220°C limit the depolymerization of cellulose only to its amorphous content (Chen et al., 2017). However, the presence of levulinic acid is relevant at 140°C and higher temperatures are assumed to increase its production. Thus, higher temperatures are not contemplated in this work, trying to balance the thermal activation by the co-presence of two catalysts (HCl and β-zeolite). Two lower temperatures were studied (120 and 130°C) considering that these conditions could minimize the HMF rehydration (Pedersen et al., 2015), increasing the selectivity by reducing its degradation into levulinic and formic acid. The main results after 8 h are summarized in Fig. 3.

As expected, cellulose conversion decreases when reducing the temperature (from 23.1% to 14.9%, from 140 to 120°C). Higher temperatures promote all the steps, decreasing the dimer selectivity (from 60.4 to 50.9) and increasing the final products, levulinic and formic acids (from 6.6% to 13.6%). As to HMF, its selectivity is maximum at 130°C (19.6%) but differences are not relevant enough to balance the differences in conversion. Thus, the maximum amount of HMF (18.6% of selectivity) is obtained at 140°C.

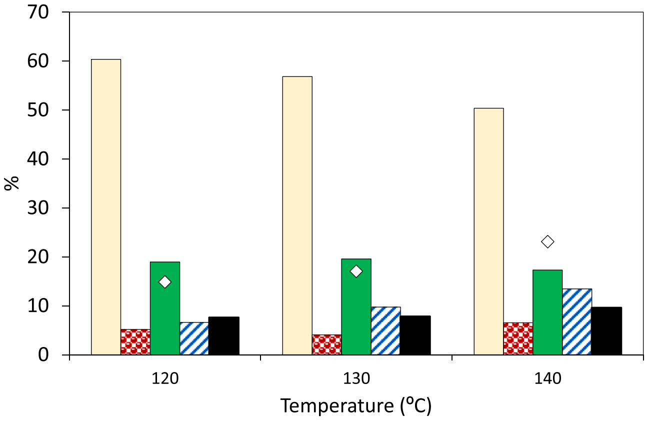


Fig. 3. Cellulose conversion (◇) and products selectivity obtained in the cellulose hydrolysis using 8% of β-zeolite and 0.02% of HCl as a function of the temperature. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black).

The temporal evolution of all the compounds (see Fig. S2) is congruent with the intermediate character of the target compound (HMF). Thus, larger reaction times increase the cellulose conversion (20.5, 28.3 and 43.1% of cellulose conversion after 24 h with 200 mg/L of HCl at 120, 130 and 140°C, respectively) but the HMF concentration slightly increases (from 4.5 to 5.0 mM, from 5.3 to 6.8 mM, and from 6 mM to 9.6 mM, after 8 and 24 h at the temperatures considered in this study) because of the promotion of further steps.

Consequently, maximizing the HMF selectivity requires an equilibrium between temperature, acidity, and time. The combined severity factor (CSF) concept was used to integrate the effects of these three conditions (Fockink et al., 2018):

$$CSF = \log\left(t \cdot \exp\left(\frac{T}{14.75}\right)\right) - pH$$

where t is the reaction time of hydrolysis in minutes, T is the reaction temperature in Celsius, and pH is the acidity of the aqueous solution measures before the reaction (4.92, 2.76, 2.03 and 1.76, for 0, 0.005, 0.02, and 0.04% of HCl, respectively).

Fig. 4 displays the effect of variations in conditions (CSF) on the HMF and levulinic acid concentration. In the case of HMF, the results show a cloud of data points where the results with 0.005 and 0.02% of HCl overlap. In other words, the concentration of HMF increases as the severity of the process increases, regardless of whether this increase was achieved by increasing reaction time, temperature, or HCl concentration.

The results obtained with the highest HCl concentration (0.04%) show a different profile, characterized by lower concentrations at low CSF values and a very narrow area of higher concentrations (never exceeding those obtained with 0.02%). This instability rules out the use of these conditions.

The evolution of levulinic acid demonstrates increasing trends with CSF, requiring a minimum CSF of 4 to star observing it, and an exponential increase for values greater than this value. However, unlike what was observed with HMF, the results are scattered depending on the acid concentration. Thus, when working with 0.04%, higher levulinic acid values are obtained at lower CSF values.

In conclusion, the maximum HMF selectivity (18.6%) obtained in

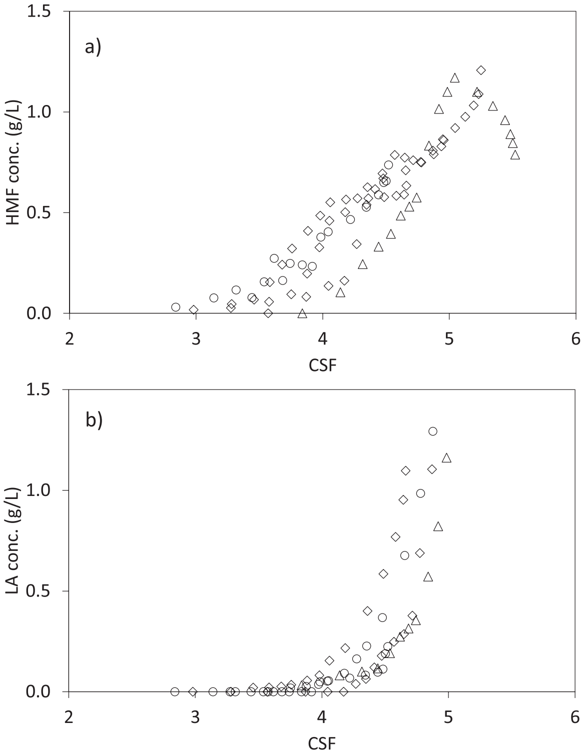


Fig. 4. Effects of CSF on concentration of (a) HMF, and (b) levulinic acid. Data obtained with 0.005% of HCl (○);0.02% of HCl (◇);0.04% of HCl (Δ).

this parametric study is higher than most of the typical values proposed in the literature for similar systems (10% at 150ºC (Gliozzi et al., 2014), 15.5% at 220ºC (Wen et al., 2019)), suggesting a good activity of the catalytic system considered. Higher selectivities (up to 33%) have recently been proposed for a similar aqueous-phase system, using modified zeolites as heterogeneous catalysts (Gromov et al., 2023). Although this result is very relevant, a direct comparison with this work is not possible because of the different crystallinity degree of the raw material used, from 33% to 55% in the case of the bibliography, >82% in this case.

On the other hand, this study also demonstrates an HMF final yield (4.3%) conditioned by the low cellulose reactivity (23% conversion). This yield is congruent with previous literature, with values in the range of 2–7% (Gliozzi et al., 2014; Wen et al., 2019), suggesting the need for other strategies to increase the reactivity of cellulose.

3.3. Improving hydrolysis behavior by chemical liquid-phase pretreatments

The production of HMF by cellulose hydrolysis under dilute acid conditions is limited by the refractory character of the cellulose. Its almost complete crystallinity restricts the access of the catalyst to surface irregularities. A previous pretreatment of this cellulose could reduce the crystallinity of the raw material, increasing the number of potential active sites in the cellulose fiber for starting hydrolysis reactions and, subsequently, increasing the HMF production.

Three different chemical pretreatments were considered in this work, using a mineral acid (HCl), an oxidant (H_2O_2), and a chemical with both properties (HNO_3). In the three cases, the influence of the dosage in the pretreatment was studied. All the pretreatments were carried out at room temperature (20–25ºC) to limit the activity of these acids to reduce the crystallinity of the cellulose, making its surface more accessible during the reaction but without promoting its hydrolysis or any degradation of the bulk structure that could produce liquid compounds during the pretreatment. Thus, pretreated cellulose could be recovered by filtration and the acid solution could be reused, minimizing the environmental and economic impact of using these chemicals.

Fig. 5 shows the results obtained after 24 h of hydrolysis. Despite the intermediate character of HMF, this reaction time corresponds to the maximum selectivity towards this compound of all the pretreated samples (the complete temporal profiles are included in the Supplementary Information, Fig. S3-S5).

In terms of conversion, pretreatments with HCl do not offer any improvement, obtaining very similar values in the three case studies (36–37.5%). These conversions are lower than the one obtained with the fresh cellulose (43%). This fact suggests that the potential surface degradation produced by this pretreatment does not lead to more accessible terminal glucose, but rather, a portion of the original terminal glucose (amorphous region) is dissolved during the pretreatment, removing the active sites of the fiber for starting hydrolysis reaction.

To support this hypothesis, fresh and pretreated celluloses were characterized by different techniques, trying to identify the main effect of each pretreatment on the cellulose structure. Figure S6 shows the diffractograms of all the samples, including the theoretical main diffraction peaks of the three polymorphs of cellulose, according to the molecular orientation and hydrogen-bonding network: cellulose I, cellulose II, and cellulose III. The analysis of these XRD results is shown in Table 1.

Native cellulose shows the typical XRD patterns of cellulose I (the expected polymorph of cotton cellulose), with diffraction peaks at $2\theta = 14.5°$, 16.5º, and 22.5º attributed to the planes of $(1\bar{1}0)$, (110) y (200), respectively (French, 2014). This cellulose has a crystallinity index of 82.5% and, according to Scherrer's equation, a crystallite size of 7.3 nm. The region around 2θ=21º could be initially attributed to the plane (200) of cellulose type III. However, the lack of signals at 11.7º and 17º (planes $(1\bar{1}0)$ and (110) of this polymorph) discards this hypothesis suggesting a contribution of a no well-ordered polymeric region. The typical rod-like structure of crystalline cellulose is observed by SEM (Fig. S7). The purity of this material is corroborated by the results after treating this sample with NaOH; the sample has a non-cellulosic material percentage of less than 2%.

Cellulose type I remains the predominant polymorph in samples pretreated with HCl, with no significant differences observed in comparison to the untreated cellulose. In fact, SEM micrographs do not reveal any significant difference (see Fig. S7). The effects of the pretreatments become evident through an increase in the crystallite size (from 7 to 9–10 nm) with a minimal rise in the crystallinity index. Both effects are congruent with the solubilization of the weakest parts of the

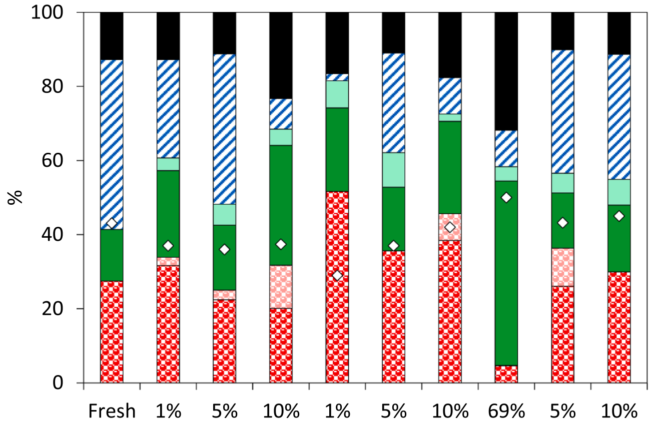


Fig. 5. Results after 24 h of cellulose hydrolysis at 140ºC using 8% of β-zeolite and 0.02% of HCl as a function of the cellulose pretreatment used. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black).

Table 1
Crystallinity index (CrI), average crystallite size and non-cellulosic phase concentration of fresh and pretreated celluloses.

Sample	CrI	Crystallite size (nm)	Non-cellulosic phase (%)
Fresh cellulose	82.1	7.3	1.8
1% HCl	82.4	9.2	3.6
5% HCl	82.4	9.5	13.4
10% HCl	82.5	9.9	24.2
5% H_2O_2	82.9	7.9	48.6
10% H_2O_2	83.2	9.2	49.1
1% HNO_3	82.8	9.3	38.3
5% HNO_3	83.1	9.5	38.8
10% HNO_3	83.2	10.0	39.9
69% HNO_3	37.8	7.8	41.9

surface (amorphous regions). The limited amount of weak β-glucosidic bonds on the parent surface (those susceptible to attack at these soft conditions) explains the low sensitivity of these results to the amount of HCl used.

The progressive increase in the percentage of non-cellulosic material, from 1.8% to 24.2%, explains the product distribution obtained, with an increasing selectivity in C5 derivatives, both sugars (arabinose) and aldehyde (furfural), as the HCl concentration increases. It is suggested that the acidic pretreatment interacts with the terminal glucose of cellulose, altering their structure in such a way that, under reaction conditions (140ºC, copresence of a heterogeneous catalyst), these terminal units suffer not only hydrolysis but also decarbonylation, leading to arabinose and its aldehyde (total selectivity of 16% with 10% HCl). The presence of these molecules, although not the most common situation, has already been referenced in the literature under oxidative conditions (Zhang et al., 2017). The hydrolysis and dehydration rates of C5 sugars are slower than the corresponding ones of glucose (Istasse and Richel, 2020), justifying the lower conversions obtained. Moreover, furfural is significantly more stable than HMF, also explaining the lower relevance of acids in the reaction mixture. As to the target compound, the selectivity to HMF increases as the HCl concentration does, reaching a maximum of 32.3%, a value almost three times higher than the one obtained in the absence of any pretreatment.

Regarding the oxidizing pretreatment (H_2O_2), the conversion obtained with 5% of H_2O_2 is the same as with the fresh sample (43%). A slight increase is obtained when using 10% of H_2O_2, reaching a final conversion of 45%. Analyzing the products, the presence of C5 sugars and aldehydes is also relevant (similar selectivities than when using HCl), but the percentage of HMF only increases from 14% to 18%.

XRD diffractograms of these samples discard a deep change in the surface crystallography, cellulose type I being the main polymorph observed. With this chemical, the effects on the crystallinity index and the crystallite size are more evident than with HCl. The high percentage of "amorphous phase" (>45% in both cases) is not congruent with the conversion reached or the product distribution, suggesting that this pretreatment partially damages the cellulose surface, obtaining a solid that cannot lead sugars by acidic hydrolysis. Based on this fact, higher H_2O_2 concentrations were not tested.

Results with HNO_3 (acidic and oxidizing activity) demonstrate a high influence of the concentration, obtaining lower conversions when using 1% (29%) and higher conversions (50%) when using a high-concentrated acid. This evolution is the result of two opposite effects: the acidic behavior of HNO_3 promotes the hydrolysis and solubilization of terminal oligomers during the pretreatment, limiting the potential conversion, whereas its oxidation activity (stronger than in the case of H_2O_2) partially degrades the cellulose surface increasing the terminal units available for the reaction. Increasing the concentration remarks this positive effect because the number of sugars available for solubilization during pretreatment is limited, while the capacity to degrade the surface through the oxidative action increases. Based on this analysis, oxidative pretreatment is more effective than the acidic one.

The morphology and crystalline structure of samples treated with 1, 5, and 10% of HNO_3 are very similar and the cellulose I polymorph is the predominant one in the three cases. 1% of nitric acid is enough to produce the main differences, both in the crystallinity index and the crystalline size, whereas almost null differences were observed when increasing the nitric acid concentration. In agreement with XRD results, a continuous but soft increase in the amount of non-cellulosic percentage is observed, highlighting that more than 95% is obtained with only 1% of HNO_3. This analysis does not allow us to determine the specific amorphous character of this fraction. Conversion results suggest that this fraction is easier to hydrolyze after being treated with high HNO_3 concentration.

The pretreatment with 69% of HNO_3 demonstrates to be significantly more effective in deeply modifying the cellulose surface. Diffraction peaks of cellulose type I and type II ($2\theta=12º$, 20º, and 22º (French, 2014)) coexist in this sample. The probable explanation for this result is that the crystalline regions swelled during the attack with HNO_3, leading to a rearrangement of the cellulose crystalline structure. This effect has been previously observed when cellulose is treated with strong mineral acids (Gong et al., 2017). Cellulose type II is more stable than cellulose type I, justifying the low effect on conversion of this relevant change.

The degradation produced by this pretreatment is very effective in terms of selectivity, reaching 50% of HMF. Furfural is also obtained, reaching a final selectivity of 4%. The low sugar selectivity (<5%) demonstrates that, despite this pretreatment having limited effectiveness in increasing the availability of hydrolysable sugars, it does reduce the stability of glucosidic bonds, favoring the progression of the reaction toward the dehydration stage.

Selectivity results are comparable to those proposed in the literature, even when using more severe pretreatment conditions (Yao et al., 2022). The selective extraction of HMF in an organic solvent could be an interesting option for increasing its selectivity. The purification of the stream is out of the scope of this work, but we have deeply studied this approach in a previous study using glucose as a reactant and the main conclusions could be extrapolated to this system (Faba et al., 2019). On the contrary, the maximum yield obtained in this study (18%) is slightly lower than the optimum values reported in the literature (up to 60% for aqueous reactions), as discussed in the review previously indicated. However, the direct comparison is unrealistic due to the different conditions under which they are conducted. Those employed in this study, both for pretreatment and reaction, including temperatures, acid concentrations, and catalyst amounts, are significantly milder than those suggested in previous studies, resulting in a more sustainable process.

3.4. *Reusability tests*

The solid after 24 h of reaction time (using cellulose pretreated with 69% of HNO_3) was recovered by filtration and resuspended in a fresh HCl solution for a new hydrolytic batch. This solid includes the zeolite as well as the non-reacted cellulose, and the lack of any reaction (conversion lower than 1%) and, more relevant, the absence of glucose is congruent with the recalcitrant character of cellulose since the first step of the hydrolysis does not need the catalytic activity of the zeolite. Thus, extending the reaction over 24 h is not a good approach to increase the HMF productivity.

This result does not give clear information about the possible zeolite deactivation since the role of this catalyst is mainly relevant for the glucose isomerization. To study the zeolite stability, a new cycle feeding the recovered solid (mixture of used zeolite and recalcitrant cellulose) into a new cellulose suspension (using pretreated cellulose as fresh reactant) was performed. In this batch, the recalcitrant cellulose is considered as an inert solid and new pretreated-cellulose (69% HNO_3) and HCl is introduced to guarantee the initial conditions. Results after 24 h are plotted in Fig. 6. As observed, the final mixture is enriched in reductive sugars, with a total selectivity of 76.3% (28.6% of arabinose, 23.6% of fructose and 24.1% glucose). A quite relevant HMF selectivity

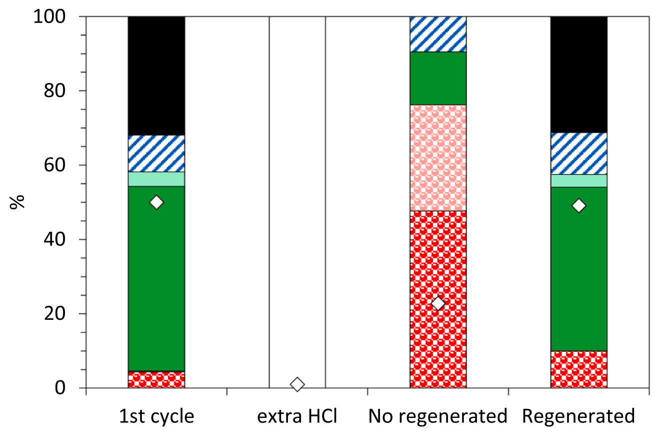


Fig. 6. Stability tests of pretreated cellulose (69% HNO3) hydrolysis at 140ºC using 8% of β-zeolite and 0.02% of HCl. Results obtained after 24 h. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black).

is also observed (14.2%). The presence of fructose indicates that the zeolite is still partially active (glucose isomerization is catalyzed by Lewis acidity). The lower conversion reached in this second cycle (22.8 % vs. 50%) as well as the lack of total fructose dehydration corroborates the initial hypothesis that Bronsted acid sites of the zeolite collaborate with HCl catalyzing the cellulose hydrolysis and the dehydration steps (see Section 3.1) and these sites are at least partially deactivated after the first cycle. A possible reason for this deactivation could be the adsorption of cellulose oligomers or humins precursors, both aspects being discarded according to the good carbon balance obtained at these mild conditions (98.4%, see Fig. 2).

An alternative explanation of these results is related to the method used to get the catalyst after the first reaction, suggesting that the remaining cellulose could be stuck on the zeolite surface, blocking the access to the active sites. To check this hypothesis, the solid recovered after the first cycle was calcined in furnace (550ºC, 8 h) to remove the cellulose. The zeolite after the thermal treatment was introduced in a new cycle with pretreated cellulose, the results after 24 h being summarized in Fig. 6. As observed, the zeolite recovers its initial activity, obtaining very similar conversion (49.1%) and a product distribution enriched in HMF (44.1%) and AHG (32.2%). These results reinforce the interesting results obtained in the cellulose hydrolysis at soft conditions using a pretreatment based on HNO_3.

4. Conclusions

The effectiveness of the bicatalytic system (HCl and beta zeolite) in the hydrolysis of microcrystalline cotton cellulose has been verified. As a result, HMF is produced due to the synergy between Bronsted centers (favoring hydrolysis) and Lewis centers (facilitating sugar dehydration through prior isomerization of glucose into fructose).

Analysis in terms of severity (CSF) rules out a preferential effect of temperature, reaction time, or acid concentration, yielding similar selectivities for equal combined severity factors. Based on this analysis, 140ºC and 0.02% of HCl are defined as the optimal parameters to maximize HMF production (19% of selectivity). However, these results are limited by the low reactivity of the cellulose (recalcitrant character). Due to this, obtaining HMF requires high temperatures and reaction times so long that the control of the reaction is poor and a relevant concentration of acids is obtained (HMF degradation).

Three chemical pretreatments (HCl, H_2O_2, and HNO_3) were proposed to solve this drawback. The mildness of these pretreatments (room temperature) does not allow for complete alteration of the crystalline structure but generates a more reactive surface (mainly after treatment with HNO_3) that produces and a significant increase in HMF production, achieving HMF selectivities higher than 50%. Reusability tests indicate that the zeolite remains active once the unreacted cellulose is removed by calcination, obtaining a perfect correspondence in conversion and product distribution (49% of cellulose conversion, >44% of HMF selectivity).

Future work in this field must integrate this reaction system that produces the HMF with high selectivity at soft conditions and using dilute acid systems, with the use of green organic solvents for the HMF selective extraction, expecting to obtain a suitable process to produce this relevant platform molecule.

CRediT authorship contribution statement

Paula Rapado: Methodology, Investigation, Data curation. **Diego Garcés:** Methodology, Investigation. **Salvador Ordonez:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Laura Faba:** Writing – original draft, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.118309.

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