

# Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules

Paula Rapado, Laura Faba, Salvador Ordóñez\*

Catalysis, Reactors and Control Research Group (CRC), Dept. of Chemical and Environmental Engineering, University of Oviedo, Oviedo 33006, Spain

\*sordonez@uniovi.es, Tel: +34 985 103 437; Fax: + 34 985 103 434

## Abstract

The effect of oxidative and reductive delignification processes on the hydrolysis of pine sawdust at mild conditions (200-1000 ppm of HCl and 140-220°C) is studied in this work. Dimers and reduced sugars are the main products obtained with the fresh sawdust (>82 %), reaching a maximum liquid phase yield of 17 % after 8 h, at the strongest conditions. This conversion increases up to almost 40 % with the pretreated sawdust, obtaining selectivities higher than 87 % of levulinic acid and a well-defined distribution of the relevant platform molecules (sugars, HMF, furfural, levulinic acid) as function of the severity of the reaction, decreasing the humins formation and being possible to define different conditions to maximize each yield. These conclusions were corroborated by the kinetic analysis, obtaining a clear decrease in the energy activation for all the individual steps involved in this process.

**KEYWORDS:** Acid hydrolysis, glucose, HMF, furfural, levulinic acid.

## 1. Introduction

Biomass is, after atmospheric CO<sub>2</sub>, the most abundant carbon source. Considering its renewable character and its well-dispersed distribution around the planet, biomass is the most promising alternative to replace the mineral sources, mainly to obtain chemical compounds at large scale, in a biorefinery concept (Gallo and Trapp, 2017; McKendry, 2002; Peters et al., 2011; Pileidis and Titirici, 2016). Thermochemical processes, such as pyrolysis, gasification or liquefaction, have been proposed for its global valorization obtaining favorable results (Dhyani and Bhaskar, 2018; Faba et al., 2015; Luque and Speight, 2015; Zhou et al., 2011). In the last years, catalytic routes have also focused the attention of many researchers (Gómez Millán et al., 2019; Mukherjee et al., 2015), considering different processes to specifically valorize one of the main fractions of the biomass: cellulose (38-50 %), hemicellulose (23-32 %) or lignin (15-30 %) (Alonso et al., 2010; Gómez Millán et al., 2019). These processes are more sustainable than thermochemical routes (mild temperatures and low pressures) and produce the intermediates of a huge variety of commodities, as well as biofuel precursors (Gómez Millán et al., 2019). The hydrolysis is one of the main alternatives proposed in this field, allowing obtaining sugar monomers and derived aldehydes and acids from hemicellulose and cellulose fractions, interesting platform molecules as intermediates of high-value chemical products.

The presence of lignin fraction affects the efficiency and product distribution obtained with this process. Working at soft conditions, lignin decreases the hydrolysis rate, since it reduces the contact between the catalyst and the (hemi)cellulose polymers. On the other hand, if reaction conditions are strong enough to alter the lignin structure, its decomposition could produce different undesired products or enhance oligomerization and humins productions,

reducing the selectivity to the desired fractions (Zhou et al., 2017). In addition, a great effort has been recently paid in the lignin upgrading, especially to obtain oxygenated aromatic compounds (Van den Bosch et al., 2015). Thus, from both points of view, understanding the effect of the lignin on the hydrolysis mechanism, as well as determining the effect of the different delignification procedures on the reactivity of the resulting (hemi)cellulosic fraction is of key interest in the integral upgrading of lignocellulosic biomass and wastes.

Different procedures have been suggested to remove the lignin from lignocellulosic biomass (delignification). Some of them are already implemented in paper-mill industries. Thus, lignin can be removed using basic catalysis, such as KOH, NaOH and Na<sub>2</sub>S (Kraft process), at moderate pressures and a temperature range of 140-170°C (Schutyser et al., 2018; Vu et al., 2004). Strong acids, H<sub>2</sub>SO<sub>4</sub> or HCl at mild conditions (120-210 °C) are also proposed, being not so often used because of the corrosion problems (Schutyser et al., 2018; Sturgeon et al., 2014). The extraction by the selective extraction in organic solvents (Organosolv process) is also proposed at industrial scale (Baig et al., 2019; Romaní et al., 2011). All these pretreatments are focused on the valorisation of cellulosic fraction, producing irreversible damage in the hemicellulosic one.

Trying to prevent the damage to the hemicellulose, two softer alternatives were considered: oxidative and reductive methods. The oxidative method usually uses sodium chlorite, which is *in situ* transformed into chlorine dioxide. This compound breaks the lignin structure by a complex and non-well defined mechanism, without altering the cellulose and hemicellulose until removing around 60 % of the lignin (Siqueira et al., 2013). On the contrary, reductive delignification is carried out with Ru/C catalyst under H<sub>2</sub> atmosphere, obtaining a “lignin oil” composed by monomers and short oligomers of aromatic compounds that are isolated from

the sugar matrix with quality enough to be valorised in subsequent steps (Van den Bosch et al., 2015).

As to the hydrolysis, it could take place catalyzed by organic acids (oxalic acid), inorganic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ), salts ( $(\text{NH}_4)_2\text{SO}_4/\text{SO}_3$ ), Lewis acids ( $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ) and ion exchange resins (Garcés et al., 2019; Kang et al., 2018). Mechanistic studies considering unaltered biomass or commercial polymers conclude that there is a sequential depolymerization, firstly in short oligomers (polysaccharides), being totally hydrolyzed in monosaccharides (mainly glucose, xylose and arabinose). Reaction conditions promote the dehydration of these sugars into the corresponding cyclic aldehydes (HMF, furfural) mainly when using Lewis acids (Marianou et al., 2018). These acids catalyze the isomerization of glucose into fructose, sugar that yields the highest HMF yields (Thapa et al., 2017). On the other hand, when using Brønsted acids, this isomerization does not take place and the cyclic dehydration is thermodynamically less favorable. In addition, Brønsted acidity promotes the degradation of HMF (cyclic break-up and rehydration), obtaining formic and levulinic acid (Garcés et al., 2017; Mukherjee et al., 2015; Van den Bosch et al., 2015). Thus, reaction conditions must be balanced to optimize the production of HMF or levulinic acid, the most relevant platform molecules (Garcés et al., 2017; Gómez Millán et al., 2019). Despite the huge number of studies in this field, there is a relevant gap related to the effect of a previous biomass delignification on the final hydrolysis results.

This work analyses the effects of the oxidative and reductive delignification pretreatments in the subsequent hydrolysis of pine sawdust. The hydrolysis is studied using  $\text{HCl}$  as catalyst, considering the influence of temperature and acid concentration. The aim of this work is to identify the optimum conditions to enhance the production of different platform molecules,

levulinic acid and HMF being the most relevant ones. Despite the HMF is faster produced after the isomerization of glucose into fructose by the presence of a Lewis acid (Rosatella et al., 2011; Toftgaard Pedersen et al., 2015), a mineral acid is proposed as catalyst considering that temperature and time could balance the kinetic without introducing a solid catalyst that could significantly reduce the kinetic of the first step of the reaction, due to the low efficiency of the solid-solid interactions (Chen et al., 2018).

## **2. Materials and methods**

### **2.1. Materials**

Pine sawdust was collected from a furniture factory located in Asturias, Spain. D-glucose ( $\geq 99.5\%$ ), xylose ( $\geq 99\%$ ), arabinose ( $\geq 99\%$ ), cellobiose (98%), maltotriose (98%) were purchased from Panreac Applichem. HMF ( $\geq 99\%$ ), furfural ( $\geq 99\%$ ), levulinic acid (98%) for HPLC calibration and acetic acid (98%) sodium chlorite (98%) and 5% Ru/C catalyst were purchased from Sigma-Aldrich. Methanol (98%) was purchased from VWR and hydrochloric acid (37%) was provided by Fisher Chemical. The reactants were used without any further purification. Solutions were prepared using distilled water.

### **2.2. Sawdust characterization**

The determination of the content of carbon, hydrogen, nitrogen and sulfur of sawdust (raw and delignified ones) has been carried out using an elemental analyzer C, H, N, S Elemental Vario EL available at the Scientific-Technical Services of the University of Oviedo. Chemical component analysis including cellulose, hemicellulose, lignin, and extractives of sawdust

(raw and delignified ones) was carried out following standard procedures (Li *et al.*, 2004; Selvaraju and Bakar, 2017).

### 2.3. Delignification procedures

The oxidative delignification was carried out according to the procedure proposed in the literature (Yu *et al.*, 2011), using sodium chlorite and acetic acid (w/v = 3:1) as reactants. 15 g of natural sawdust was mixed to 600 mL distilled water in a ball flask with a reflux. When the temperature reaches 80 °C, 7.5 g of acetic acid were added, and 22.5 g sodium chlorite were dosed in four times (every 30 min). After this time, the delignified sawdust was washed with distilled water until washings were colorless, then rinsed again with distilled water for 3 times. Finally, the sample was dried in an oven at 110 °C and milled to a particle size of 200 µm.

The reductive delignification was performed according to Van den Bosch proposal (Van den Bosch *et al.*, 2015). 10 g of raw sawdust, 1.5 g of 5% Ru/C and 200 mL of methanol were loaded into a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal). The reactor was purged with N<sub>2</sub> and pressurized with 25 bar H<sub>2</sub> at room temperature. The mixture was stirred at 700 rpm and the temperature was increased to 150 °C for 6 h.

### 2.4. Sawdust hydrolysis

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) with a back-pressure regulator and a PID temperature controller. 3 g of pine sawdust were suspended in 0.2 L of reaction volume. Once the desired temperature was reached (140-220 °C as function of the experiment), 12 mL of an HCl solution were added to achieve the desired concentration in each experiment (from 200 to 1000 ppm). Air was

purged with N<sub>2</sub>, and the hydrolysis was carried out with 10 bar of N<sub>2</sub> with a stirring of 700 rpm for 8h. Samples were taken from the sampling port, filtered using 0.22 µm Nylon syringe filters and diluted in a 1:2 ratio. Reactants and products of hydrolysis were quantified by HPLC (1200 Series, Agilent) equipped with a RI detector and a Hi-Plex H column, using 0.5 mL/min of 5 mM H<sub>2</sub>SO<sub>4</sub> as a mobile phase.

The sawdust conversion is calculated in terms of liquid-phase carbon yield, a concept involving the theoretical sawdust required to obtain all compounds detected in the liquid phase, extensively used in biomass conversion (Garcés et al., 2019; Giannakopoulou et al., 2010; Kluska et al., 2019). The direct use of the conversion calculated from solid weight measurement before and after the reaction is discarded since the temporal evolution cannot be analyzed based on this parameter, and the accurateness is limited by the presence of humins or other insoluble products (mainly the trimers). The liquid-phase carbon yield is calculated according to Equation (1):

$$\varphi_s = \frac{V \cdot \sum(n_i \cdot C_i) \cdot MW_C}{\%C \cdot m_{sawdust}} \cdot 100 \quad [1]$$

Where “V” is the volume of the solution; “C<sub>i</sub>”, the molar concentration of each compound detected in each liquid phase; “n<sub>i</sub>”, the number of carbons in the molecule of “i” compound; “m<sub>sawdust</sub>” is the mass of cellulose introduced in the reactor at the initial point; “MW<sub>C</sub>” is the molar mass of carbon; and “%C” corresponds to the mass percentage of carbon in this sawdust, according to the elemental analysis.

The selectivity to any individual product quantified in the liquid phase is indicated in carbon basis, according to Equation (2):

$$S_i (\%) = \frac{n_i \cdot C_i}{\sum_{j=1...i}^n n_i \cdot C_i} \cdot 100 \quad [2]$$

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

With the aim to guarantee the reproducibility of these analyses, each reaction was carried out at least twice. Considering the heterogeneity and complexity of this raw material, results were validated if the standard deviation between two experiments is lower than 7 %. In case of a higher discrepancy, a third experiment allowed defining the good results. As consequence, all the values shown in this work correspond to the average of two experiments.

### 3. Results and discussion

#### 3.1. Sawdust characterization before and after delignification

The amount of cellulose, hemicellulose and lignin was determined before and after the delignification pretreatments, the results being summarized in **Table 1**. Each analysis was carried out twice obtaining deviations lower than 3%. Results shown in Table 1 are the average values obtained with both analyses.

Data obtained for natural sawdust are in good agreement with typical composition of softwood, with percentages from 25 to 35 % of the three main polymers and less cellulose than hardwood (Cotana et al., 2014). From a macroscopic point of view, the oxidative pretreatment seems to be quite efficient, since the original brown color of the pine sawdust



disappears, obtaining a white material. This evolution is a clear consequence of the lignin removal (Trisant and Gunardi, 2020), and it is not totally observed in the case of the reductive pretreatment. However, the use of a carbonaceous support could alter this appreciation.

Considering the quantitative analysis, the lignin content decreases considerably after both pretreatments, with the subsequent increase in the relative percentage of cellulose or hemicellulose. Thus, 81.5 % of lignin is removed in case of the oxidative delignification, whereas this value increases up to more than 88 % with the reductive method. These values are in good agreement with previous literature applied to other raw materials, suggesting that the reductive pretreatment is more effective than the oxidative one (Hubbell and Ragauskas, 2010; Van den Bosch et al., 2015). Despite the similar delignification efficiency, significant differences between both methods related to the effects on the hydrocarbon structure are observed. It can be concluded that the reductive method mainly affects the lignin fraction, since the decrease in the proportion of this fraction directly correlates with the increase in the cellulose and hemicellulose ones (theoretical values corresponding to this delignification ratio: 42.2 % of cellulose and 53.4 % of hemicellulose), with slight differences (less than 4 %) in favor of hemicellulose. This fact indicates that only a small fraction of cellulose is partially degraded, obtaining a less crystalline structure with similar behavior as the hemicellulose. On the other hand, when the oxidative method is used, the expected percentages of cellulose and hemicellulose if only lignin was removed would be 41 and 52 %, respectively. Considering the high discrepancy with respect to the values obtained, a partial degradation of hemicellulose is produced. It removes a relevant fraction of external functional groups, obtaining a high ordered polymer, with a structure closer to cellulose than to the initial hemicellulose one. This conformation evolution could affect the sawdust

behavior in hydrolysis conditions, being not possible to determine if this is a positive or a negative effect before being tested in the reaction. According to these results, the reductive pretreatment is less aggressive with the hemicellulosic structure of the sawdust, obtaining a more selective delignification than with the oxidative one.

This hypothesis is corroborated by the elemental analysis, whose results are also summarized in Table 1. Regarding to the fresh material, values are similar to those proposed in the literature for other softwoods (Shen et al., 2010). Results related to delignified samples are congruent with the removal of lignin, with a decrease in N and C, and a slight increase in the oxygen percentage (present in high amount in sugar structures). The decrease in the C/H ratio is also congruent with the removal of aromatic rings, typical structures of lignin fractions, and the prevalence of saturated compounds. The more marked changes observed with the oxidative method are in good agreement with its more aggressive character. This fact suggests that samples after reductive pretreatment have lost the lignin fixed structure, but the total decomposition is not achieved, with some S and N still remaining in the solid sample.

### 3.2. Hydrolysis of fresh sawdust

The acidic hydrolysis of fresh sawdust (without any pretreatment) was carried out using HCl as catalyst, in the range 200 – 1000 ppm, in order to identify the optimum conditions, and to determine the effect the pH in these reactions. The mineral acid has been reported as an active catalyst for the hydrolysis of biomass polymers (Marianou et al., 2018; Sarno et al., 2020; Yang et al., 2012), but it could also enhance the subsequent steps of sugar dehydrations and degradations, obtaining acids and humins (Clauser et al., 2020; Garcés et

al., 2017; Garcés et al., 2019). Thus, a balance between positive and negative effects requires a well-defined concentration, different for each type of wood, trying to enhance the production of desired platform molecules. A blank experiment was done to discard the hydrothermal hydrolysis, despite being not expected considering the temperatures of the non-catalytic hydrolysis reported in the literature (Kruse and Gawlik, 2003; Toor et al., 2011). The evolution of the liquid-phase carbon yield with the time is analyzed in **Figure 1a**. Values plotted in this figure correspond to the average ones after two repetitions, obtaining standard deviations lower than 7 % in all the cases, as observed by the small error bars than, in some cases, cannot be appreciated.

Results obtained with 200 ppm indicate an almost negligible degradation activity at these conditions, reaching constant yield in less than two hours (0.9 %). Considering the total amount of carbohydrates present in the sawdust (cellulose and hemicellulose), this liquid-phase carbon yield represents 1.8 % of the maximum theoretical grade of hydrolysis. A clear evolution is observed when increasing the acidity up to 600 ppm, with a maximum carbon yield obtained after 4 h of reaction (12.5 %). This value corresponds to the hydrolysis of 24.6 % of the total sugar fractions in this sawdust. Once the maximum is reached, it keeps constant with the time, without observing any evolution when the reaction is extended up to 24 h. This result suggests that conditions are not severe enough to degrade the recalcitrant structure of biomass polymers. This hypothesis is congruent with results obtained with 1000 ppm of HCl, observing a faster hydrolysis that only reaches a maximum of 15.6 % (equivalent to 31.4 % of the sugar polymers). This value, obtained after 5 h, is not stable, followed by a continuous decrease for products detected, up to 9.8 % after 24 h. Considering the irreversible character of this reaction, the decreasing trend suggests that, at these conditions, different side reactions involving solid products (humins production) take

place. According to the literature, humins are formed by cross-polymerization reactions between HMF, furfural and sugars during the acid catalyzed hydrothermal hydrolysis (Patil et al., 2012; van Zandvoort et al., 2013). The fact that this is only observed at the most severe conditions suggests a different product distribution, which is analyzed in **Figure 2**.

This figure analyses the results in terms of carbon selectivities. The compounds considered for this analysis represent a carbon balance closure higher than 60 % in all the cases, the value being higher as the acidity decreases (70.4, 75.4 and 60.5 %, for 200, 600 and 1000 ppm of HCl, respectively). Seven compounds derived from the typical route of acid-catalyzed biomass hydrolysis are detected: dimers (corresponding mainly, but not only, to cellobiose), three reduced sugars (glucose, arabinose and xylose), HMF (cyclic aldehyde derived from hexose), furfural (cyclic aldehyde derived from pentoses), levulinic and formic acids. These last two products are obtained by the rehydration of HMF in equimolar amounts. Considering that there is not any other reaction that consumes any of these acids, same concentrations of both acids are obtained, so only levulinic acid is shown in the graphs (to prevent repeated information). An almost perfect carbon balance closure is obtained (higher than 90 % in all the cases) if this analysis is completed with light alcohols detected at significant extent. These alcohols are identified as terminal units of sugar polymers, this location justifying the high amount obtained. However, as these compounds do not interfere in the main reaction scheme, they are not included in the following analyses.

As anticipated by the soft conditions (low temperature and low acidity), dimers are the main product obtained during the first 7 h, despite the HCl concentration used. The absence of glucose and the detection of arabinose and xylose during the first 2 h is congruent with the recalcitrant structure of cellulose and the presence of pentoses in the external structure of

hemicellulose (weakest bonds, the most easily hydrolyzed ones). With 200 and 600 ppm of HCl, the relative relevance of these pentoses decreases as the incomplete hydrolysis of cellulose increases, observing low amount of glucose and suggesting that most of the dimers correspond to cellobiose (experimentally tested). Thus, stable selectivities around 7 % of total reduced sugars (TRS) are obtained during the first 7 h. A slight improvement with the time is observed, with an increase up to 17 and 13.7 % of TRS, with 200 and 600 ppm. However, considering the low hydrolysis degree, these values only correspond to 68 and 277 ppm of TRS, respectively. As anticipated, no aldehydes or acids are observed at these conditions. The evolution with 1000 ppm is considerably different, with a relevant formation of TRS (24 % after 7 h, 52.8 % after 24 h, corresponding with 686 and 1020 ppm, respectively). Aldehydes formation is clearly observed after 24 h, with 8 % of HMF and 10.2 % of furfural, whereas levulinic acid is not detected in these experiments. The presence of aldehydes in the liquid phase is congruent with the promotion of humins and the decrease in the carbon balance.

According to these results, increasing the reaction temperature working with 1000 ppm of HCl is suggested as the following approach, trying to balance the promotion of the desired steps with the avoidance of side reactions. The influence of temperature was studied in the range 140-220 °C, obtaining the evolution of the liquid-phase carbon yield observed in

**Figure 1b.**

Experimental results follow the anticipated trend considering the positive effect of temperature in the kinetics and the relevance of side reactions obtained when working at 140 °C. Thus, there is a first increase in the liquid-phase carbon yield, reaching a maximum value of around 16 %, despite the temperature. This result indicates the maximum hydrolysis

efficiency at these conditions, corresponding with 34 % of the potential amount of sugars.

This result suggests that temperature is not the key parameter for this variable. However, it is worth noticing that this first step requires less time as the temperature increases, i.e., 4-5 h, 2 h and around 1.5-2 h at 140, 180 and 220°C, respectively. After these maximums, the relevance of side reactions is clearly observed, being promoted by the temperature. In good agreement, final carbon balance closures after 24 h decrease from 59 % to 54 and 33 %, as the temperature increases.

These results only consider the solubilization of sugar fractions, the analysis of selectivities being required to determine the optimum conditions for recovering each platform molecule. The simultaneous comparison after different reaction times is plotted in **Figure 3**.

A clear influence of reaction temperature is observed, being all the products observed from the first hour when temperature is higher than 140 °C. Xylose is the main product detected at intermediate temperatures and short times, whereas a fast dehydration is observed at 220 °C, aldehydes and acids prevailing over the TRS. The similar amount of arabinose obtained at 180 and 220 °C, not only in selectivity but also in concentration. This result suggests that furfural is mainly produced by the dehydration of xylose, pentose for which the differences are more marked. The glucose dehydration to produce HMF is observed at 180 and 220 °C, with selectivities of 5.6 and 14.5 %, respectively, in less than 1 h. According to the previous literature, Lewis acidity is defined as a key factor to promote the HMF via glucose isomerization, since the fructose dehydration is thermodynamically favored (Marianou et al., 2018). The role of temperature in this step is more relevant when the catalyst is a Brønsted acid (such as the HCl), because of the higher activation energy of the direct glucose dehydration (Yang et al., 2012).

At larger reaction times, side reactions determine the observed product distribution. On the one hand, the almost total rehydration of HMF into levulinic and formic acid is clearly observed at 220 °C, with the disappearance of this aldehyde and a relevant increase of levulinic acid selectivity (60, 66 and 68 % after 4, 7 and 24 h). This effect is less marked at 180 °C. On the other hand, the furfural total amount reaches a maximum of 330 ppm at 180 °C after 4 h (selectivity of 21 %), with a soft decrease to 250 ppm after 24 h (equivalent to 18 % of selectivity). However, this effect is much more relevant at 220 °C, reaching the maximum furfural concentration (270 ppm) after only 2 h, with a total disappearance of this compound in less than 5 h, due to the promotion of humins.

According to these results, there is not a clear range of conditions to maximize the productivity and selectivity of almost any compound. This fact seems to be determined by the low rate of the first step of the process: the sugar solubilization to produce TRS. Thus, all the concentrations are quite low, and the reaction conditions required to promote this step are so strong that the subsequent steps occur too fast. In this context, the lignin pretreatment could play a relevant role since a feasible degradation of the recalcitrant structure of sugar polymers could reduce the severity requirements to enhance the hydrolysis. Then, the temperature and reaction time would have a key role in maximizing the productivity and selectivity of the platform molecules.

### 3.3. Influence of the oxidative and reductive pretreatments

To identify the effect of both pretreatments, the comparative analysis of liquid-phase carbon yield obtained is shown in **Figure 4** (Fig. 4a and 4b). In these plots, values over and below the diagonal line indicate higher or lower values once the pretreatments are applied with respect to the reaction with fresh sawdust, always comparing data at same conditions

(temperature and acidity) and time on reaction. The discrepancies between results of each pair of experiments were lower than 8 % in all the cases, 2-3 % being the typical errors obtained. The error bars are included in the temporal profiles of concentration evolutions.

The comparison considering the total amount of sawdust treated (Fig. 4a) indicates that both pretreatments have a positive effect in the liquid-phase carbon yield, duplicating the values at almost all the conditions, reaching maxima close to 40 % when the oxidative pretreatment is applied, at 180 and 220 °C. In addition, the humins production slows down, in good agreement with the increase of the carbon yield increases observed for the pretreated samples. For example, at 220 °C, a decreasing trend is observed after 2 h of reaction, this time being increased up to 5 and 7 h, after the reductive and oxidative pretreatment, respectively. However, if same values are analyzed considering only the potential maximum amount of sugars (Fig. 4b), these values are quite different, since they are strongly affected by the almost total absence of lignin in the pretreated samples. In this case, the differences between reductive and oxidative pretreatments are more evident, with a clear prevalence of the oxidative one, when working at with 1000 ppm of HCl and 180 or 220 °C. Softer conditions (600 ppm and 140 °C) do not imply any improvement with respect to the hydrolysis of fresh sawdust. Despite the low values obtained when working with 200 ppm of HCl, around 10 % of liquid-phase carbon yields is reached with both pretreatments whereas no reaction is observed with the fresh material. Two main conclusions of these results can be drawn: i) pretreatments do not modify the potential amount of sugar polymers (increase or reduction) that can be hydrolyzed at these conditions; ii) these pretreatments seem to debilitate the glycosidic bonds, reducing the severity to obtain a similar hydrolytic efficiency. A deeper study of these pretreatments requires the analysis of the products distribution, these data being shown in **Figure 5**.



Reactions carried out with 200 ppm of HCl mainly produce dimers and TRS, the dimer concentration being always higher with the oxidative pretreatment than with the reductive one. Thus, in the case of the oxidative pretreatment, dimers correspond to 90 % of the total liquid products during the first 4 h of reaction, decreasing only to 75 % after 7 h. On the contrary, an initial 41 % of dimer is obtained with the reductive pretreatment, with less than 6 % observed after 7 h, when more than 89 % of the total selectivity corresponds to TRS and small traces of aldehydes can be observed (1.5 % of HMF and 3.7 % of furfural). Thus, these conditions are identified as the optimum ones to selectively obtain these sugar monomers, the mixture being always enriched in xylose (75 and 80 % when working with the oxidative and reductive treated sawdust). In concentration values, working with 200 ppm, 1.55 g/L of TRS is obtained when working with the treated sample (reductive pretreatment), this value being more than 3 times higher than the value obtained with the oxidative pretreated sample, and 140 times higher than the corresponding one obtained with the fresh sample.

A logical evolution with the acidity, temperature and reaction time is obtained, despite the samples analyzed, with an increase in the degradation process as all these parameters increase. In general, reactions with the oxidized samples suggest a more sensitivity to the reaction parameters, being difficult to control the reaction in the intermediate steps. Thus, levulinic and formic acid are the main compounds identified in the samples at 220 °C after only 1 h of reaction, 79 % of selectivity, whereas the corresponding value obtained with the samples pretreated with Ru/C is lower than 10 %. These results conclude that the oxidative pretreatment is the optimum one to maximize the production of these platform molecules, obtaining almost a total degradation of all the sugars in less than 7 h (selectivity to levulinic acid higher than 86 %). This selectivity cannot be reached without a previous pretreatment, even increasing the reaction time up to 24 h. In concentration terms, this selectivity

corresponds to 3.2 g/L of levulinic acid produced with the oxidative pretreatment. With the reductive pretreatment, this amount is limited to 2.4 g/L, these two values being significantly higher than the one obtained during the hydrolysis of the fresh sample (0.8 g/L). An analysis of variance (ANOVA) comparing values obtained with fresh and pretreated samples corroborates the statistical significance of these differences, obtaining F-values more than one order of magnitude higher than the maximum ones that could be accepted to consider the results as equal, with a level of confidence of 95 %.

Concerning the aldehydes (HMF and furfural), a selective production of these intermediates is not possible, since HMF is faster degraded to levulinic acid and a high selectivity of furfural is limited by the undesired oligomerization. In any case, the pretreatments also imply an improvement at this point, the reductive process being the optimum to enhance the particular selectivity of furfural (19 % after 3 h of reaction at 180 °C with 1000 ppm of HCl, this selectivity being reduced to 16 % at 4 h). The maximum value obtained with the sawdust after the oxidative process is limited to 11 %. Seeing both aldehydes together, 35.4 % of both compounds are obtained in less than 1 h of reaction at 220°C with the reductive pretreatment. This selectivity corresponds with the maximum concentration observed for these compounds (1.2 g/L). This concentration is 1.8 times higher than the maximum one obtained with the fresh sawdust, 0.68 g/L after 4 h at 180°C with 1000 ppm of HCl. A similar selectivity than with the reductive process (34 %) is obtained with the oxidative pretreatment, even at softer conditions (180 °C, 4 h). However, considering the total conversion, this selectivity only corresponds with 0.75 g/L, this value being only half of the concentration reached after the oxidative pretreatment. As explained before, the ANOVA analysis of these results corroborates the significance of these results.

To globally identify the impacts of delignification processes in the sawdust hydrolysis, and considering the simultaneous effect of acidity, temperature and reaction time, the evolutions of different intermediates and final products are compared considering the combined severity factor (CSF). This parameter has been previously proposed in the literature to unify the role of all the variables involved in one coefficient, according to the following expression (Lee and Jeffries, 2011; Rogalinski et al., 2008):

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

where “ $t$ ” is the reaction time of hydrolysis in minutes, “ $T$ ” is the reaction temperature in Celsius, “ $T_{ref}$ ” is the reference temperature, most often 0 °C, and pH is the acidity of the aqueous solution measured before reaction. In this case, these values correspond to 2.1, 1.8 and 1.6, for reactions with 200, 600 and 1000 ppm of HCl, respectively. The concentrations of total reduced sugars (TRS), aldehydes and acids as function of the CSF values are plotted in **Figure 4** (parts c to e).

The soft trends obtained for all the compounds studied corroborate the utility of this parameter, showing distributions with clear maxima, which indicates a common evolution as function of the acidity, temperature, and reaction time for all the platform molecules. A similar effect of both pretreatments in the TRS productivity is observed (Fig. 4c), with a maximum clearly concentrated in CSF values 4.5 – 5 and a fast decrease in the concentration at both, lower and higher CSF values. In these two cases, the maximum concentration is close to 3 g·L<sup>-1</sup>. More severe conditions are required in the hydrolysis of the fresh sawdust, with and more extensive optimum CSF range from 5 to 6. Even at the optimum conditions, the total amount of sugars obtained is significantly lower than with the pretreated sawdust (maximum 0.75 g·L<sup>-1</sup>).

As to the aldehydes (HMF and furfural), the maximum obtained with the fresh sawdust is concentrated in a very narrow range (5.8 -6.4), without observing HMF nor FFL with CSF values under 5. The concentration at these optimum conditions,  $0.8 \text{ g}\cdot\text{L}^{-1}$ , is also the optimum obtained with the oxidative pretreatment, the most relevant difference being the presence of aldehydes even at CSF values lower than 5. The most extended range is observed for the sawdust after the reductive pretreatment, obtaining aldehydes almost at all the conditions tested. However, this sawdust follows a flat evolution in the range 5 – 6.5, being not possible to identify clear optimum conditions, and with a maximum concentration lower than  $0.5 \text{ g}\cdot\text{L}^{-1}$ .

In concentration terms, acids (levulinic and formic acid considered together) are the compounds more affected by the pretreatment used. However, the general trends are the same, and CSF values higher than 6.5 are required in all the cases to obtain these compounds in significant amounts. The clearest difference is then the slope of this increasing trend, the oxidative pretreatment being the most efficient one to increase acid yields.

According to this analysis, the oxidative delignification method is considered as the best one to clearly identify different optimum conditions, in terms of productivity and selectivity, for each platform molecule. On the contrary, these optimum values are partially overlapped with the reductive pretreated and fresh sawdust.

### 3.4. Kinetic study

To sum up, relevant influences are observed as function of the pretreatment carried out.

These higher reaction progresses can be analyzed in kinetic terms, proposing a kinetic model

to describe the solubilization of hexoses and pentoses present in sawdust as well as their degradation to HMF, furfural and levulinic and formic acids. For this model, the quantity of sugar polymers is obtained as the difference between the initial amount (experimentally determined) and the sum of all compounds detected in liquid phase. The evolution of all the compounds (grouped by families) with the time could be assimilate to a sequence of irreversible first-order steps in series configuration, see Eq. 3:



Where:

$C_P$  is the sum of hemicellulose and cellulose in the sawdust;  $C_D$  and  $C_M$  are the dimer and monomer (hexoses and pentoses) concentrations detected in the liquid phase, respectively;  $C_{ald.}$ , the sum of HMF and furfural; and  $C_{ac.}$  the amount of formic and levulinic acid. All concentrations are expressed in g/L.

To guarantee the absence of any limitation because of the amount of HCl, only the set of reactions obtained with 1000 ppm of this catalyst were considered for the adjustment. This decision is justified by the negligible pH evolution observed in these experiments during the 8 h analyzed. Considering the possible humins formation, as well as the subsequent alteration in the theoretical amount of polymers, a fifth rate was evaluated, being the responsible of aldehyde oligomerization to obtain these solid deposits. Experimental data were fitted to this kinetic model using MATLAB code ("ode45"). The fitting of the unknown parameters was accomplished by the least-square method using the "lsqcurvefit" function and the Levenberg-Marquardt algorithm, obtaining the kinetic rates summarized in **Table 2**. The comparison of these data requires corroborating the reliability of these values. An

ANOVA analysis confirms that temperature is a significant model terms that influences the kinetic of the hydrolysis, for fresh and pretreated samples, with p-values lower than 0.5 in all the cases (0.028, 0.022 and 0.016 for fresh samples and sawdust after oxidative and reductive pretreatments, respectively). The sawdust pretreatments also produce a relevant influence in the kinetic, mainly at 220°C, when the p value is 0.036. This influence is not so significant at lower temperatures, with p-values a bit higher: 0.17 and 0.11, for 140 and 180°C, respectively. These values are too high to conclude a clear influence of these pretreatments at low temperatures at this level of confidence (95 %). The p-values decrease up to less than 0.07 if only the first steps of the reaction are considered (sugar solubilization), in good agreement with the suggested hypothesis of a main effect of these pretreatments making easier the cellulose and hemicellulose hydrolysis, whereas the subsequent steps of the process are mainly conditioned by the acidity of the medium.

The good fit of this model with experimental values is shown in **Figure 6**, including the reactions at 220°C as examples. The good regression coefficients of kinetic rates as function of the temperature indicates an optimum adjustment of experimental data according to Arrhenius model. This model, previously proposed in the literature (Clauser et al., 2020; Rodríguez-Chong et al., 2004; Tsoutsos and Bethanis, 2011) represents a first approach to the kinetic since a deeper analysis would require individual steps for the hydrolysis of each sugar polymer, as well as particular steps of degradation of each monomer. However, the common existence of glucose in both polymers, cellulose and hemicellulose, prevents this possibility. Despite this general character, the influence of delignification pretreatments is clearly observed, with significant decreases in the activation energy of all the kinetic rates of the hydrolysis pathway. On the contrary, significant increases in the activation energy of undesired reaction is observed after both pretreatments, being more evident in the case of

the oxidation one. All these results are congruent with the initial assumption, considering that removing lignin has a positive effect increasing the accessibility to the sugar polymers, promoting their solubility and the subsequent steps. In addition, removing lignin as well as the external functional groups of hemicellulose (more evident in the case of oxidative pretreatment) significantly decreases the humins formation, preventing the oligomerization of aldehydes involved in the reaction.

#### **4. Conclusions**

Lignin strongly limits the hydrolysis of pine sawdust requiring so strong conditions that humins production restricts the process. Reductive and oxidative delignifications produce a positive effect, marked by a productivity of TRS 140 times higher than with the fresh sawdust and a relevant decrease in humins production. The best results obtained are 3.2 g/L of levulinic acid with a selectivity of 86% after 7 h of reaction at 220 °C and 1000 ppm of HCl applying the oxidative pretreatment, and 1.2 g/L of aldehydes (selectivity of 35.4 %) in less than 1 h, with the reductive pretreatment.

#### **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.

## Acknowledgments

This study has been financial supported by the Spanish Ministry of Economy and Competitiveness (CTQ2017-89443-C3-2-R). Paula Rapado thanks the financial support from the Principado de Asturias (contract FC-GRUPIN-IDI/2018000116).

## Electronic supplementary material

E-supplementary data for this work can be found in e-version of this paper online.

## References

1. Alonso, D.M., Bond, J.Q., Dumesic, J.A., 2010. Catalytic conversion of biomass to biofuels, *Green Chem* 12, 1493-1513.
2. Baig, K.S., Wu, J., Turcotte, G., 2019. Future prospects of delignification pretreatments for the lignocellulosic materials to produce second generation bioethanol, *Int. J. Energ. Res.* 43, 1411-1427.
3. Clauser, N.M., Felissia, F.E., Area, M.C., Vallejos, M.E., Gutiérrez, S., 2020. An energy-saving re-use strategy for the treatment of lignocellulosic biomass applied to the production of levulinic acid, *J Clean. Prod.* 257, 120549.
4. Cotana, F., Cavalaglio, G., Gelosia, M., Nicolini, A., Coccia, V., Petrozzi, A., 2014. Production of bioethanol in a second generation prototype from pine wood chips, *Energy Procedia.* 45, 42-51.
5. Chen, S.S., Wang, L., Iris, K., Tsang, D.C., Hunt, A.J., Jérôme, F., Zhang, S., Ok, Y.S., Poon, C.S., 2018. Valorization of lignocellulosic fibres of paper waste into levulinic acid using solid and aqueous Brønsted acid, *Bioresour. technol.* 247, 387-394.
6. Dhyani, V., Bhaskar, T., 2018. A comprehensive review on the pyrolysis of lignocellulosic biomass, *Renew. Energ.* 129, 695-716.
7. Faba, L., Díaz, E., Ordóñez, S., 2015. Recent developments on the catalytic technologies for the transformation of biomass into biofuels: A patent survey, *Renew. Sust. Energ. Rev.* 51, 273-287.
8. Gallo, J.M.R., Trapp, M.A., 2017. The chemical conversion of biomass-derived saccharides: an overview, *J Brazil Chem. Soc.* 28, 1586-1607.



9. Garcés, D., Díaz, E., Ordóñez, S., 2017. Aqueous phase conversion of hexoses into 5-hydroxymethylfurfural and levulinic acid in the presence of hydrochloric acid: mechanism and kinetics, *Ind. Eng. Chem. Res.* 56, 5221-5230.
10. Garcés, D., Faba, L., Díaz, E., Ordóñez, S., 2019. Aqueous-Phase Transformation of Glucose into Hydroxymethylfurfural and Levulinic Acid by Combining Homogeneous and Heterogeneous Catalysis, *ChemSusChem*. 12, 924-934.
11. Giannakopoulou, K., Lukas, M., Vasiliev, A., Brunner, C., Schnitzer, H., 2010. Conversion of rapeseed cake into bio-fuel in a batch reactor: Effect of catalytic vapor upgrading, *Micropor. Mesopor. Mat.* 128, 126-135.
12. Gómez Millán, G., Hellsten, S., Llorca, J., Luque, R., Sixta, H., Balu, A.M., 2019. Recent Advances in the Catalytic Production of Platform Chemicals from Holocellulosic Biomass, *ChemCatChem*. 11, 2022-2042.
13. Hubbell, C.A., Ragauskas, A.J., 2010. Effect of acid-chlorite delignification on cellulose degree of polymerization, *Bioresour. technol.* 101, 7410-7415.
14. Kang, S., Fu, J., Zhang, G., 2018. From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis, *Renew. Sust. Energ. Rev.* 94, 340-362.
15. Kluska, J., Ochnio, M., Kardaś, D., Heda, Ł., 2019. The influence of temperature on the physicochemical properties of products of pyrolysis of leather-tannery waste, *Waste Manage.* 88, 248-256.
16. Kruse, A., Gawlik, A., 2003. Biomass conversion in water at 330– 410 C and 30– 50 MPa. Identification of key compounds for indicating different chemical reaction pathways, *Ind. Eng. Chem. Res.* 42, 267-279.
17. Lee, J.-W., Jeffries, T.W., 2011. Efficiencies of acid catalysts in the hydrolysis of lignocellulosic biomass over a range of combined severity factors, *Bioresour. Technol.* 102, 5884-5890.
18. Li, S., Xu, S., Liu, S., Yang, C., Lu, Q., 2004. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas, *Fuel Process. Technol.* 85, 1201-1211
19. Luque, R., Speight, J.G., 1 - Gasification and synthetic liquid fuel production: an overview, in: R. Luque, J.G. Speight (Eds.) *Gasification for Synthetic Fuel Production*, Woodhead Publishing 2015, pp. 3-27.
20. Marianou, A.A., Michailof, C.M., Pineda, A., Iliopoulou, E., Triantafyllidis, K., Lappas, A., 2018. Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media, *Appl. Catal. A* 555, 75-87.
21. McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass, *Bioresour. Technol.* 83, 37-46.

22. Mukherjee, A., Dumont, M.-J., Raghavan, V., 2015. Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities, *Biomass Bioenerg.* 72, 143-183.
23. Patil, S.K., Heltzel, J., Lund, C.R., 2012. Comparison of structural features of humins formed catalytically from glucose, fructose, and 5-hydroxymethylfurfuraldehyde, *Eneg. Fuel* 26, 5281-5293.
24. Peters, M., Köhler, B., Kuckshinrichs, W., Leitner, W., Markewitz, P., Müller, T.E., 2011. Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain, *ChemSusChem.* 4, 1216-1240.
25. Pileidis, F.D., Titirici, M.M., 2016. Levulinic acid biorefineries: new challenges for efficient utilization of biomass, *ChemSusChem.* 9, 562-582.
26. Rodríguez-Chong, A., Alberto Ramírez, J., Garrote, G., Vázquez, M., 2004. Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment, *J. Food Eng.* 61, 143-152.
27. Rogalinski, T., Ingram, T., Brunner, G., 2008. Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures, *J Supercrit. Fluid.* 47, 54-63.
28. Romaní, A., Garrote, G., López, F., Parajó, J.C., 2011. Eucalyptus globulus wood fractionation by autohydrolysis and organosolv delignification, *Bioresour. Technol.* 102, 5896-5904.
29. Rosatella, A.A., Simeonov, S.P., Frade, R.F.M., Afonso, C.A.M., 2011. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications, *Green Chem.* 13, 754-793.
30. Sarno, M., Iuliano, M., De Pasquale, S., Ponticorvo, E., 2020. A new nano-catalyst for sawdust hydrolysis, *Appl. Catal. A* 602, 117686.
31. Schutyser, W., Renders, a.T., Van den Bosch, S., Koelewijn, S.-F., Beckham, G., Sels, B.F., 2018. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, *Chem. Soc. Rev.* 47, 852-908.
32. Selvaraju, G., Bakar, N.K.A., 2017. Production of a new industrially viable green-activated carbon from Artocarpus integer fruit processing waste and evaluation of its chemical, morphological and adsorption properties, *J. Clean. Prod.* 141, 989-999
33. Shen, J., Zhu, S., Liu, X., Zhang, H., Tan, J., 2010. The prediction of elemental composition of biomass based on proximate analysis, *Energ. Convers. Manage.* 51, 983-987.
34. Siqueira, G., Várnai, A., Ferraz, A., Milagres, A.M., 2013. Enhancement of cellulose hydrolysis in sugarcane bagasse by the selective removal of lignin with sodium chlorite, *Appl. Energ.* 102, 399-402.

35. Sturgeon, M.R., Kim, S., Lawrence, K., Paton, R.S., Chmely, S.C., Nimlos, M., Foust, T.D., Beckham, G.T., 2014. A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: implications for lignin depolymerization in acidic environments, *ACS Sustain. Chem. Eng.* 2, 472-485.
36. Thapa, I., Mullen, B., Saleem, A., Leibig, C., Baker, R.T., Giorgi, J.B., 2017. Efficient green catalysis for the conversion of fructose to levulinic acid, *Appl. Catal. A* 539, 70-79.
37. Toftgaard Pedersen, A., Ringborg, R., Grothkjær, T., Pedersen, S., Woodley, J.M., 2015. Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose-fructose mixtures, *Chem. Eng. J.* 273, 455-464.
38. Toor, S.S., Rosendahl, L., Rudolf, A., 2011. Hydrothermal liquefaction of biomass: a review of subcritical water technologies, *Energ.* 36, 2328-2342.
39. Trisant, P.N., Gunardi, I., 2020, The Influence of Hydrolysis Time in Hydrothermal Process of Cellulose from Sengon Wood Sawdust, *Macromolecular Symposia*, Wiley Online Library, pp. 2000016.
40. Tsoutsos, T., Bethanis, D., 2011. Optimization of the dilute acid hydrolyzator for cellulose-to-bioethanol saccharification, *Energies.* 4, 1601-1623.
41. Van den Bosch, S., Schutyser, W., Vanholme, R., Driessen, T., Koelewijn, S.-F., Renders, T., De Meester, B., Huijgen, W., Dehaen, W., Courtin, C., 2015. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps, *Energ. Environ. Sci.* 8, 1748-1763.
42. van Zandvoort, I., Wang, Y., Rasrendra, C.B., van Eck, E.R., Bruijninx, P.C., Heeres, H.J., Weckhuysen, B.M., 2013. Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions, *ChemSusChem.* 6, 1745-1758.
43. Vu, T.H.M., Pakkanen, H., Alén, R., 2004. Delignification of bamboo (*Bambusa procera* acher): Part 1. Kraft pulping and the subsequent oxygen delignification to pulp with a low kappa number, *Ind. Crop. Prod.* 19, 49-57.
44. Yang, G., Pidko, E.A., Hensen, E.J.M., 2012. Mechanism of Brønsted acid-catalyzed conversion of carbohydrates, *J Catal.* 295, 122-132.
45. Yu, Z., Jameel, H., Chang, H.-m., Park, S., 2011. The effect of delignification of forest biomass on enzymatic hydrolysis, *Bioresour. Technol.* 102, 9083-9089.
46. Zhou, C.-H., Xia, X., Lin, C.-X., Tong, D.-S., Beltramini, J., 2011. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, *Chem. Soc. Rev.* 40, 5588-5617.

47. Zhou, C., Zhao, J., Yagoub, A.E.A., Ma, H., Yu, X., Hu, J., Bao, X., Liu, S., 2017. Conversion of glucose into 5-hydroxymethylfurfural in different solvents and catalysts: Reaction kinetics and mechanism, Egypt. J. Petrol. 26, 477-487.

## FIGURE CAPTION

**Figure 1:** Temporal evolution of the liquid-phase carbon yield obtained in the hydrolysis of fresh sawdust as function of: (a) the acid concentration and (b) the reaction temperature. Data analyzed considering the total amount of sawdust (left axes) and only the potential sugars, cellulose, and hemicellulose (right axes). Results corresponding to (▲) 200 ppm of HCl, 140°C; (●) 600 ppm of HCl, 140°C; (◆) 1000 ppm of HCl, 140 °C; (▲) 1000 ppm of HCl, 180 °C, (●) 1000 ppm of HCl, 220 °C.

**Figure 2:** Comparative distribution of products selectivities obtained with fresh sawdust as function of the acidity. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue).

**Figure 3:** Comparative distribution of products selectivities obtained with the fresh sawdust as function of the reaction temperature. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue); and levulinic acid (purple).

**Figure 4:** Comparative analysis of liquid-phase carbon yields obtained with the pretreated (circles for the reductive delignification, diamonds for the oxidative one) and fresh sawdust considering (a) the total amount of sawdust; and (b) cellulose and hemicellulose. Results corresponding to: 200 ppm of HCl and 140°C (green), 600 ppm of HCl and 140°C (light blue), 1000 ppm of HCl and 140°C (dark blue), 1000 ppm of HCl and 180°C (gold), 1000 ppm of HCl and 220°C (red). Evolution of (c) TRS, (d) aldehydes, and (e) acids as function of the CSF factor. Data correspond to (▲) fresh sawdust; delignified sawdust using (◆) oxidative and (●) reductive pretreatments.

**Figure 5:** Comparative distribution of products selectivities obtained with the hydrolysis of pretreated sawdust as function of the reaction time. Left graphs related to reductive pretreatment; right graphs related to the oxidative one. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue); and levulinic acid (purple).

**Figure 6:** Kinetic adjustment of experimental data according to the kinetic model proposed. Results corresponding to hydrolysis at 220°C with 1000 ppm of HCl of the (a) fresh sawdust; (b) pretreated sawdust by oxidative method; and (c) pretreated sawdust by reductive method. Symbols: (◇) sugar polymer; (■) dimers; (▲) TRS; (◆) aldehydes; (●) acids.

## **TABLE CAPTION**

**Table 1.** Sawdust characterization, in terms of fractionation and elemental analysis, before and after delignification pretreatment. Result expressed in dry basis.

**Table 2:** Kinetic model parameters for the hydrolysis of sawdust catalyzed by 1000 ppm of HCl.

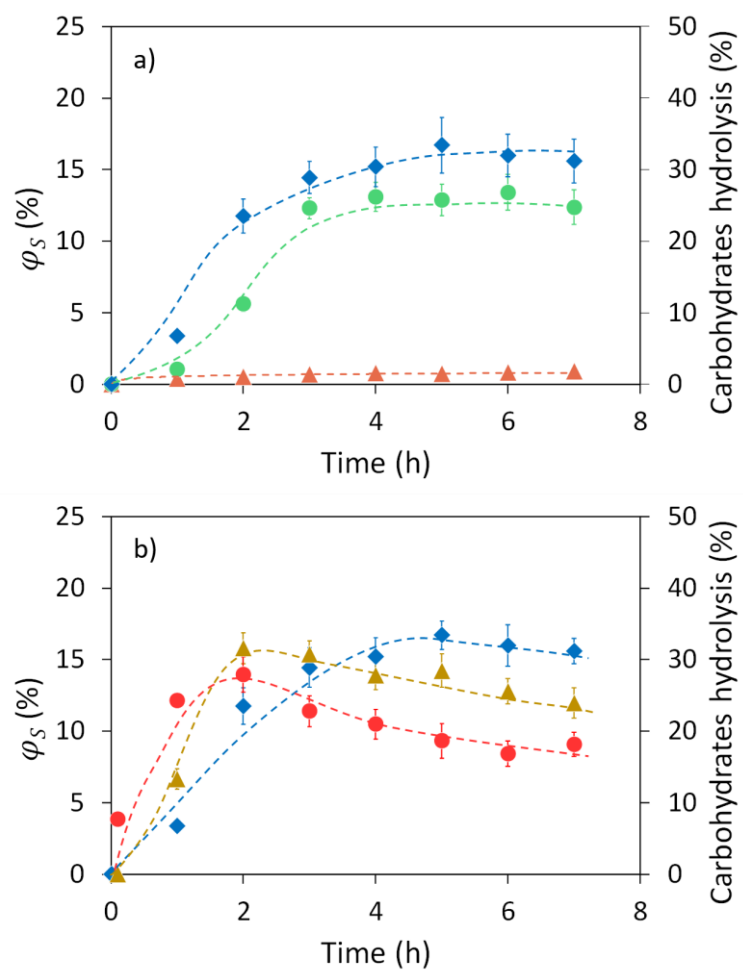


Figure 1

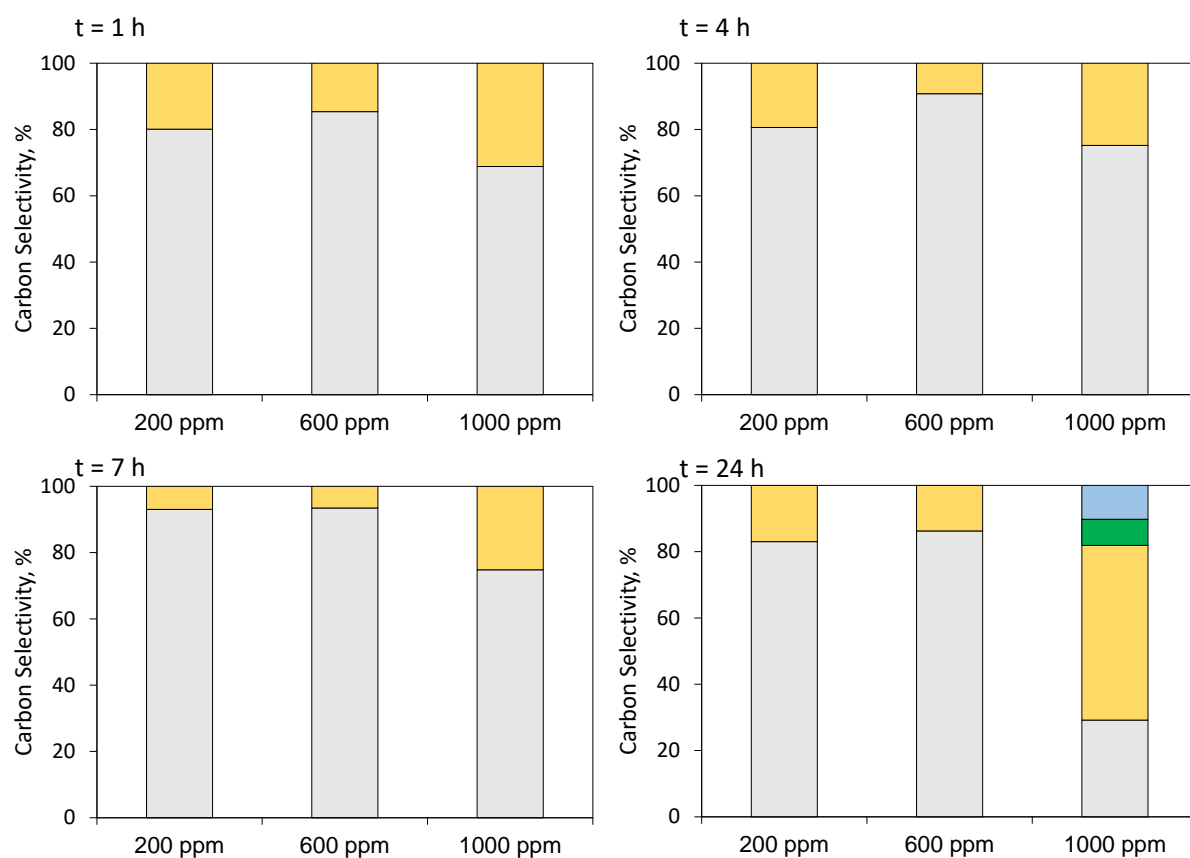


Figure 2



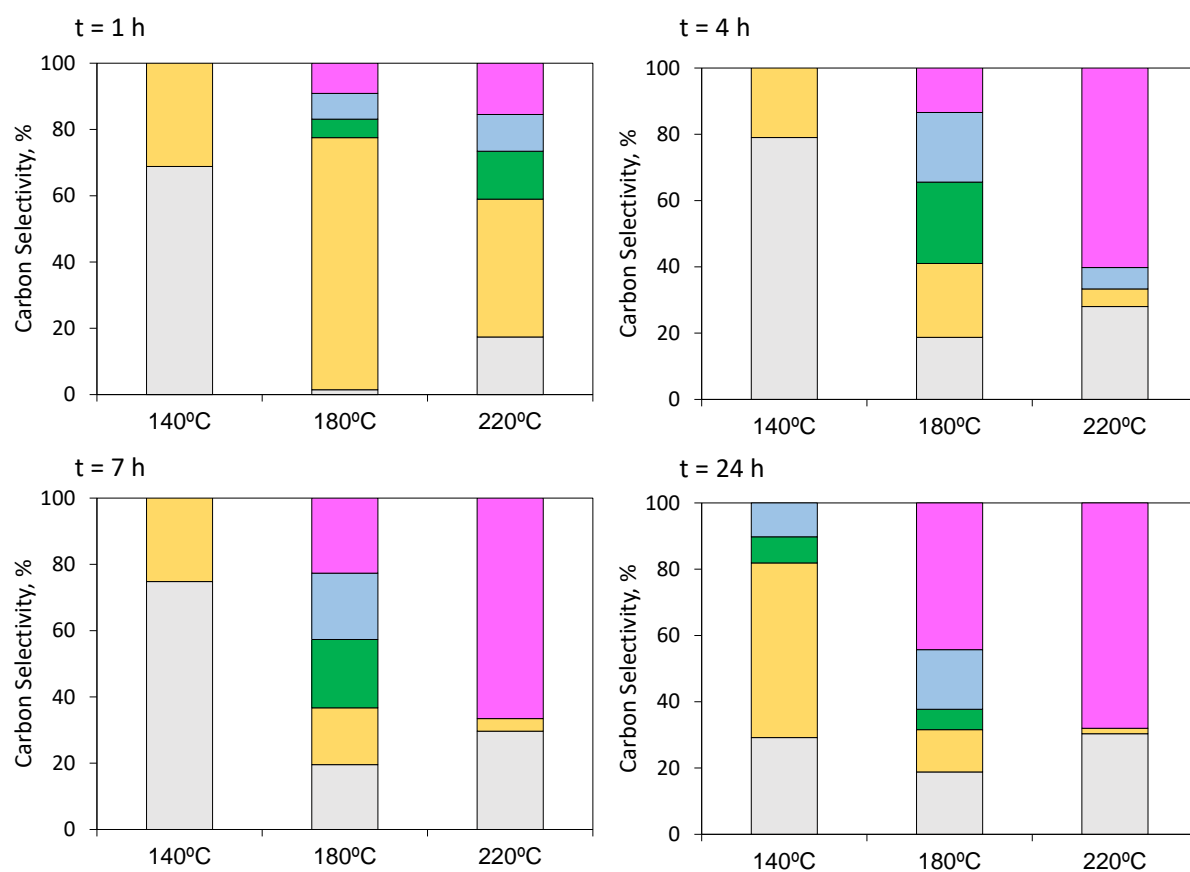


Figure 3

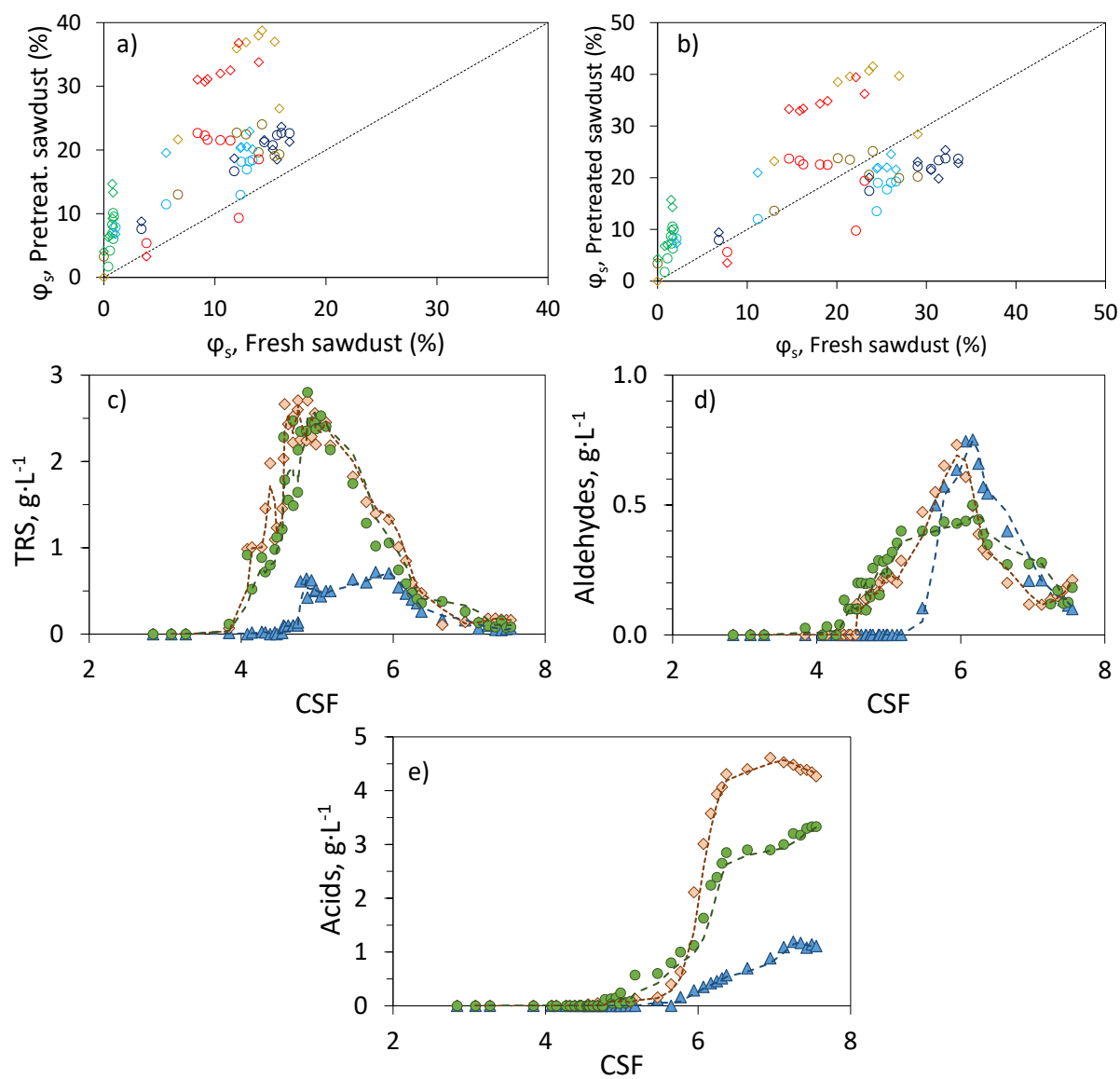


Figure 4

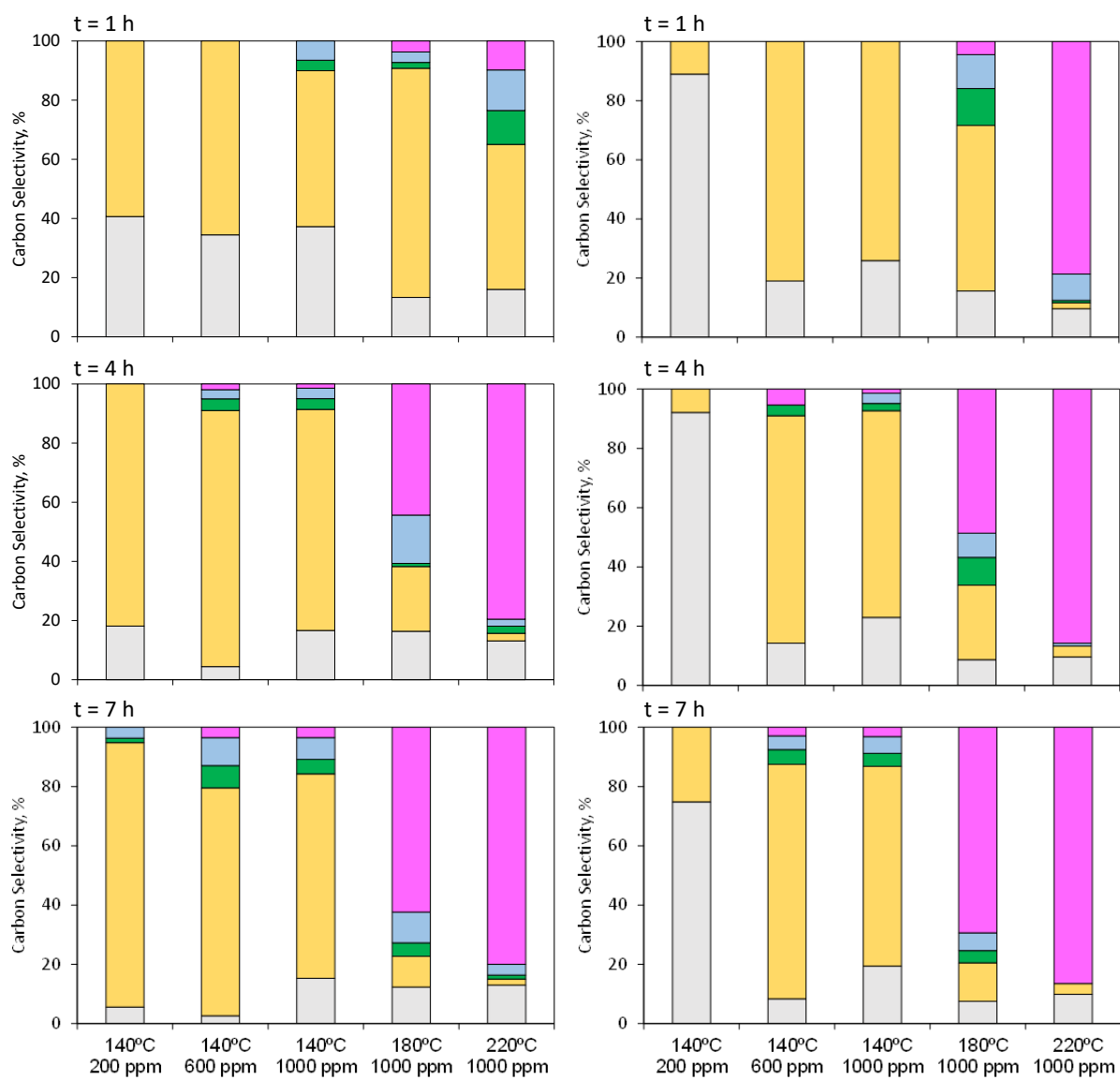


Figure 5

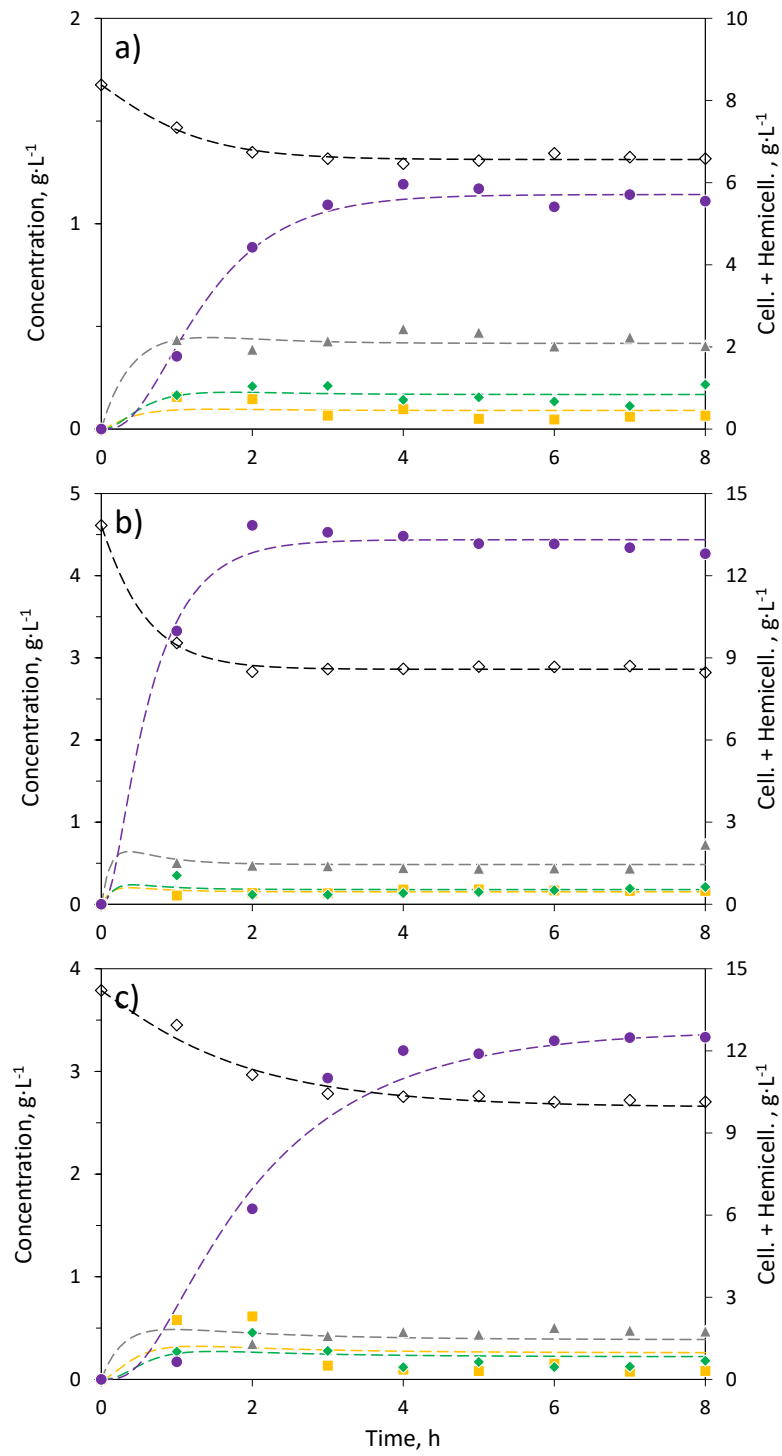


Figure 6

**Table 1.** Sawdust characterization, in terms of fractionation and elemental analysis, before and after delignification pretreatment. Result expressed in dry basis.

	Natural Sawdust	Oxidative delignification	Reductive delignification
Extractives (%)	6.9	-	-
Cellulose (%)	24.9	58.1	38.5
Hemicellulose (%)	31.5	35.2	57.1
Lignin (%)	36.6	6.7	4.4
C (%)	46.9	40.7	42.6
O (%)	43.6	52.0	49.1
H (%)	6.2	6.3	5.5
N (%)	2.2	0.4	0.7
S (%)	1.1	0.6	2.1

**Table 2.** Kinetic model parameters for the hydrolysis of sawdust catalysed by 1000 ppm of HCl.

Raw Material	Temp. (°C)	$k_1$ (s <sup>-1</sup> )	$k_2$ (s <sup>-1</sup> )	$k_3$ (s <sup>-1</sup> )	$k_4$ (s <sup>-1</sup> )	$k_5$ (s <sup>-1</sup> )
Fresh sawdust	140	$4.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	$2.5 \cdot 10^{-7}$	$7.0 \cdot 10^{-5}$
	180	$7.7 \cdot 10^{-5}$	$8.5 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
	220	$2.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$
	Ea (kJ·mol <sup>-1</sup> )	33.7	54.1	120.0	193.3	31.9
	r <sup>2</sup>	0.93	0.95	0.99	0.96	0.93
Delignified by oxidative method	140	$4.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	0
	180	$8.6 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$
	220	$1.6 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$	$9.1 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$
	Ea (kJ·mol <sup>-1</sup> )	27.8	49.1	78.9	113.9	205.1
	r <sup>2</sup>	0.999	0.95	0.83	0.999	0.999
Delignified by reductive method	140	$1.1310^{-5}$	$5.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$3.4 \cdot 10^{-5}$	$4.7 \cdot 10^{-8}$
	180	$2.9 \cdot 10^{-5}$	$7.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$5.3 \cdot 10^{-4}$	$7.0 \cdot 10^{-5}$
	220	$3.9 \cdot 10^{-5}$	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$
	Ea (kJ·mol <sup>-1</sup> )	29.0	14.0	45.9	84.1	202.0
	r <sup>2</sup>	0.93	0.997	0.95	0.97	0.94