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*Corresponding author: corazza@ufpr.br

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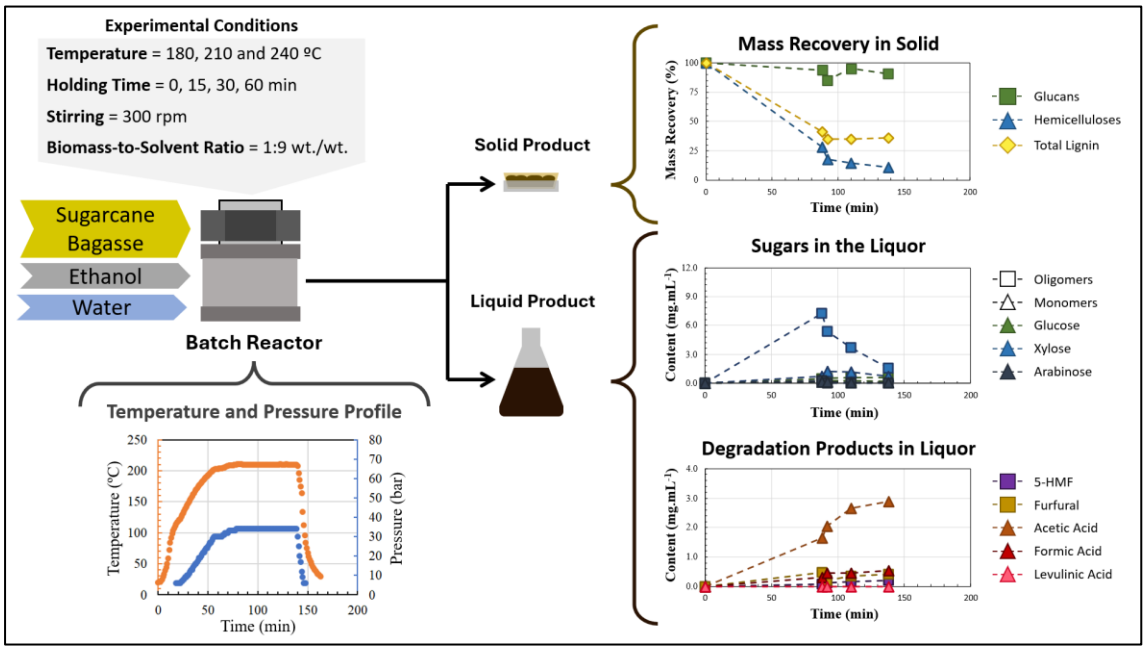
GRAPHICAL ABSTRACT



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Hydrothermal liquefaction (HTL) uses compressed water at high temperatures (≥250 °C) to convert wet biomass into a synthetic crude oil (bio-crude). Here, sugarcane bagasse was treated in batch mode using water, ethanol, and a water+ethanol (1:1, w/w) mixture at a 1:9 biomass-to-solvent mass ratio to evaluate the effects of solvent, non-isothermal heating, temperature (180, 210, and 240 °C), and holding time at the setpoint temperature (0 to 60 min) on product distribution under pre-HTL conditions. With water at 240 °C and 60 min holding time, solid recovery was 48% and non-volatile liquor products were 16%. Under the same conditions, the water+ethanol mixture improved fractionation, yielding the highest extraction (35%) and the lowest solid recovery (36%). Ethanol addition inhibited humins formation and favored lignin and hemicellulose fractionation (solid recoveries of 27% and 1% at 240 °C and 60 min), while 56% of glucans remained in the residual solids. Under the best sugar recovery treatment (water, 180 °C, 0 min), 62% of hemicelluloses were recovered in the liquor at a 1:6 mono-to-oligosaccharide ratio. Under harsher conditions, even in the presence of ethanol, slow heating promoted depolymerization but also substantial sugar degradation, with acetic acid being identified as the main component of liquid streams.

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Keywords: Sugarcane bagasse; Hydrothermal treatment; Organosolv; Fractionation; Batch reactor

*Contact information: Department of Chemical Engineering, Federal University of Paraná, P. O. Box 19011, Curitiba 81531-980, State of Paraná, Brazil; * Corresponding author: corazza@ufpr.br*

INTRODUCTION

Global energy demand continues to rise, driven largely by the rapid economic and population growth of emerging and developing countries (Wolfram *et al.* 2012; McKinsey & Company 2025). According to the International Energy Agency, liquid biofuel demand increased to 4.6 EJ in 2023 (5.6% of the global liquid fuel demand (on volume basis) and is projected to reach 5.7 EJ (215 billion liters) by 2030 (IEA 2024). This expansion, supported by a series state-level policy measures (International Energy Agency 2025) has raised interest in biomass as a fuel feedstock due to its widespread availability at relatively low cost and its potential to help closing the carbon cycle (Kazmi *et al.* 2023).

Brazil is one of the world's largest sugarcane producers (≈ 39% of global production), which leads to the generation of large quantities of sugarcane bagasse (SCB), a residual biomass with significant potential for energy applications. SCB is classified as a lignocellulosic biomass, as it is mostly composed of cellulose, hemicelluloses, and lignin (Toscano Miranda *et al.* 2021). It is often employed in co-generation systems for electricity and heat. However, this application has low efficiencies, making the exploration of alternative thermochemical conversion routes imperative (Motta *et al.* 2018). Carbohydrates from SCB (cellulose and hemicelluloses) can be fractionated into monomeric sugars, which can subsequently be directed to

fermentation or chemical conversion to polyols, organic acids, and biofuels, among others (Isikgor and Becer 2015; Brown *et al.* 2024). This fractionation can be carried out using water as the primary solvent, either alone or with the aid of enzymes or catalysts (Sun and Cheng 2002; Vasić *et al.* 2021). In addition, the incorporation of an organic co-solvent such as ethanol can enhance biomass fractionation, characterizing a typical organosolv process (Alves *et al.* 2025).

SCB is also being explored as feedstock for other thermochemical conversion techniques, such as pyrolysis, gasification, or hydrothermal liquefaction. Among the routes for direct biomass conversion into biofuels, hydrothermal liquefaction (HTL) stands out, as it does not require feedstocks with low moisture content, thereby avoiding the energy-intensive drying and other pre-treatments steps (Amadei *et al.* 2023). HTL consists of several reactions that take place between 250 and 374 °C using compressed (sub and supercritical) water in the range of 4 to 22 MPa (Ong *et al.* 2019). Under these conditions, changes in water properties (*e.g.*, solubility, density, and dielectric constant) enhance interactions with organic compounds and facilitate the thermal conversion of biomass macromolecular components. HTL products include a solid known as biochar, a liquid referred to as bio-crude, and non-condensable volatiles (gases) (Amadei *et al.* 2023). From a process perspective, the goal of HTL is to maximize the conversion of biomass into an energy-dense bio-crude suitable for integration into a biorefinery for upgrading into biofuels and platform chemicals. An overview of the transformations that each fraction (cellulose, hemicelluloses, and lignin) undergo at high temperatures in the presence of water are presented in Fig. 1.

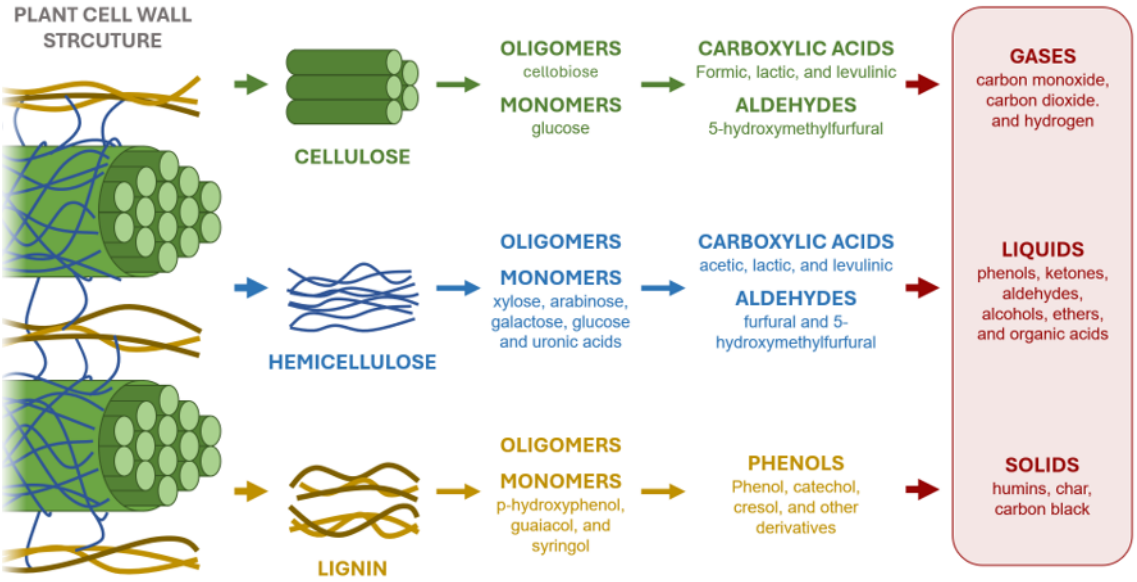

Fig. 1. Graphical representation of the plant cell wall structure and the sequence of possible hydrothermal transformations involving cellulose, hemicelluloses, and lignin. Gas, liquid, and solid products indicated in red can be derived from all three biomass macromolecular components.

Cellulose, a linear homopolysaccharide composed of glucosyl units, is the main structural component of plant cell walls. Its thermal hydrolysis begins at around 180 °C, producing short-chain oligomers (2 to 10 monomeric units) that can be further cleaved into their monomeric unit, glucose (Toscano Miranda *et al.* 2021). Then, glucose can be isomerized to fructose, which is dehydrated to 5-hydroxymethylfurfural (HMF), and further rehydrated to form levulinic and formic acids or follow retro-aldol chain splitting to lactic acid (Fernandes *et al.* 2024). However, biomass chemistry is

rarely simple: a variety of other chemicals including ketones, aldehydes, furans, and organic acids are also generated with yields and selectivity heavily dependent on reactants concentration, catalytic effects, and temperature (Jing and Lü 2008; Knežević *et al.* 2009; Yu and Wu 2011). As temperature continues to increase, these compounds may either decompose into gases (*e.g.*, H_2, CO, and CO_2) or condense to form humins (Jing and Lü 2008; Yang *et al.* 2020).

Hemicelluloses, a group of branched heteropolysaccharides, encase the cellulose chains within plant cell walls (Toscano Miranda *et al.* 2021). Unlike cellulose, hemicelluloses are heteropolysaccharides containing a variety of glycosyl units including xylose, arabinose, galactose, glucose, mannose, and uronic acids such as glucuronic and 4-O-methyl-glucuronic acids (Xie *et al.* 2020). Under hydrothermal treatment, hexoses (*e.g.*, glucose, galactose, mannose, and hexuronic acids) generally follow reaction pathways like those described for cellulose, whereas pentoses (*e.g.*, xylose and arabinose) follow a different route. After initial hydrolysis to oligomers and subsequent cleavage to monomeric units, pentoses can undergo dehydration to form furfural. As in the case of six-carbon sugar compounds, this description omits a complex network of other species, and as in the case of glucose, hemicellulose derivatives can be converted to gases and humins (Wang *et al.* 2025).

Lignin, an amorphous aromatic heteropolymer, plays a vital role in providing structural integrity and rigidity to plant cell walls (Toscano Miranda *et al.* 2021). Its depolymerization typically requires temperatures exceeding 270 °C and the use of catalysts, such as strong bases or oxides. Under hydrothermal depolymerization conditions, lignin predominantly yields monomeric products such as p-hydroxyphenol, guaiacol, and syringol (Nguyen *et al.* 2014), depending on the feedstock used. These intermediates can undergo secondary reactions to form more stable compounds, such as phenol and cresol. Compared to cellulose and hemicelluloses, lignin exhibits significantly greater resistance to hydrothermal conversion (Yang *et al.* 2019).

In a catalyst-free aqueous thermal treatment of lignocellulosic materials, the aforementioned transformations start at 150 ºC with the hydrolytic fractionation of hemicelluloses (Tunc and van Heiningen 2008). As temperature increases, the released monomeric units become increasingly susceptible to secondary transformations, which are commonly intensified around 180 ºC (Lin *et al.* 2020). Nonetheless, it is only at HTL conditions (above 250 ºC) that the residual solids are characterized as char rather than as fractions of biomass macromolecular components (cellulose, hemicellulose and lignin). Likewise, it is only then that the liquid fraction no longer contains sugars in significant amounts and is not addressed as a liquor but rather as bio-crude – the main HTL product. In this work, the intermediate range between these two regimes (fractionation and HTL), within 180 °C ≤ T ≤ 250 °C, is referred to as pre-HTL.

Although most studies utilize non-isothermal batch reactors due to the challenges of continuous lignocellulose HTL (Tran 2016; Ghadge *et al.* 2022), little focus has been placed on how the temperature profile influences the reaction pathways when HTL conditions are reached. This paper describes the behavior of SCB in a system that was operated under pre-HTL conditions, with results being correlated with the corresponding heating profiles. At the same time, inspired by the organosolv process of biomass fractionation, the effect of ethanol as cosolvent was accessed. The impact of different solvents (water, ethanol, and an equal-mass water/ethanol mixture) on extracting and depolymerizing SCB components was evaluated at three processing temperatures (180, 210, and 240 °C) in a batch reactor with constant stirring, with holding times ranging from 0 to 60 min at the temperature set-point.

EXPERIMENTAL

Materials

Sugarcane bagasse (SCB) was supplied by Santa Terezinha, an industrial sugarcane mill located in Tapejara (PR, Brazil). Deionized water, anhydrous ethanol (99.5%, Carbon – Ringaskiddy, C, Ireland), and their mixture were used as solvents. Nitrogen gas (99.9%, White Martins – Rio de Janeiro, RJ, Brazil) was used to provide an inert atmosphere in the reactor headspace. Sulfuric acid was purchased in two varieties: 72 wt.% from Exodo Científica (Sumaré, SP, Brazil) for biomass compositional analysis and P.A. from Química Moderna (Santana de Parnaíba, SP, Brazil) for the preparation of liquid chromatography mobile phase. Chromatography standards were acquired from Sigma-Aldrich (St. Louis, MO, USA). Other reagents and solvents were bought from local suppliers according to the specification required for analytical procedures.

Experimental Procedures

As summarized in Fig. 2, experiments were performed with ground SCB (average particle size of 0.21 mm) in a stirred batch reactor. The reactor output was vacuum filtered and washed for solid-liquid separation. Reaction products including a solid phase (recovered solids) and a liquid phase (liquor) were recovered and characterized according to NREL protocols.

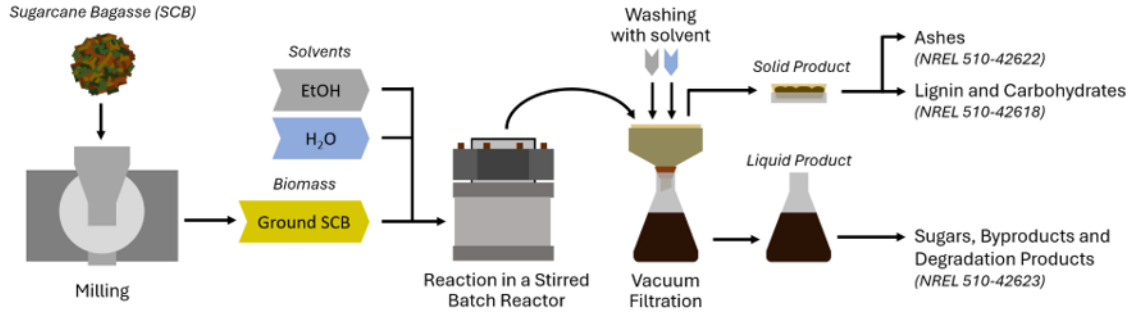

Fig. 2. Experimental procedure for biomass conversion under pre-HTL conditions (T = 180, 210, or 240 ºC)

Initially, biomass was milled in a grinding mill (Perten, LM3100 – Shelton, CT, USA) equipped with a 20-mesh screen size (0.841 mm). Reactions were performed with 15 g of SCB (dry basis) and 135 g of deionized water, anhydrous ethanol, or a water/ethanol equal-mass mixture. In the latter case, the moisture content initially present in SCB was subtracted from the water added to the system.

The reactants were loaded into a 300 mL stainless-steel batch reactor (Parr Instrument Company, model 4561 – Moline, IL, USA) equipped with a temperature controller (model 4848). Pressure was monitored using the reactor-mounted manometer. After sealing, the reactor headspace was purged with a gentle nitrogen flow to remove residual air. Heating was then initiated and stirring was set to 300 rpm. The reactor was heated to the setpoint temperature (T_{SP} = 180, 210, or 240 °C) and maintained at this temperature for specific holding times (t_{hold}) of 0, 15, 30, or 60 min. For experiments performed with 0 min of holding time, the heating jacket was removed and cooling was initiated immediately after the setpoint temperature was reached. For the other holding times, the setpoint temperature was maintained for t_{hold} before cooling. The reaction system was then cooled to 30 °C using a fan and the reactor cooling system supplied with cold water.

In batch reactors, heating profiles may vary amongst runs. Hence, the severity

factor (S_O) was used to keep consistency and make different profiles comparable. This factor is a dimensionless parameter that combines reaction temperature and residence time into a single metrics to quantify the overall harshness of a thermochemical or hydrothermal treatment (Overend and Chornet 1987). It was calculated using Eq. 1,

$$S_O = ln \int_0^t \left(exp \left[\frac{T(t)-100}{14.75} \right] \right) dt \quad (1)$$

where the integral considers the heating curve over time using temperature (T) in ºC and time (t) in minutes.

The reactor output, consisting of a mixture of residual solids and liquor, was subjected to a vacuum-assisted filtration using a Solab SL60 vacuum pump (Piracicaba, SP, Brazil) operated at an absolute pressure of 100 mmHg (0.13 bar). During filtration, 200 g of solvent – matching the solvent composition used in the reaction – were added to wash the solid. The resulting fractions were subjected to characterization for determining the overall process yields.

Characterization of Feedstock

Moisture in milled SCB was determined in triplicates using an infrared moisture analyzer (Shimadzu, Moc63u – Barueri, SP, Brazil). Extractives in ethanol and water were determined using a Soxhlet extractor following the NREL 510-42619 protocol (Sluiter *et al.* 2008d). For ash content determination, samples were calcined in a muffle furnace (EDG, Model 7000 – São Carlos, SP, Brazil) equipped with ramping program, following the NREL 510-42622 protocol (Sluiter *et al.* 2008a).

Structural carbohydrates (cellulose and hemicelluloses) and lignin were determined following the NREL 510-42618 protocol (Sluiter *et al.* 2008c), which involves a two-stage sulfuric acid hydrolysis (72 wt.% H_2SO_4 at 30 ºC for 1 h, followed by 3 wt.% H_2SO_4 at 121 ºC for 1 h). After vacuum-assisted filtration of the acid hydrolysate, ash-free acid-insoluble lignin (AIL) was determined by gravimetric analysis. Acid-soluble lignin (ASL) was determined in the filtrate by UV spectrophotometry (Global Analyzer – Calgary, AB, Canada) at 240 nm. Finally, carbohydrates were quantified in the filtrate by high-performance liquid chromatography (Agilent Technologies, 1260 Infinity HPLC – Santa Clara, CA, USA), equipped a Bio-Rad Aminex HPX-87H column (300 x 7.8 mm – Hercules, CA, USA) and a refractive index detector. Quantitative analysis was carried out by external calibration using standard solutions of cellobiose, glucose, xylose, arabinose, and acetic acid. However, results were expressed in terms of their parent polysaccharides to enable a direct comparison with the initial feedstock chemical composition.

Characterization of Solid Products

Solid products obtained from vacuum-assisted filtration and washing were dried at 40 ºC for 48 h in an air circulating oven (Nova Ética – Piracicaba, SP, Brazil). Dried solids were characterized in terms of moisture, ash, structural carbohydrates, and total lignin, which were determined following the same procedures described above.

The solids recovery percentage (RS) was calculated on a dry basis in relation to the initial SCB input. This calculation is given in Eq. 2,

$$RS(\%) = \frac{m_{RS} \cdot (1 - MC_{RS})}{m_{SCB} \cdot (1 - MC_{SCB})} \cdot 100\% \quad (2)$$

where m_{RS} is the dry mass of the recovered solids (g), m_{SBC} is the dry mass of SCB used as reactant (g), and MC_{RS} and MC_{SCB} represent the corresponding moisture contents in decimal form, respectively.

Another metric employed to follow the reaction performance was the mass removal ratio of a specific fraction (MR_i), where i can represent either a specific carbohydrate (*e.g.*, glucose, xylose, and arabinose), a lignin type (*e.g.*, acid-soluble and acid-insoluble lignins), or a group of biomass constituents (*e.g.*, glucans, hemicelluloses, and total lignin). MR_i calculations were based on Eq. 3,

$$MR_i\ (\%) = SR(\%) \cdot \frac{x_{i,RS}}{x_{i,SCB}} \quad (3)$$

where $x_{i,RS}$ represents the dry-basis content (%) of the target fraction in the recovered solid, and $x_{i,SCB}$ is the dry-basis content (%) of the same fraction in the feedstock.

Characterization of Liquid Products

Determination of sugars and byproducts in the reaction liquor was performed following the NREL 510-42623 protocol (Sluiter *et al.* 2008b) using the same HPLC system described above. This procedure involves direct analysis of the liquor to quantify free monosaccharides, followed by a second analysis after hydrolysis with 4 wt.% H_2SO_4 at 120 ºC. The difference between both measurements provided an estimate for the liquor oligosaccharide content and composition.

Ethanol had to be removed prior to sample analysis because its presence interfered with both acid hydrolysis and HPLC. For runs using anhydrous ethanol or an ethanol/water mixture as solvent, approximately 120 g of liquor were transferred to a round-bottom flask.

In the case of liquors obtained using anhydrous ethanol as the sole solvent, 60 g of water were added prior to ethanol evaporation to maintain the dissolved components in solution and prevent drying. Ethanol removal was performed by evaporation at 60 to 68 °C for approximately 45 min using a rotary evaporator (Gehaka, RD-180 – São Paulo, SP, Brazil) equipped with a thermostatic bath (Ethik Technology, 521-5D – Vargem Grande Paulista, SP, Brazil) and a vacuum pump (BIOMEC ECO, 260 – Araucária, PR, Brazil) operating at an absolute pressure of 250 mmHg (3.3 bar). Evaporation was considered complete when the estimated ethanol mass had been removed. Then, deionized water was added to restore the original solvent balance of the reaction liquor.

Quantitative analysis was initially obtained on an ethanol-free basis. However, reported values were corrected to account for the presence of ethanol. This correction was performed using density values for water (0.997 g/cm^3), ethanol (0.786 g/cm^3), and ethanol-water equal-mass mixture (0.908 g/cm^3) at 298 K, based on the experimental data reported by Khattab *et al.* (2012). Since liquors analyzed by HPLC were obtained after washing the recovered solids, a dilution factor of 2.48 was applied to report concentrations that were representative of the reactor outlet.

The extraction yield (EY) was defined in the present work as the total mass of non-volatile solids present in the liquor divided by the dry-basis mass of SCB employed in the run. To determine the mass of solids, samples (*circa* 5 g) were weighed in an amber flask and then set to dry in same air circulating oven as the solid phase for 48 h. The extraction yield was calculated by Eq. 4,

$$EY\ (\%) = \frac{m_{liq} \cdot \left(\frac{m_{sol}}{m_{samp}}\right)}{m_{SCB} \cdot (1 - MC_{SCB})} \cdot 100\% \quad (4)$$

where m_{sol} is the final mass of solids after drying (g), m_{samp} is the initial sample mass (g), and m_{liq} is the total liquor mass (g).

RESULTS AND DISCUSSION

Characterization of Feedstock

In dry basis, ground SCB employed in the experiments presented 12.7% ± 0.2% ash, 5.5 ± 0.6% extractives, 3.7% ± 0.4% acid soluble lignin (ASL), 18.7% ± 0.3% acid insoluble lignin (AIL), 36.2% ± 0.7% glucans, 18.2% ± 0.3% xylans, and 2.1% ± 0.1% arabinosyl residues plus 2.2% ± 0.1% acetyl groups linked to xylan backbones. Based on these values, SCB contained 22.4% total lignin content (AIL plus ASL) and 22.4% total hemicellulose content.

The glucans in biomass should not be interpreted as a direct measurement of cellulose, since they can be present in at least three different formats: crystalline cellulose, amorphous cellulose, and hemicellulose. For instance, Xie *et al.* (2020) found that hemicellulose fractions isolated from SCB pith contained between 4.34 and 10.31% of glucans. Additionally, cellulose crystallinity in sugarcane bagasse has been reported to range from 50 to 81% (Caliari *et al.* 2017), and amorphous cellulose domains are generally more accessible to hydrolysis than crystalline domains (Zhao *et al.* 2006). Therefore, changes in glucan content observed in the recovered solid cannot be attributed solely to cellulose hydrolysis but are rather to the combined contribution of different glucose-containing structures.

It is also important to comment on a limitation of the chromatographic method used: the HPX-87H column does not resolve xylose, mannose, and galactose, which are therefore collectively quantified as xylose. This does not substantially compromise the estimation of total hemicelluloses, since these monosaccharides (mannose and galactose) have similar response factors to xylose and are present in relatively low amounts in SCB.

Reaction Yields

For all runs, after loading and sealing biomass and solvents inside the reaction chamber, heating and stirring were turned on. However, for batch reactors with a temperature controller, heating profiles are normally curved rather than linear. Fig. 3 shows how temperature and pressure varied over time for two reaction set-ups: zero holding time and fixed holding time at 240 °C. Three segments were identified in these profiles: the heating ramp up to the setpoint temperature, the isothermal plateau (holding time), and the cooling down to 30 °C.

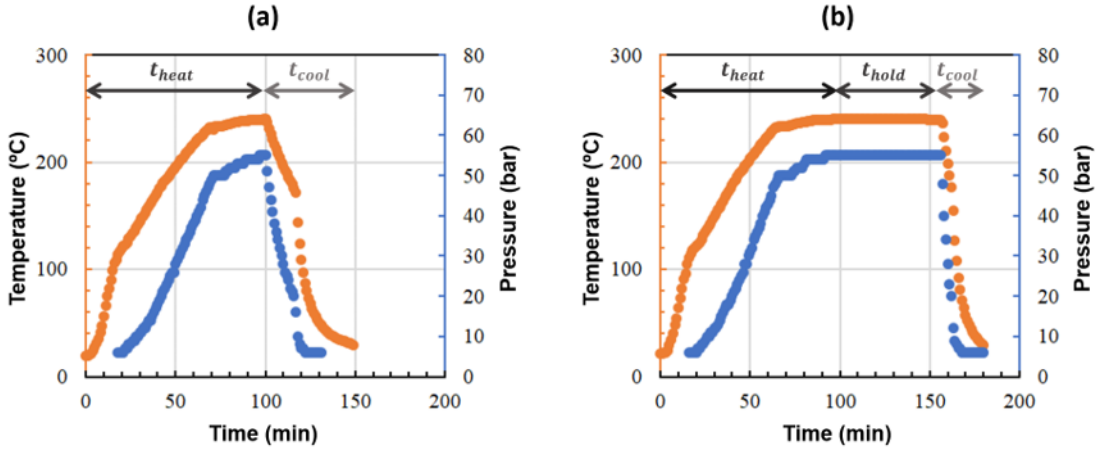

Fig. 3. Temperature and pressure profiles for experiments using water and ethanol and 240 ºC as the setpoint temperature for (a) 0 min and (b) 60 min holding times (t_{hold}). The initial heating time is given by t_{heat}, while t_{cool} is the cooling time between the end of the holding time and the system reaching 30 ºC.

For runs with 0 min holding time (t_{hold}), heating was turned down and cooling begun as soon as the setpoint temperature was reached. Since the cooling time (t_{cool}) was faster than the heating time (t_{heat}) especially at higher temperatures, due to the efficiency of the temperature controller, most of the chemical transformations took place during t_{heat} and t_{hold}.

The severity factor (S_O in Eq. 1) was used to make runs using a different solvent comparable regarding the applied temperature and holding time. Table 1 presents the mass inputs for each experiment, as well as values for the severity factor (S_O), recovered solids (*RS*), and extraction yields (*EY*). Some conditions (specified in Table 1) were performed in duplicate to determine the experimental error. Deviations for non-replicate conditions were assumed as the average standard deviation of duplicated experiments (1.0% for *RS* and 1.0% for *EY*).

Table 1. Mass Inputs, Solids Recovered (*RS*), and Extraction Yields (*EY*) for All Experiments

Solvent	*T* (ºC)	t_{hold} (min)	S_O	*RS* (%)	*EY* (%)
Water	180	0	3.724	71.8	23.4
Water †	180	60	4.291	64.4 ± 2.5	15.4 ± 3.2
Water	210	0	4.556	63.7	13.4
Water	210	60	5.215	62.2	12.0
Water	240	0	5.577	54.8	14.7
Water	240	60	6.095	48.9	16.3
Water+Ethanol	180	0	3.840	81.6	15.2
Water+Ethanol †	180	15	4.012	76.5 ± 1.6	17.9 ± 1.8
Water+Ethanol †	180	30	4.122	74.3 ± 1.2	19.7 ± 0.3
Water+Ethanol †	180	60	4.304	68.3 ± 1.0	23.1 ± 0.7
Water+Ethanol †	210	0	4.740	59.0 ± 0.1	32.5 ± 1.1
Water+Ethanol	210	15	4.909	54.1	30.6
Water+Ethanol	210	30	5.020	54.1	31.7
Water+Ethanol	210	60	5.177	52.5	31.0
Water+Ethanol	240	0	5.658	47.8	32.3
Water+Ethanol	240	15	5.816	45.2	32.3
Water+Ethanol	240	30	5.951	42.5	33.6
Water+Ethanol	240	60	6.100	37.0	35.1
Ethanol	180	0	3.675	90.7	5.3
Ethanol †	180 *	60	4.333	89.6 ± 0.1	5.9 ± 0.1
Ethanol	210	0	4.529	86.4	8.3
Ethanol	210	60	5.210	79.3	11.0
Ethanol	240	0	5.531	76.1	14.1
Ethanol †	240	60	6.110	69.1 ± 0.6	17.4 ± 1.1
† = *Experimental conditions performed in duplicate (mean value ± standard deviation).*					

A graphical representation of both *RS* and *EY* is given in Fig. 4. The gap between bars and 100% is related the formation of non-condensable volatiles (gases) and physical losses in the downstream procedure. Although the composition of the gas phase was not analyzed, gas formation was indicated by final reactor pressures above 6 bar observed in some experiments after cooling the reactor to 30 °C. Experiments performed with different solvents but the same setpoint temperature (T_{SP}) and holding time (t_{hold}) presented S_O differences below 5%. This enabled a direct comparison between runs, as they were submitted to similar heating severities. In addition, *RS* decreased as S_O increased for a given solvent and T_{SP}. This provides further evidence

that, although runs differed in t_{heat}, the treatment became more severe with an increase in t_{hold}.

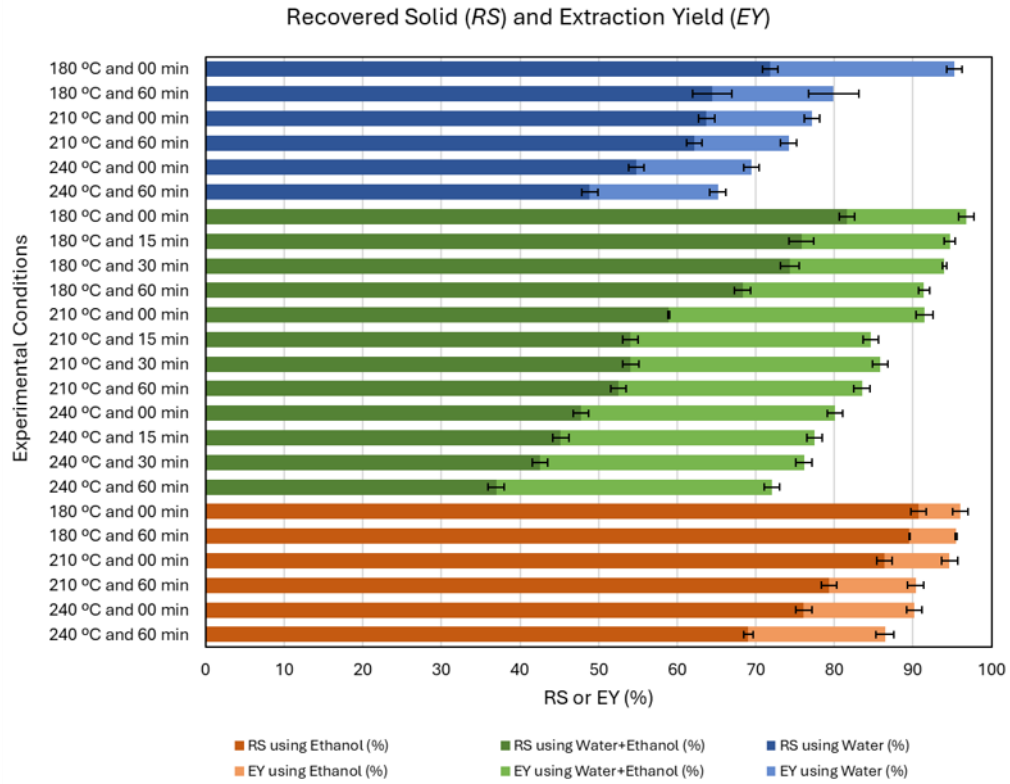

Fig. 4. Recovered solids (Eq. 2) and extraction yield (Eq. 4) for experiments using water, ethanol, and water+ethanol (1:1 mass ratio) as solvent and a 1:9 biomass-to-solvent mass ratio, totalizing 150 g of mass in a 300 mL Parr batch reactor. T is the temperature setpoint (maximum temperature reached) and (t_{hold}) is the holding time at this maximum temperature.

Looking at recovery and extraction yields in Fig. 4, employing water at 180 °C was the best strategy for SCB fractionation since more mass was removed from the starting material and transported to the liquor when compared to the other solvents. Literature suggests that 180 °C is already beyond the optimal point for sugar recovery as degradation reactions are already taking place (Lin *et al.* 2020). Said reactions could explain why *EY* and *RS* decreased concomitantly for runs at 210 °C. As T_{SP} was raised to 240 °C, the slight increase in *EY* was likely due to the system approaching HTL conditions (Ong *et al.* 2019).

When mixing water and ethanol, *RS* decreased steadily with longer holding times and higher temperatures, while *EY* seemed to remain stable for reactions carried out with different holding times at 210 and 240 °C. While using only water at 240 °C and holding of 60 min, *RS* reached 48% and *EY* 16%, water+ethanol treatment under the same conditions resulted in the highest *EY* (35%) and the lowest *RS* (36%). In comparison to water-only runs, the solvent mixture seemed to keep the solid fractionation products in the liquid phase, with comparatively lower mass losses. Lower *RS* and higher *EY* values are explained by the ethanol's ability to support delignification (Escobar *et al.* 2022), a reaction stage that water alone demands higher temperatures to reach (Nguyen *et al.* 2014).

Yields from runs using only ethanol performed the worst. Longer holding times (60 min) and higher temperatures (≥ 210 °C) were necessary to match results obtained at 180 °C for water-only runs. Likewise, Yamazaki *et al.* (2006) reported retention of over 50% of alcohol insoluble matter after processing lignocellulosic biomass *via* alcohol-thermal treatment at 270 °C.

Overall, the water and ethanol mixture minimized *RS* while maximizing *EY* under the temperatures and holding times evaluated in this study. To understand how each solvent affects biomass fractionation, the chemical composition of the residual solids was evaluated.

Solid Products

Following the same procedure employed for feedstock characterization, the compositions of recovered solids were analyzed and presented on dry basis in Table 2. Standard deviations for non-replicated experiments were calculated from analytical triplicates of the same sample, whereas for duplicate experiments, triplicates from both runs were considered in this calculation. Composition standard deviations of duplicate experiments averaged 1.8% for glucans, 1.0% for hemicelluloses, and 2.2% for total lignin. Mass recoveries (MR_i in Eq. 3) in relation to the original SCB chemical composition are given in Fig. 5. Vertical arrows correlate the ending of holding time and the corresponding MR_i value for each run.

Table 2. Mass Composition of Different Fractions of Lignocellulosic Biomass (Glucans, Hemicelluloses, and Total Lignin) in the Solid for All Experiments

Solvent	T (ºC)	t_{hold} (min)	$x_{(Glc)n}$ (%)	x_{hemi} (%)	x_{tl} (%)
Water	180	0	44.4 ± 2.1	9.1 ± 0.4	31.7 ± 1.5
Water †	180	60	48.9 ± 1.1	2.3 ± 0.3	35.1 ± 1.9
Water	210	0	43.1 ± 3.8	0.8 ± 0.1	36.6 ± 0.4
Water	210	60	45.0 ± 0.4	<loq	46.1 ± 0.5
Water	240	0	30.7 ± 2.2	<loq	52.1 ± 2.8
Water	240	60	7.5 ± 0.1	<loq	75.5 ± 0.2
Water+Ethanol	180	0	41.5 ± 0.7	20.0 ± 0.9	19.7 ± 1.0
Water+Ethanol †	180	15	44.8 ± 2.4	20.0 ± 0.6	19.9 ± 1.3
Water+Ethanol †	180	30	43.1 ± 3.2	17.7 ± 1.4	21.4 ± 1.4
Water+Ethanol †	180	60	47.1 ± 3.8	16.2 ± 2.0	22.0 ± 3.8
Water+Ethanol †	210	0	58.1 ± 1.1	9.7 ± 1.3	17.5 ± 2.0
Water+Ethanol	210	15	57.1 ± 0.8	7.4 ± 0.7	14.5 ± 0.5
Water+Ethanol	210	30	63.5 ± 1.4	6.0 ± 0.8	14.5 ± 1.4
Water+Ethanol	210	60	62.4 ± 5.5	4.8 ± 0.5	15.4 ± 1.1
Water+Ethanol	240	0	65.6 ± 0.6	1.8 ± 0.1	15.3 ± 1.6
Water+Ethanol	240	15	63.0 ± 0.5	2.2 ± 0.3	13.2 ± 0.9
Water+Ethanol	240	30	64.3 ± 1.2	1.3 ± 0.1	15.1 ± 0.9
Water+Ethanol	240	60	55.7 ± 1.2	0.6 ± 0.1	16.4 ± 0.7
Ethanol	180	0	41.1 ± 1.5	25.5 ± 1.1	24.9 ± 1.2
Ethanol †	180	60	36.7 ± 0.6	21.8 ± 1.0	22.6 ± 2.2
Ethanol	210	0	38.5 ± 0.6	23.1 ± 0.3	24.0 ± 0.1
Ethanol	210	60	45.6 ± 4.0	23.0 ± 1.6	22.5 ± 0.2
Ethanol	240	0	41.4 ± 5.4	20.8 ± 2.8	24.3 ± 4.1
Ethanol †	240	60	46.8 ± 0.5	18.2 ± 0.4	18.7 ± 2.8

(Glc)n = glucans; hemi = hemicelluloses; tl = total lignin; <loq = lower than the Limit of Quantification of the method; † = Values obtained using all triplicate analysis of each replicate experiments (mean value ± standard deviation).

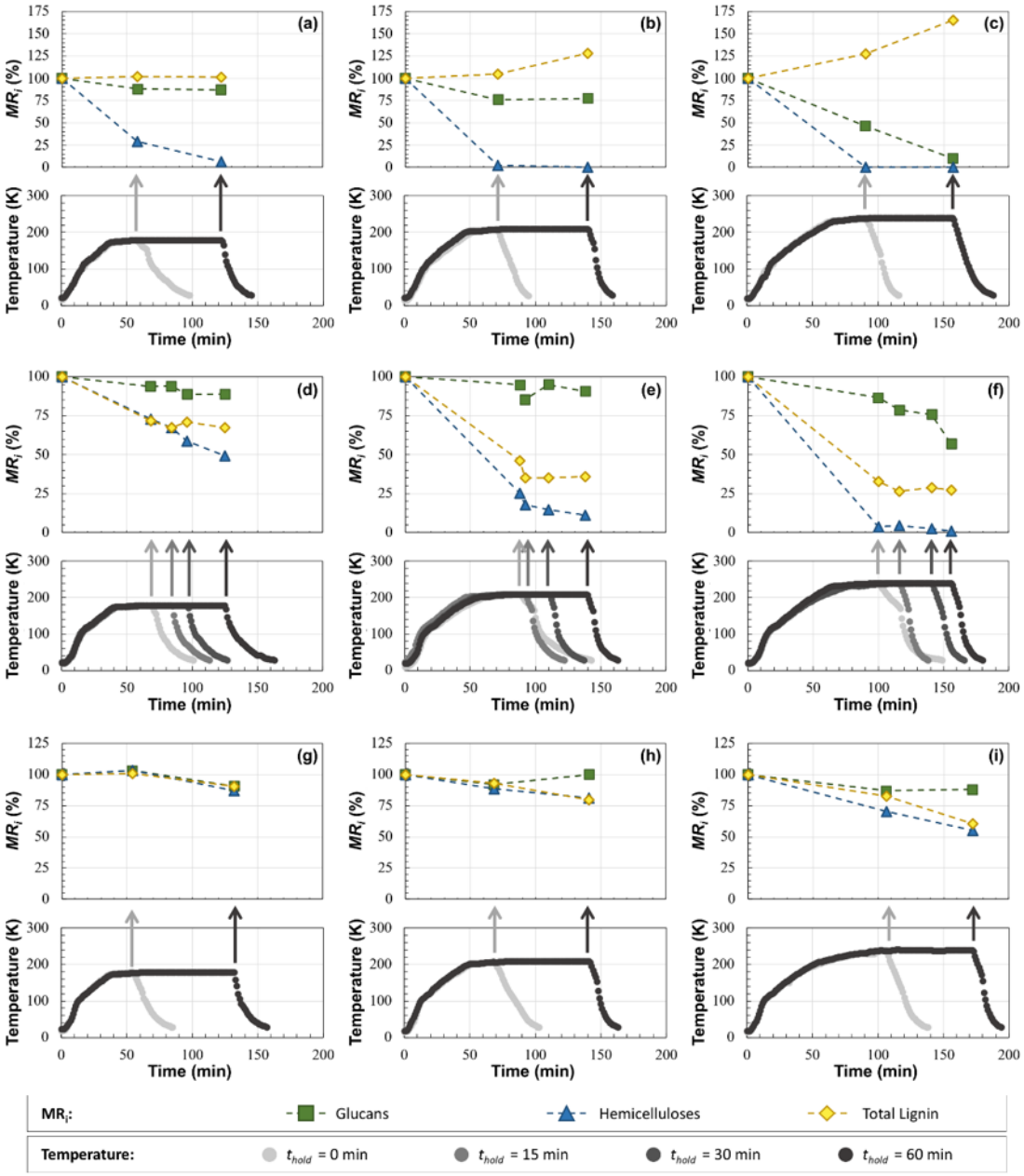

Fig. 5. Graphical correlation between heating profiles and mass recoveries of different SCB fractions in residual solids (glucans, hemicelluloses, and total lignin) for experiments carried out with different holding times using (a) water at 180 ºC, (b) water at 210 ºC, (c) water at 240 ºC, (d) water+ethanol at 180 ºC, (e) water+ethanol at 210 ºC, (f) water+ethanol at 240 ºC, (g) ethanol at 180 ºC, (h) ethanol at 210 ºC, and (i) ethanol at 240 ºC.

Water-only experiments (Fig. 5) showed a strong capacity to remove sugars, particularly hemicelluloses. For example, at 180 °C and a 60 min holding time, only 7% of hemicelluloses remained in the recovered solids while, at higher temperatures (210 and 240 °C), hemicelluloses were completely removed. These results are consistent with the use of liquid hot water to remove hemicelluloses (mainly xylans) and hemicellulose-bound lignin fragments from lignocellulosic materials to obtain cellulose-enriched solids for fermentation (Gladysheva 2025). Sasaki *et al.* (2003) explored this concept in a semi-batch system in which the solvent (water) was preheated before passing through the fractionation vessel containing SCB. Within the 200 to 230 °C window, most hemicellulose and lignin were removed, yielding residual solids mostly composed of cellulose. However, in the present work, batch fractionation did

not result in extensive lignin removal from SCB.

Water at 180 °C (0 and 60 min holding time) removed little more than 10% of SCB glucans likely originated from hemicelluloses or amorphous cellulose (Fig. 5), while more than one quarter was fractionated at 210 °C (0 and 60 min holding time). At 240 °C and no holding time, more than half of SCB glucans were removed, whereas after a 60 min holding time, only 10% remained in the recovered solids. Therefore, batch treatment of SCB at 240 °C resulted in extensive glucan hydrolysis, while lignin was the predominant fraction in the recovered solid.

In Fig. 5, as polysaccharides disappear from the recovered solids, the lignin content grows beyond the original amount. The increase in total lignin content, based on the quantification of higher amounts of lignin-like acid insoluble residues, may be partially due to the formation of humins – complex, dark, water insoluble, amorphous organic polymers that are formed by condensation of sugar dehydration byproducts with probable involvement of lignin substructures (Jing and Lü 2008; Poerschmann *et al.* 2017). Figure 6 provides visual support for this hypothesis, as the aspect of the recovered solid from experiments with water grows darker with an increase in temperature and total lignin contents.

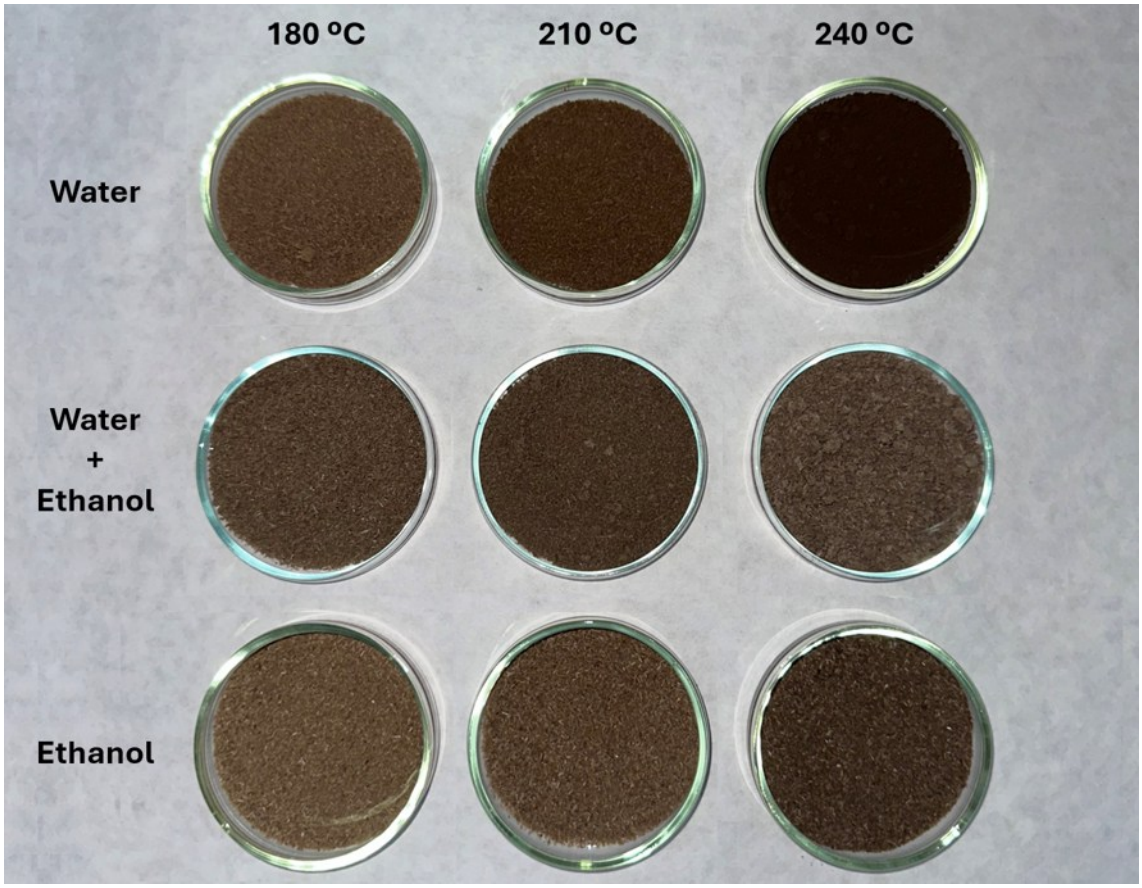

Fig. 6. Picture of recovered solids from all experiments carried out at no holding time (t_{hold} = 0 min). Experiments on the same row were performed with the same solvent (water, ethanol, and water+ethanol equimassic mixture) and those on the same column were performed at the same setpoint temperature (T_{SP} = 180, 210, or 240 ºC).

The hypothesis that humins are formed from both glucose and xylose is supported by other works. For example, when studying the kinetics of glucose hydrothermal decomposition, Jing and Lü (2008) showed that humic matter was formed beyond 180 °C. Poerschmann *et al.* (2017) claimed that under batch hydrothermal carbonization (no inert atmosphere and no stirring), 68 to 78% of the feedstock carbon

(glucose, xylose, and fructose) was converted to a solid residue named hydrochar at 220 °C. Although hydrochar was hypothesized to come mostly from 5-HMF (glucose dehydration product), Köchermann *et al.* (2019) showed that humic matter can also come from furfural (xylose dehydration product). These reports are in line with Fig. 5 (lignin recoveries beyond 100%) and Fig. 6 (gradual darkening of the recovered solids). Since the methodology employed for lignin determination (NREL protocol 510-42618) relies on classifying all acid insoluble matter as AIL, humic matter (if present) is likely being misclassified.

When ethanol is added as a cosolvent, humins formation is not evidenced. Köchermann *et al.* (2019) reported that the use of an equimass water+ethanol mixture during the catalytic hydrotreatment of xylose between 180 and 220 °C increased furfural yields from 36 to 52% up to 90% and reduced humins formation by 60%.

Even so, hemicelluloses were found to become depolymerized significantly in water+ethanol experiments, with only 49% remaining in the recovered solids at 180 °C with a 60 min holding time and almost complete removal at 240 °C. Likewise, when comparing organosolv (water+ethanol) and hydrothermal (water only) pre-treatments, Alves *et al.* (2025) reported the extraction of over half of SCB hemicelluloses in batch experiments at 180 °C (120 min holding time, 200 psi, water+ethanol mixture at 1:1 volumetric ratio as solvent, and 10:1 solvent-to-biomass ratio).

While hemicelluloses were hydrolyzed, the solvent mixture helped in retaining SCB glucans in the recovered solids, with recoveries remaining above 85% at 180 °C and 210 °C but dropping to 56% at 240 °C with a 60 min holding time. This fraction was more difficult to fractionate compared to water-only experiments, but even so, the addition of ethanol as co-solvent enabled the lowest *RS* and highest *EY* values as already discussed elsewhere (see section about Reaction Yields).

Delignification bared a striking difference between experiments using water and water+ethanol: with 0 min holding time at 180 °C, only 71% total lignin was recovered in the solids, with this value lowering to 46% at 210 °C (0 min), 32% at 240 °C (0 min) and 27% at 240 °C (60 min). In terms of ASL and AIL recovery, both had reduced recoveries while the reaction temperature was raised. ASL recovery dropped from 67.5 (180 °C and 0 min) to 18.1% (240 °C and 0 min), while AIL recovery was reduced from 72.5 to 35.5% under the same conditions. Ethanol presence in the solvent mixture also enhanced lignin fractionation, which justifies its application as cosolvent in organosolv delignification (Alves *et al.* 2025). The same effect was also evidenced by Vallejos *et al.* (2015), who were able to remove 57.5% of the total lignin from SCB when treating it in a batch system at 190 °C for 30 min using aqueous ethanol (1:1 water-to-ethanol mass ratio) and a 9:1 solvent-to-solids ratio.

In experiments carried out with ethanol and 0 min holding time at 180 °C, almost none of the biomass components were fractionated. At 210 °C with a holding time of 60 min, nearly one quarter of both hemicelluloses and lignin were removed. Finally, at 240 °C and a 60 min holding time, almost half of these two SCB structural components were removed. Although ethanol helped partial delignification, the absence of water imparted hemicellulose hydrolysis and limited lignocellulose depolymerization. Yamazaki *et al.* (2006) investigated the use of ethanol as the sole solvent for extracting beech wood lignocellulosic components. Using 150 mg biomass and 4.9 mL ethanol, a nearly complete delignification was achieved at 270 °C with a holding time of 30 min, paralleled by a retention of over 80% of cellulose and 60% of hemicelluloses from feedstock.

The combined effects of carbohydrate hydrolysis and ethanol-assisted delignification enhanced lignocellulose fractionation as, compared to water-only experiments, lower *RS* values were achieved at $T \geq 210$ °C under equivalent reaction

conditions. In contrast, reactions conducted in water alone tend to promote humins formation, whereas ethanol partially suppress these condensation pathways. Considering 250 °C as threshold for the onset of HTL, changes in residual solids chemical composition indicate that ethanol had a marked effect on biomass fractionation. Next, a detailed analysis of the liquid phase is provided to characterize the chemical transformations following depolymerization.

Liquid Products

Figures 7 and 8 provide a visual representation of the kinetics governing the transformations occurring in the liquid phase, correlating each experimental point with the corresponding heating profile. For clarity, monomeric and oligomeric sugars are presented separately from compounds formed by subsequent transformation reactions. The composition of liquors collected at the reactor outlet are presented as mass concentration per unit volume (mg/mL) in Tables 3 and 4.

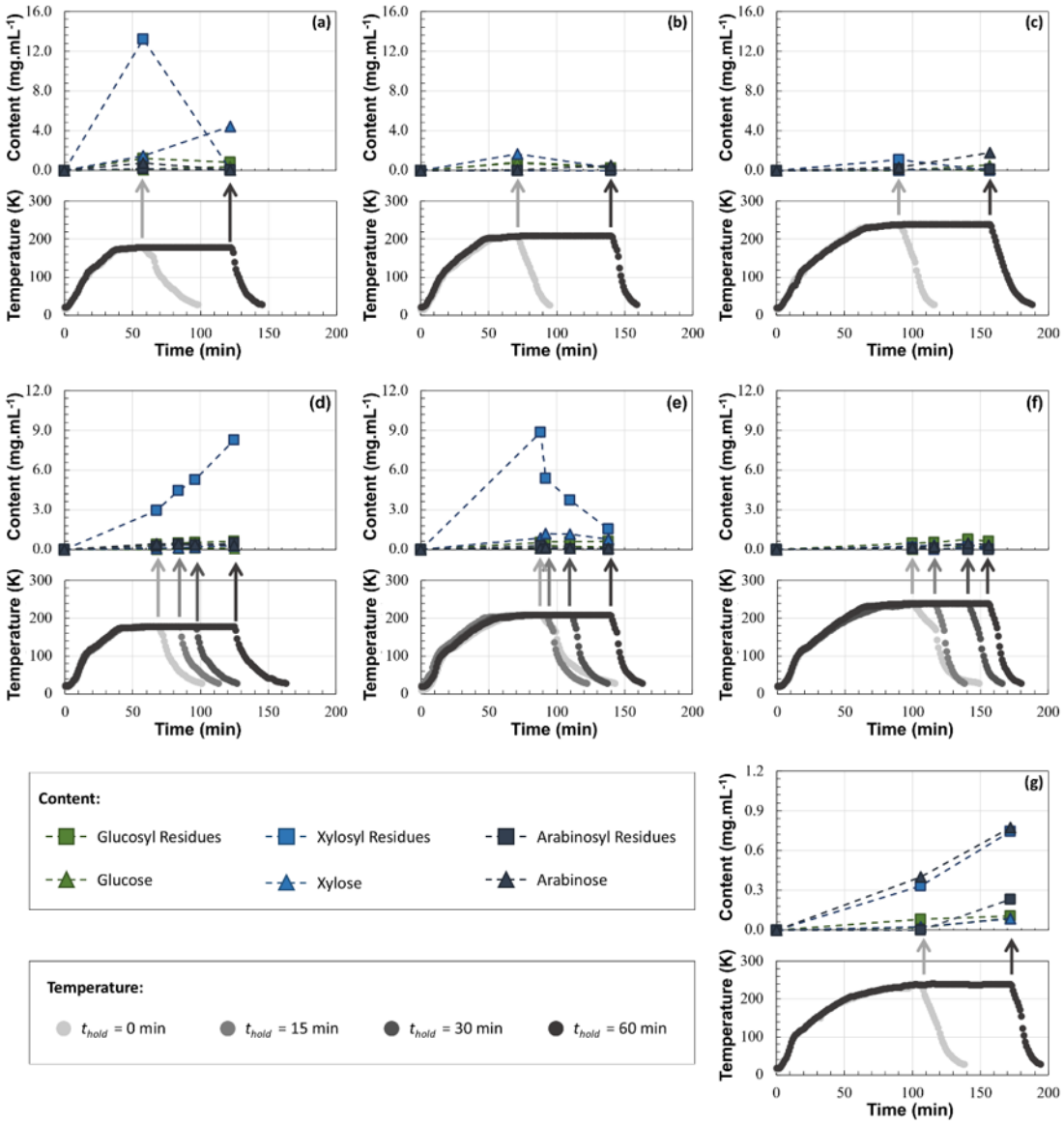

Fig. 7. Graphical correlation between heating profiles and monomeric (glucose, xylose, and arabinose) and oligomeric (glucosyl, xylosyl, and arabinosyl residues) sugars found in the reaction liquor (reactor outlet) for experiments carried out with different holding times using (a) water at 180 ºC, (b) water at 210 ºC, (c) water at 240 ºC, (d) water+ethanol at 180 ºC, (e) water+ethanol at 210 ºC, (f) water+ethanol at 240 ºC, and (g) ethanol at 240 ºC

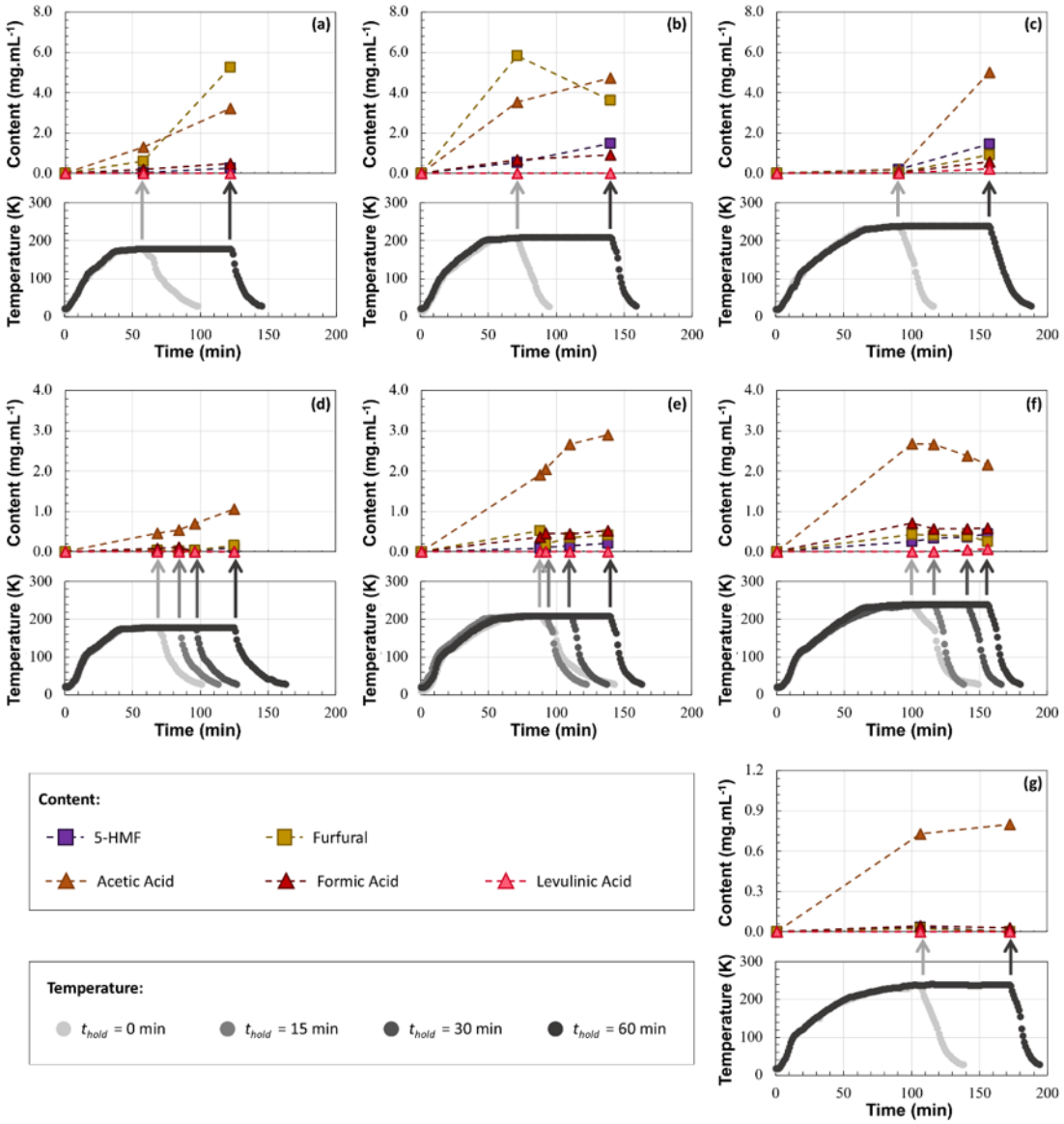

Fig. 8. Graphical correlation between heating profiles and degradation products (5-HMF, furfural, formic acid, acetic acid, and levulinic acid) found in the liquor (reactor outlet) for experiments carried out with different holding times using (a) water at 180 ºC, (b) water at 210 ºC, (c) water at 240 ºC, (d) water+ethanol at 180 ºC, (e) water+ethanol at 210 ºC, (f) water+ethanol at 240 ºC, and (g) ethanol at 240 ºC

Liquors were analyzed for all runs performed using only water or the water+ethanol mixture as solvent. For ethanol-only experiments, however, this analysis was limited to the runs conducted at 240 °C, as preliminary results showed that milder conditions produced very low concentrations of sugars and related degradation by-products (<0.1 $mg.mL^{-1}$). As evidenced in Fig. 7A, the highest sugar release (considering glucose, xylose, arabinose plus glucosyl, xylosyl, and arabinosyl residues) was obtained when only water was used as solvent at 180 °C and 0 min holding time (16.8 $mg.mL^{-1}$). Considering the feedstock was composed of 22.4% hemicelluloses, this value represented a 62% hemicellulose recovery in the reaction liquor. Holding times of 60 min at 180 °C reduced oligomers while ascending the presence of xylose, as longer reaction times favored hydrolysis. Also, sugar recovery at 180 °C exceeded those of hydrothermal treatments at more severe reaction conditions (higher temperatures with and without holding time, as presented in Fig. 7B and Fig. 7C) because degradation reactions became more expressive.

Table 3. Content of Monomeric (Glucose, Xylose, and Arabinose) and Oligomeric (Glucosyl, Xylosyl, and Arabinosyl Residues) Sugars Found in the Liquor (Exit of the Reactor)

Solvent	*T* (ºC)	t_{hold} (min)	Oligomers (mg.mL^{-1})			Monossacharides (mg.mL^{-1})		
			Glucosyl	Xylosyl	Arabinosyl	Glucose	Xylose	Arabinose
Water	180	0	1.20 ± 0.02	13.19 ± 0.38	0.16 ± 0.02	0.08 ± 0.01	1.46 ± 0.01	0.75 ± 0.01
Water	180	60	0.84 ± 0.03	0.07 ± 0.21	0.04 ± 0.01	0.39 ± 0.02	4.47 ± 0.04	0.05 ± 0.02
Water	210	0	0.73 ± 0.01	< loq	< loq	0.79 ± 0.01	1.69 ± 0.02	0.03 ± 0.01
Water	210	60	0.26 ± 0.01	< loq	< loq	0.37 ± 0.02	0.22 ± 0.01	0.52 ± 0.02
Water	240	0	0.11 ± 0.01	1.08 ± 0.01	0.09 ± 0.01	< loq	0.05 ± 0.01	0.30 ± 0.01
Water	240	60	< loq	< loq	0.12 ± 0.13	0.56 ± 0.06	0.20 ± 0.03	1.80 ± 0.04
Water+Ethanol	180	0	0.36 ± 0.01	2.93 ± 0.47	0.24 ± 0.03	< loq	0.11 ± 0.01	0.41 ± 0.01
Water+Ethanol	180	15	0.46 ± 0.10	4.46 ± 0.12	0.39 ± 0.01	0.04 ± 0.01	0.15 ± 0.01	0.40 ± 0.01
Water+Ethanol	180	30	0.53 ± 0.07	5.25 ± 0.13	0.32 ± 0.14	0.10 ± 0.01	0.18 ± 0.01	0.38 ± 0.01
Water+Ethanol	180	60	0.63 ± 0.09	8.29 ± 2.01	0.46 ± 0.06	0.06 ± 0.01	0.27 ± 0.01	0.33 ± 0.01
Water+Ethanol †	210	0	0.15 ± 0.03	0.87 ± 0.05	< loq	0.51 ± 0.03	8.86 ± 0.68	0.27 ± 0.10
Water+Ethanol	210	15	0.55 ± 0.01	5.39 ± 0.03	0.03 ± 0.01	0.26 ± 0.01	1.22 ± 0.01	0.11 ± 0.01
Water+Ethanol	210	30	0.59 ± 0.01	3.70 ± 0.04	< loq	0.23 ± 0.01	1.14 ± 0.01	0.10 ± 0.01
Water+Ethanol	210	60	0.60 ± 0.01	1.53 ± 0.02	< loq	0.19 ± 0.01	0.74 ± 0.01	0.09 ± 0.01
Water+Ethanol	240	0	0.45 ± 0.16	0.13 ± 0.12	< loq	0.02 ± 0.01	0.22 ± 0.02	0.13 ± 0.01
Water+Ethanol	240	15	0.54 ± 0.13	< loq	0.07 ± 0.05	0.33 ± 0.01	0.34 ± 0.08	0.23 ± 0.01
Water+Ethanol	240	30	0.76 ± 0.12	0.18 ± 0.06	< loq	0.20 ± 0.01	0.34 ± 0.01	0.47 ± 0.02
Water+Ethanol	240	60	0.62 ± 0.10	< loq	< loq	0.22 ± 0.01	0.18 ± 0.01	0.34 ± 0.11
Ethanol	240	0	0.08 ± 0.01	0.33 ± 0.01	< loq	0.02 ± 0.01	0.02 ± 0.01	0.40 ± 0.01
Ethanol	240	60	0.10 ± 0.03	0.74 ± 0.16	0.23 ± 0.17	0.09 ± 0.01	0.09 ± 0.01	0.77 ± 0.01

loq = Limit of Quantification; † = Values obtained using all triplicate analysis of each replicate experiments (mean value ± standard deviation).

Table 4. Content of Degradation Products (5-HMF, Furfural, Formic Acid, Acetic Acid, and Levulinic Acid) Found in the Liquor at the Reactor Outlet

Solvent	T (ºC)	t_{hold} (min)	5-HMF (mg.mL^{-1})	Furfural (mg.mL^{-1})	Acetic Acid (mg.mL^{-1})	Formic Acid (mg.mL^{-1})	Levulinic Acid (mg.mL^{-1})
Water	180	0	0.04 ± 0.01	0.62 ± 0.01	1.29 ± 0.03	0.22 ± 0.01	< loq
Water	180	60	0.26 ± 0.01	5.26 ± 0.03	3.23 ± 0.08	0.49 ± 0.05	< loq
Water	210	0	0.56 ± 0.01	5.83 ± 0.10	3.52 ± 0.27	0.68 ± 0.02	< loq
Water	210	60	1.48 ± 0.05	3.62 ± 0.08	4.73 ± 0.10	0.91 ± 0.01	< loq
Water	240	0	0.21 ± 0.01	0.05 ± 0.01	0.20 ± 0.01	0.03 ± 0.01	< loq
Water	240	60	1.45 ± 0.01	0.94 ± 0.01	5.02 ± 0.02	0.58 ± 0.01	0.23 ± 0.01
Water+Ethanol	180	0	0.02 ± 0.01	0.03 ± 0.01	0.46 ± 0.01	0.08 ± 0.01	< loq
Water+Ethanol	180	15	0.02 ± 0.01	0.02 ± 0.01	0.54 ± 0.01	0.11 ± 0.01	< loq
Water+Ethanol	180	30	0.04 ± 0.01	0.04 ± 0.01	0.69 ± 0.01	< loq	< loq
Water+Ethanol	180	60	0.11 ± 0.01	0.16 ± 0.01	1.06 ± 0.02	< loq	< loq
Water+Ethanol †	210	0	0.09 ± 0.01	0.52 ± 0.05	1.90 ± 0.05	0.37 ± 0.05	< loq
Water+Ethanol	210	15	0.11 ± 0.01	0.20 ± 0.01	2.06 ± 0.02	0.46 ± 0.01	< loq
Water+Ethanol	210	30	0.15 ± 0.01	0.36 ± 0.01	2.66 ± 0.01	0.45 ± 0.01	< loq
Water+Ethanol	210	60	0.21 ± 0.01	0.41 ± 0.01	2.90 ± 0.01	0.53 ± 0.01	< loq
Water+Ethanol	240	0	0.25 ± 0.01	0.42 ± 0.01	2.67 ± 0.02	0.71 ± 0.01	< loq
Water+Ethanol	240	15	0.34 ± 0.01	0.41 ± 0.01	2.67 ± 0.01	0.58 ± 0.01	< loq
Water+Ethanol	240	30	0.37 ± 0.01	0.39 ± 0.02	2.37 ± 0.04	0.58 ± 0.01	0.05 ± 0.01
Water+Ethanol	240	60	0.45 ± 0.01	0.25 ± 0.01	2.15 ± 0.02	0.59 ± 0.01	0.07 ± 0.01
Ethanol	240	0	0.04 ± 0.01	0.03 ± 0.01	0.73 ± 0.01	0.04 ± 0.01	< loq
Ethanol	240	60	< loq	< loq	0.80 ± 0.06	0.03 ± 0.01	< loq

** loq = Limit of Quantification; † = Values obtained using all triplicate analysis of each replicate experiments (mean value ± standard deviation).*

The sugar content obtained in liquor at 180 °C and 0 min holding time was comparable to other biomass hydrothermal fractionation reports in terms of hemicellulose recovery. Boussarsar *et al.* (2009) studied the hydrothermal treatment of SCB in water (5 wt.%) at 150, 170, and 190 °C. The authors obtained 4.5 and 6 mg.mL^{-1} xylose at 170 and 190 °C, respectively, by performing the reaction for a little over 60 min holding time. For reactions at 190 °C, a higher xylose content of 6.5 mg.mL^{-1} was obtained when employing a 125 min holding time, with longer reactions incurring in a decrease with an almost parabolic behavior. Considering that the liquor contained 0.6 mg mL^{-1} arabinose, and that the reported SCB hemicellulose content was 26%, total hemicellulose recovery approached 52%. Although based on a more dilute reaction system, and despite the fact that monomeric and oligomeric sugars were not reported separately, the highest hemicellulose recovery found by Boussarsar *et al.* (2009) was comparable to the present findings. A similar experiment was performed by Alves *et al.* (2025). SCB was hydrotreated at 180 °C with a 45 min holding time using a biomass-to-water mass ratio of 1:4, with additional water for extraction added latter resulting in a 1:7.53 mass ratio. A monomeric sugar concentration (glucose, xylose, and arabinose) of 16.5 mg.mL^{-1} was obtained, with the content of oligomers estimated via enzymatic hydrolysis as 9.98 mg.mL^{-1}. Although glucose was not distinguished from other monomeric sugars in the reported values, assuming that the liquor contained only hemicellulose-derived sugars and considering that SCB contained 29.3% hemicelluloses, the total hemicellulose recovery was 57% with a monomer-to-oligomer ratio of 1:0.6. This value is comparable to the best hemicellulose recovery from the present work, however, with a more expressive presence of monomeric sugars. From that, is possible to hypothesize that the heating profile of a batch reactor held significant influence over hydrolysis of oligomers in reaction liquor.

When ethanol was used to replace part of the solvent water, hydrolysis rates were slower at 180 °C, as shown by the increased xylo-oligomer contents contrasting with low xylose release (Fig. 7D). As temperature was raised to 210 °C, hydrolysis rates were increased with a corresponding increase in xylose concentrations at shorter holding times (Fig. 7E), which decreased afterward due to dehydration and other secondary reactions.

Alves *et al.* (2025) reported 11.14 mg.mL^{-1} monomers (glucose, xylose, and arabinose) and 2.3 mg.mL oligomers in organosolv liquors prepared from SCB using an water+ethanol (1:1 v./v.) mixture at 180 °C with a 120 min holding time and a 1:10 biomass-to-solvent ratio. Assuming these sugars to be derived from hemicelluloses, this would correspond to a recovery of 38% of hemicelluloses in liquor in a 1:0.2 mono-to-oligosaccharides ratio. Comparatively, in the present work a recovery of 34% of hemicelluloses in a 1:14.5 mono-to-oligosaccharides ratio was obtained at 180 °C with 60 min of holding time. In the present study, a 34% hemicellulose recovery with a 1:14.5 mono-to-oligosaccharide ratio was achieved at 180 °C and a residence time of 60 min. Once again, the sugar recovery in liquor is similar, but the oligomeric content is higher.

Compared with the remaining experiments performed with water and water–ethanol mixtures at 180 and 210 °C, the reaction liquors exhibited lower total sugar concentrations, including both oligomeric and monomeric species. In the ethanol-only systems (Fig. 7G), hydrolysis to monomers was attributed to the intrinsic SCB moisture content and to the water released during carbohydrate dehydration.

In most runs, pentose oligomers and monomers (mostly arabinose and xylose) were in concentrations higher than those of glucose. Although the previous section reports significant glucan fractionation in water-only experiments performed in T ≥ 210 °C, the relatively low water-soluble glucose recovery is likely tied to its conversion into humins.

In experiments using water+ethanol as solvent, the presence of gluco-oligomers became more evident at 240 °C, consistent with the observed decrease in glucan recovery in the residual solids (Fig. 5F).

Based on the products disclosed in Fig. 8 and Table 4, a simplified graphical representation was created based on their parental carbohydrates (Fig. 9).

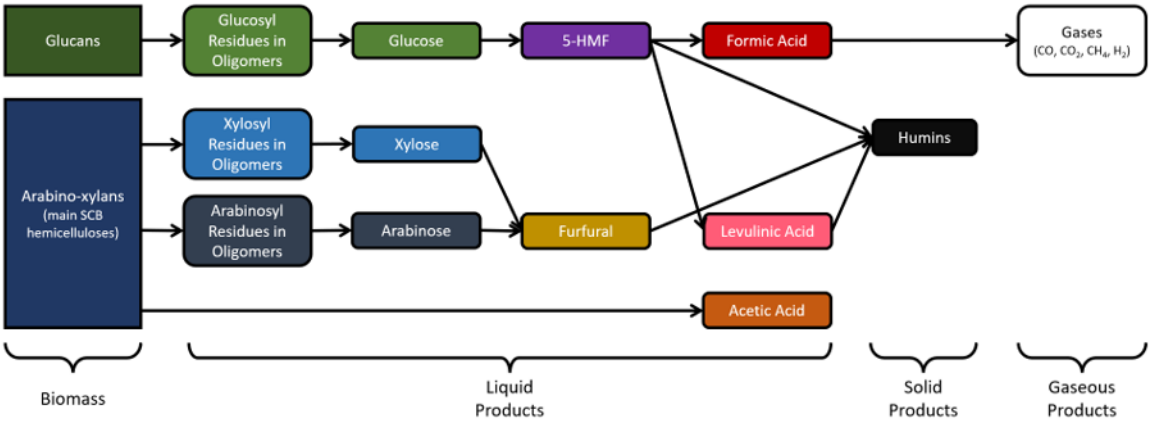

Fig. 9. Pathways for formation of degradation products from pentose and hexose sugars under hydrothermal treatment

The main degradation products from water-only runs were furfural and acetic acid, followed by a more pronounced formation of 5-HMF at temperatures ≥ 210 °C. Furfural formation was more pronounced at lower temperatures, particularly at 180 °C, where its concentration exceeded that of all monomeric sugars. In higher temperatures, acetic acid predominated. In terms of chemical origin, both furfural and 5-HMF are dehydration products from pentoses (xylose and arabinose) and hexoses (glucose), respectively (Knežević *et al.* 2009; Shimizu *et al.* 2021). However, acetic acid is mainly associated with hemicellulose deacetylation (Garrote *et al.* 2001).

Qiu *et al.* (2023) showed that temperature plays a limiting role in the catalytic conversion of biomass to furfural. The authors argue that, despite the fact that hydrothermal treatments are normally performed at temperatures up to 300 °C, optimal furfural yields are obtained between 160 and 210 °C. This is mostly attributed to secondary reactions forming short-chain organic acids and aldol condensation forming humins (Köchermann *et al.* 2019; Qiu *et al.* 2023). In the present work, the highest furfural yield was obtained at 210 °C, with decreased contents spotted at 240 °C (Figs. 8B and 8C).

Shimizu *et al.* (2021) studied the batch hydrothermal liquefaction of wood chips in a 0.19 L reactor using a 1:10 biomass-to-water mass ratio for temperatures ranging from 180 to 425 °C with different holding times. 5-HMF concentration peaked at 1.1 $mg.mL^{-1}$ when HTL was performed at 180 °C with a 30 min holding time, but reactions at 250 °C reduced it to 0.3 $mg.mL^{-1}$. In the present report, despite working with a similar biomass-to-solvent ratio, 5-HMF release was lower at 180 °C with a 60 min holding time (0.26 $mg.mL^{-1}$) and higher at 210 and 240 °C (maximum at 1.48 $mg.mL^{-1}$). By examining 5-HMF conversion pathways, hydration leads to levulinic and formic acids (Jing and Lü 2008). None of these products were detected in significant amounts at 180 °C (Fig. 8A) because the extent of glucan depolymerization at this temperature was low.

Finally, acetic acid formed from hemicellulose deacetylation act as catalyst for carbohydrate hydrolysis and dehydration (Garrote *et al.* 2001; Area *et al.* 2009). Shimizu

et al. (2021) showed that acetic acid is a stable HTL product as it was produced in concentrations between 3 and 5 $mg.mL^{-1}$ for reactions carried out between 180 and 425 °C. Given that these authors employed a biomass-to-solvent ratio (1:10) like that of the present study (1:9), these concentrations are both comparable and consistent with those presented in Fig. 8A to Fig. 8C.

When ethanol was added as co-solvent, acetic acid predominated over all other reaction products at 210 °C (Fig. 8E). Since carbohydrate depolymerization was more pronounced in the absence of ethanol, acetic acid may have been formed from lignin under organosolv conditions at temperatures between 150 and 200 °C (Li *et al.* 2019). Nevertheless, acetic acid content in water+ethanol system (Fig. 8E and 8F) was lower than that observed in water-only reactions (Fig. 8B and 8C). This finding may be explained by its esterification with ethanol, with the forming of ethyl acetate. This reaction competes with hydrolysis, which is favored by water. Although esterification is slow at room temperature, experimental studies considering the chemical equilibria of this quaternary system (water, ethanol, acetic acid, and ethyl acetate), such as those described by Kang *et al.* (1992) and Golikova *et al.* (2017), indicate that higher temperatures and acidified reaction media can accelerate the esterification kinetics.

Besides acetic acid, formic and levulinic acids, formed by 5-HMF rehydration, were present in very low concentrations in reaction liquors. Levulinic acid was detected only at 240 °C, while formic acid was present in most reaction liquors, reaching its highest concentrations at 210 °C when water was used as the sole solvent and at 240 °C when ethanol was added as a co-solvent.

Area *et al.* (2009) performed lignocellulosic biomass (wood chips) fractionation in ethanol+water (14:1 v./wt. solvent-to-biomass ratio with a 1:1 v./v. water-to-ethanol ratio) using a continuous liquor circulation system. With results expressed as mass of extracted compound per SCB dry mass, yields of 0.14% glucose, 1.05% xylose, 0.25% arabinose, 0.70% furfural, 2.14% acetic acid, and 0.25% formic acid were reported for experiments carried out at 180 ºC for a 90 min holding time. Performing the same calculation strategy for experiments carried out at 180 ºC for 60 min in this work, 0.05% glucose, 0.22% xylose, 0.27% arabinose, 0.13% furfural, and 0.85% acetic acid were obtained, with no 5-HMF being detected. Lower yields of monomeric sugars and degradation products may be attributed to the use of a lower solvent-to-biomass ratio. However, differences in particle size distribution may also have contributed to the observed discrepancy, along with the depithing process adopted by the former authors.

Figures 8B and 8C show that with an increase in the set-point temperature, the presence of other secondary biomass derivatives declined in the reaction liquors. This was evident not only in catalyst-free hydrothermal treatments, but also in other systems such as dilute acid hydrolysis. After dilute sulfuric acid hydrolysis of SCB using a 1:10 biomass-to-solvent mass ratio, xylose recovery was almost complete at 122 °C but, when the temperature was raised to 128 °C, there was a decrease in all monomeric sugars and their main hydrothermal derivatives (5-HMF, furfural, and acetic acid) (Aguilar *et al.* 2002).

The pathway proposed in Fig. 9 was partially based on the findings of Knežević *et al.* (2009), who studied the formation of gases from different components of lignocellulosic biomass HTL condensates. For instance, 0.16 g of gas was obtained for each gram of glucose (16 wt.% yield) submitted to hydrothermal treatment (5 wt.% glucose in water, 350 °C, and 30 min holding time). Formic acid presented the highest gas yield (103 wt.%), forming CO_2 and H_2 primarily, while all other species discussed in this work presented lower values (12 wt.% for furfural, 3 wt.% for 5-HMF, and 5 wt.% for acetic acid).

The results of this section indicate that, as HTL conditions are approached, most SCB hemicellulose sugars are converted into degradation products, regardless of whether ethanol is used or not as a co-solvent. Although small amounts of oligosaccharides are still detected at 240 °C, their contents are significantly lower than those observed at 180 °C. The concentration of monomeric sugars in reaction liquors was also low, especially compared to acetic acid, which predominated in water-only liquors even at 240 °C. Acetic acid concentration decreased when ethanol was added as co-solvent, partially due to its esterification to ethyl acetate. Ethanol as co-solvent acts as a delignification agent and an inhibitor for humins formation. Finally, the gases formed in the system were probably originated from formic acid decomposition, which accumulated in the reaction liquor as carbohydrates were thermally decomposed.

Future Work

The present work considered treatment of sugarcane bagasse using only water and ethanol as solvent. In future research, adding liquor components (*e.g.*, acetic, levulinic, and formic acids) to the reaction medium before processing may be tested to evaluate autocatalytic and selectivity effects on pre-HTL reaction performance. Complementary future studies may focus on the kinetic modeling of biomass conversion under pre-HTL conditions, considering structural lumps (glucans, hemicelluloses, and total lignin), non-isothermal temperature profiles, and solvent composition. Such work might be useful to provide valuable insights for HTL process optimization.

CONCLUSIONS

1. Reaction severity in batch reactors was determined by the heating profile of the reaction chamber. Slow heating resulted in higher depolymerization of sugarcane bagasse (SCB) macromolecular components, with an extensive degree of biomass transformation even before reaching hydrothermal liquefaction (HTL) reaction conditions.
2. If the aim is to recover sugars (mono and oligosaccharides) for further processing, SCB should be treated with only water as solvent at temperatures up to 180 ºC and short residence times.
3. Despite recovering 62% of SCB hemicelluloses in the reaction liquor under hydrothermal treatment at 180 ºC with 0 min holding time, lower recovery values were found under all other solvents, temperatures, and holding times tested due to degradation reactions.
4. Within 180 and 240 ºC, water almost completely hydrolysed SCB cellulose and hemicellulose components. However, yield losses were observed due to condensation reactions involving carbohydrate dehydration derivatives (furans and organic acids) forming water-insoluble humins.
5. If the goal is to depolymerize biomass while retaining the generated chemical species in the reaction liquor, addition of ethanol and increased reaction temperatures can maximize extraction yields and minimize recovery of residual solids.
6. Acetic acid was the main component in all reaction liquors, with higher concentrations observed when water was used as the sole solvent.

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Conflict of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

Use of Generative AI

The authors used AI-assisted writing tool (ChatGPT 5.4) solely for language editing, rephrasing, and grammatical refinement. The authors take full responsibility for the content and its accuracy. No AI tools were used to generate scientific content, analyze data, or produce figures.

Data Availability

Data not included in this article, such as individual temperature profiles for the experiments, will be made available by the authors upon reasonable request.

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