Identification and quantification of valuable platform chemicals in aqueous product streams from a preliminary study of a large pilot-scale steam explosion of woody biomass using quantitative nuclear magnetic resonance spectroscopy

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Abstract
Steam explosion breaks down the polymeric matrix and enables the recovery of valuable compounds from lignocellulosic feedstock. In the steam explosion process, biomass is treated with high-pressure steam which subsequently generates large quantities of a condensed aqueous liquid (process effluent) and a filtered aqueous liquid (filtrate) that contain furfural, 5-hydroxymethylfurfural, 5-methylfurfural, methanol, and acetic acid as major constituents. This study addresses the identification and quantification of value-added chemicals in the aqueous product streams using quantitative analytical nuclear magnetic resonance spectroscopy with water suppression. This work reports a screening study for two different types of sawdust (Norway spruce and birch) at two different scales (4 L and 10 L reactors) using different reaction temperatures (190–223 °C) and corresponding pressures (13–24 bar), with and without the addition of SO_2 gas. The duration of all experiments was 8 min. The process effluents contained acetic acid, methanol, formic acid, 5-methylfurfural, and furfural. Acetic acid (0.5 g/kg dry input biomass) and furfural (1.0 g/kg dry input biomass) were more abundant than methanol, formic acid, and 5-methylfurfural for both feedstocks. The addition of SO_2 increased the furfural yields, indicating more efficient hydrolysis of hemicelluloses under acidic conditions. Filtrate samples also contained 5-hydroxymethylfurfural, with the highest concentrations (5.7–6.0 g/kg dry input biomass) in the filtrates from spruce. The different feedstocks and steam explosion temperatures strongly influenced the overall yields of the target compounds, in some cases tripling the concentrations. The results can be used to improve the profit margins in a pellets and chemicals biorefinery, as demonstrated in the ArbaOne pellets plant.

Keywords Lignocellulosic biomass · Steam explosion · Biorefinery · Aqueous product streams · Furfural · 5-Hydroxymethylfurfural

1 Introduction

Modern society is overdependent on petroleum-based resources and is thus seriously challenged by dwindling fossil fuel reserves and growing environmental concerns [1–3]. As a result of this, the production of biofuels and chemical building blocks from renewable feedstocks is a developing trend in the chemical industry for replacing fossil resources while simultaneously mitigating climate change [3–5]. When considering alternative carbon-based raw materials for the petrochemical industry, options are limited, as there are only two large-scale sources of renewable carbon on this planet: plants and atmospheric carbon dioxide [6]. Established manufacturing processes for bio-based chemicals are mainly based on first-generation biomass, i.e., edible vegetable oils and sources of carbohydrates, and this is normally in direct competition with food and fodder production. Thus, developing new processes for producing second-generation biofuels and products from non-edible resources such as lignocellulosic biomass can prevent this predicament [5, 7].

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However, the development of economically viable and energy-efficient processes for converting low-value lignocellulosic biomass into commercially useful biofuels and products is a considerable challenge. At present, most of the proposed processes are unable to compete economically with petroleum refineries in part due to incomplete utilization of the biomass feedstock. The biorefinery approach, to improve biomass utilization, and thus, the economic outputs of biomass-derived processes encompass an integrated and diversified processing plant where the incoming biomass feedstock is completely converted into a wide range of valuable products, including fuels, power, heat, chemicals, and materials [5, 8–10].

Lignocellulosic biomass comprising residues from forestry, agriculture, municipal sources, and industry is considered a sustainable feedstock for this purpose since it is renewable, readily available, and has a wide spatial distribution in nature. Lignocellulosic biomass is heterogeneous and composed of three principal constituents with different structural compositions: approximately 30–50% cellulose, a polymer of glucose; 20–35% hemicellulose, a heteropolymer containing mostly xylose; and 15–35% lignin, a complex heteropolymer of monolignols. The structural rigidity of the polymeric matrix provided by the strong intermolecular interactions has proven problematic for the efficient utilization of lignocellulosic biomass [1, 5, 6, 11]. Successfully replacing fuels and chemicals derived from petroleum with bio-based products derived from lignocellulosic biomass will therefore require high-yield, low-cost, and energetically efficient targeted upgrading processes. Hence, new industrial technologies must strive to minimize the consumption of energy and chemicals, while limiting the generation of downstream pollutants such as waste gas, wastewater, and solid waste materials [1, 6, 11].

For lignocellulosic biomass, a pretreatment step can be used to disrupt the plant cell structure and overcome its recalcitrance, making polysaccharides easily available for reactions like enzymatic hydrolysis, and increasing the surface area [4, 12, 13]. The most widely investigated pretreatment techniques for woody biomass include dilute acid hydrolysis, steam explosion, organosolv, and sulfite pretreatment [5, 14]. Among these pretreatments, steam explosion, which includes a degree of autohydrolysis, is an efficient and widely used technique. During the steam explosion, the lignocellulosic biomass undergoes a sequence of defibrillation, delignification, and hydrolysis of the hemicelluloses. However, the crystallinity of cellulose tends to increase due to the crystallization of amorphous portions, which can be a disadvantage of the technology since the hydrolysis processes will generally be more difficult with high crystallinity [13, 15–17]. Advantages of steam explosion pretreatment include low capital investment, moderate energy requirements, and low environmental impacts as no acids, bases, or solvents are

normally required, which simplifies the subsequent biorefinery stages and reduces their cost. Additionally, uncatalyzed steam explosion pretreatment avoids the additional chemical costs and associated problems derived from equipment corrosion [4, 15, 18]. Steam explosion pretreatment has proven effective for a wide range of different biomasses [8, 19–22].

The steam explosion process involves exposing the lignocellulosic material to high-pressure saturated steam for a specified period and then reducing pressure swiftly, thus making the materials undergo an explosive decompression which results in the deconstruction of the lignocellulosic matrix [8, 13, 15]. During this treatment, the high-temperature steam causes the release of organic acids such as formic acid and acetic acid from a formyl and acetyl functional groups in biomass. These compounds can catalyze hydrolytic degradation of the chemical bonds connecting the woody polymers. The autohydrolysis reactions result in the loss of hemicellulose, which is dissolved in the hot condensed water and can be recovered in the liquid fraction to be further converted into value-added products [8, 23–25]. Acetic acid hydrolyzes xylan polymers into monomeric xylose units and xylose oligomers, and the acidic conditions can lead to further dehydration of the monomeric sugars. This pretreatment can also cause the melting of lignin and its partial depolymerization through the cleavage of the predominant β-O-4 ether and other acid-labile linkages producing a series of lignin monomer derived alcohols and condensation byproducts [8, 15, 26]. The main factors that affect the steam explosion process are temperature, residence time, particle size, and moisture content. Typically, the steam explosion process operates at temperatures ranging from 160 to 260 °C for 1 to 30 min, depending on the feedstock. Optimal hemicellulose solubilization and hydrolysis can be achieved either by high temperature and short residence time or lower temperature and longer residence time. Furthermore, sugar degradation products such as furfural and 5-hydroxymethylfurfural, and soluble phenolic compounds such as catechol and vanillin can be generated in the process with increasing yields at high temperature and long residence time [8, 16, 27].

The optimal solubilization and hydrolysis conditions are also highly dependent on the structural composition of the feedstock. Therefore, a distinction must be made between hardwoods and softwoods [5, 15, 18]. Softwoods have a higher cellulose content (40–45%), higher lignin (26–34%), and lower pentosan (7–14%) content compared to hardwoods (cellulose 38–49%, lignin 23–30%, and pentosans 19–26%) [28]. Acetylated xylans are the predominant hemicellulosic species found in hardwoods, whereas softwoods are mainly composed of glucomannans. Hardwood xylans mainly consist of xylose and glucuronic acid and are relatively labile and will therefore undergo autohydrolysis under milder conditions compared to softwood xylans due to the high content

of acetyl groups. In contrast, softwoods have a higher proportion of partly acetylated glucomannans and galactoglucomannans, and xylans correspond to only a small fraction of their total hemicellulosic content. Hence, the steam explosion is found to be less effective for softwoods due to the low content of acetyl groups in the hemicellulose portion and high lignin content [5, 18, 29].

According to a review on pretreatment techniques, acid-catalyzed steam treatment using H_2SO_4 or gaseous SO_2 is the most suitable pretreatment technique for softwoods [30]. In general, 1–5% w/w of SO_2 is used to treat the biomass at temperatures of 190–210 °C for hardwoods and 200–220 °C for softwoods. The SO_2 gas penetrates the biomass and by explosive decompression, hemicellulose will be hydrolyzed to soluble sugars as a result of glycosidic bonds cleavage [22, 31, 32]. Carrasco et al. reported in 2010 that between 50 and 60% of the xylan could be recovered as soluble xylose from the steam treatment of sugarcane bagasse at 190 °C for 5 min using 2% w/w of SO_2 as a catalyst [33]. In a study from 2005, Öhgren et al. reported that a high overall yield of xylose (78%) can be achieved with one-step steam explosion pretreatment of corn stover using 2% w/w SO_2 as catalyst [34]. However, issues such as equipment corrosion, high purchase costs of SO_2, and additional costs for neutralization as well as recycling must be taken to account when considering the application of SO_2-catalysis in a full-scale steam explosion process [18, 31].

A plethora of valuable products can be synthesized from bio-based platform chemicals, where a special group of furan derivates is identified as among the top 10 value-added molecular platforms by the US Department of Energy (DOE) due to their widespread application as feedstocks for bulk chemicals and fuels. The most important furans are furfural, 5-hydroxymethylfurfural (5-HMF), and 2,5-furandicarboxylic acid (FDCA). Additionally, furans are highly carbon efficient during their synthesis as they retain all five carbon atoms initially present in the pentoses and 5-HMF retains all six carbon atoms initially present in the hexoses [5, 35]. Several recent studies have shown that furfural and 5-HMF can be produced from biomass at high yields and at low costs (1000–5000 USD/ton) if produced at scales above 10 kton/year [10, 36]. According to Trivedi et al., the global bio-based platform chemicals market accounted for 13.83 billion USD in 2017 and is expected to reach 31.56 billion USD by 2026 growing at a compound annual growth rate (CAGR) of 9.6% during the forecast period [37].

Furfural is a key platform chemical produced from acid-catalyzed dehydration of biomass-derived C5 sugars, mainly xylose (from xylan), with a global market of around 400 kilotons per year. Furfural can further be transformed into fuels and value-added chemicals which are widely used in oil refining, plastics, pharmaceutical, and agrochemical industries [1, 35, 36]. Currently, 90% of furfural is produced

by China, South Africa, and the Dominican Republic. From 2006 to 2016, the cost of furfural has been between 800 and 1600 USD/ton. The furfural price increased to 2700 USD/ton at the end of 2017 due to environmental regulations enforced on China's furfural production industry. Thus, in 2017, the furfural market was valued at around 400 million USD. However, the furfural market is expected to undergo a considerable expansion in the coming years due to a rapidly growing demand for furfuryl alcohol. Indeed, the largest amount of furfural (around 60% of the global furfural market) is converted to furfuryl alcohol which is primarily used to produce foundry resins [5, 36, 38, 39]. In addition, furfural can undergo successive hydrogenation and/or hydrogenolysis reactions to produce polymer precursors such as furfuryl alcohol, tetrahydrofurfuryl alcohol, and 1,5-pentanediol, as well as renewable solvents including 2-methyltetrahydrofuran and cyclopentanone. Succinic acid which is a versatile building block with a wide range of applications can be derived from furfural through oxygenation [36, 40].

5-Hydroxymethylfurfural (5-HMF) is also considered one of the top 10 value-added bio-based chemicals by the US DOE. 5-HMF and its derivates are versatile precursors to produce medicines and pharmaceuticals, bioplastics, biopolymers, and biofuels [41–43]. 5-HMF contains two different functional groups, a hydroxyl group, and an aldehyde group, making it an attractive starting material for transformation into a wide range of chemicals with important industrial applications. 5-HMF is a product of acid-catalyzed dehydration of cellulose and all types of C6 sugars, including monomeric and polymeric carbohydrates such as fructose, glucose, mannose, galactose (from glucomannan), and starch [36, 41, 42]. 5-HMF can undergo successive oxidation, rehydration, and hydrogenation reactions to produce platform chemicals and liquid fuels such as 2,5-furandicarboxylic acid (FDCA), adipic acid, levulinic acid, 2,5-dimethylfuran, and gamma-valerolactone (GVL) [40, 41]. FDCA is one of the most extensively investigated products from 5-HMF and is another key bio-derived platform chemical, which can be converted to succinic acid and adipic acid, both of which have a wide range of applications [41, 44]. The global 5-HMF market was valued at around 55,900 K USD in 2018 and is expected to reach 62,700 K USD by the end of 2025 [45]. Unfortunately, the industrial production of 5-HMF remains an economic challenge for large-scale applications. The main reasons impeding the rapid expansion of 5-HMF production are the low reactivity of glucose, the relatively high price of the starting material (fructose), and the low yields of 5-HMF obtained from simple processes in aqueous reaction media [5].

The work presented here was performed as a preliminary study in the development of a full-scale commercial biorefinery in Eastern Norway, producing black wood

pellets and platform chemicals. Steam explosion is considered a sustainable and promising technology for improving the pelletizing properties for co-firing biomass pellets and coal. The pellets from steam-exploded biomass have increased calorific value, higher density, and are more impact and abrasion resistant and water-repellent, making them superior to conventional pellets in terms of storage and handling. They thus have the potential to become a valuable part of the future sustainable energy supply chain [46, 47]. During the full-scale steam explosion process, large quantities of a condensed aqueous liquid (process effluent) and a filtered aqueous liquid (filtrate) are generated. These fractions contain considerable amounts of furfural and 5-hydroxymethylfurfural (5-HMF), and also methanol, acetic acid, acetone, and formic acid. Filtrates have also been shown to contain various amounts of dissolved sugar monomers and oligomers. However, these components were not considered in this study.

Currently, only a few studies have analyzed organic compounds in the aqueous phase streams from hydrothermal treatment of lignocellulosic biomass [48, 49]. Analysis of small organic molecules in aqueous product streams can be challenging due to limitations in the application of chromatographic methods, such as signal overlap due to similar chromatographic properties especially in HPLC (high-pressure liquid chromatography) and solvent delay in GC-based (gas chromatography) analysis that can exclude a wide range of components. To provide improved analytical data, quantitative NMR spectroscopy has recently developed into a well-established technique and has been widely used for the analysis of organic compounds at low concentrations in metabolomics, pharmaceuticals, natural products, and food and beverage. In 2017, Elliot et al. reported a quantitative ^{13}C NMR procedure for the detection and accurate quantification of α-hydroxy acids, esters, and lactones from Sn-beta-catalyzed conversion of xylose, without using reference standard compounds [50]. In 2020, Halleraker and Barth published a quantitative NMR study of aqueous phase products from the hydrothermal conversion of lignin. Acetic acid, acetone, methanol, formic acid, dimethyl ether, phenol, and catechol were reported to be compounded with the highest concentrations [51]. In 2018, Yue et al. reported a study where various qualitative and quantitative NMR techniques were applied in the analysis of process waters from hydrothermal carbonization (HTC) of furfural residues. Without separation and purification, 5-hydroxymethylfurfural, glycerol, formic acid, methanol, acetic acid, levulinic acid, hydroxyacetone, and acetaldehyde were identified and quantified to be the main detectable compounds [52]. In a recent study, Løhre et al. reported a preparative laboratory procedure combined with subsequent ^{1}H NMR spectroscopy for the identification and quantification of biorefinery products in aqueous product streams [53]. The procedure gives highly

accurate results with excellent reproducibility for quantitative analytical purposes.

In this study, we aim to identify and quantify the molecular platform compounds generated in the aqueous product streams from the steam explosion of woody biomass at the pilot scale. The concentration of furfural, 5-HMF, and the other major organic components (acetic acid, acetone, methanol, and formic acid) in the process effluents and filtrates from the steam explosion of two different types of woody biomass (Norway spruce and birch) are compared. The study also aims to find the optimal steam explosion parameters for maximizing furfural and 5-HMF in the product streams. This is done by evaluating the composition of organic compounds in the aqueous phases as a function of reactor scale and experimental pretreatment conditions. The effect of adding SO_2 as an acid catalyst during steam treatment is also evaluated. The quantification of the aqueous organic components was performed by using quantitative nuclear magnetic resonance spectroscopy (qNMR).

2 Materials and methods

2.1 Chemicals

All reagents and solvents were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification. All standard components are commercially available.

2.2 Large pilot-scale steam explosion

The steam explosion processing was performed on a large pilot scale at Lund University Biobased Industry Research Center (LUBIRC) in Sweden. Two different types of woody biomass, Norway spruce (softwood), and birch (hardwood) were investigated as feedstocks, and experiments were conducted at two different scales (4 L and 10 L reactors) using different reaction temperatures (190–223 °C) and pressures (13–24 bar). The duration of the pressurized step was 8 min in all experiments. At the decompression, a gas phase product is formed. This gas, which is mainly steam and some small organic compounds, is condensed and collected through an outlet connected to the decompression valve of the reactor. This product is referred to as effluent/condensate in this work. Samples produced at LUBIRC, i.e., the wet steam-exploded biomasses and process effluents, were sent to RISE PFI for further distribution. The wet steam-exploded biomass was vacuum filtered at RISE PFI to give the filtrate samples.

In total, 10 effluent samples and 10 filtrate samples are included in this study. An extended overview over investigated steam explosion parameters and sample information is given in Table 1. As shown in Table 1, experiments using

Table 1 Extended overview of experimental large pilot-scale steam explosion conditions

Experiment name	Biomass type	Amount of dry biomass (g)	Reactor scale (L)	Residence temp. (°C)	Residence time (s)	Residence pressure (bar)	SO_2 injection
Reference 4 L	Norway spruce	800	4	223	480	24	
Reference 10 L		700	10	223		24	
Warm flash tank		800	4	223		24	
Low temp		800	4	210		20	
Low temp. + SO_2		800	4	210		20	3% w/w
Reference 4 L	Birch	800	4	200		16	
Reference 10 L		700	10	200		16	
Warm flash tank		800	4	200		16	
Low temp		800	4	190		13	
Low temp. + SO_2		800	4	190		13	1.5% w/w

birch as feedstock have been conducted at milder severity to maintain the quality of the produced pellets. According to previous investigations performed at LUBIRC and unpublished internal results birch requires temperatures below 200 °C to provide high-quality pellets while simultaneously generating high furfural and 5-HMF yields in the aqueous product streams.

The parameters investigated in this experimental sequence include two temperatures, the effect of keeping the exploded mass uncooled for the duration of the two batches of 400 g biomass when using the 4 L reactor (termed "Warm flash tank") and the effect of changing the scale to a 10 L reactor with one run using 700 g biomass. The loading capacity of the 10 L reactor is 700 g dry material, while the 4 L reactor can be loaded with 400 g dry material. In addition, in two of the experiments conducted in the 4 L reactor, SO_2-gas was used as an acid catalyst to improve hemicellulose hydrolysis. The amount of steam added to the reactor depended on the degree of filling. The optimal filling level used in LUBIRC is 70%, as a higher degree of filling leads to uneven heat transfer and variable conversion of the material. The most abundant organic species present in the effluent and filtrate samples were quantified using the procedure described in Sections 2.3, 2.4, and 2.5.

2.3 Preparation of samples for qNMR analysis

Samples for q-NMR analysis were prepared by using 8 mL of each aqueous sample and adding 400 µL (for the effluent samples) and 200 µL (for the filtrate samples) of a 2.1 M solution of dimethyl sulfone in distilled water (TraceCERT® DMSO$_2$, $(CH_3)_2SO_2$) as internal standard (IS). The target concentration of IS in the effluent and filtrate samples at this stage was approx. 0.100 M and 0.052 M, respectively, ensuring analysis within its optimal range of quantification. A stock solution containing 0.010 M sodium phosphate dibasic dihydrate buffer ($\geq$ 99.0% $Na_2HPO_4\cdot2H_2O$) and 20%

deuterium oxide (99.9 atom % D D_2O containing 0.05 wt. % TSP (3-(trimethylsilyl)-propionic-2,2,3,3-d4 acid), sodium salt) was prepared and added to the sample in a volume ratio of 1:1, giving the analyzed sample a 10% volume of deuterium oxide. The NMR samples were prepared according to the protocol reported by Løhre et al. [53]. The stepwise preparation of the NMR samples is illustrated in Figs. 1 and 2.

2.4 NMR spectral acquisition

NMR acquisition was engaged by Topspin 4.0 and IconNMR on a 600 MHz Bruker AVANCE NEO NMR-spectrometer equipped with a QCI CryoProbe with four RF channels. NMR acquisition parameters in this study, using pre-saturated water suppression, are described elsewhere [53].

2.5 Identification and quantification

Compound identity was determined by using online databases and NMR spectra of standard compounds. The most abundant compounds in the effluent samples were selected for quantification. They comprised acetic acid (1.93 ppm), acetone (2.24 ppm), methanol (3.37 ppm), formic acid (8.47 ppm), 5-methylfurfural (2.43, 6.44, 7.51, and 9.33 ppm), 5-hydroxymethylfurfural (4.70, 6.68, 7.54, and 9.46 ppm), and furfural (6.77, 7.58, 7.93, and 9.50 ppm). The final 5-methylfurfural, 5-hydroxymethylfurfural, and furfural concentrations were calculated based on the average value of their corresponding signals. To ensure stable values for the NMR chemical shifts from one spectrum to another, the pH should be held constant. In this context, the buffer concentration can be increased ($\leq$ 200 mM). However, the spectra acquired in this study did not display shift variations because of pH variations.

Integration regions for quantification were selected as the region around each signal out to but not including ^{13}C
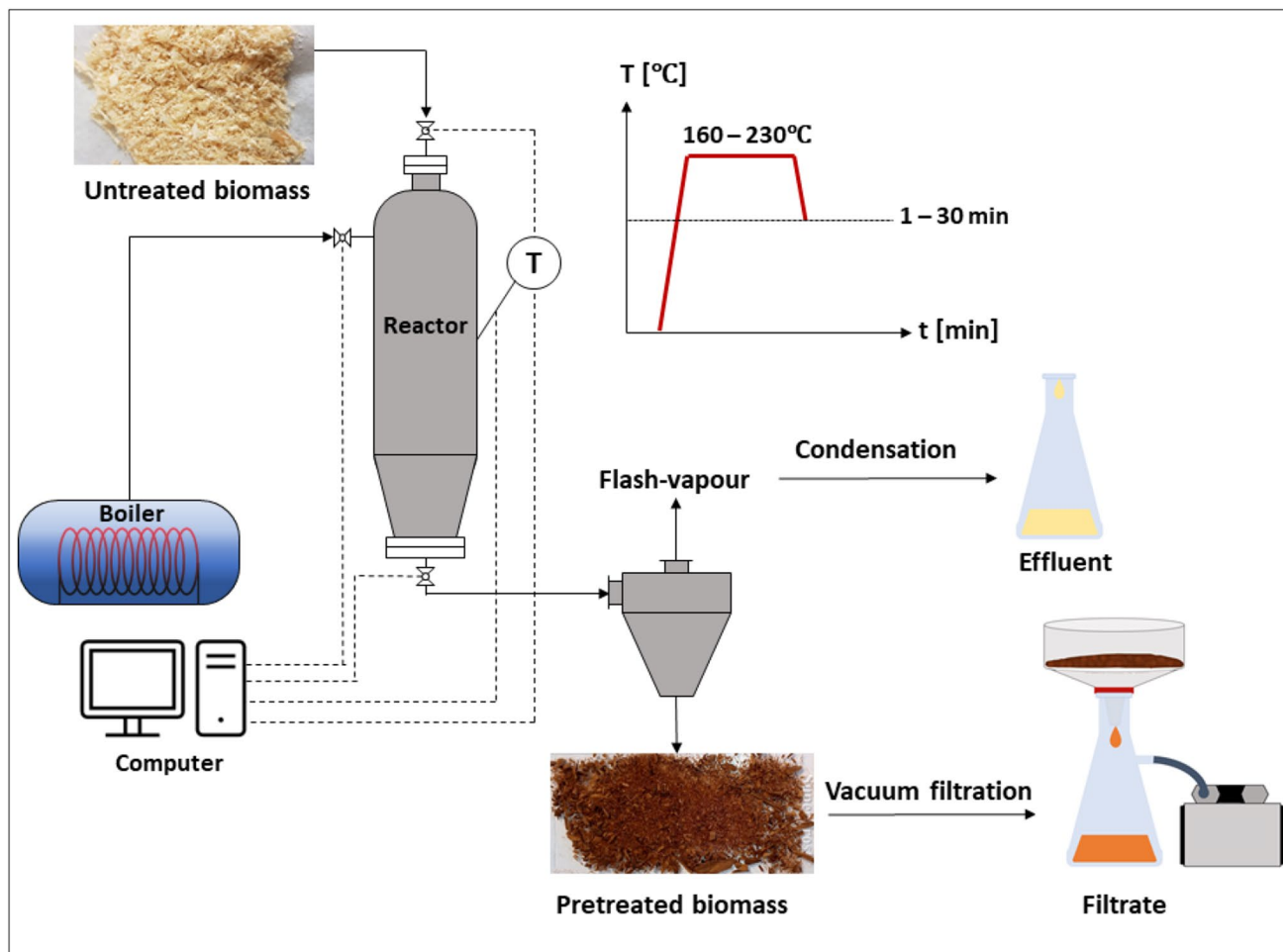
Fig. 1 Flow chart illustrating steam explosion unit at LUBIRC and the origin of the aqueous samples

satellite signals. All components were quantified relative to the internal standard (DMSO$_2$) concentration. Quantification of components was performed by direct calculation from the resonance peak integrals, together with internal standard concentration, initial volumes of samples, molecular masses, and a normalization of the number of protons giving rise to the respective signals. NMR data were processed using a line broadening of 0.30 Hz, and signals were integrated (10 − 0 ppm) using TopSpin 4.0.7 software. Signals from labile protons, such as − OH and − NH$_2$, were not considered in this study [53]. The concentration of each component [A], given as millimolar (mM), was calculated according to Eq. (1), where I$_A$ is an integral of the component and NP$_A$ is the number of protons giving rise to the signal. I$_{DMSO2}$ is the integral of the DMSO$_2$ signal, NP$_{DMSO2}$ is the number of DMSO$_2$ protons giving rise to the signal (6 protons), and [DMSO$_2$] is the concentration of DMSO$_2$ in the NMR sample.

$$[A] = \frac{I_A \times NP_{DMSO2} \times [DMSO2]}{NP_A \times I_{DMSO2}} \tag{1}$$

The yield of each component (m$_A$), given as g of component/kg of dry input material, was calculated according to Eq. (2), where [A] is the concentration of each component measured according to Eq. (1) and M$_A$ is the molar mass of each component.

$$m_A = \frac{[A] \times total\ amount\ of\ aqueous\ sample \times M_A}{amount\ dry\ input\ material \times 1000} \tag{2}$$

The recovery of biomass after the steam explosion process, given as (%), was calculated according to Eq. (3).

$$Recovery\ of\ biomass\ (\%) = \frac{Amount\ of\ dry\ pretreated\ biomass\ (g)}{Amount\ of\ dry\ input\ biomass\ (g)} \times 100 \tag{3}$$

Fig. 2 Stepwise preparation of the qNMR samples including the addition of the internal standard to the effluent and filtrate samples
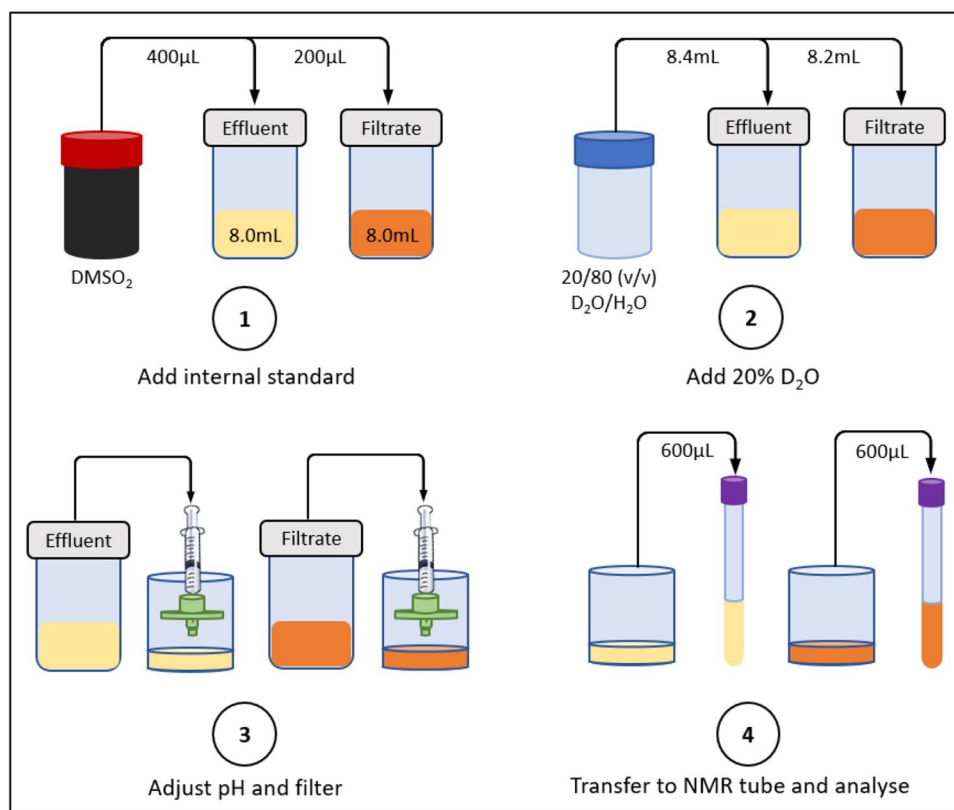
2.6 Reproducibility

In order to evaluate the precision related to the reproducibility of the sample workup and subsequent NMR quantification procedure, three repeated workups using three different effluent samples (*Warm flash tank* and *Low temp. + SO$_2$* from Norway spruce and *Low temp. + SO$_2$* from birch) and two different filtrate samples (*Reference 10 L* from Norway spruce and *Low temp. + SO$_2$* from birch) were prepared. The parallel quantifications are noted as *p1*, *p2*, and *p3*.

3 Results and discussion

3.1 Samples

The quantitative results from 10 steam explosion processes are shown in Table 2. It was unfortunately not possible to measure the exact volume of produced process effluents during steam explosion due to sampling issues. Thus, the amounts of the effluent samples in Table 2 are

Table 2 Quantitative results showing product output from the steam explosion experiments

| Experiment name	Biomass type	Amount of wet steam-exploded biomass (g)	Dry matter (%)	Amount of dry steam-exploded biomass (g)	Recovery of biomass (%)	Estimated amount of effluent (mL)	Amount of filtrate (mL)
Reference 4 L	Norway spruce	3176	23.9	760	95.1	182	1220
Reference 10 L		3306	19.2	636	90.9	194	1575
Warm flash tank		3350	23.8	796	99.5	191	1110
Low temp		3209	23.7	762	95.2	47	710
Low temp. + SO$_2$		3363	19.8	667	83.8	41	1300
Reference 4 L	Birch	3317	22.9	758	94.7	58	750
Reference 10 L		2691	23.5	631	90.1	64	1050
Warm flash tank		2635	29.7	782	97.8	60	635
Low temp		2925	27.3	799	99.8	46	370
Low temp. + SO$_2$		3142	22.5	705	88.1	41	1150

estimated volumes based on internal results obtained from comparable steam explosion processes. As shown in Table 2, for both feedstocks, a higher amount of process effluent is measured for experiment *Reference 10 L* compared to experiment *Reference 4 L*, which can be due to a higher volume of injected steam during the heating stage in experiment *Reference 10 L*. As expected, the lowest amounts of effluents are recovered from the experiments conducted at low residence temperatures and pressures. Furthermore, the lowest filtrate yields are recovered in the experiment *Low temp.* when using both feedstocks. The lowest yields of the exploded biomasses were obtained in the experiments performed using SO_2 as an acid catalyst, which can be due to the more efficient hydrolysis of hemicelluloses under acidic conditions.

3.2 Effluent/condensate composition

3.2.1 Identification and quantification of organic components in the process effluents

A ^{1}H spectrum for the effluent sample from experiment *Low temp.* + SO_2 using Norway spruce as feedstock is depicted in Fig. 3, including proton signal identification. The peak at 4.7 ppm is a residual water signal from the pre-saturated water suppression acquisition. The most abundant compounds identified in the effluent samples are acetic acid, methanol, formic acid, 5-methylfurfural (5-MF), and furfural. ^{1}H signals from 5-MF are very small and are therefore not marked in Fig. 3. The proton signals at 2.1 ppm and 3.7 ppm have not yet been identified, despite analysis of standards of relevant compounds such as 2-acetylfuran and diacetyl.

Signal integrals of the components and calculated concentrations, given as mM, are presented in Table S1 in the supplementary material. Concentration calculations are performed according to Eq. (1) given in Section 2.5
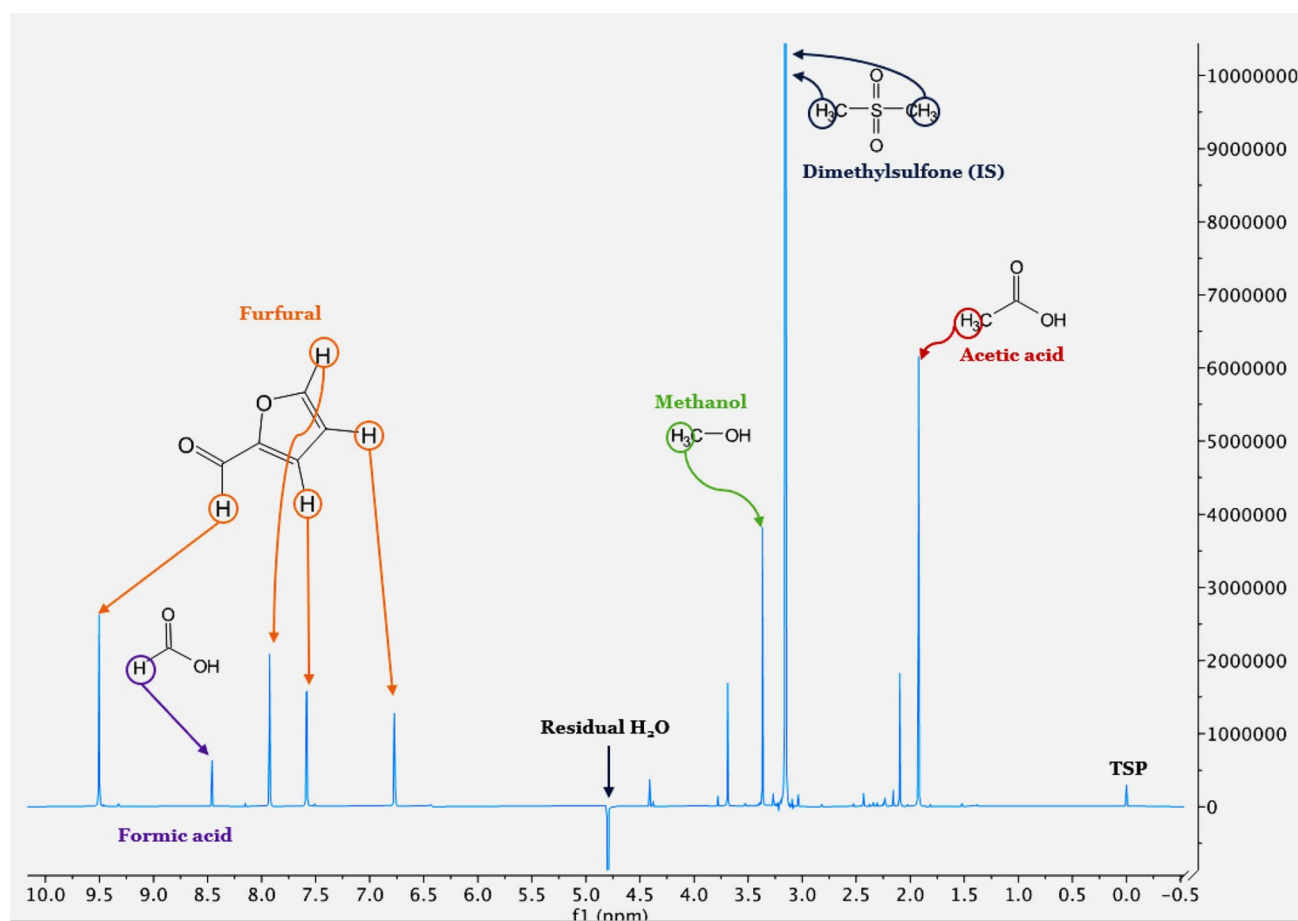
Fig. 3 Proton spectrum for the process effluent recovered from experiment *Low temp.* + SO_2 using Norway spruce as feedstock. Dimethyl sulfone (DMSO$_2$) is used as an internal standard (IS)

and the internal standard (DMSO$_2$) integral was standardized to 6.000 (corresponding to the number of protons in DMSO$_2$).

As shown in Fig. 4, acetic acid, methanol, and furfural are found in considerably higher concentrations than formic acid and 5-methylfurfural in the process effluents from both feedstocks. The concentration of all identified components, except methanol, was lowest in the process effluents from the experiment *Low temp.* A comparison of experiment *Reference 10 L* with experiment *Reference 4 L*, shown in Fig. 4a, which are performed at the same pretreatment temperature, indicates an increase in the concentration of the components with increased amounts of raw material. The highest concentrations of furfural were achieved in experiment *Low temp. + SO$_2$* where SO$_2$-gas has been used as an acid catalyst to improve the hydrolysis of the hemicelluloses. In order to quantify the relationship between the pretreatment parameters and the formation of the identified compounds, more experiments are required.

3.2.2 Yields on a feedstock basis

The relationship between the estimated yields of the major compounds in the process effluents on an input weight basis and the residence temperature of the steam explosion processes is shown in Fig. 5. Since the volumes of the effluents reported in this study are estimated values, the reported yields (given as g compound/kg dry input material) have a larger uncertainty than the measured concentrations. The results can still be used to compare the effect of different processing conditions. For the replicated samples, the average yield of each component is shown in Fig. 5.

As shown in Fig. 5, the yields of acetic acid and furfural decreased significantly as a function of decreased pretreatment temperature when the reactor scale and amount of input material were kept constant. The higher yields of acetic acid and furfural in the effluent samples performed at higher temperatures and pressures can be attributed to the more efficient release of acetic acid from acetyl groups in the biomass structure. Acetic acid catalyzes hydrolytic reactions

Fig. 4 Concentration of the identified components in the process effluents from the steam explosion of Norway spruce (**a**) and birch (**b**)
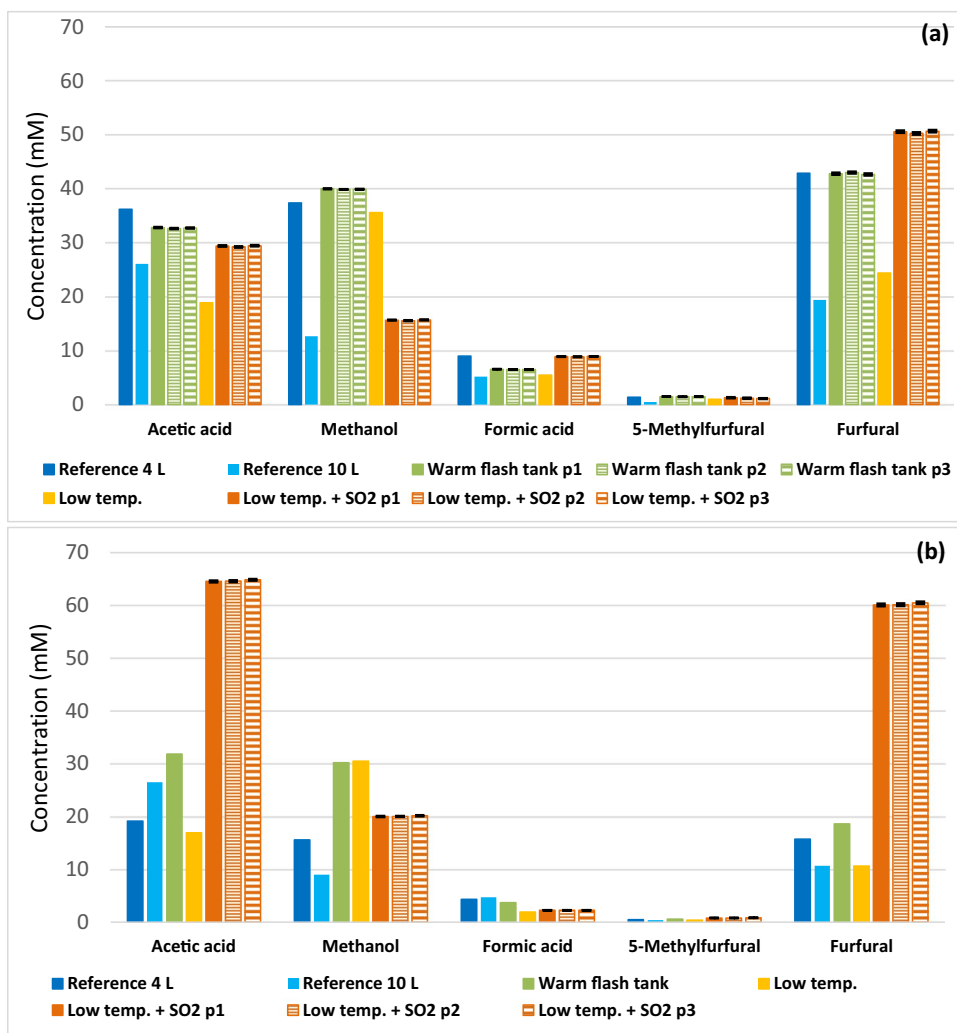
Fig. 5 Schematic overview of the relationship between the yield (g/kg dry input biomass) of the components in the effluent samples from the steam explosion of Norway spruce (**a**) and birch (**b**) and the residence temperature (°C)
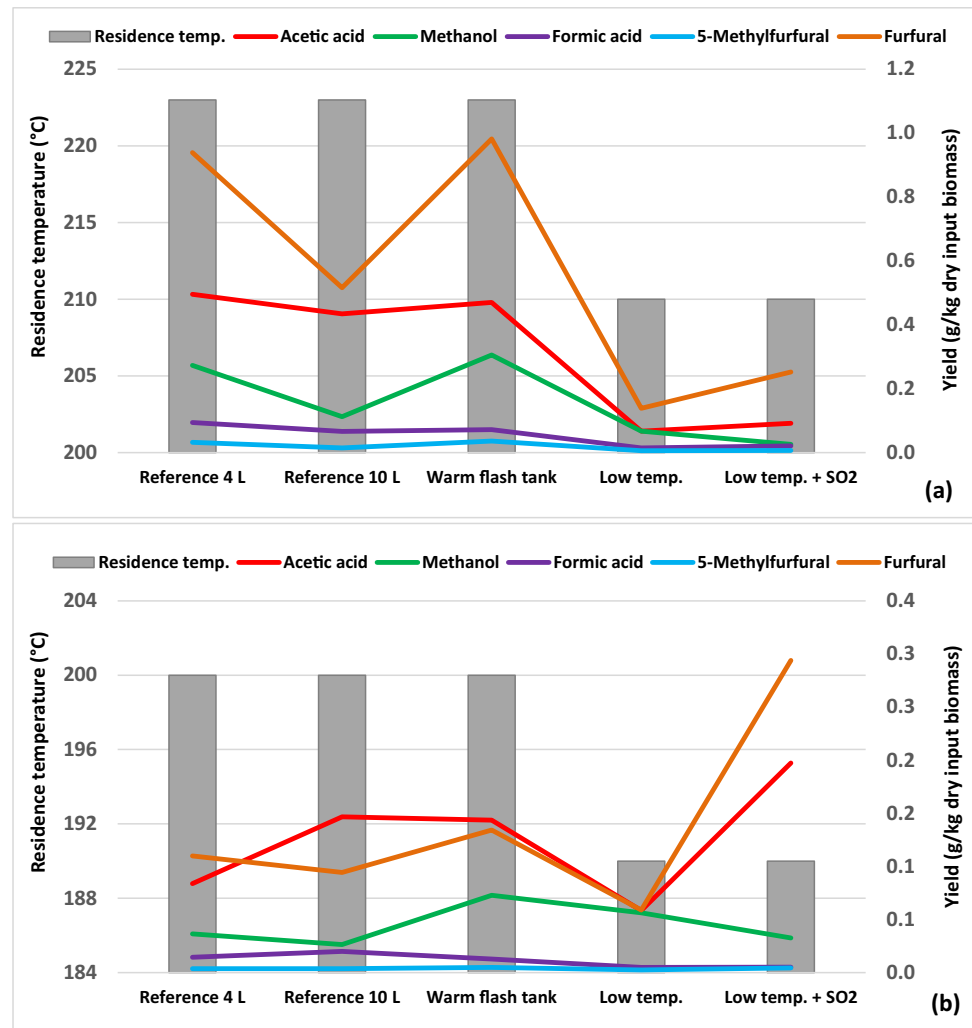
in the wood polymers by more efficient conversion of the dissolved hemicelluloses in the aqueous fractions to furan derivates, including furfural (autohydrolysis). A maximum in the approximate yield of acetic acid has been found to be 0.5 g/kg dry input biomass in the effluent samples produced from the experiments *Reference 4 L* and *Warm flash tank* using Norway spruce as feedstock. The higher amount of acetic acid found in the effluent samples from Norway spruce does not reflect the fact that softwoods have a lower content of acetyl groups in the hemicellulose part, making softwoods generally less susceptible to pretreatment using steam explosion than hardwoods.

As previously described and shown in Fig. 5a, the yield of all components is considerably higher in the effluent sample from experiment *Reference 4 L* compared to the effluent sample from experiment *Reference 10 L*. This was expected due to higher substrate loading in the experiment *Reference 4 L*. In addition, the injected steam volume used in the heating stage was also higher in the experiment *Reference 10 L*, thereby diluting the final product stream.

Since no experiments in this work give a direct comparison between the composition of an effluent sample from a 4 L scale and an effluent sample from a 10 L scale, the role of the reactor scale on the concentration/yield of the components remains unresolved. However, the yield of all the components in the effluent samples from the experiments *Warm flash tank* and *Reference 4 L* that are conducted at the same scale under the same reaction conditions have shown to be quite similar (see Fig. 5a).

As shown in Fig. 5b, the effluent sample obtained from experiment *Reference 4 L* contains higher amounts of furfural, 5-MF, and methanol in comparison with experiment *Reference 10 L*. In addition, the yield of all components is considerably lower in the effluent sample from experiment *Reference 4 L* using birch as feedstock compared to the effluent sample from experiment *Reference 4 L* using Norway spruce as feedstock. Moreover, the yield of acetic acid and furfural is highest in the effluent sample from the experiment *Low temp. + SO_2* when using birch as feedstock.

The higher yield of furfural in the process effluents produced from the steam explosion of Norway spruce compared to the effluent samples from the steam explosion of birch was expected due to more severe steam explosion conditions. Moreover, a comparison of experiment *Low temp.* with experiment *Low temp.* + SO_2 shows that the addition of SO_2-gass has significantly increased the yields of furfural, indicating, as expected, more efficient hydrolysis and subsequent dehydration of hemicelluloses under acidic conditions. The lowest furfural yields were found in the *Low temp.* experiments. A possible explanation for this could be that these experiments were conducted using lower temperatures and pressures, thus resulting in a less efficient hydrolysis of the hemicellulose and ultimately leading to poor furfural yields. However, the noticeably high furfural yield in the effluent samples from the experiments *Reference 4 L* and *Warm flash tank*, between 0.9 and 1.0 g/kg dry input biomass, makes the recovery of furfural from the effluent samples very relevant and is considered to have a good economic potential.

The optimal utilization of hemicellulose in lignocellulosic biomass for furfural production should include selective dissolution of hemicellulose from raw biomass and selective formation of furfural from dissolved hemicellulose derivatives. Based on the results obtained in this work, the production of furfural with high yields and selectivity from the hemicellulose fraction of woody biomass is challenging but should be achievable. As mentioned in Section 1, this study is in the preliminary stage

for implementation in a full-scale commercial biorefinery in Eastern Norway. In preliminary investigations of distillation for the recovery of furfural from the process effluents (unpublished results), furfural fractions with quite high purity containing only trace amounts of impurities, mainly consisting of furanic compounds and water, have been recovered.

3.2.3 Analytical precision and accuracy for process effluents

Furfural and 5-MF contain 4 ^{1}H signals each (see Table S1). The proton signal at 7.51 ppm was excluded from the calculation of the 5-MF concentration average in the effluent samples due to a significantly higher peak integral compared to the integrals from the other three 5-MF signals. The measured concentration averages of furfural and 5-MF based on 4 and 3 ^{1}H signals, respectively, resulted in standard deviations of $< 4\%$ and $< 9\%$, giving a $\sigma < 2.1$ mM of furfural and $\sigma < 0.1$ mM of 5-MF concentrations.

As shown in Table 3, the preparative laboratory procedure combined with qNMR spectroscopy provides excellent reproducibility for three repeated sample workups with standard deviations of $< 0.5\%$ of each compound average, except 5-MF with a standard deviation of $< 7\%$, which can be due to uncertainties associated with the integration of the weak 5-MF proton signals.

Table 3 Quantification data from three workup replicates of effluent samples from experiments *Warm flash tank* and *Low temp.* + SO_2 from Norway spruce, and *Low temp.* + SO_2 from birch

Biomass type	Experiment name	Concentration (mM)				
		Acetic acid	Methanol	Formic acid	5-MF	Furfural
Norway spruce	**Warm flash tank p1**	32.81	40.01	6.58	1.38	42.80
	Warm flash tank p2	32.63	39.88	6.53	1.37	43.01
	Warm flash tank p3	32.73	39.92	6.51	1.38	42.66
	Average	32.72	39.94	6.54	1.38	42.83
	σ	0.09	0.07	0.03	0.01	0.18
	Standard deviation (%)	0.28	0.18	0.46	0.72	0.42
	Low temp. + SO₂ p1	29.39	15.66	8.92	1.16	50.58
	Low temp. + SO₂ p2	29.22	15.57	8.87	1.02	50.26
	Low temp. + SO₂ p3	29.45	15.70	8.94	1.07	50.67
	Average	29.35	15.64	8.91	1.08	50.50
	σ	0.12	0.07	0.04	0.07	0.21
	Standard deviation (%)	0.41	0.45	0.45	6.48	0.42
Birch	**Low temp. + SO₂ p1**	64.50	20.00	2.24	0.78	60.03
	Low temp. + SO₂ p2	64.55	20.01	2.25	0.79	60.08
	Low temp. + SO₂ p3	64.80	20.14	2.26	0.81	60.45
	Average	64.62	20.05	2.25	0.79	60.19
	σ	0.16	0.08	0.01	0.02	0.23
	Standard deviation (%)	0.25	0.40	0.44	2.53	0.38

3.3 Filtrate composition

### 3.3.1 Identification and quantification of organic components in the process filtrates

The chemical composition of the dissolved organic compounds in the filtrate samples is different from the effluent samples as the less volatile components adsorbed to the solid residue are collected in addition to the remaining volatiles. A ^{1}H spectrum for the filtrate sample from experiment *Low temp. + SO$_2$* using Norway spruce as feedstock is depicted in Fig. 6, including proton signal identification. The most abundant compounds identified in the filtrate samples are acetic acid, acetone, methanol, formic acid, 5-methylfurfural (5-MF), 5-hydroxymethylfurfural (5-HMF), and furfural. 5-HMF and acetone are examples of the additional components relative to the effluent. Signals from sugar residues and other minor peaks were not considered in this study. Integrals of each component and calculated concentrations (mM) are presented in Table S2 in the supplementary material.

As depicted in Fig. 7a, the concentration of all the components in the filtrate samples from the experiments performed using Norway spruce as feedstock was lowest in the experiment conducted at a low temperature, except for the concentration of methanol. In general, the concentration of all components increased with increasing pretreatment severity. Additionally, a comparison of experiment *Low temp.* with experiment *Low temp. + SO$_2$*, which were carried out at the same temperature (210 °C), indicates a significantly higher concentration of all components (except methanol) in the filtrate samples from the experiment conducted using SO$_2$-gas as an acid catalyst in the process, which concur with previously discussed results. Moreover, the concentration of all the components has shown to be lower in the filtrate sample from experiment *Reference 10 L* compared to the filtrate sample from experiment *Reference 4 L*, which was expected due to higher substrate loading in the experiment *Reference 4 L*, as well as higher volume of the produced filtrate in the experiment *Reference 10 L* which dilutes the final product stream.
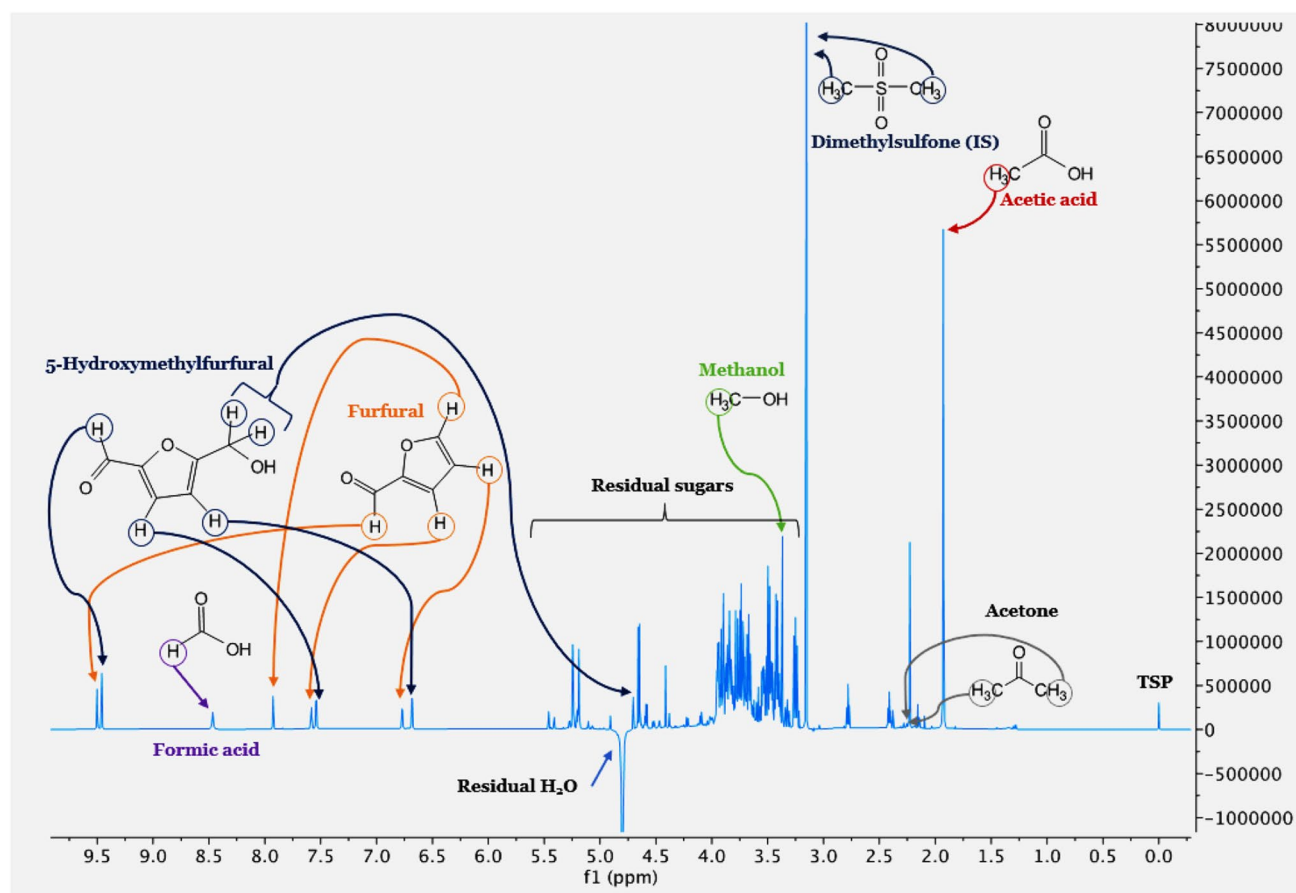
Fig. 6 Proton spectrum for the process filtrate from experiment *Low temp. + SO$_2$* using Norway spruce as feedstock. Dimethyl sulfone (DMSO$_2$) is used as an internal standard (IS)

Fig. 7 Concentration of the identified components in the process filtrates from steam explosion of Norway spruce (a) and birch (b)
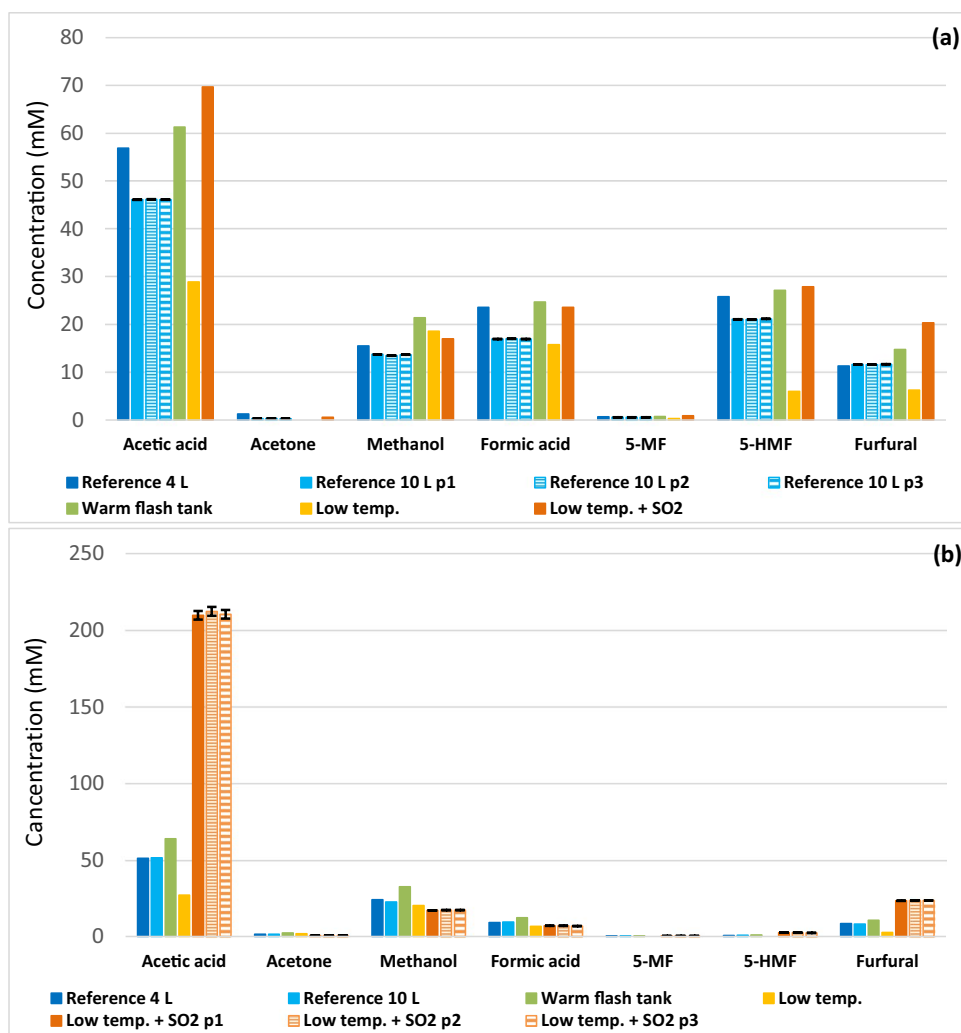

Based on the results shown in Fig. 7b, variations in the concentration of the organic components in the filtrate samples from experiments using birch as feedstock have shown to be proportional to variations in the residence temperature, except for the results obtained from experiment *Low temp.* + SO_2. Thus, the concentration of the components has decreased as a function of decreasing pretreatment temperature but remains almost unchanged in the experiments conducted at the same residence temperature. When comparing experiment *Reference 10 L* with experiment *Reference 4 L*, both of which are performed at the same pretreatment temperature, no significant increase in the concentration of the components as a function of increased substrate loading is observed. This can most probably be due to a smaller amount of filtrate generated in experiment *Reference 4 L*, resulting in smaller amounts of each compound in total.

3.3.2 Yields on a feedstock basis

The relationship between the calculated yields of the major compounds in the process filtrates on an input weight basis and the residence temperature of the steam explosion processes is shown in Fig. 8. For the replicated samples, the average yield of each component is shown in Fig. 8.

As depicted in Fig. 8a, variations in the yield of the components in the different filtrate samples follow a similar trend. Acetic acid and 5-HMF have considerably higher yields than furfural, methanol, and formic acid. Acetone and 5-MF have the lowest yields in the process filtrates from the steam explosion of Norway spruce. The low yield of acetic acid, 5-HMF, and furfural in the filtrate sample was performed at low temperature and pressure, experiment *Low temp.* confirms less efficient depolymerization of the biomass at low temperatures, resulting in lower cleavage of

Fig. 8 Schematic overview of the relationship between the yield of the components in the filtrate samples from steam explosion of Norway spruce (a) and birch (b) and the residence temperature (°C)
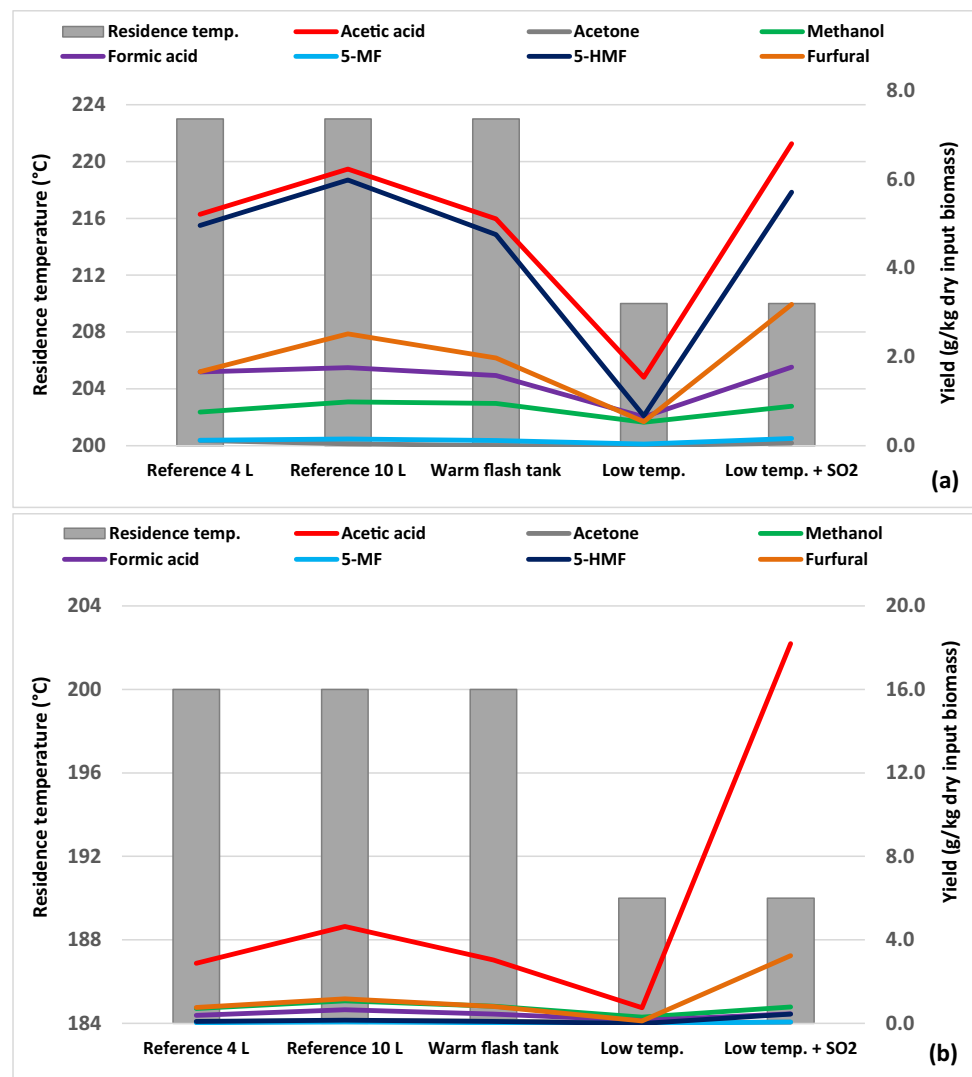
acetic acid from acetyl groups in the native biomass structure and thus less efficient hydrolysis and subsequent dehydration of hemicellulose units to furanic derivatives. The yield of acetic acid has been found to be quite similar, between 5.1 and 5.2 g/kg dry input biomass, in the filtrate samples from experiment *Reference 4 L* and *Warm flash tank*, using Norway spruce as feedstock. However, the highest acetic acid yield, 18.1–18.3 g/kg dry input biomass, was obtained in the filtrate sample from the experiment *Low temp. + SO₂*, when birch was used as raw material. Moreover, the results indicated that a major part of the produced acetic acid remained adsorbed on the steam-exploded biomass, which makes an additional washing procedure after the steam explosion process worth considering for maximizing the recovery of acetic acid.

As shown in Fig. 8, the yield of 5-HMF is considerably higher in the filtrate samples from the steam-exploded Norway spruce compared to the filtrate samples from the steam explosion of birch, which is due to the high content of

galactoglucomannan in the softwood hemicellulose. A comparison of the yield of 5-HMF based on pretreatment conditions shows that the highest 5-HMF yields were obtained in the filtrate samples from the experiments *Reference 10 L* and *Low temp. + SO₂*. Moreover, significant differences were observed between the composition of the filtrate sample from experiment *Reference 4 L* compared to the composition of the filtrate sample from experiment *Reference 10 L* using both feedstocks. The higher yields of the components in the filtrates from experiment *Reference 10 L* compared to experiment *Reference 4 L* indicate that higher amounts of the volatiles remain in the solid residues from experiment *Reference 10 L* most probably as a result of less efficient removal of volatiles during the pressure release stage at 10 L scale.

However, significantly higher yields of formic acid were observed for the process filtrates compared to the process effluents. Formic acid can be produced both from the elimination of formyl groups in the hemicellulose units and from the rehydration of 5-HMF in the aqueous reaction media.

5-HMF can undergo a rehydration process and decompose to formic acid and levulinic acid. However, the absence of levulinic acid in the aqueous product streams can most probably be related to secondary reactions including the formation of humins. The presence of sugar residues in the filtrate samples indicates incomplete decomposition of the carbohydrate fractions of the biomasses when using the investigated steam explosion conditions. However, the low standard deviations ($< 2\%$) measured for each identified component based on three repeated sample preparations of filtrate samples from the experiments *Reference 10 L* and *Low temp. $+ SO_2$*, again confirms the outstanding reproducibility of the reported sample preparation technique as well as the qNMR spectrometric method used.

The results obtained in this study indicated that the filtrate samples obtained from steam explosion contained significant amounts of valuable platform chemicals that can be recovered for commercial use. Acetic acid, 5-HMF, furfural, and formic acid are the components with the highest yields in the filtrate samples from the steam explosion of Norway spruce, respectively, and acetic acid, furfural, and methanol are the components with the highest yields in the filtrate samples from the steam explosion of birch. The yields are sufficient to confirm that washing of steam-exploded biomass is worth performing for maximizing economic outputs from this type of biomass. On the other hand, washing steam-exploded biomass could perhaps influence the pelletizing properties of the biomass. Hence, additional analyses are required to ensure that physicochemical pellet properties like calorific value, impact and abrasion resistance, etc., are maintained. All in all, more research is needed to get a better understanding of the relationship between the pretreatment conditions and the generation of the identified organic components.

3.3.3 Analytical precision and accuracy for process filtrates

The 5-HMF signal at 4.70 ppm was excluded from the quantification due to the proximity of the methylene resonance to the H_2O solvent peak. Spillover from the pre-saturated H_2O resonance to the CH_2 resonance causes saturation of the methylene signal, consistently reducing its relative intensity, making it inaccurate for quantitative purposes. This is a good example of how the dynamic range problem can affect signal intensity when working with aqueous samples, as big solvent peaks can influence the signal intensity of adjacent signals [54]. In addition, the 5-MF ^{1}H signal at 9.33 was excluded from the calculation of the 5-MF concentration average in the filtrate samples due to deviating peak integral compared to the other 5-MF peak integrals. In addition, the 5-HMF ^{1}H signal at 9.46 ppm has also been excluded from the calculation of 5-HMF concentration averages in the filtrate samples from birch due to significantly lower peak integral relative to 5-HMF peak integrals at 7.54 and 6.68 ppm. Uncertainties

related to the integration values of 5-MF and 5-HMF can be associated with the relatively low concentrations of these components in the aqueous samples studied in this work. However, this illustrates the flexibility of the qNMR quantification, as the normalization of the peak areas to the specific protons providing the signal makes the exclusion of the more variable signal unproblematic. The measured concentration averages of furfural, 5-MF, and 5-HMF in the process filtrates based on 4, 3, and 2 ^{1}H signals, respectively, resulted in standard deviations of $< 4\%$, $< 34\%$, and $< 10\%$. The high standard deviations for the 5-MF and 5-HMF averages are caused by the low concentration of these compounds, which are lower than the quantification limit (1 mM) of the NMR instrument.

As shown in Table 4, the three repeated sample workups of two different filtrate samples resulted in standard deviations of $< 2\%$ of each compound average, which again confirms the excellent reproducibility of the quantitative procedure/method reported here. The only exception was 5-MF with a standard deviation of $< 7\%$, which can be associated with the uncertainty related to the integration of the weak proton signals of 5-MF.

3.4 Implications of results for a steam explosion-based biorefinery

By applying the results from this research to real-world biorefineries and using estimated market values of the identified value-added products, it is possible to estimate the potential revenue each product can give to a biorefinery. A basic commercial-size steam explosion biorefinery, as being presently demonstrated in Norway [55], has the potential to produce upwards of 40,000 tons or 4×10^7 L of effluent each year, from which furfural and 5-MF are the major target products. The co-produced acetic and formic acid can be processed by bacteria to generate methane gas that can be burned with the low-boiling compounds, typically methanol, to improve the energy efficiency of the refinery.

Following the results from Section 3.2, the yearly production can be estimated to 204.2 tons of furfural (95% purity) and 5.2 tons of 5-MF, obtained from the treatment of Norway spruce using the *Low temp. $+ SO_2$* conditions, while approximately 243.4 tons of furfural (95% purity) and 3.6 tons 5-MF can be obtained from birch using the same conditions. For reaction conditions without acid catalysis, the highest concentrations are obtained from the *Warm flash tank* and *Reference 4 L* conditions with Norway spruce and give 173.5 tons of furfural (95% purity) and 6.0 tons of 5-MF, while similar conditions for birch are not worth estimating as the furfural and 5-MF concentrations are too low to have any commercial value.

If we assume that a commercial biorefinery can process 130,000 tons of biomass per annum and that from

Table 4 Quantification data from three workup replicates of filtrate samples from experiment *Reference 10 L* and *Low temp. + SO$_2$* from Norway spruce and birch, respectively

Biomass type	Experiment name	Concentration (mM)						
		Acetic acid	Acetone	Methanol	Formic acid	5-MF	5-HMF	Furfural
Norway spruce	**Reference 10 L p1**	46.10	0.30	13.75	16.94	0.61	21.09	11.62
	Reference 10 L p2	46.18	0.31	13.46	17.02	0.60	21.03	11.60
	Reference 10 L p3	46.11	0.30	13.67	16.94	0.62	21.17	11.69
	Average	46.13	0.30	13.63	16.97	0.61	21.10	11.64
	σ	0.04	0.004	0.15	0.05	0.01	0.07	0.05
	Standard deviation (%)	0.09	1.33	1.10	0.29	1.64	0.33	0.43
Birch	**Low temp. + SO$_2$ p1**	209.68	0.63	17.10	7.00	0.43	2.51	23.32
	Low temp. + SO$_2$ p2	212.25	0.62	17.30	7.00	0.43	2.52	23.59
	Low temp. + SO$_2$ p3	210.41	0.63	17.30	6.80	0.39	2.49	23.59
	Average	210.78	0.63	17.23	6.93	0.42	2.51	23.50
	σ	1.32	0.01	0.12	0.12	0.03	0.02	0.16
	Standard deviation (%)	0.63	1.59	0.70	1.73	7.14	0.80	0.68

every 3 kg of treated biomass can produce about 1 L of filtrate, the following amounts of chemicals can be extracted: 89.4 tons of furfural, 152.5 tons of 5-HMF, and 4.3 tons of 5-MF from Norway spruce and 103.1 tons of furfural, 13.9 tons of 5-HMF, and 2.2 tons of 5-MF from birch with *Low temp. + SO$_2$*. As for the best non-catalyzed alternative, *Warm flash tank* with Norway spruce, 64.8 tons of furfural, 148.6 tons of 5-HMF, and 3.5 tons of 5-MF can be extracted annually.

Under the assumption that market prices for these compounds are stable, one can estimate the additional value of the biorefinery. From a refinery using the *Low temp. + SO$_2$* condition with birch as feedstock, an estimated 866,000 \$/year from furfural, 64,000 \$/year from 5-HMF, and 235,000 \$/year from 5-MF can be added to the annual revenue of the biorefinery. Similarly, *Low temp. + SO$_2$* condition with Norway spruce can add 735,000 \$/year from furfural, 702,000 \$/year from 5-HMF, and 391,000 from 5-MF. For the *Warm flash tank* conditions, on the other hand, potential profits are somewhat lower with estimated earnings from furfural, 5-HMF, and 5-MF of 596,000 \$/year, 684,000 \$/year, and 388,000 \$/year, respectively.

These results clearly show that extraction of furfural, 5-HMF, and 5-MF from effluents and filtrates has the potential to drastically increase the profit margins of modern biorefineries. It also shows that more value can be extracted from Norway spruce than from birch and that depending on the cost, using SO$_2$ as an acid catalyst may not increase the revenue from Norway spruce, but is indicated to be able to extract additional value from birch.

4 Conclusion

The results presented in this paper show that the aqueous product streams generated from the steam explosion of woody biomass contain platform chemicals of high value that are suitable for recovery for commercial use. The most abundant compounds identified in the process effluents were acetic acid, methanol, formic acid, 5-methylfurfural (5-MF), and furfural, while the most abundant components identified in process filtrates were acetic acid, acetone, methanol, formic acid, 5-methylfurfural (5-MF), 5-hydroxymethylfurfural (5-HMF), and furfural. These platform chemicals can be recovered and utilized in the production of other value-added chemicals, medicines, biofuels, polymers, bioplastics, additives, etc. In addition, filtrate samples contain considerable amounts of sugar residues that were not addressed in this study.

Acetic acid (0.1–0.50 g/kg dry input biomass) and furfural (0.1–1.0 g/kg dry input biomass) were found to be the components with the highest yields in the process effluents. The use of SO$_2$-gas in addition to steam in the steam explosion processes conducted at low residence temperatures led to more efficient hydrolysis of hemicellulose units present in the biomass, resulting in a higher concentration (mM) and yield (g/kg dry input biomass) of furfural in the process effluents. However, the problems associated with the use of SO$_2$ do not make the pretreatment beneficial in a full-scale commercial biorefinery. Additionally, with respect to the investigated parameters, birch has proven to have an advantage since it required lower pretreatment

temperature with regard to furfural production. Furthermore, results obtained from process filtrates indicated that acetic acid (0.8–18.3 g/kg dry input biomass), 5-HMF (0.1–6.0 g/kg dry input biomass), furfural (0.1–3.3 g/kg dry input biomass), formic acid (0.1–1.8 g/kg dry input biomass), and methanol (0.3–1.1 g/kg dry input biomass) were the components with highest concentrations in the process filtrates. The highest yield of these components was achieved in the experiments performed using SO_2-gas as an acid catalyst. The yield of 5-HMF was considerably higher in the filtrate samples from the steam-exploded Norway spruce compared to filtrate samples from the steam-exploded birch, which is consistent with the high content of hexoses in the softwood hemicellulose. However, the yield of furfural in the filtrate sample from the experiment *Low temp.* + SO_2 from both feedstocks was quite similar.

In order to approach optimal conditions for this biorefinery concept, which aims for simultaneous production of high-quality brown pellets (Arbacore pellets) and value-added platform chemicals recovered from the process effluents and filtrates, further in-depth investigations are required. The furfural and 5-HMF recovery must be balanced against the physicochemical properties of the pellets achieved. The result presented in this study shows that the steam explosion conditions strongly influence the amounts of furfural and 5-HMF produced in the pretreatment step. The results also suggest that it is possible to drastically increase the concentrations of the targeted compounds by making only moderate adjustments to the process conditions.

Declarations

Conflict of interest The authors declare no competing interest.

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