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Research Article

# Laboratory- to Pilot-Scale Fractionation of Lignocellulosic Biomass Using an Acetone Organosolv Process

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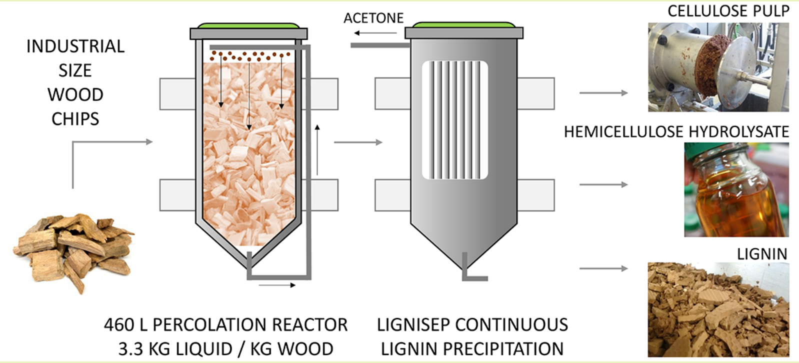

**ABSTRACT:** Acetone organosolv fractionation of beech and birch wood at the lab-scale results in high sugar yields from the (hemi)cellulose and the isolation of a high-purity lignin. In this study, the process is scaled up to validate the technology at the pilot scale using industrial-size beech and birch wood chips and low liquid-to-solid ratios as a next step toward commercialization. Translation of the fractionation process to the pilot-scale showed a similar performance as compared to the lab-scale processing with a good conversion of the wood polymeric pentoses to mostly monomeric sugars and a high delignification. Continuous lignin precipitation by solvent evaporation using the LigniSep process resulted in the formation of nonsticky lignin aggregates with a good filterability. The improved lignin yields and advanced process design as compared to the traditional dilutive lignin precipitation approaches are likely to translate to a better process economy. The pulp washing efficiency and the recovery of (nonprecipitable) lignin from the aqueous hemicellulose stream still need to be improved for an efficient process design. However, the fractionation performance and high product concentrations in the spent liquor provide an excellent start position for improved process design at the commercial scale.

**KEYWORDS:** *Biomass organosolv pretreatment, Lignocellulose biorefinery, Scale-up, Process intensification, Cellulose, Hemicellulose, Lignin*

## INTRODUCTION

Increased global demand for earth's natural resources and climate change through the emission of greenhouse gases are two major challenges of our time. Increased price volatility, supply risks, and competition for these resources as well as pressure of environmental regulations are a major concern for the manufacturing industry.[1] To help mitigate these challenges, a transition to a biobased circular economy is pursued through the development of biorefineries. This enables the use of biomass as a resource and its conversion to fuels and chemical building blocks for biobased, and preferably circular, products.[2] However, the requirements for biorefineries are high regarding process economy, sustainability, and product quality.[3,4] Pretreatment processes that enable the isolation of a high-purity lignin or its derivatives from biomass to complement the production of cellulose and sugars have the advantage of creating more product value by maximizing biomass valorization toward fuels and chemicals.

Organosolv pretreatment is widely studied and can fractionate lignocellulosic biomass into its main constituents, cellulose, hemicellulose, and lignin.[5−7] The use of volatile solvents in organosolv processes enables the isolation of a high-purity lignin after solvent recovery. However, contrary to aqueous processes, organosolv pretreatment is more complex and is characterized by relatively high costs and energy

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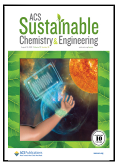

Table 1. Fractionation Conditions for Lab- and Pilot-Scale Fractionation Experiments

| | | beech L-BEC | beech P-BEC-1 | beech P-BEC-2 | beech P-BEC-3 | birch L-BIC | birch P-BIC |
|---|---|---|---|---|---|---|---|
| feedstock | [kg dry weight wood] | 2.8 | 55 | 70 | 70 | 2.8 | 54 |
| liquid/solid ratio | [kg liquid/kg dry weight wood] | 4.4 | 4.5 | 3.3 | 3.3 | 4.4 | 3.7 |
| acetone concentration start[a] | [% w/w] | 50 | 58 | 58 | 59 | 50 | 60 |
| temperature | [°C] | 140 | 140 | 140 | 140 | 140 | 140 |
| time at $T_{max}$ | [min] | 90 | 118 | 115 | 115 | 90 | 83 |
| acid dose | [% w/w dry weight wood] | 2.5 | 2.0 | 2.0 | 2.0 | 1.5 | 1.5 |
| ANC feedstock[b] | [mol $H^+$/kg dry weight wood] | 0.15 | 0.16 | 0.16 | 0.16 | 0.07 | 0.07 |
| aqueous acetone wash liquid | [kg] | 6.3 | 121 | 380 | 380 | 6.3 | 380 |
| water wash liquid | [kg] | 6.3 | 1330 | 1450 | 1450 | 6.3 | 1350 |

[a] Calculated acetone concentration at the start of fractionation, derived from the quantity of added steam and reaction liquid mass/composition.
[b] Acid neutralizing capacity.

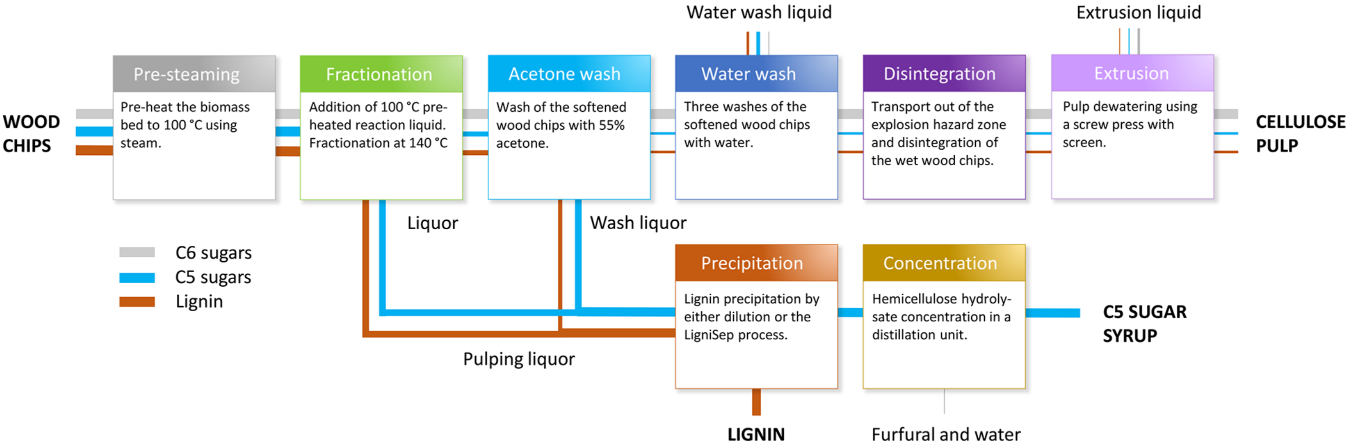

**Figure 1.** Process design for pilot-scale fractionation of hardwood chips and downstream processing of liquor and solids to obtain a cellulose pulp, a C5 sugar syrup, and lignin. Colored lines provide an impression of the main routes for C6 sugars (glucan, galactan, mannan, and rhamnan), C5 sugars (arabinan and xylan), and lignin.

demand[8,9] challenging its competitiveness and market implementation.

Mild acetone organosolv fractionation of herbaceous biomass and hardwood has shown promising results at the lab scale and excellent lignin solubilization.[10,11] The so-called Fabiola process aims to balance the high severity requirements for optimal biomass fractionation and mild process conditions needed to minimize sugar and lignin degradation. Replacing the state-of-the-art ethanol organosolv fractionation process by an acetone-based process prevents undesired ethylation of sugars and lignin and directly improves sustainability performance mainly via reduced energy demand and investments.[9,10]

In previous work, mild acetone organosolv fractionation of a selection of herbaceous biomass and hardwood was conducted at the lab scale using a 2 L batch stirred autoclave. Milled hardwood was fractionated at 140 °C for 2 h using 4.4 kg of 50% w/w aqueous acetone/kg dry feedstock and sulfuric acid as a catalyst. The combination of lab-scale processing and the use of small feedstock particle sizes enables relatively efficient downstream processing and recovery of products.[10]

However, fractionation of industrial-size wood chips using low liquid-to-solid (L/S) ratios is preferred for full-scale biorefineries to obtain a viable process economy and to meet sustainability criteria.[8] Furthermore, downstream processes such as lignin precipitation and solvent recovery can be energy intensive, especially when the pulping liquor is diluted with water in order to precipitate the lignin as previously performed at the lab scale.[12] Reported assessments of the organosolv pretreatment of wood chips showed that, besides operational costs, the process is sensitive to variation in feedstock prices, sugar and lignin revenue, and capital costs.[13,14] Together, this shows that a variety of factors must be addressed to obtain a robust and viable process. After promising lab-scale results, the next step toward a commercialization of the mild acetone organosolv process is the validation at the pilot scale, an important step as technical immaturity often impairs a successful commercial implementation of biorefinery processes.[15]

An integrated pilot plant is available at Fraunhofer CBP that was designed for the ethanol organosolv fractionation of wood chips.[16] It consists of a 460 L percolation reactor and downstream equipment for pulp disintegration and dewatering, precipitation of lignin from process liquors, solvent recovery, and concentration of sugar streams.

Lignin precipitation and solvent recovery from the pulping liquor are important downstream processes that have significant impact on the process economy. Herein, high lignin yield and solvent recovery rate, as well as good filterability of the lignin particles, are important performance indicators. The novel LigniSep process enables continuous lignin precipitation and controlled particle agglomeration with integrated solvent recovery.[17,18] This process was initially developed for ethanol organosolv pulping liquors at the lab scale[19] and was later upscaled to the dedicated pilot plant at Fraunhofer CBP.[17]

In this study, the mild acetone organosolv fractionation technology is validated at the pilot scale using industrial-size

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wood chips and low cooking-liquor-to-wood-chips ratios. In addition, the recent process for continuous LigniSep precipitation of lignin from process liquors and other major downstream processing (DSP) steps are conducted using scalable equipment. This enables the provision of reliable process data for improved process design, technoeconomic assessment, and representative product samples for application tests.

## ■ MATERIALS AND METHODS

**Fractionation.** Lab-scale fractionation experiments were conducted in a 20 L autoclave reactor (Büchi Glas Uster AG) using commercially purchased beech wood from Rettenmaier (Räuchergold, 0.75−2 mm particle size) and birch wood from Sappi Belgium (chips milled over a 4 mm sieve). For the beech (L-BEC) and birch (L-BIC) lab-scale fractionation experiments, the feedstock was mixed with 50% w/w aqueous acetone (corrected for the biomass moisture content) and sulfuric acid (Table 1). The mixture was heated to 140 °C and kept isothermal for 90 min, while stirring with an anchor stirrer at 500 rpm. After cooling to below 25 °C, the slurry was measured for pH and filtered. The solids were first washed with 50% w/w aqueous acetone (2.5 L/kg initial dry biomass) followed by a wash with water (2.5 L/kg initial dry biomass) to remove acetone from the pulp. A subsample was dried at 50 °C to determine the dry pulp yield. The filtrate and first wash liquor were combined to form the pulping liquor and processed for lignin precipitation.

Pilot-scale fractionation experiments were conducted using a 460 L percolation reactor (Table 1, Figure 1, and Figure S2). The feedstock was preheated to a temperature of 100 °C by direct application of steam inside of the reactor. The aqueous acetone mixture (corrected for feedstock moisture, mass of condensed steam, and tube dead volumes) was preheated in a separate vessel and transferred to the reactor. Further heating to the target temperature was conducted using a heat exchanger implemented in the percolation system. A pressure of 14 bar was applied by adding nitrogen. Samples of the fractionation liquor were taken during the process to monitor progress. After holding time, the liquor was pumped out from the bottom of the reactor, and 121 kg of 55% w/w acetone washing solution at 100 °C was added from the top of the reactor for pulp washing of P-BEC-1. For P-BEC-2, P-BEC-3, and P-BIC, the liquor was displaced from the bottom to the top using 380 kg of fresh 55% w/w acetone washing solution at 100 °C. The liquor and first wash liquor were combined (pulping liquor) and processed for lignin precipitation.

The fractionated and softened wood chips were washed three times with 450 kg of water at ambient temperature to remove acetone from the fractionated wood chips. Each wash was performed for 30 min from the bottom to the top of the reactor (displacement washing) to avoid preferential flow through channels and because of the density difference between the hot liquor and colder wash liquid. The pulp was then discharged outside of the ATEX zone (explosive atmosphere zone) into a blow tank, disintegrated, and dewatered using a screw press. The liquid obtained after pulp extrusion was not analyzed and may contain small pulp fibers that pass through the extruder mesh screen. Pulp dry weight was determined by drying a subsample at 105 °C. The liquid solutions were stored in intermediate bulk containers (IBCs).

**Lignin Precipitation.** Dilutive lab-scale lignin precipitation was conducted by adding the pulping liquor (L-BEC and L-BIC) to water (4 °C, 4:1 w/w dilution ratio $H_2O$/liquor). The lignin precipitate was collected by centrifugation at 3488*g* for 5 min. The wet lignin pellet was weighed, and residual noncovalently bonded carbohydrates were removed by heating the pellet at 50 °C for 2 h. The liquid contained in the wet lignin contains around 10% acetone, and at 50 °C, a softening and agglomeration occurs (Figure S6) that causes the liquid and sugars to be expelled. Subsequently, the expelled liquid was decanted and the lignin dried at 50 °C in a vacuum oven.

Dilutive pilot-scale lignin precipitation from pulping liquors of P-BEC-1, P-BEC-2, and P-BIC was conducted by adding three parts w/w of deionized water to the pulping liquor in two batches in a 1200 L precipitation tank. The suspension was stirred overnight at 6 °C and then filtered using a membrane chamber filter press. The lignin was washed on the filter press with 150 kg of water and subsequently dried in a vacuum oven at 50 °C. During hydrolysate concentration, nonprecipitated lignin fragments precipitate to a sticky solid coating on parts of the distillation equipment. This lignin was removed using a large volume of diluted sodium hydroxide solution and could not be recovered for quantification and characterization.

LigniSep lab-scale continuous lignin precipitation was conducted in an experimental plant reported earlier[17] which was modified to fit the demands for the processing of acetone (see the SI for a detailed process description). The operation conditions of the process were derived from lignin phase behavior investigations (see the SI and Figures S5 and S6 for detailed information). A lignin dispersion with a targeted 6−7% w/w acetone concentration was cycled between the reactor and a falling film evaporator using a cycle pump. The pulping liquor (P-BEC-2 and P-BIC) with adjusted pH (4−5) was continuously fed into this evaporator cycle leading to immediate lignin precipitation in the acetone-lean liquid. The acetone was continuously evaporated from this liquid in the falling film evaporator to maintain a constant acetone concentration in the dispersion. The acetone content was controlled by the feed rate of pulping liquor and heat input to the evaporator and was monitored via an in-line infrared spectroscopy probe and associated calibration function (Figure S11). The temperature of the dispersion (35−43 °C) was controlled by the vacuum pressure (140−180 mbarA) and regulated so that the primary precipitated lignin particles were slightly softened and subsequently agglomerated to larger particles with improved filterability. The particle size was monitored by in-line microscopy and particle size measurement probes. The pH of the dispersion was 3−4 which is near a $\zeta$ potential of 0 mV (data not shown), leading to improved agglomeration. Up to 300 ppm silicon-based antifoam agent was added to prevent excessive foaming. The L-BEC and L-BIC pulping liquors were processed at similar conditions using a 20 L rotary evaporator setup instead of a falling film evaporator.

LigniSep pilot-scale continuous lignin precipitation was conducted using P-BEC-3 pulping liquor (see the SI for a detailed process description). The pH of the pulping liquor was adjusted to 3.5 by adding 2.99 kg of 30% w/w NaOH. The liquor was continuously fed into a 500 L precipitation vessel containing a 6 ± 1% w/w acetone start solution. The feed was positioned next to the stirrer to allow immediate mixing of the pulping liquor with the dispersion and facilitate rapid lignin precipitation. The system was heated using a falling film evaporator that is connected to a vacuum heating steam system operated at 130 mbarA/47 °C. In the precipitation tank, a pressure of 170 mbarA was set to reach a temperature of 40 ± 2 °C. Lignin particle agglomeration was monitored by visual inspection of the sedimentation behavior of lignin dispersion samples. The acetone content in the dispersion was monitored by an FTIR probe and associated calibration function. The lignin suspension was periodically transferred to a storage tank to maintain a constant volume in the precipitation tank. Lignin precipitate was then recovered using filtration and washed, identical to the pilot-scale dilutive precipitation approach. The filtered liquid (i.e., hydrolysate) mostly contained hemicellulose sugars as well as varying concentrations of extractives, organic acids, furanics, phenolics, and nonprecipitated lignin.

**Analysis.** The acetone content of liquid subsamples from pilot-scale fractionation was analyzed on an Agilent 1260 Infinity HPLC system equipped with an HPX-87H column. An infrared spectrometer (Bruker Alpha with ATR window and flow cell) and calibration models (Figures S9 and S10) were used for the determination of acetone contents in off-line samples (e.g., pulping liquor, distillate, and lignin dispersion).

Biochemical composition analysis of feedstocks and pulps (L-BEC and L-BIC) as well as quantification of sugars and derivatives were conducted as described in previous work.[10] Compositional analyses of the pilot-scale feedstock and samples were performed by Celignis Analytical as described in the work of Pisano et al.[20] Lignin characterization methods (SEC, $^{31}$P NMR, and 2D HSQC-NMR)

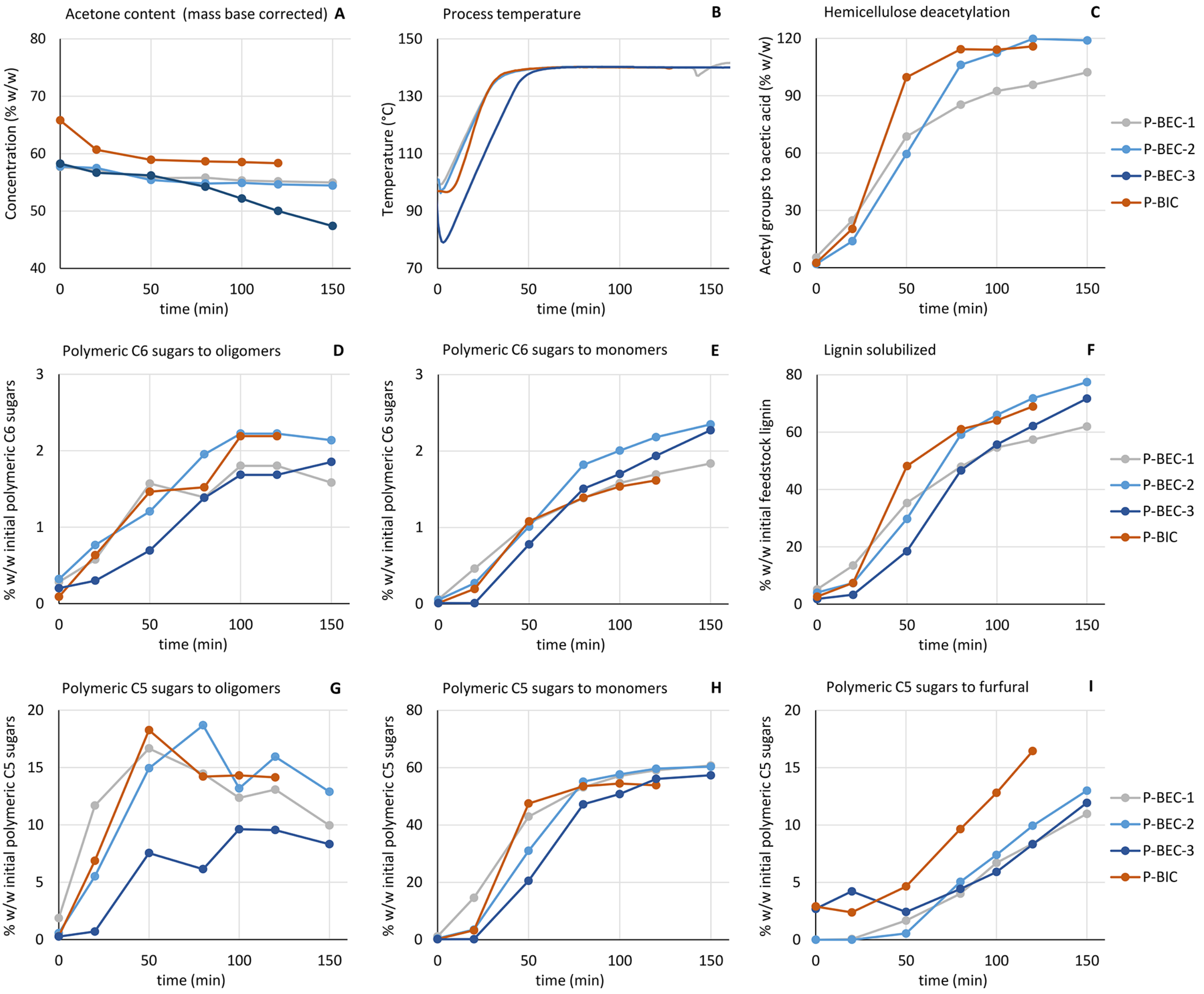


**Figure 2.** Pilot-scale fractionation development over time for beech wood chips fractionated with an L/S ratio comparable to lab-scale processing (P-BEC-1) and a duplicate beech wood fractionation experiment (P-BEC-2 and P-BEC-3) and birch wood (P-BIC), using low L/S ratios.

were conducted as described in the Supporting Information and in previous work.[21] The water-insoluble lignin (WIL) content in the pulping liquors was determined gravimetrically. The pulping liquor was first dried (60 °C/10 mbarA) until the weight was constant. The dry solids were suspended in a mass of water equal to the initial mass of the pulping liquor solution to dissolve the water-soluble compounds such as sugars, minerals, and water-soluble lignin fragments. The water-insoluble solid lignin fraction was filtered, washed with additional water, and dried.

## ■ RESULTS AND DISCUSSION

**Fractionation.** The composition of beech and birch wood chips used for the fractionation experiments (Table S1) is similar to reported hardwood compositions with a high lignocellulose (mainly glucan, xylan, and lignin) content and limited amounts of ash and extractives.[22,23]

P-BEC-1 was the first pilot-scale experiment using beech wood chips at an L/S ratio of 4.5 kg liquid/kg dry feedstock to reproduce the lab-scale conditions. However, as compared to the lab-scale experiment (L-BEC), a lower sulfuric acid dose and a longer reaction time were applied (Table 1) to provide better control over process severity (i.e., optionally adjusting the reaction time depending on process monitoring results). P-BEC-2 and P-BEC-3 are duplicate pilot-scale experiments where the L/S ratio was reduced to 3.3 kg/kg by increasing the feedstock loading. For P-BIC, the reactor loading was less than expected due to a lower bulk density of the used birch wood chips resulting in a higher L/S ratio of 3.7 kg/kg. The applied low L/S ratios represent the minimum liquid usage for fractionation in the percolation reactor and provide important information regarding the potential for process intensification and improved process economy. After presteaming and the addition of preheated solvent, the temperature of the mixture ranged between 80 and 100 °C (Figure 2B). Further heating to $T_{\max}$ was much faster (up to 50 min) compared to the lab scale (up to 80 min). Therefore, holding time at $T_{\max}$ was increased based on the H-Factor concept at the pilot scale.[24] During pilot-scale fractionation, a loss of acetone was observed due to automatic venting by the pressure control system implemented in the plant (Figure S3). This was balanced by applying a higher starting concentration of approximately 60% w/w aqueous acetone. After an initial equilibration, the liquor acetone content stabilized to 55−58% w/w in the liquor

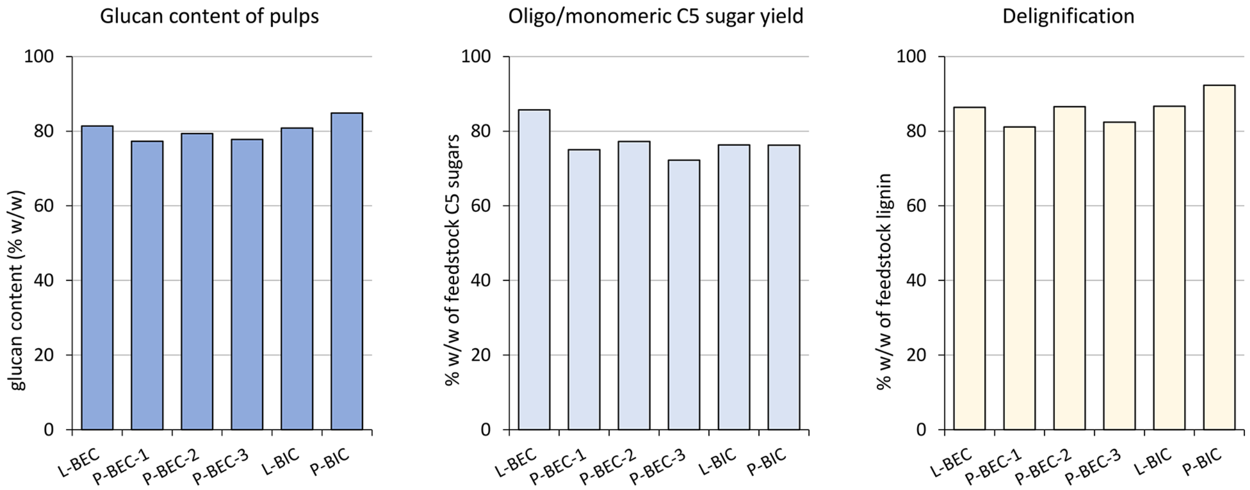


**Figure 3.** Fractionation performance indicators for lab- and pilot-scale fractionation: (left) glucan (cellulose) content of pulps, (middle) oligomeric and monomeric sugars recovered in the liquor and water wash liquid, and (right) delignification derived from feedstock and pulp nonextractable lignin content.

(corrected for solubilized wood constituents, Figure 2A). However, for P-BEC-3, the acetone concentration steadily declined to 47% after 150 min of fractionation time. Process monitoring showed no obvious reason for the apparent solvent loss (Figure S4). Detailed information regarding acetone self-condensation rates in model liquids and beech fractionation experiments is available in the Supporting Information (Tables S7 and S8 and Figures S18 and S19).

Figure 2D−I shows how hardwood fractionation develops over time for the pilot-scale experiments. In these graphs, the hexose, pentose, and lignin content are set to 100% for each feedstock individually. The pulping liquor was analyzed, and the component yield was expressed as % w/w of the polymer source from which they were derived (including a correction for sugar hydration and dehydration during hydrolysis and degradation, respectively).

Polymeric C6 sugar hydrolysis to soluble oligomeric and monomeric sugars remains relatively low during fractionation (Figure 2D,E). Sugar degradation to hydroxymethylfurfural (HMF) was minor and represented less than 0.3% w/w of feedstock C6 sugars after 150 min of reaction time, and levulinic acid was not detected (data not shown). Polymeric C5 sugar hydrolysis to oligomers (Figure 2G) proceeds relatively quickly (except for P-BEC-3) and shows, despite some variation, a downward trend toward the end of the fractionation. The average composition of the P-BEC-1, P-BEC-2, and P-BEC-3 sugar oligomers after 50 min of fractionation is 82% xylan, 7% galactan, 4% glucan, 4% rhamnan, 3% mannan, and 1% arabinan. The composition is slightly enriched in C6 sugars in the final fractionation liquor with 69% xylan, 10% glucan, 9% galactan, 7% mannan, 3% rhamnan, and 2% arabinan. Production of monomeric C5 sugars accelerates after 20 min of reaction time (Figure 2H), likely due to increased process temperature and hydrolysis of solubilized oligomeric sugars (Figure 2G). C5 sugar degradation to furfural steadily increases to 11−13% w/w for beech wood fractionation (Figure 2I). The sugar degradation rate is slightly higher for P-BIC, in line with a faster solubilization of C5 sugars and lignin.

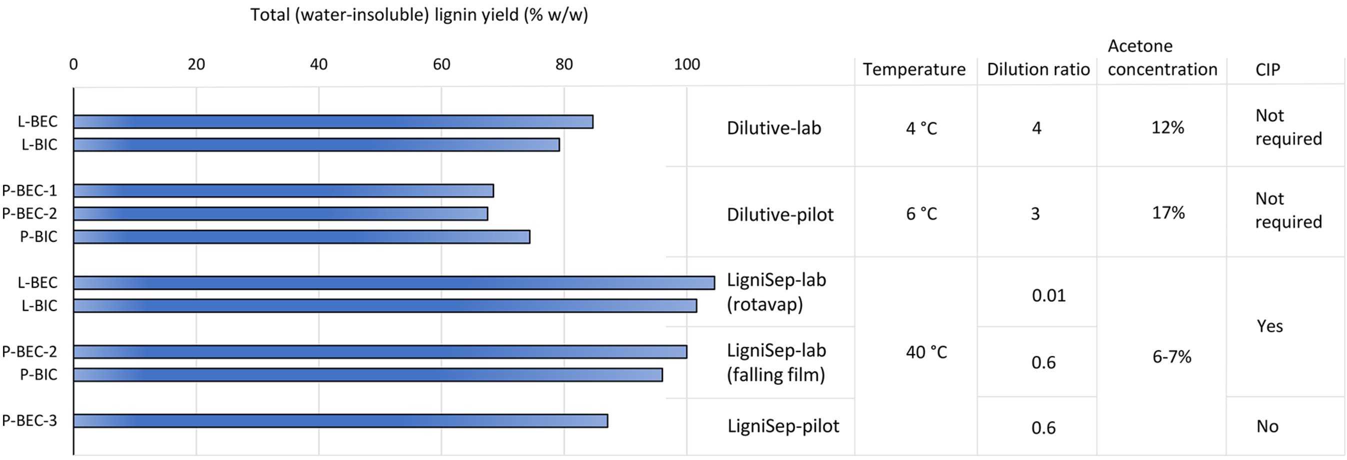
The effect of the recycling of the recovered acetone from previous runs was tested for P-BEC-3 and P-BIC. Distillation of P-BEC-1 and P-BEC-2 hydrolysates (obtained after dilutive lignin precipitation) recovered acetone as well as part of the furfural from these hydrolysates. As a result, higher furfural concentrations were found at the start of P-BEC-3 and P-BIC.

The concentration of acetic acid is calculated to % w/w of feedstock hemicellulose acetyl groups in Figure 2C. The total deacetylation exceeds 100% for P-BEC-2 and P-BIC fractionation, indicating the additional release of acetic acid from lignin.[25]

The solubilized lignin in the percolation liquor (Figure 2F) is measured as the water-insoluble lignin (WIL) fraction. Note that water-soluble lignin (WSL) is not included in the WIL. After 150 min of fractionation time, 62−77% of feedstock lignin is quantified as WIL in the process liquor with the remainder either solubilized as WSL or in polymeric form as pulp residual lignin.

The lab-scale fractionation experiments did not allow for time series sampling, preventing a direct comparison of fractionation performance between the lab and pilot scales. Additionally, a comparison of the final product yields in the obtained fractions is a combined effect of fractionation performance and recovery/loss of product during downstream processing (see mass balance section for a detailed discussion). To allow for a comparison between lab- and pilot-scale fractionation with minimal downstream processing effects, three fractionation performance indicators are shown in Figure 3. These represent the target for fractionation which is to maximize hemicellulose solubilization toward oligo/monomeric sugars and lignin solubilization with minimal lignin degradation while preserving the more crystalline cellulose (glucan) in the pulp.

Lab-scale fractionation of beech wood (L-BEC) resulted in high glucan enrichment in the pulp, C5 sugar recovery (in the pulping liquor and water wash liquid), and delignification. Lab-scale fractionation of beech wood was translated to pilot-scale processing with minor changes to the process conditions. Beech wood used for L-BEC was ambient dry (~10% w/w moisture content) and had a particle size of <2 mm. For P-BEC-1, P-BEC-2, and P-BEC-3, industrial-size wood chips with a moisture content of 20−38% w/w were used without additional screening or milling. Fractionation screening experiments at the lab scale showed that feedstock particle size and moisture content had no significant effect on the



| | Temperature | Dilution ratio | Acetone concentration | CIP |
|---|---|---|---|---|
| Dilutive-lab | 4 °C | 4 | 12% | Not required |
| Dilutive-pilot | 6 °C | 3 | 17% | Not required |
| LigniSep-lab (rotavap) | 40 °C | 0.01 | 6-7% | Yes |
| LigniSep-lab (falling film) | | 0.6 | | |
| LigniSep-pilot | | 0.6 | | No |

**Figure 4.** Lignin precipitation yield using dilutive and LigniSep precipitation methods at lab and pilot scales. Process conditions that affect lignin yield are shown on the right side and include temperature and acetone concentration in the precipitation mixture, the dilution ratio (L of water used per kg of pulping liquor), and cleaning in place (CIP).

fractionation performance (Tables S3 and S4). The main difference between L-BEC and P-BEC-1, aside from scale and operation, is the slightly higher acid dose and shorter reaction time for L-BEC (Table 1).

The results in Figure 3 show only slightly lower values for P-BEC-1 as compared to L-BEC, indicating a good translation from lab- to pilot-scale processing. Furthermore, despite some variability, fractionation at low L/S ratios as applied for P-BEC-2 and P-BEC-3 does not lead to reduced process performance with a high C5 sugar yield and feedstock delignification. This is an important result because lower L/S conditions are advantageous for the energy demand and economy of an industrial process.

Birch wood chips were fractionated using a lower acid dose of 1.5% w/w to compensate for the lower acid neutralizing capacity of birch wood as compared to beech wood (0.07 versus 0.15 mol $H^+$/kg, respectively). The pilot-scale run P-BIC was stopped after 83 min at the target temperature instead of the planned 115 min. The on-line measurements showed that the dry matter content of the liquor samples reached a plateau, indicating that no further liberation of lignin and hemicellulose sugars took place. P-BIC fractionation was slightly faster than P-BEC-1, P-BEC-2, and P-BEC-3 (Figure 2) with a high level of delignification, comparable C5 sugar yield (Figure 3), and increased furfural formation (Figure 6C). Note that the same acid dose (per feedstock weight) was used for both lab- and pilot-scale fractionation, but a reduced L/S ratio at the pilot scale may result in higher free acid concentrations which may promote fractionation and reduce sugar stability. Overall, the estimation of process conditions during pilot-scale experiments could be successfully derived from the lab-scale experiments without substantial errors.

**Lignin Precipitation.** Lignin was precipitated from the pulping liquor of P-BEC-1, P-BEC-2, and P-BIC using a dilutive approach at the pilot scale. In this process, three parts of (ambient temperature) water were added to the liquor which results in the formation of filterable lignin particles that were recovered using a filter press. The relatively polar nature of the acetone organosolv lignin combined with the applied dilution resulted in low yields (67−74%) of recovered lignin at the pilot scale (Figure 4).

Lab-scale dilutive precipitation consisted of adding liquor to four parts of water which was precooled to 4 °C. This approach resulted in the formation of a lignin precipitate that cannot be filtered but is obtained by centrifugation. The lower acetone concentration in the lab-scale diluted mixture increases the yield slightly as compared to the pilot-scale dilution method (79−85%).

The LigniSep process involves solvent evaporation, leading to the concentration of the pulping liquor instead of water dilution. Lab-scale LigniSep experiments reached the highest lignin yields due to lower acetone and higher lignin concentrations (Figure 4). In particular, those lignin fractions with a lower molar mass are precipitated to a larger extent with LigniSep than with the dilution methods (Figure S21). The WIL content of L-BEC and L-BIC pulping liquors was 92% and 88% of the total amount of lignin solubilized from the beech and birch, respectively. The lignin precipitation yield exceeding 100% (L-BEC LigniSep-lab, Figure 4) indicates additional precipitation of lignin which is not included in the WIL, especially at low dilution ratios. This result suggests that part of the otherwise WSL is also captured in the LigniSep precipitation process. Overall, all isolated lignins showed a low sugar content ranging from 0.7% to 1.1% w/w. Similarly, the ash contents of the isolated lignins were below 0.3% w/w.

The LigniSep method results in superior filterability of the lignin particles due to the controlled particle agglomeration in the process (Figure S14). The pH of the dispersion was found to affect the extent of lignin deposition on glass parts of the experimental plant. The zeta ($\zeta$) potential (ZP) of lignin particles is influenced by the pH of the dispersion. Lignin deposition was lowest at a ZP of 0 mV at pH 3.5 (measured by a Malvern Zetasizer nano ZS instrument). Zero ZP also led to improved lignin particle agglomeration due to less repellent forces between particles. A cleaning-in-place (CIP) strategy for the recovery of lignin deposits from the lab plant involved filling the setup with pulping liquor or distillate and moderate heating. Afterward, the CIP liquor was processed using LigniSep precipitation to recover lignin, solvent, and hydrolysate. The average lignin yield could be increased from 87% to nearly 100% w/w by the CIP strategy (Figure S12 and Table S6).

An average acetone recovery of 95% w/w was achieved in the LigniSep lab experiments (Figure S13), which can be prospectively improved by closing leaks in the lab plant as well as improved condensation/recovery of the solvent. Acetone

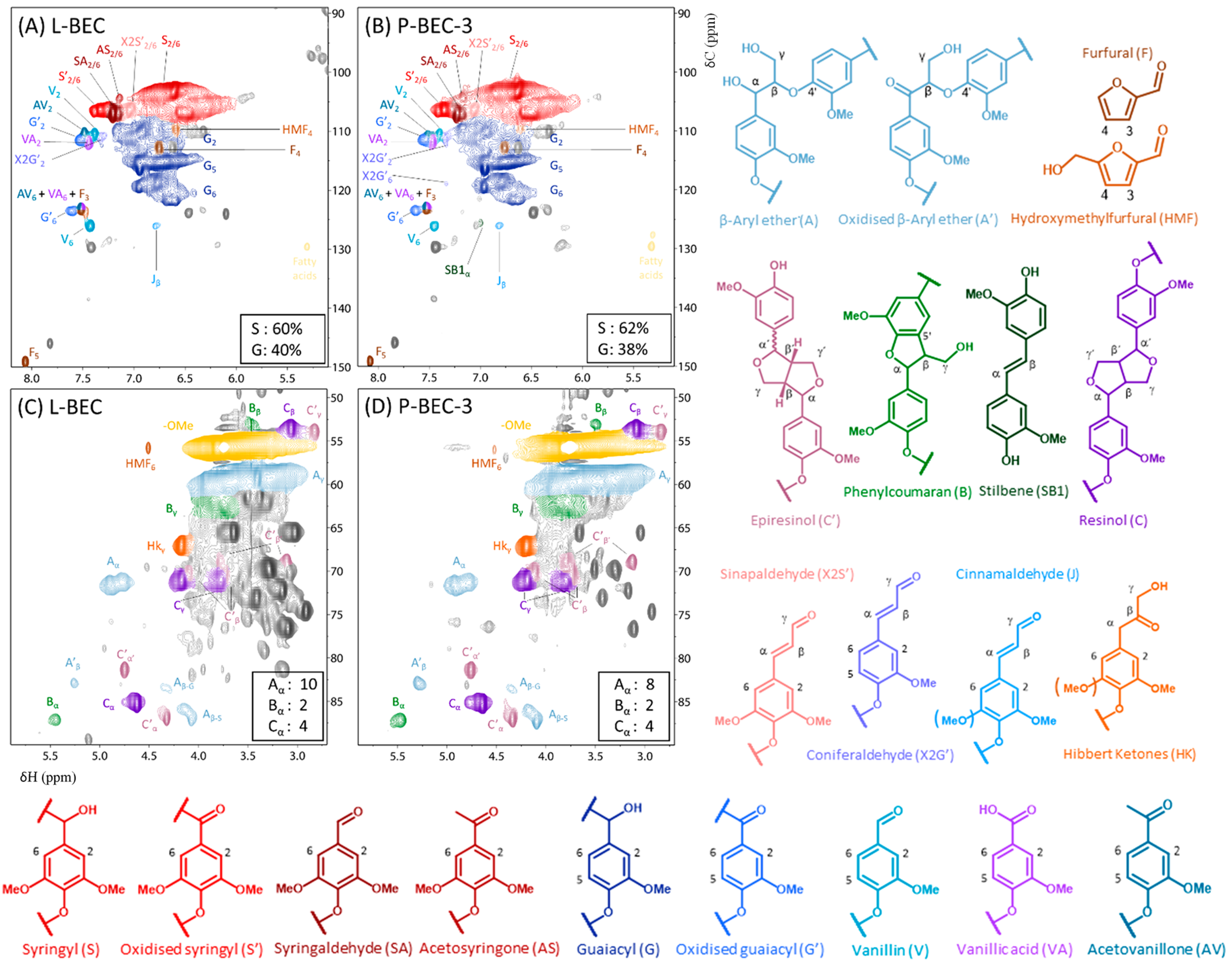


**Figure 5.** 2D HSQC NMR spectra of lignin obtained from lab-scale (L-BEC) and pilot-scale (P-BEC-3) fractionation of beech wood. The insets in the aromatic/unsaturated region (A, B) represent the aromatic units expressed as percent of total S + G. Oxygenated aliphatic side chain region (C, D) insets represent linkage/structure abundance per 100 aromatic S + G units. Methoxy group peaks (OMe) are depicted in yellow. The main identified structures are shown at the right and bottom.

has a 19% lower heat of evaporation as compared to ethanol, which allows for more energy-efficient separations in the downstream solvent recovery. Process design evaluations showed that the higher vapor pressure of acetone does not lead to unrealistically high operating pressures or refrigerant requirements (data not shown).

P-BEC-3 was the first pilot-scale test of LigniSep lignin precipitation from acetone pulping liquor using conditions that were derived from lab-scale results and a feed rate of 70−80 kg pulping liquor/h. Contrary to the lab-scale tests, no excessive formation of foam was observed during the pilot-scale precipitation, and no antifoam agent was used. Thus, the foaming seems to be a more scale-related problem, which is less prominent at larger scales, e.g., due to a higher volume/surface ratio and larger headspace for foam collapse. The lignin yield increased significantly as compared to the dilutive approach used for P-BEC-1 and P-BEC-2. However, some losses were observed due to an adhesion of lignin particles on the large surface areas of the pilot equipment. These deposits appeared loose and easily removable but were not recovered by CIP, leading to a lower yield as compared to lab-scale results. There is a high potential for optimization when the plant is in continuous operation mode with a CIP procedure scheduled on a regular basis.

**Lignin Characteristics.** Lignin depolymerization and subsequent solubilization during organosolv-type processes primarily occur via cleavage of labile *β*-aryl ether bonds that have a high abundance in native lignin. Cleavage of these ether bonds results in the formation of Hibbert ketones and benzylic aldehydes which can undergo significant repolymerization to condensed lignin structures depending on process severity.[26−28] Organosolv lignin molar mass is thus affected by these two mechanisms, i.e., reduced molar mass by ether bond cleavage leading to lignin depolymerization and an increase in molar mass as a result of lignin condensation. *β*-Aryl ether bond cleavage typically results in the loss of aliphatic hydroxyl groups and an increase in lignin phenolic OH content, where an increase in the 5-substituted OH group abundance suggests recondensation via new ether bonds and C−C coupled units.[27,29]

L-BEC and P-BEC-3 lignin obtained from the LigniSep process (Figure 4) were selected for characterization to minimize the effect of lignin precipitation yields on lignin molar mass and characteristics. The molar mass distribution

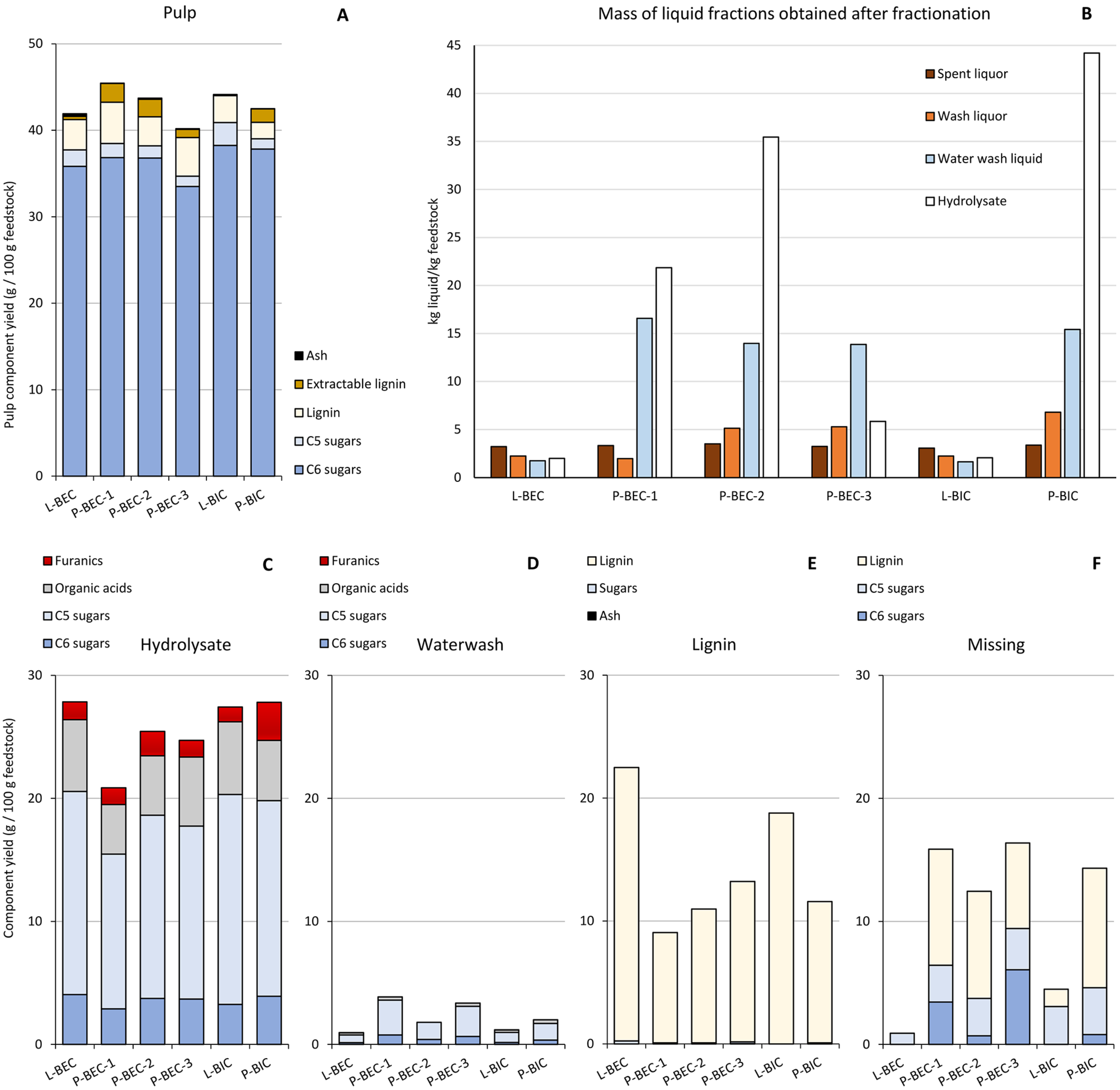


**Figure 6.** Feedstock component yield in the isolated solid pulp (A), hydrolysate (C), water wash liquid (D), isolated solid lignin (E), components missing in the total mass balance (F), and mass of obtained processing liquids, expressed in kg/kg processed dry feedstock (B).

(Table S10) was determined using size exclusion chromatography (SEC) and showed a higher weight-average molecular weight ($M_w$) for L-BEC than for P-BEC-3 with 2940 and 2780 g/mol, respectively. $^{31}$P NMR analysis (Table S10) shows a higher aliphatic OH content for L-BEC as compared to P-BEC-3 (2.3 and 1.9 mmol OH/g dry lignin, respectively) and a slightly lower 5-substituted OH content (2.3 and 2.4 mmol OH/g dry lignin, respectively). Lignin structural characterization by semiquantitative 2D HSQC-NMR shows relatively similar characteristics for L-BEC and P-BEC-3 (Figure 5, Table S10). Note that L-BEC lignin was initially not washed with water after precipitation, and the 2D HSQC-NMR spectra show increased signals from typical sugar peaks in the oxygenated aliphatic region in Figure 5. The lignin yield in Figure 4 was corrected for sugar content, and the $^{31}$P NMR analysis was conducted on water-washed lignin.

Overall, P-BEC-3 seems to be slightly more affected by the process severity as compared to L-BEC as indicated by a lower abundance of $\beta$-aryl ethers and aliphatic hydroxyl groups and a higher abundance of oxidized structures and Hibbert ketones. However, these minor differences can be understood from the process conditions, and the results indicate that the laboratory- and pilot-scale experiments yield lignin with mostly similar characteristics. Significant structural differences are observed between acetone and ethanol organosolv lignins (Table S10). Beech wood fractionation using L-BEC process conditions and ethanol as the solvent provided a lignin similar to L-BEC except for significant ethylation of $\beta$-aryl ether bonds. Fractionation at a higher temperature of 190 °C using ethanol as the solvent and a lower acid dose caused more pronounced changes in the lignin structure showing similar ethylation, a lower abundance of $\beta$-aryl ether bonds and aliphatic OH content, and slightly increased formation of stilbenes.

**Mass Balance.** As shown in Figure 3, fractionation performance translates well from lab to pilot scales even when industrial-size wood chips are used in combination with low L/S ratios. However, downstream processing is significantly different at the pilot scale and not optimized for cost-effectiveness, as only single experiments are conducted.

The mass balance in Figure 6 shows how the fractionation products are distributed (in g/100 g initial dry feedstock) over the recovered pulp, hydrolysate, water wash liquid, and lignin. The smaller wood particle sizes used for the lab-scale experiments allowed for efficient pulp washing with aqueous acetone using limited amounts of liquid (Table 1, Figure 6B). As a result, most solubilized products were obtained in the pulping liquor and, consequently, the hydrolysate (Figure 6C). A pulp water wash yielded only minor amounts of remaining product in the wash liquid (Figure 6D). A small quantity of lignin precipitate was collected after evaporation of acetone from the water wash liquid. This isolated lignin represented only 1% and 2% of total isolated lignin from beech and birch wood, respectively (amounts were added to the total isolated lignin in Figure 6E). In addition, lab-scale LigniSep precipitation of lignin was conducted using a low pulping liquor dilution ratio resulting in a high yield of precipitated lignin while limiting the amount of hydrolysate produced in the lab-scale experiments (Figure 6B). Together, efficient downstream processing and equipment cleaning result in a minor loss of product as shown for the lab-scale experiments in Figure 6F. Note that loss of (mainly) C5 sugars may partly result from alternative sugar and furanics degradation routes and inclusion of furanics in the isolated lignin.

The pilot-scale processing experiment P-BEC-1 was conducted using a similar fractionation L/S ratio and a top−down aqueous acetone washing to replicate the lab-scale conditions. As a result, the amount of obtained liquor and wash liquor per kg of wood is comparable to that in L-BEC (Figure 6B).

Contrary to the lab-scale experiments, extensive pulp water washing of the nondisintegrated wood chips is required for further pulp processing outside of the ATEX zone. This resulted in a good recovery of solubilized sugars in the water wash liquid (pulp extractable sugar content was low, data not shown). However, the water wash induced the precipitation of unwashed solubilized lignin in the pulp which partly precipitated onto the pulp as extractable lignin (Figure 6A). Another (unquantified) part was found at the bottom of the storage IBCs containing water wash liquid. Glucose yield from enzymatic saccharification of pulps was significantly lower for the pulp obtained from pilot-scale processing (Figure S23). Enzyme deactivation due to irreversible binding to the pulp extractable lignin may have affected saccharification rates. Dilutive pilot-scale precipitation resulted in relatively low isolated lignin yield (Figure 4) while producing large volumes of hydrolysate. Nonprecipitated lignin in the hydrolysate partly precipitated over time in the storage IBC, while the still solubilized lignin formed a sticky coating on the distillation unit upon hydrolysate concentration which could not be quantified. Together, these losses sum up to a considerable amount of lignin missing in the mass balance in Figure 6F. Loss of pulp fibers through the mesh screen during extrusion may have caused the relatively high amount of missing C6 sugars (and additional C5 sugar and lignin) in Figure 6F.

P-BEC-2 and P-BIC were both conducted using low L/S ratios for fractionation, and top−down pulp aqueous acetone washing was replaced by bottom−up displacement washing with 3 times more washing liquid. This slightly improved the sugar (and lignin) recovery for P-BEC-2 and P-BIC (Figure 6D) while significantly increasing the amount of obtained pulping liquor and subsequent water usage for the dilutive lignin precipitation process (Figure 6B). Here again, the isolated lignin yields for P-BEC-2 and P-BIC were relatively low (Figure 6E,F).

LigniSep lignin precipitation from the pulping liquor of P-BEC-3 improved lignin yield as compared to the dilutive approach that was performed for P-BEC-1 and P-BEC-2 (Figure 4). The minimal dilution effects with LigniSep, combined with CIP, have the potential for full recovery of WIL as observed for the lab-scale LigniSep results. Furthermore, the production of concentrated hydrolysates will limit energy demand for concentrating such streams at the biorefinery scale. Optimization of the lignin washing step by integration with biorefinery aqueous process streams is then still required. Hydrolysate purification prior to concentration using, for example, activated carbon to capture WSL and phenolics may prevent fouling of distillation equipment. Concentration of the partially purified hydrolysate can then remove most of the furanics and volatile organic acids.[30]

P-BEC-3 deviated from P-BEC-2 with a lower washing efficiency and higher suspected pulp losses during extrusion, which shows the variation that can occur between duplicate experiments.

Overall, acetone organosolv fractionation of beech and birch wood chips at low liquid-to-solid ratios, combined with LigniSep lignin precipitation, reduces process energy demand and investment requirements as compared to the benchmark ethanol organosolv, which leads to a significantly improved sustainability performance. The initial target of 30% reduction in greenhouse gas emissions was exceeded by a significant margin, as confirmed by an integrated sustainability assessment that used a range of data modeled for the industrial scale based on learnings from the pilot scale.[9] However, for clear climate change mitigation, other aspects must be optimized further, including efficient replacement of energy-intensive fossil-based materials and chemicals by products from biorefinery intermediates and an integrated utilities concept based on renewable energy sources. Furthermore, the flexible processing of unused residual biomass streams, which is made possible by Fabiola technology, needs to be taken advantage of in sustainable feedstock supply chains to ensure that direct climate change mitigation is not outweighed by indirect additional greenhouse gas emissions and other environmental impacts of unsustainable biomass.

## ■ CONCLUSIONS

Lab-scale mild acetone organosolv fractionation of beech and birch wood showed a good recovery of cellulose in the pulp and efficient solubilization of polymeric C5 sugars and lignin. Translation of the fractionation process to a pilot-scale percolation reactor was excellent with a similar performance as compared to the lab-scale processing. Importantly, the results were obtained using industrial-size wood chips and low liquid-to-solid ratios at the pilot scale.

Pilot-scale process design is not yet optimized for cost-efficient downstream processing of solids. Consequently, pulp washing requires large volumes of washing liquid to achieve reasonable washing efficiencies. Additionally, pulp disintegration and extrusion resulted in a minor loss of (hemi)cellulose and lignin, preventing its isolation and quantification. Optimization of pilot-scale downstream processing should be addressed before further scale-up of the mild acetone organosolv process. Improved pulp washing using dedicated equipment has the potential to significantly improve downstream processing economy and product recovery and reduce the pulp extractable lignin content.

Continuous lignin precipitation from pulping liquors by the LigniSep process resulted in the formation of nonsticky lignin aggregates with a good filterability and at high yields. The process design and improved lignin yields are likely to translate to a better process economy as compared to the more traditional dilutive approaches. Additionally, improved lignin yield may reduce the requirements for capture of non-precipitated lignin from hydrolysates prior to concentration. Isolated lignin contained low concentrations of ash and sugars and showed similar structural characteristics for beech lignin obtained from lab- and pilot-scale processing.

Overall, this study shows that scale-up of the two most critical steps in organosolv biorefining, i.e., fractionation and lignin precipitation, can be achieved while maintaining fractionation performance and improving process intensity. Together, this provides an excellent position for further improved process design at the commercial scale. For further advances in process sustainability, technology development should aim, among other aspects, to include low-density feedstocks such as straw and grasses while maintaining process intensity.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c01425.

> Additional experimental details, materials, and methods, including photographs of samples and the experimental setup (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

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