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Reductive Catalytic Fractionation of straw digestates for the production of biogenic aromatic monomers

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ABSTRACT

Lignin is hardly degraded and presumably only scarcely structurally modified during the anaerobic digestion of straw and thus accumulating in the digestate remaining after digestion. As available industrial residue stream and due to the accumulation of unmodified lignin, such a digestate appears as promising substrate for the production of biogenic aromatics. One process for recovering monomeric aromatics from structurally unmodified lignin is the Reductive Catalytic Fractionation (RCF). Here, the RCF of straw digestates from a lab fermentation and from an industrial plant was investigated and compared to the RCF of unfermented straw as well as beech wood. It turned out that monomeric aromatics can be recovered from straw digestates by RCF. Removing impurities from the digestates by washing, increasing the hydrogen pressure and extending the reaction time to at least 7 h further increased the monomer yield. The selectivity towards γ-OH groups in the monomers can be controlled by the hydrogen pressure and the choice of hydrogenation catalyst. No yield-reducing influence of hydroxycinnamic acids found in straw got evident, however, only their purely ester-bound fraction could be easily removed and quantified. Compared to the straw digestates, monomer yields on biomass basis were lower from unfermented straw, but significantly higher from beech wood for all tested catalysts. Thus, although having a comparable lignin content, beech wood represents a higher yielding source for monomeric biogenic aromatics compared to straw digestates.

1. Introduction

Aromatics are almost exclusively obtained from fossil raw materials today, mostly by cracking or reforming crude oil [1,2]. In view of the ambition to become less dependent on fossil carbon to contribute to the goals defined within the Paris Agreement, interest moves increasingly towards the production of aromatics from biogenic sources. The respective approaches can be distinguished in two groups:

- One approach is to synthesize aromatics from small chemicals like glucose, methanol, ethanol or acetic acid easily obtained from biogenic material. The synthesis can be performed by thermochemical approaches like the methanol to aromatics process [3] or by biotechnological approaches where microorganisms are used for the production of aromatics [4].
- The second approach, followed in this paper, makes use of the abundant natural occurrence of the aromatic polymer lignin within the natural composite lignocellulose; i.e. the approach is here to recover aromatic molecules by lignin depolymerization.

On the one hand side, lignocellulosic biomass is an attractive biomass type for further industrial exploitation, as it is abundant worldwide and, in contrast to many other biomasses, not in direct conflict with food production. On the other hand side, its robust and highly interconnected structure poses a major challenge for its industrial exploitation [5]. The industrial, non-energetic valorization of lignocellulosic biomass is so far predominantly limited to the valorization of the carbohydrate polymers cellulose and, in part, hemicellulose [6]. In order to make these polymers available or even isolate them, harsh conditions (i.e. high temperatures and/or extreme pH values) are usually applied. The third main constituent of lignocellulose, the aromatic polymer lignin, is

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Abbreviations

FA	ferulic acid
HA	hydroxycinnamic acid
pCA	p-coumaric acid
RCF	Reductive Catalytic Fractionation

degrading under these harsh conditions due to diverse condensation reactions [7]. In native lignin, the monomers (different phenylpropanoids) are predominantly linked by ether bonds and to a lower extend by C-C-bonds. These ether bonds are cleaved under harsh process conditions, however, the lignin fragments formed are reactive and tend to repolymerize and form new C-C-bonds under such harsh conditions (these reactions are summarized as “condensation reactions”). The formed condensed (“technical”) lignin is a heterogeneous, polymeric solid, where C-C-bonds are dominating. However, the shift from ether bonds to C-C-bonds lowers the depolymerization ability of such a technical lignin, making these molecules difficult to valorize. That is the reason why they are currently mainly incinerated [8].

Different strategies have been developed to stabilize the lignin and avoid such condensation reactions; these concepts are summarized under the term "lignin-first" strategies [9]. One of these strategies is the Reductive Catalytic Fractionation (RCF), which resembles the organosolv process in that lignocellulosic biomass is fractionated in an organic solvent (e.g. methanol or ethanol) at high temperatures (e.g. 200–250 °C) and pressures (e.g. 20–60 bar). Under these conditions, lignin fragments and unsaturated monomers are released from biomass by ether bond cleavage [10,11]. However, monomer yields are typically low under these conditions and the lignin is mostly obtained as a heterogeneous solid due to repolymerization reactions (condensation) [12]. For RCF, a hydrogenation catalyst in combination with hydrogen gas are added compared to the organosolv process in order to stabilize reactive lignin fragments by catalytic reduction. With this stabilization, the repolymerization of the lignin fragments and released monomers can be avoided and lignin is obtained as an oil with a high monomer content [12,13]. It is believed that the addition of a hydrogenation catalyst furthermore supports ether bond cleavage by hydrogenolysis [10,11,14]. But essentially, the catalyst provides the crucial stabilization of monomers through hydrogenation. Partially, also the hydrogenolysis of the hydroxyl group at the γ-position (γ-OH) may be catalyzed before hydrogenation (Fig. 1) [15].

The RCF of different lignocellulosic biomasses has been investigated already, among them are a huge variety of hardwoods (e.g. birch, beech) [16,17], softwoods (e.g. pine, spruce) [18,19] and, to a lesser extent, also herbaceous biomass (e.g. corn stover, miscanthus) [20,21]. The results show that under identical process conditions, the highest monomer yields on lignin basis can be obtained from hardwood due to its high ether bond content, which is one requirement for high yields. For wood, a correlation can be established between the ether bond content in lignin and the lignin monomer yield [16,22,23]. However, for herbaceous biomass the correlation is not that evident, as usually an even higher ether bond content (considering just ether and carbon bonds) compared to hardwood is detected by NMR analysis [24,25], while yields from RCF or other selective ether-cleaving methods like thioacidolysis are generally considerably lower [26–28]. This “mystery” [29] is still not yet definitely clarified, however, there are clear structural differences between these types of biomass and thus possible causes: lignin in herbaceous biomass is more heterogeneous with a higher variety of monomers, rendering both structural analysis and detection of released monomers more challenging. Besides the classical alcoholic monomers p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (also termed as “core lignin” monomers [29]), also phenolic acids, mainly the hydroxycinnamic acids p-coumaric acid and ferulic acid (also termed as “clip-offs” [29]), and further aromatic compounds like tricin are incorporated in herbaceous biomass but hardly found in wood [30–32]. Especially the presence of ferulic acid is presumed to induce lower yields due to its involvement in diverse cross-linkings [29]. The higher ash content in herbaceous biomass compared to wood might have further negative impact on the monomer yield due to catalyst deactivation [33,34].

Thermochemical pre-treatment of lignocellulose typically leads to a structural lignin degradation as described above. Consequently, thermochemically pre-treated biomasses are less attractive for RCF which gives highest yields from biomass with native lignin structures (i.e., lignin with high ether bond contents). However, no structural degradation is expected during mild biological pre-treatments like anaerobic digestion without any further chemical pre-treatment. Lignin is hardly degraded under anaerobic conditions and accumulating in the solid digestates remaining after anaerobic digestion of lignocellulosic materials [35–38]. Thus, lignocellulosic digestates as by-product of biogas production could represent a more attractive substrate than straw and wood from an economic perspective due to the higher lignin content and the preceding value creation by biogas production, however, to the best of our knowledge, they have not been considered as substrates for RCF yet.

Therefore, the RCF of such digestates is investigated exemplarily for straw digestates in this paper. The behavior of straw digestate during RCF in dependence of the reaction conditions in small-scale experiments is characterized and compared to the behavior of unfermented straw and typically used hardwood. Based on the aforementioned, it is hypothesized that higher amounts of lignin monomers can be recovered from straw digestate (on dry biomass basis) than from unfermented straw due to the higher relative lignin content (hypothesis 1). On a pure lignin basis, monomer yields are hypothesized to be in a similar range, as no structural lignin degradation is expected during anaerobic digestion (hypothesis 2). Straw digestates are herbaceous, thus containing non-classic building blocks like hydroxycinnamic acids and furthermore they are characterized by increased contents of impurities like ash and microorganisms presumably reducing the monomer yields. Therefore,

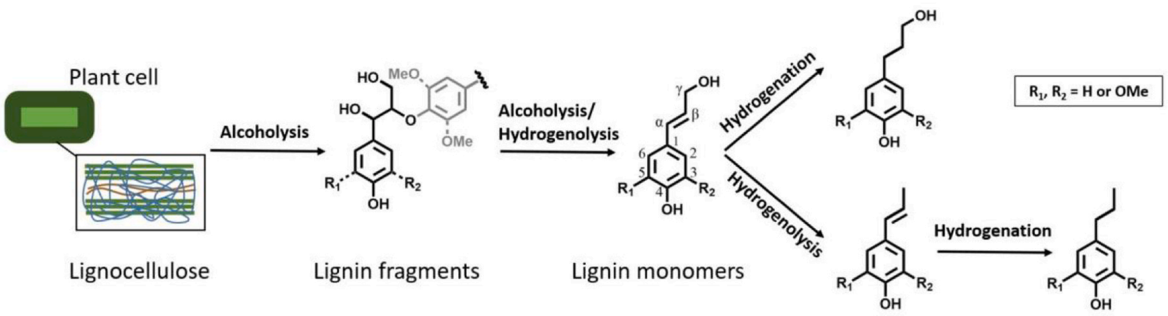


Fig. 1. Lignin depolymerization by RCF. Schematic representation of the anticipated reactions occurring during RCF of lignocellulose.

also the fate of ester-bound hydroxycinnamic acids and the influence of impurities during RCF are assessed.

2. Materials and methods

Details about used materials, biomass treatments (anaerobic digestion of rye straw, ester hydrolysis by alkaline treatment), RCF, as well as analytical methods (biomass composition, ester bound phenolic acids, lignin monomers, gas-phase, catalyst characterization) can be found in the Supporting Information (chapters S1 and S2). In the following, the used nomenclature and parameters for evaluation are explained.

By RCF, the lignin fraction of biomass is partly depolymerized and obtained as an oil, composed of monomers and oligomers. Here, only the monomer fraction was characterized. Monomers obtained by RCF are phenylpropanoids and can be related to the three alcoholic monolignols coniferyl alcohol, sinapyl alcohol, and para-coumaryl alcohol. They differ with regard to the side groups of the aromatic ring (H with only one hydroxyl group, G with one hydroxyl and one methoxy group and S with one hydroxyl and two methoxy groups), the existence of unsaturated C-C double bonds in the aliphatic side chain and the existence of an OH-group at the γ-position of the aliphatic side chain. Besides the alcoholic monolignols, there are also hydroxycinnamic acids linked to the lignin polymer. During lignin biosynthesis, such hydroxycinnamic acids are precursors of the alcoholic monolignols and during RCF in methanol, they are predominantly obtained as methyl esters.

A uniform nomenclature of abbreviations shown in Table 1 is used for the monomeric products (for denotation according to IUPAC nomenclature, see Table S2).

The hydroxycinnamates are not only linked to lignin, but also to arabinoxylan polysaccharides; this is why they are distinguished from the "core-lignin" [29,30,39]. However, due to their strong structural similarity with the alcoholic monomers and their proximity in the metabolic pathway, they are still regarded as lignin-related components and thus included here in the calculation of monomer yields. Monomer yields are given in two different ways: Yield Y_{BM} on biomass-basis in mg/g (Eq. (1)) and yield Y_{Lig} on lignin-basis in C-mol% (Eq. (2)).

$$Y_{BM} = \frac{\sum_i m_i}{m_{biomass,dry}} \times 1000\, mg \Big/ g \qquad \text{(Eq. 1)}$$

$$Y_{Lig} = \frac{M_C \times \sum_i \left(\frac{m_i}{M_i} \times n_{C\text{-}BM,i} \right)}{m_{biomass,dry} \times \omega_{Lig} \times \omega_{C,Lig}} \times 100\% \qquad \text{(Eq. 2)}$$

m_i is the mass of monomer i detected after RCF (including all quantified monomers marked in black in Table 1), M_i is the molar mass of monomer i and $n_{C\text{-}BM,i}$ corresponds to the number of biomass-derived C-atoms per monomer i (C-atoms originating from the solvent methanol contained in the added methyl groups in the monomers GPaMe and HPaMe are excluded). ω_{Lig} is the mass fraction of lignin in the respective biomass, $\omega_{C,Lig}$ the mass fraction of carbon atoms in the lignin of the respective biomass and M_C the molar mass of carbon (12 g/mol).

In order to characterize the nature of the monomers more precisely, three shares (in mol%) are calculated. The share of S-monomers %S is calculated following Eq. (3):

$$\%S = \frac{n_{SP} + n_{SPOH}}{n_{SP} + n_{SPOH} + n_{GP} + n_{GPOH}} \qquad \text{(Eq. 3)}$$

The share of γ-OH-monomers %γ-OH is calculated via Eq. (4):

$$\%\gamma\text{-OH} = \frac{n_{GPOH} + n_{SPOH}}{n_{SP} + n_{SPOH} + n_{GP} + n_{GPOH}} \qquad \text{(Eq. 4)}$$

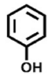
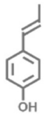
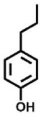
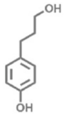
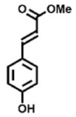
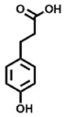
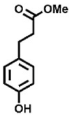
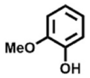
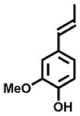
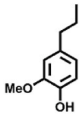
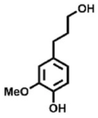
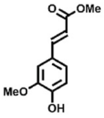
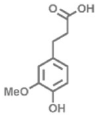
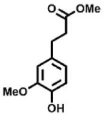
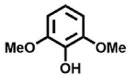
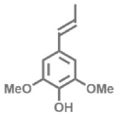
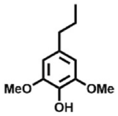
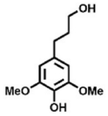
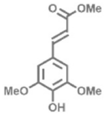
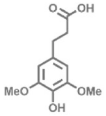
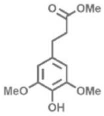
Using Eq. (5), the share of hydroxycinnamic acid monomers %HA, representing the "non-core lignin", is assessed:

$$\%HA = \frac{n_{HPeaMe} + n_{HPaMe} + n_{GPeaMe} + n_{GPaMe}}{n_{HPeaMe} + n_{HPaMe} + n_{GPeaMe} + n_{GPaMe} + n_{SP} + n_{SPOH} + n_{GP} + n_{GPOH}} \qquad \text{(Eq. 5)}$$

There in, n_i corresponds to the number of moles of monomer i detected after RCF. As the H monomers HP and HPOH were barely detected, they were excluded from the calculations in Eq. (3) to Eq. (5). It wasn't quantified for HPe, HPOH, SPe, GPa, SPeaMe, SPa and SPaMe; however, among these monomers, relevant peaks were only detected for SPe in the experiments without catalysts (chapter S5.1.1).

Table 1

Applied nomenclature for typical monomers obtained from RCF (the GC/MS was calibrated for compounds in black (Fig. S3) and, due to a lack of standards, not calibrated for compounds in grey; more details like the CAS number and denotation according to IUPAC about the calibrated compounds are presented in Table S2).

Basic aryl group	Aliphatic side chain					
	Derived from alcoholic monolignols			Derived from hydroxycinnamic acids		
	-propen	-propane	-propanol	-propenoic acid methyl ester	-propanoic acid	-propanoic acid methyl ester
 H-	 HPe (not calib.)	 HP (calib.)	 HPOH (not calib.)	 HPeaMe (calib.)	 HPa (calib.)	 HPaMe (calib.)
 G-	 GPe (calib.)	 GP (calib.)	 GPOH (calib.)	 GPeaMe (calib.)	 GPa (not calib.)	 GPaMe (calib.)
 S-	 SPe (not calib.)	 SP (calib.)	 SPOH (calib.)	 SPeaMe (not calib.)	 SPa (not calib.)	 SPaMe (not calib.)

3. Results and discussion

3.1. Substrate composition

Different biomasses were used (i.e., beech wood, rye straw, solid digestate obtained after lab scale anaerobic digestion of the rye straw and solid digestate obtained from an industrial straw mono-fermentation plant). Their elemental composition using CHNS analysis is shown in Table S3 and their cumulative particle size distribution is given in Fig. S1. The composition of these substrates is depicted in Table 2.

The compositional analysis shows that lignin is accumulated within the digestates verifying their similar or even higher lignin contents compared to beech wood. Also, the lignin to holocellulose ratio is increasing during anaerobic digestion indicating a higher carbohydrate degradation than lignin degradation. Furthermore, as expected, straw and straw digestates contain more ash than beech wood.

One further difference between straw and wood is in the acylation with carboxylic acids (Table 3). The rye straw used, as typical for herbaceous biomass, contains a considerable amount of purely ester-bound ferulic acid (FA) (0.2 wt%) and para-coumaric acid (pCA) (1 wt%), which are structurally related to lignin, but might be linked to both lignin and carbohydrates [30,39]. These are partly retained during anaerobic digestion, but in contrast to lignin, their content is decreasing and not increasing in the digestates indicating that they are anaerobically degraded to a certain extent (Table 3). However, the purely ester-bound FA given in Table 3 represents only one part of the total contained FA, as FA is predominantly both ester- and ether-bound in straw [31,40]. In contrast, pCA is mainly ester-bound to lignin in straw, i.e., it can be assumed that approximately the total pCA content is given in Table 3 [31,40]. Beech wood hardly contains any purely ester-bound FA or pCA, but is highly acylated with acetate.

3.2. RCF of beech wood – catalyst screening

Hardwood like beech wood is often applied as a substrate for RCF and typically shows the highest yields among the different types of lignocellulose. For the verification of the experimental setup and a first screening of different catalysts, beech wood was used as a substrate.

Based on the catalyst screening presented in Fig. 2, it appears that Pd is the most productive metal, as for both carbon- and alumina-supported catalysts, highest monomer-yields are obtained from the Pd-containing catalysts. Ni-based catalysts, on the contrary, showed the lowest productivity, especially if their higher loading is taken into account. H_2-TPR measurements (Fig. S2 and Table S8) reveal interesting metal-activity correlations. While Ru showed its first reduction peak already at around 150 °C, Ni has its main reduction peak at around 330 °C while Pd just starts to reduce at above 500 °C, which is indicating the different oxidation states of these metals under the applied RCF conditions (chapter S4.2).

Fig. 2 shows that for all active metals, higher monomer yields were obtained with the respective carbon-supported catalysts than with the corresponding alumina-supported analogs having the same metal loading. If no hydrogenation catalyst was added, mainly unsaturated monomers were released and monomer peaks were significantly reduced indicating the crucial role of the catalyst (Table S9). Blank experiments using neat support materials without active metal also led to mainly unsaturated monomers with reduced monomer peaks. But even here, in line with the observations made when comparing carbon- and alumina-supported catalysts, the addition of neat carbon support led to clearly higher yields of unsaturated GPe compared to the use of neat alumina support or the absence of both catalyst and support (Table S10). One explanation for the higher activity of carbon supported catalysts might be their significantly higher BET surfaces between 788 and 1196 m^2/g compared to only 105–283 m^2/g for alumina-supported catalysts (see Table S7). In the blank experiments using neat support materials without active metal, where hardly any hydrogenation of monomers was achieved, a better stability of released unsaturated monomers and a reduction in repolymerization reactions were apparently achieved using carbon as a support. This might indicate a less favorable interaction of lignin fragments with the alumina support compared to the carbon support as discussed in other studies that observed a similar trend when comparing carbon-and alumina-supported catalysts [15,33]. Another difference possibly playing a role is the higher acidity of alumina supports compared to carbon supports [41,42]. However, opposed to this, an increase in yield with an increase of acidity was found for the case of acidified carbon supports [20].

Consequently, among the catalysts investigated, 5 wt% Pd/C

Table 2
Composition of the used substrates, including the mean values and standard deviations calculated from quadruplicates. Furthermore, the lignin to holocellulose ratio for each substrate is given, where holocellulose comprises the glucan, arabinoxylan and acetate content (the latter is given in Table 3).

	Beech wood	Rye straw	Washed rye straw digestate	Washed industrial straw digestate
	in wt% (based on dry mass)			
Glucan	40.5 ± 0.3	35.3 ± 0.3	18.5 ± 0.2	36.2 ± 0.3
(Arabino-) Xylan[a]	20.6 ± 0.1	25.1 ± 0.3	17.3 ± 0.4	24.7 ± 0.3
Lignin	24.6 ± 0.5	15.2 ± 0.2	28.3 ± 0.2	25.6 ± 0.4
Ash content	0.9 ± 0.1	7.0 ± 0.03	10.5 ± 0.1	3.7 ± 0.1
Lignin to holo- cellulose ratio	0.37	0.24	0.76	0.42

[a] No Arabinan was detected in case of beech wood.

Table 3
Acylation with acetic acid, purely ester-bound ferulic acid (FA) and purely ester-bound para-coumaric acid (pCA) of the different assessed substrates, including the mean values in mg per g of dry biomass and standard deviations calculated from duplicates.

	Beech wood	Rye straw	Washed rye straw digestate	Washed industrial digestate
	in $mg/g_{dry\ biomass}$			
Acetate	57.2 ± 0.5	24.3 ± 0.3	14.4 ± 0.7	7.8 ± 0.2
Purely ester-bound FA	0.04 ± 0.001	2.15 ± 0.02	0.88 ± 0.01	1.1 ± 0.2
Purely ester-bound pCA	0.31 ± 0.002	10.0 ± 0.6	8.07 ± 0.09	8.6 ± 0.5
(FA+pCA)[a] per lignin in %	0.1	8.0	3.2	3.8

[a] Purely ester-bound.

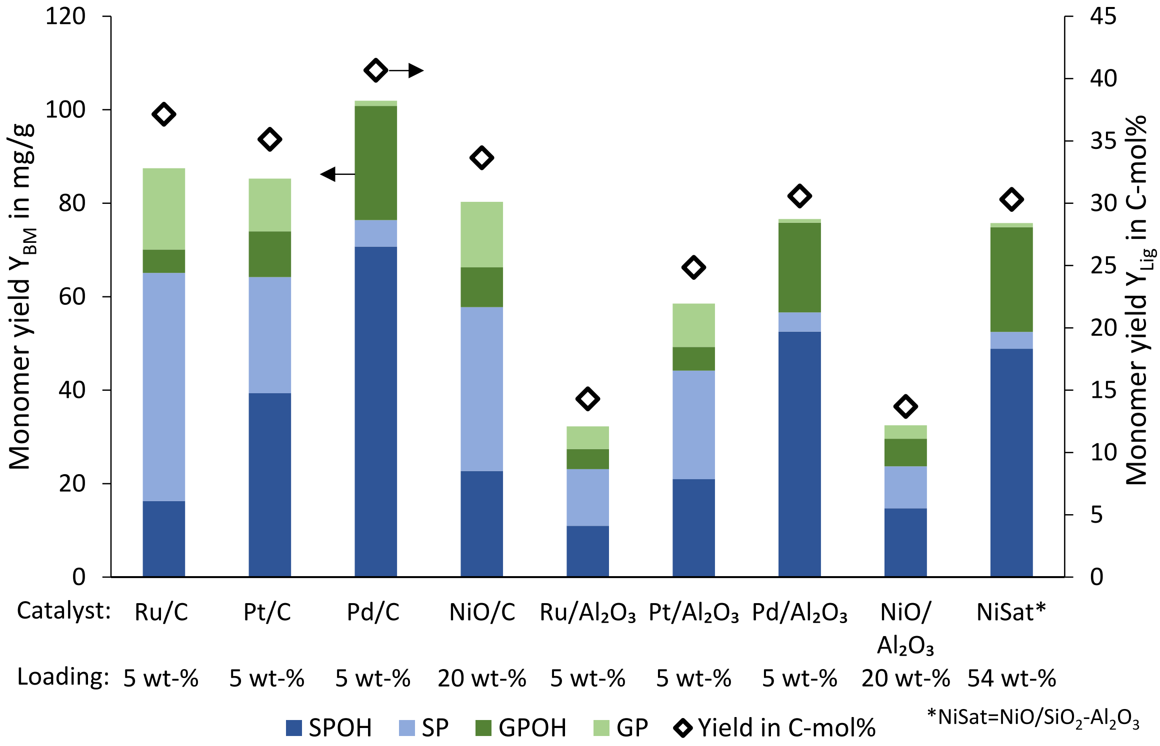


Fig. 2. Catalyst screening. Monomer yields Y_{BM} based on biomass dry weight (left axis) and monomer yields Y_{Lig} based on lignin-related carbon (right axis) obtained after RCF of beech wood using different catalysts (loading given in wt%). Reaction conditions: 10 mL methanol, 250 mg beech wood, 50 mg catalyst, T = 200 °C, 50 bar H_2, t = 24 h, n = 1000 rpm.

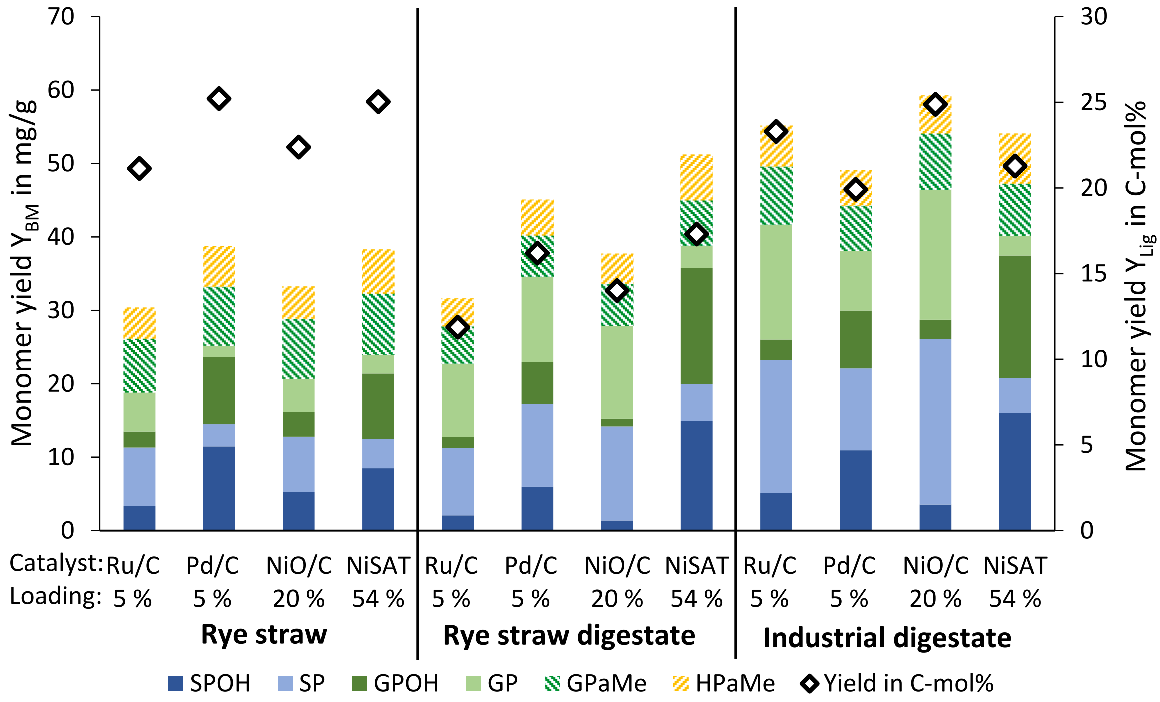


Fig. 3. Screening of alternative substrates. Monomer yields Y_{BM} based on biomass dry weight (left axis) and monomer yields Y_{Lig} based on lignin-related carbon (right axis) obtained after RCF of rye straw, rye straw digestate or industrial straw digestate using different catalysts. Reaction conditions: 10 mL methanol, 250 mg biomass, 50 mg catalyst, T = 200 °C, 50 bar H_2, t = 24 h, n = 1000 rpm.

Table 4

The total monomer yield Y_{Lig} on lignin basis is split into the yield of alcoholic monomers (HP, GP, GPe, GPOH, SP, SPOH) and the yield of hydroxycinnamic acid monomers (HPeaMe, HPaMe, GPeaMe, GPaMe). Furthermore the p-coumaric acid (pCA) and ferulic acid (FA) recovery are given corresponding to the ratio of pCA- and FA-derived monomers (HPeaMe and HPaMe from pCA and GPeaMe and GPaMe from FA) over the content of purely ester-bound pCA and FA, respectively. Yields are given for the RCF experiments of rye straw, washed rye straw digestate and washed industrial digestate using NiSat catalyst. The same data for the experiments with other catalysts are summarized in Table S12.

	Yield of alcoholic monomers	Yield of hydroxycinnamic acid monomers	pCA recovery (related to purely ester-bound pCA)	FA recovery (related to purely ester-bound FA)
	in C-mol% on lignin basis		in mol%	
Rye straw	16.4	8.6	54.1	356.0
Washed rye straw digestate	13.5	3.9	70.1	653.2
Washed industrial straw digestate	16.2	5.0	72.6	593.3

performed best for beech wood with a biomass-based yield of around 100 mg/g and a lignin-based monomer yield of around 41 C-mol% (corresponding to 41.5 wt% on lignin basis). This is slightly lower, but comparable to results from other hardwoods. As an example, under comparable conditions, a yield of 46.6 wt% on lignin basis from birch wood with Pd/C has been reported [43].

Additionally, it was verified that the monomer selectivity regarding the share of γ-OH-monomers (%γ-OH) is well controllable via the catalyst choice [44,45]. Under the applied process conditions, Pd/C and Pd/Al_2O_3 led to a higher %γ-OH, while NiO/C and Ru/C rather yielded monomers without aliphatic γ-OH-groups, indicating with regard to the anticipated reaction scheme in Fig. 1, different hydrogenolysis and hydrogenation activities of these catalysts. To some part, this selectivity seems to be influenced by the active metal, as the trend regarding %γ-OH for Pd and Ru is similar for both carbon- and alumina-supported catalysts. However, for Ni, a change in γ-OH selectivity is observed from 36.9 %γ-OH using NiO/C to 69.8 %γ-OH using NiO/Al_2O_3 and 65.9 %γ-OH using NiSat (NiO/SiO_2-Al_2O_3) so that a further influence of the support and metal loading is evident. As typical for hardwood, S-monomers are dominating recognizable by shares of S-monomers around 70 % for all experiments from Fig. 2; the share of S-monomers is not influenced by the catalyst choice.

Small carbon losses in form of CO, CO_2, CH_4, C_2H_6 and C_3H_8 via the gas phase were also detected (Table S19) and showed to be below 2 C-mol% on biomass basis for most catalysts and around only 0.3 C-mol% for blank experiments. However, higher carbon losses around 10 C-mol % were observed for Ru-based catalysts and a very high carbon loss around 37 C-mol% was observed for the NiSat-catalyst favoring methane formation [46]. As indicated in other studies [47] and further supported by a carbon balance that does not add up if methane losses are included (Table S21), it is assumed that methane is predominantly originating from the methanol solvent. For all metals, slightly higher carbon losses via the gas phase were observed for the alumina-supported catalysts than for the carbon-supported catalysts. Carbon losses in the form of other volatiles like furans are possible, but were not further investigated here.

3.3. *RCF of straw and straw digestates – screening of alternative substrates*

From the catalyst screening using beech wood as a substrate, four catalysts were selected for further investigations using straw and straw digestates as alternative substrates. The selected catalysts were Pd/C and Ru/C, as these gave the highest monomer yields and NiO/C and NiSat, as these are associated with lower costs than noble metal-based catalysts. Monomer yields that were obtained by RCF of rye straw, washed rye straw digestate and washed industrial straw digestate using these catalysts can be seen in Fig. 3.

3.3.1. *Comparison of yields from straw and straw digestate with yields from beech wood*

From all straw-based substrates shown in Fig. 3 and Table S11, monomer yields are clearly lower than from beech wood both on biomass and on lignin basis, which is in accordance with the observations of other authors handling herbaceous biomass [26,27,48]. One further difference compared to the RCF of beech wood is the release of two more monomers from the straw-based biomasses: The hydroxycinnamates ferulate (FA) and p-coumarate (pCA) present in straw were obtained as methyl esters (HPaMe from pCA and GPaMe from FA; in small quantities also HPeaMe and GPeaMe) due to a supposed transesterification with the solvent methanol [20]. These hydroxycinnamates are not regarded as “core-lignin”, but nevertheless included in yield calculations [29].

Among the straw-based substrates shown in Fig. 3, highest monomer yields on biomass basis were obtained from washed industrial straw digestate with values between 50 and 60 mg/g. For unfermented rye straw, the biomass-based yield was between 30 and 40 mg/g, being still a lot higher than the biomass-based yield of around 17 mg/g, which Brienza et al. detected under comparable conditions from wheat straw [33]. Comparing rye straw and its corresponding digestate, slightly higher yields on biomass basis tend to be obtained from washed rye straw digestate than from rye straw, i.e., the results for both digestate types are in harmony with hypothesis 1 (higher monomer yields on biomass basis from straw digestate than from unfermented straw). On lignin basis however, monomer yields are lower from the rye straw digestate than from rye straw. The latter observation contradicts hypothesis 2 of similar monomer yields on lignin basis from straw and straw digestate. It might indicate that, against the hypothesis, a slight lignin degradation is taking place during anaerobic degradation. However, also the catalysis could be inhibited to a larger extent by the increased ash content in rye straw digestate. Furthermore, the yields on lignin basis rely on an accurate determination of the lignin content, which is however not certain.

The determination of lignin content is challenging and no method could be identified as clearly most accurate yet [49]. The compositional analysis method used in this paper (chapter S2.2), is typically also used in lignin-first-studies, providing a basis for comparability [9]. However, two specific challenges became apparent in the context of straw and straw digestates.

- A first challenge is the influence of impurities. The digestates were in contact with digestion sludge containing mainly microorganisms and minerals. These impurities have been largely removed by washing and extracting. Furthermore, lignin values were corrected for ash and protein. However, other impurities like plastic particles expectedly present in sludge from a municipal wastewater plant might have led to an overestimation of lignin content especially in the rye straw digestates from lab fermentation (chapter S5.3).

- A second challenge is the influence of hydroxycinnamic acids, which are fully considered for yield calculations but seem to contribute only partially to the lignin content during compositional analysis (chapter S3.2) [50], rendering yield comparisons on lignin basis difficult for straw and straw digestates considering their different hydroxycinnamics-to-lignin ratios (Table 3). Indeed, based on lignin content, in particular the yield of hydroxycinnamic acid derived monomers is lower from the digestates than from the unfermented straw, while the yield of alcoholic monomers ("core lignin" monomers) is on average only slightly lower for washed rye straw digestate and even slightly higher for industrial straw digestate (Table 4 and Table S12).

Consequently, according to hypothesis 2, no clear final statement is possible due to the uncertainty in lignin content determination not allowing for a direct comparison. It can be concluded that there is a need for further research on the fate of hydroxycinnamic acids during lignin content determination.

3.3.2. *Recovery of hydroxycinnamic acids*

Consistently observed lower yields from straw compared to wood cannot be explained only by ether bond content, if NMR determinations are correct (chapter 1). Possible reasons might be the higher ash content and the more heterogeneous structure of straw, including other monomers like tricin not detected as monomers within this and most other studies. Estimated tricin contents around 30 mg/g on lignin basis for different types of straw explain a reduction in yield, but do not close the entire gap [32]. Furthermore, tricin is assumed to be only ether-bound and thus wouldn't hinder the release of other monomers by ether cleavage [51].

Another difference between straw and wood maybe influencing the depolymerization behavior is the high content of hydroxycinnamic acids in straw. Clearly more hydroxycinnamic acid derived monomers (mostly unsaturated HPeaMe and GPeaMe) than alcoholic monomers were released during blank runs without catalyst from straw-based biomasses. This can be seen from Tables S11 and S12 and it indicates that these hydroxycinnamic acids are easier released or more stable (less involved in condensation reactions) under the applied condensation-prone conditions (i.e., absence of hydrogenation catalyst) than alcoholic monomers. This is not only due to the cleavage of ester bonds but obviously also more stable ether bonds are cleaved, as significantly more ferulic acid (FA) is obtained by RCF than by pure ester cleavage, which can be seen by FA recoveries between 200 and 700 % compared to purely ester-bound FA in Table 4 and Table S12. However, maximally about two third of the contained ester-bound p-coumaric acid (pCA) is recovered as pCA-derived monomers (mainly HPaME) during RCF even with the application of a catalyst (Table S12). To a certain extent, this recovery gap for pCA can be explained by degradation reactions to other monomers; one side-reaction is the decarboxylation of pCA and FA to phenols with ethyl side-chain, however, these were detected but not quantified here [20].

Altogether, these results do not indicate a strong involvement of hydroxycinnamic acids in condensation reactions, but do not completely exclude them either. A more comprehensive investigation requires a method for determining the total FA content, quantifying ester-, ether- and C-C-bound FA. Heavily cross-coupled FA suggested as a reason for lower monomer yields from grasses, would be neither detected by ester hydrolysis nor by RCF if also C-C-bonds are present [29].

3.3.3. *Influence of active metal*

For rye straw and washed rye straw digestate, Pd/C and NiSat gave the highest yields, respectively, whereas for washed industrial straw digestate, NiO/C performed best in terms of the monomer yield. Regarding the share of γ-OH-monomers, the respective catalysts mostly showed a similar behavior for straw and straw digestates as for beech wood. NiSat is highly selective for γ-OH-monomers, whereas with the application of Ru/C and NiO/C rather monomers without γ-OH are obtained. However, a shift in γ-OH-selectivity was observed for Pd/C, which predominantly yields γ-OH-monomers for beech wood and rye straw, but predominantly yields monomers without γ-OH in case of both investigated straw digestates. As the type of biomass was the only parameter varied, this change in selectivity can certainly be attributed to some characteristics of the digestates. Preserving the γ-OH-functionality might be advantageous for different industrial applications [44] and as the highest γ-OH-selectivity and the highest yield of γ-OH-monomers from both straw digestates were obtained using NiSat, it was decided to use this NiSat catalyst for further investigation and optimization of the RCF of straw digestates.

Concerning the carbon losses via the gas phase (Table S19), a similar trend was observed for the straw-based biomasses as for beech wood. Carbon losses higher than 2 C-mol% were observed only for Ru/C and NiSat. By far the highest losses, mostly in the form of methane, were observed from NiSat again. Rough mass balances, indicating the loss of biomass solids during reductive catalytic fractionation and their recovery as gases and mono-aromatics are presented in chapter S5.5.

3.4. *Effect of a preceding removal of ester-bound hydroxycinnamates*

In order to investigate the influence of ester-bound hydroxycinnamic acids further, washed industrial straw digestate and beech wood were treated in an aqueous 1 M NaOH solution at 30 °C. In this way, among other compounds, purely ester-bound hydroxycinnamic acids as well as alkali-soluble lignin were released from the biomass and could be separated from the alkali-insoluble residue of the biomass by centrifugation in a first procedure. In a second procedure instead, the pH was lowered to about 1 after the treatment with 1 M NaOH to precipitate and separate the acid-insoluble residue after alkaline treatment, containing the solid biomass residue plus the polymeric lignin fragments that were extracted and solubilized by alkaline treatment, but not the free hydroxycinnamic acids [52]; in Fig. 4 these different procedures are schematically presented. The two different fractions obtained after alkaline treatment (i.e., the alkaline insoluble residue and the acid insoluble residue) were used as substrates for RCF and the resulting monomer yields are shown in Fig. 5.

In accordance with literature, especially the lignin in straw-based biomass like the washed industrial straw digestate showed to be highly extractable by alkali (Fig. 5, Table S13) [53]. Only very few amounts of lignin-derived monomers are obtained from the alkaline insoluble residue of the industrial straw digestate. After precipitating the alkali-soluble lignin with acid however, the monomer yield from the resulting acid-insoluble residue is drastically higher and comparable with the yield from untreated washed industrial straw digestate. This shows that a part of the lignin in the straw digestate is extracted and solubilized by alkaline treatment and that either hardly any lignin is remaining in the solid biomass during alkaline treatment or the remaining lignin has a condensed structure (i.e., low ether bond content). The solubilized lignin, however, can be easily precipitated by the addition of acid. Comparing the hydroxycinnamic acids released from untreated industrial digestate with the hydroxycinnamic acids released from its acid soluble residue after alkaline treatment, it is getting evident that most of the ferulic acids (FA) contained are ester- and ether- bound, as the yields of FA-derived GPaMe are similar from untreated biomass and the acid insoluble residue; thus hardly any FA was released by ester-bond-cleavage (Table 3). Although reduced in quantity, p-coumaric acid (pCA) -derived HPaMe is still obtained from the acid-insoluble residue. Thus, either also a fraction of pCA is ether- and ester-bound or the release of ester-bound acids according to the method used (chapter S2.2) is incomplete, which would mean that the pCA recovery is actually lower than calculated in Table 4. However, it seems that the partial removal of pCA from the acid insoluble residue doesn't lead to an increase in the yield of alcoholic monomers, which would be the expectation, if pCA would be strongly involved in condensation

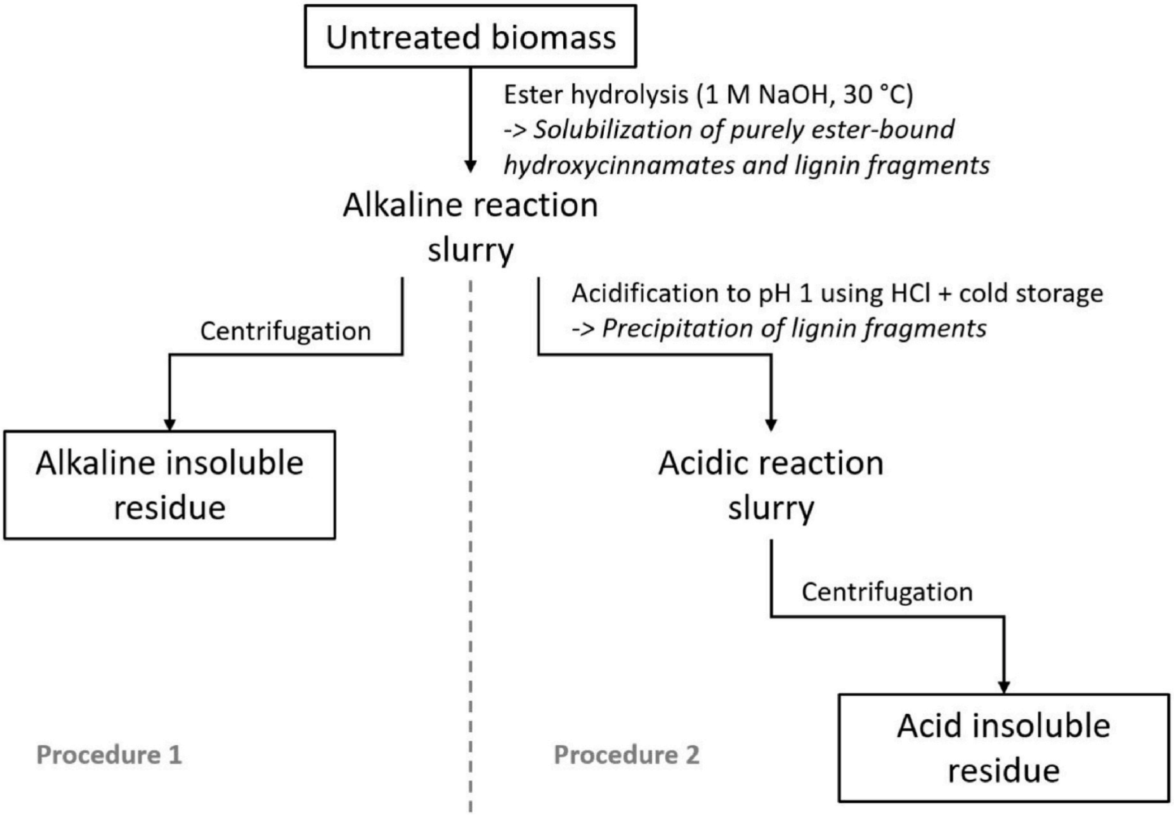


Fig. 4. Alkaline treatment procedure. Schematic representation of the experimental procedure of alkaline treatment and the following steps to get either the alkaline insoluble residue or the acid insoluble residue after alkaline treatment of the respective biomass. In italics is described, which components should theoretically dissolve or precipitate by the corresponding treatment.

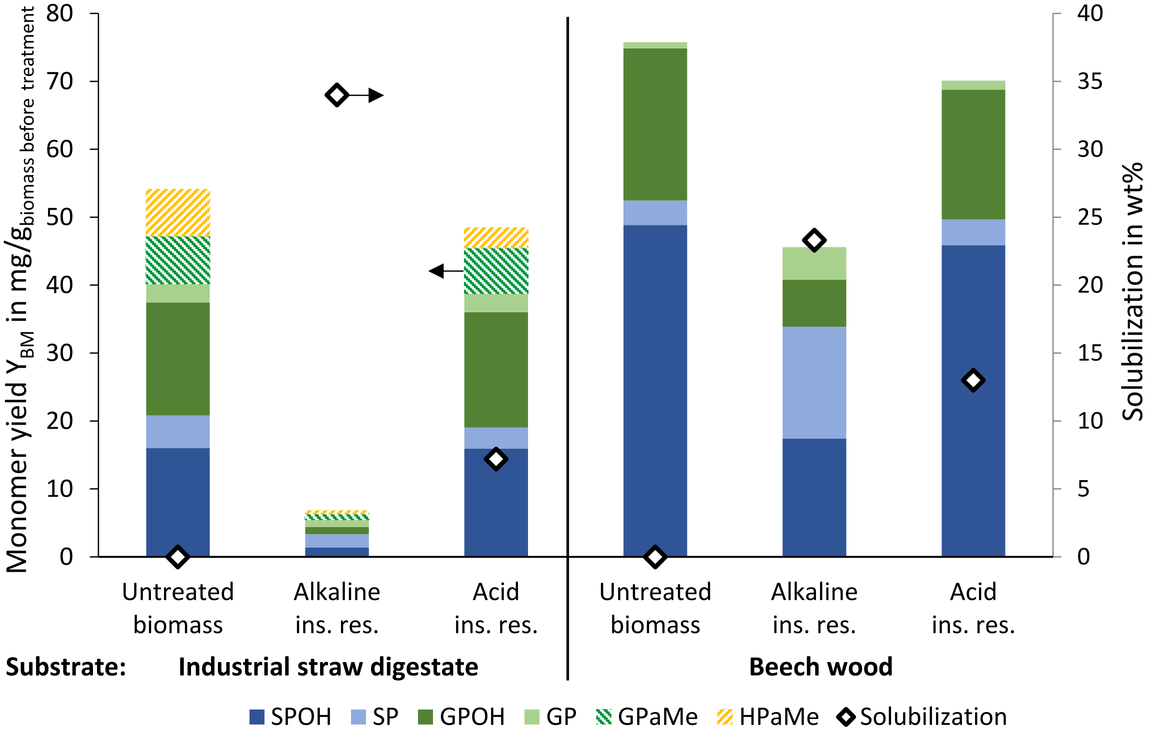


Fig. 5. Effect of alkaline pretreatment (1 M NaOH for 24 h at 30 °C) of industrial straw digestate and beech wood on the monomer yields Y_{BM} obtained by RCF. RCF reaction conditions: 10 mL methanol, 250 mg biomass, 50 mg 54 wt% NiO/SiO_2-Al_2O_3 catalyst, T = 200 °C, 50 bar H_2, t = 24 h, n = 1000 rpm.

reactions. It has been suggested to remove hydroxycinnamic acids from herbaceous biomasses before RCF by a preceding ester hydrolysis in order increase selectivity of "core lignin" monomers and facilitate downstream processing [29]. However, in case of the ester hydrolysis performed here, it could be seen that the shift in selectivity is low and that no type of hydroxycinnamic acids, even not pCA, is fully removed.

Regarding beech wood, the decrease in monomer yield from the alkaline insoluble residue compared to untreated beech wood is a lot lower, indicating that a major part of the beech wood lignin is not alkali-extractable under the applied conditions. Interestingly, there is a shift in γ-OH-selectivity from around 80 % for untreated beech wood to around 40 % from the alkaline insoluble residue, which is reversible, as from its acid insoluble residue, the γ-OH-selectivity is around 80 % again.

In summary, the RCF experiments of different biomass fractions after ester hydrolysis by alkaline treatment confirmed the different behavior of lignin from herbaceous biomass compared to lignin from hardwoods; more precisely, a clear difference in lignin dissolvability in alkali was apparent from the experiments. The removal of ester-bound hydroxycinnamic acids has not led to a detectable increase in monomer yield, however, the majority of hydroxycinnamic acids seems to be additionally ether-bound and thus not releasable by simple ester hydrolysis.

3.5. *Variation of RCF reaction conditions for industrial straw digestate*

The previous biomass and catalyst screening experiments showed that the RCF of washed industrial straw digestate using NiSat as a RCF catalyst gives the highest biomass-based yield of γ-OH-monomers among the straw-based substrates. Below, the influence of the performed digestate washing and furthermore of reaction time and hydrogen pressure on the RCF of industrial straw digestate is further investigated by a parameter variation.

3.5.1. *Effect of washing digestate fibers*

After anaerobic digestion of straw, the digestate fibers were separated from the liquid phase by decantation in an industrial scale. In the raw digestate, impurities (e.g. minerals, ammonia and microorganisms) from the liquid phase are still present [37]. In order to remove these impurities, the digestates were extensively washed with tap water until a fully clear effluent was obtained (chapter S1.1). The washing of the digestate leads to a strong increase in yields and γ-OH-selectivity: A biomass-based yield of around 54 mg/g, a lignin-based yield of around 21 % and a γ-OH-selectivity of around 80 % were obtained from washed industrial straw digestate whereas a biomass-based yield of around 27 mg/g, a lignin-based yield of around 12 % and γ-OH-selectivity of around 57 % were obtained from raw industrial straw digestate (Table S14), showing the negative impact of the impurities on RCF. Impurities seem to impair the catalysis and thus, washed digestates were used for all the other experiments presented.

3.5.2. *Effect of reaction time*

The influence of the reaction time on RCF with washed industrial straw digestate as substrate is presented in Fig. 6. Timing was started, once the reaction temperature of 200 °C was reached. However, already at that time, just from the heating phase, monomers with a biomass-based monomer yield of around 14 mg/g were released. Subsequently, the yield was quickly increasing within the first 7 h up to a yield of around 54 mg/g. Afterwards, no further significant change in yield (all yields for reaction times $\geq$ 7h are within the estimated relative standard deviation of 6 % (chapter S5.2)) is apparent; thus, a reaction time of 7 h is sufficient for achieving maximal yields. This is in line with the findings for the RCF of corn stover using Ni/C, where no further considerable increase in yield was detected between 6 h and 24 h reaction time [20].

The share of γ-OH-monomers is slightly decreasing within the first 7 h, indicating that the direct hydrogenation to γ-OH-monomers occurs slightly faster than the subsequent hydrogenolysis and hydrogenation reactions theoretically necessary for monomers without γ-OH group. Within the first 2 h, there is furthermore a slight increase observable for both the share of S-monomers and the share of hydroxycinnamic acid (HA) monomers, indicating that G-monomers are slightly faster released than S-monomers and that alcoholic monomers are slightly faster released than hydroxycinnamate-derived monomers. However, after about 2 h, these shares remain rather constant.

A further look at the gas phase analysis (Table S20) reveals that the methane formation catalyzed by NiSat further increases with increasing reaction time up to an amount of 28 C-mol% after 48 h. The methane formation is thus independent from the formation of lignin monomers, which is not further increasing after 7 h; however, the methane formation rate appears to decrease which could indicate a certain catalyst

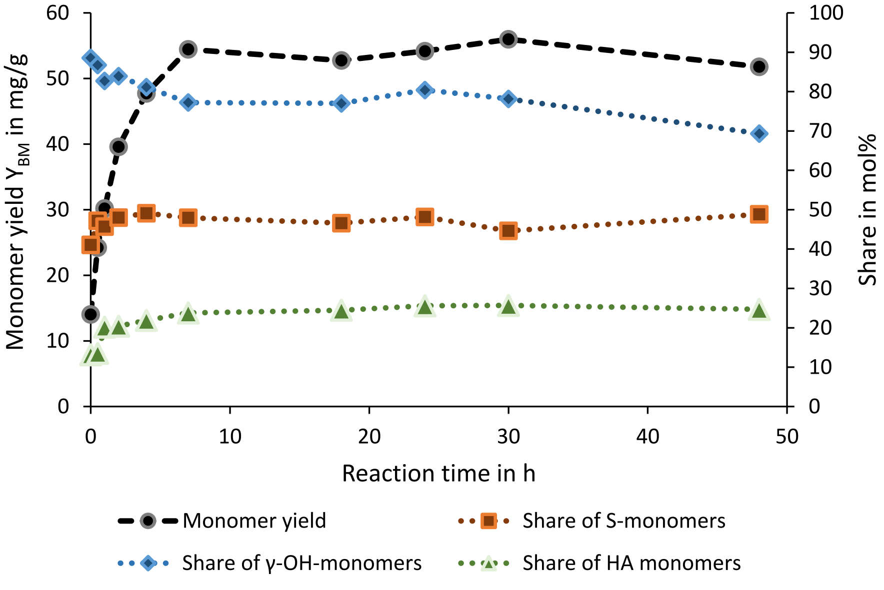


Fig. 6. Effect of the reaction time on the biomass-based monomer yield (referring to the left y-axis) and the shares of S-monomers, γ-OH monomers and HA (hydroxycinnamic acid) monomers (all shares referring to the right y-axis) during RCF of washed industrial straw digestate. Reaction conditions: 10 mL methanol, 250 mg biomass, 50 mg 54 wt% NiO/SiO_2-Al_2O_3 catalyst, T = 200 °C, 50 bar H_2, n = 1000 rpm.

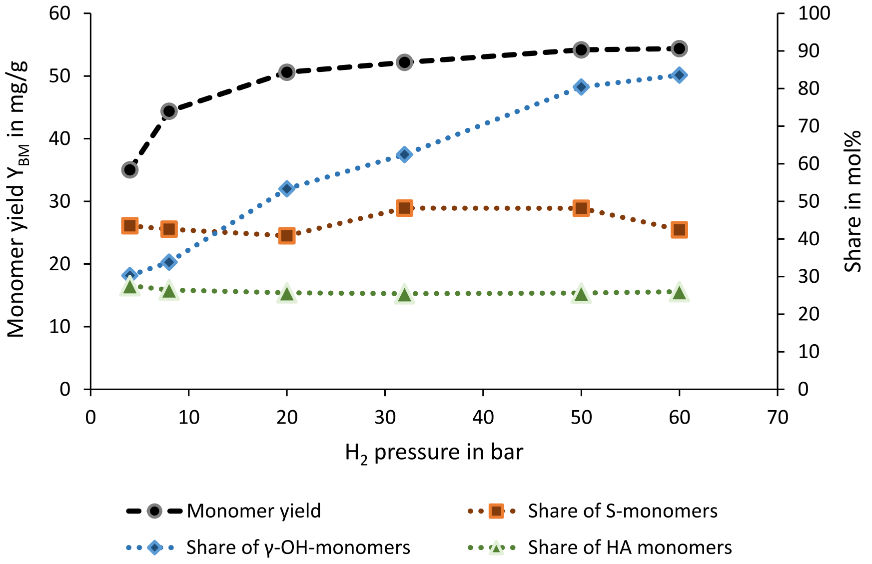


Fig. 7. Effect of the H_2 pressure (at 200 °C) on the biomass-based monomer yield (referring to the left y-axis) and the shares of S-monomers, γ-OH monomers and hydroxycinnamic acid (HA) monomers (all shares referring to the right y-axis) during RCF of washed industrial straw digestate. Reaction conditions: 10 mL methanol, 250 mg washed industrial straw digestate, 50 mg 54 wt% NiO/SiO_2-Al_2O_3 catalyst, T = 200 °C, t = 24 h, n = 1000 rpm.

deactivation, if methane formation by methanol reforming is assumed.

3.5.3. Effect of gas atmosphere and pressure

A strong reductive atmosphere is necessary to effectively hydrogenate unsaturated monomers in RCF processing [54]. However, it has been shown in other studies using wood and herbaceous biomass that hydrogen does not necessarily have to be supplied externally via the gas atmosphere, since the solvent or components of the biomass can also act as hydrogen donors [10,14,16]. This could be confirmed also with washed industrial straw digestate, as under absence of external hydrogen with a nitrogen gas atmosphere (8 bar N_2 pressure at 200 °C), still around 36 mg/g of monomers per biomass (corresponding to 14.6 C-mol%) were released with a share of γ-OH monomers of around 27 mol% (Table S16). Adding H_2 gas with a partial pressure of 4 bar led to similar yields. However, as a clear trend, monomer yields increased with H_2 pressures within the applied range from 4 to 60 bars up to around 54 mg/g (corresponding to 21.4 C-mol%) (Fig. 7). While the share of S-monomers and the share of HA monomers are hardly changing with H_2 pressure, the share of γ-OH monomers is increasing with increasing H_2 pressures from around 27 mol% in the absence of external H_2 to around 84 mol% at 60 bar H_2 pressure. Thus, alcoholic G- and S- monomers and HA monomers were released in similar proportions for each respective H_2 pressure, however, the amount and the γ-OH-functionality of the released monomers was strongly influenced by the H_2 pressure. A similar observation was made for the RCF of eucalyptus sawdust in n-butanol/water [15]. This can be explained by considering the reaction scheme in Fig. 1: Monomers with γ-OH-functionality are formed by direct hydrogenation of released monolignols, whereas monomers without γ-OH-functionality are formed by first hydrogenolysis, leading to the formation of propenyl-substituted phenols (GPe and SPe), followed by the hydrogenation of unsaturated double bonds leading to GP and SP. Even though the hydrogenolysis-hydrogenation pathway stoichiometrically requires more hydrogen than the pathway with direct hydrogenation, it diminishes with higher hydrogen pressure as indicated by the change in γ-OH-selectivity. One explanation for this might be that the hydrogenolysis reactions taking place are inversely dependent on hydrogen pressure as was observed also for other hydrogenolysis reactions, whereas hydrogenation reactions are favored by higher hydrogen pressures [55–57]. Furthermore, the total monomer yield is increasing with increasing H_2 pressure also on a molar basis, indicating an increased release of monomers or a decrease in condensation reactions of released monomers. The latter can be explained by the transition of the reaction system from a reduction-limited state to a solvolysis-limited state at higher H_2 pressures and the described shift in reaction pathway to a direct hydrogenation with higher H_2 pressure [58]. Both effects lead to a faster reductive stabilization of unsaturated monomers, which are prone to repolymerization reactions if not stabilized.

An additional reaction parameter is the reaction temperature. It was not varied here as the used reactors didn't allow temperatures above 200 °C. Published studies with herbaceous biomass indicate that a further increase in yield could be achieved by raising the reaction temperature up to 250 °C, accompanied by a higher lignin extraction and a faster hydrogenolysis [20,33]. As a trade-off, the same studies report a decrease in both retention and enzymatic degradability of the carbohydrates with higher temperatures. Similarly, the addition of an acid or the utilization of an acidic catalyst support could increase monomer yield and decrease the carbohydrate retention [20]. The fate of the carbohydrates, as well as the quantity and types of the remaining lignin di- and oligomers, were not investigated further in this study and should be the subject of subsequent investigations on a larger scale. The structure of the remaining lignin di- and oligomers is also of interest for further utilization options. While the lignin oil from softwood has already been analyzed in extensive studies, to our knowledge such studies are still lacking for lignin from straw-like biomass [59,60].

4. Conclusions

The goal of this study was to investigate the Reductive Catalytic Fractionation (RCF) of two straw digestates, one from a batch fermentation in lab scale and one from a continuous fermentation in industrial scale, in comparison to the RCF of rye straw and beech wood.

The results have shown that biogenic aromatics can be recovered from straw digestates by RCF in methanol at 200 °C. As lignin is accumulated in digested straw, higher yields of aromatic monomers on biomass basis are achieved from straw digestates than from unfermented straw. A parameter screening using industrial straw digestate showed that the digestates should be freed from impurities by washing, as yields are clearly lower also on lignin basis from raw, unwashed digestates containing more impurities like minerals and microorganisms. Maximal yields are achieved after about 7 h of reaction time; however, yields are not significantly decreasing also with longer reaction times up to 48 h, indicating the successful stabilization of the monomers released. Medium monomer yields could be obtained even without addition of external hydrogen; however, yields increased with hydrogen pressure. Furthermore, the share in γ-OH monomers increases with increasing H_2 pressure; thus, besides the catalyst choice, the H_2 pressure is an important parameter to influence the monomer selectivity.

In general, from all straw-based biomasses lower yields (maximally around 60 mg of monomers per g of washed industrial straw digestates) were obtained than from beech wood (maximally around 100 mg of monomers per g of beech wood). This is typically observed when herbaceous biomasses are compared with hardwoods, but still not fully understood. One difference is the occurrence of hydroxycinnamic acids (HAs), which are abundant in straw but hardly found in wood. However, no clear evidence about a yield-reducing influence of HAs could be found when their release under condensation-prone conditions (i.e., under absence of a hydrogenation catalyst) was regarded and when purely ester-bound HAs were released by ester cleavage prior to RCF. Purely ester-bound HAs seem to be partially degraded during anaerobic digestion as their contents decrease in straw digestates. Consequently, less HA-derived monomers were recovered from straw digestates than from unfermented straw, also on lignin basis. Just considering alcoholic "core-lignin" monomers, however, yields on lignin basis seemed to be in a comparable range for straw and straw digestates, which is highlighting the uncertainty regarding the attribution of HAs to lignin.

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CRediT authorship contribution statement

Timo Steinbrecher: Writing – original draft, Investigation. **Magdy Sherbi:** Formal analysis, Data curation. **Fabian Bonk:** Writing – review & editing, Resources. **Oliver Lüdtke:** Writing – review & editing, Resources. **Jakob Albert:** Writing – review & editing, Supervision, Conceptualization. **Martin Kaltschmitt:** Writing – review & editing, Supervision, Conceptualization.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2024.107136.

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