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ORIGINAL PAPER

Comparison of Acidic and Alkaline Oxidative Catalytic Fractionation Processes to Recover Aromatic Monomers from Native Poplar Wood and Straw Digestates: A Critical Lab-to-Lab Comparison

Timo Steinbrecher[1] · **Adrian Stöver**[1] · **Jakob Albert**[2] · **Martin Kaltschmitt**[1]

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Abstract

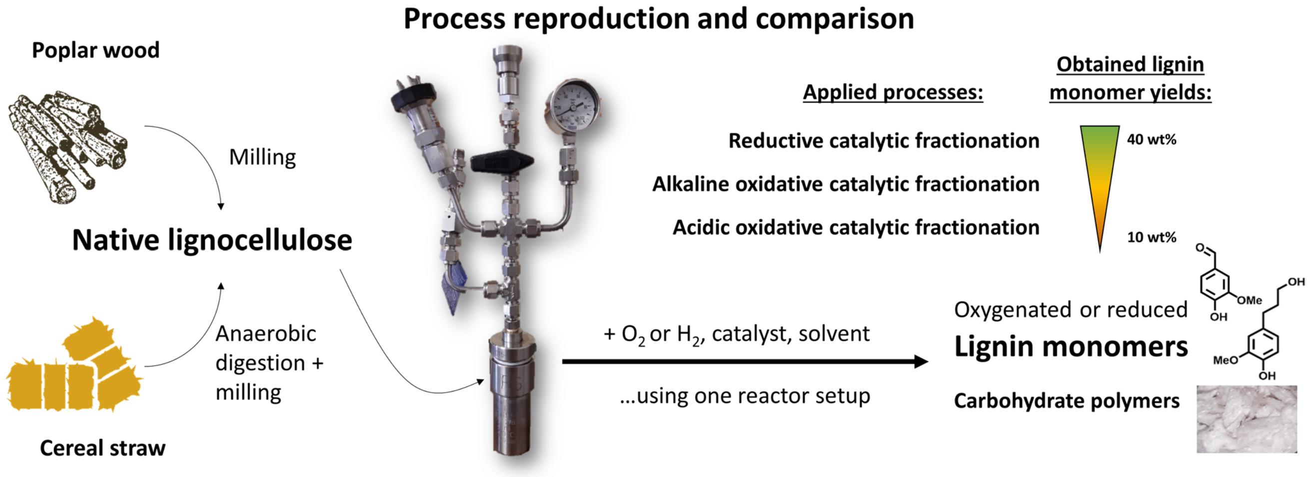
Lignin from native lignocellulose is a potentially attractive raw material for the production of bio-based aromatics due to its high abundance and its aromatic structure rich in ether bonds. Several oxidative catalytic fractionation processes have been presented in literature, through which oxygenated aromatics can be obtained from native lignocellulose-containing biomass in high yields. These processes can be divided into acidic processes using catalysts such as heteropolyacids in alcoholic solvents and alkaline processes using copper catalysts in aqueous NaOH solutions. Some of these processes have been tested only in one laboratory so far and the comparability among each other is very limited. Consequently, it is the aim and main novelty of this study to reproduce these processes with poplar wood and to compare them among each other and with the well-established reductive catalytic fractionation using the same reactor setup and biomass sample. The reaction conditions from selected reference processes were reproduced, with the main deviation that a smaller reactor size was used. Highest monomer yields on lignin basis around 40 wt% were obtained by reductive catalytic fractionation, leading to reduced instead of oxygenated monomers. The tested one-step alkaline oxidative catalytic fractionation process resulted in monomer yields up to around 30 wt%. Lowest yields around 10 wt% were obtained for one-step acidic catalytic processes using a methanol–water mixture as solvent and phosphomolybdic acid as catalyst, for which similar monomer yields could be achieved using sulfuric acid instead of phosphomolybdic acid. An acidic two-step process yielded very low monomer yields around 2 wt% largely deviating from literature values. For all oxidative catalytic processes, lower yields compared to literature values were observed, which is comprehensively discussed. It appears that, compared to the stable monomers obtained by reductive catalytic fractionation, the instability of the oxygenated monomers leads to a higher vulnerability to changes in the reaction process, probably shifting the optimal conditions. Straw digestate was applied as alternative substrate and yielded significantly less monomers than poplar wood.

✉ Timo Steinbrecher
timo.hannes.steinbrecher@tuhh.de

[1] Institute of Environmental Engineering and Energy Economics (IUE), Hamburg University of Technology (TUHH), Eißendorfer Straße 40, 21073 Hamburg, Germany

[2] Institute for Technical and Macromolecular Chemistry, University of Hamburg (UHH), Bundesstraße 45, 20146 Hamburg, Germany

Graphical Abstract



Highlights

- Reproduction and comparison of recently developed lignin-first processes
- Higher lignin monomer yields from poplar wood than from straw digestate
- Highest monomer yields achieved by reductive catalytic fractionation
- Higher yields from alkaline than from acidic oxidative catalytic fractionation
- In acidic processes, heteropolyacids replaceable by sulfuric acid for similar yields

Keywords Lignocellulosic biorefinery · Lignin depolymerization · Lignin-first processes · Oxidative catalytic fractionation · Reductive catalytic fractionation · Reproducibility study

Introduction

Aromatic compounds play an important role both in nature and in the chemical industry. In biomass, most aromatics are phenylpropanoids like mainly coniferyl or sinapyl alcohol polymerized in lignin, which, along with the carbohydrate polymers cellulose and hemicellulose, is a main component of lignocellulose. In the chemical industry, more basic aromatic molecules like benzene, xylene and their derivatives are used, which are almost exclusively obtained from fossil raw materials and hardly from lignin [1].

The high structural complexity and reactivity of lignin pose major challenges for its utilization. Technically isolated lignin (e.g., from the alkaline Kraft pulping process or the acidic Sulfite process) is typically highly degraded structurally (condensed), mainly through repolymerization reactions including the formation of stable C–C bonds, occurring during lignin isolation and hampering its depolymerization into monomers [2]. In lignin-first processes, the aim is to avoid such condensation in order to ensure a high depolymerizability of the lignin without preventing the valorization of the other biomass compounds [3]. This is achieved in particular by two characteristics of lignin-first processes: firstly, by the use of native (only mechanically treated) lignocellulosic biomasses as substrates and secondly, by an active stabilization of lignin to avoid condensation reactions.

Special care is taken for the lignin structure: it should not be condensed in the biogenic substrate and should not condense during the fractionation process. To avoid lignin condensation during fractionation, the lignin polymer might be stabilized in a way that prevents its degradation and depolymerization, e.g., by stabilizing labile ether bonds through acetal formation [4]. Another option is the stabilization of depolymerization products to prevent their repolymerization, e.g., by reduction [3]. One example are reductive catalytic fractionation processes where conditions are harsh enough that lignin is depolymerized, e.g., by solvolysis. Typically, unsaturated C=C bonds prone to react with other unsaturated bonds through a radical oligomerization are forming within the aliphatic side chain during solvolysis, however, if these unsaturated bonds are saturated by reduction as it is the case in reductive catalytic fractionation processes, the resulting lignin fragments are stable under the applied reaction conditions [2]. The reduced aromatics have a low content of functional groups, though these might be of special interest for selected industrial applications [5].

In oxidative processes, aromatics with such attractive functional groups can be obtained (phenolic aldehydes or carboxylic acids). However, opposed to the reductive processes, these compounds are typically not stable under the applied reaction conditions [6]. Accordingly, there are few oxidative lignin-first processes, as these can theoretically treat native lignocellulose (1st characteristic), but have difficulties fulfilling the 2nd characteristic of lignin stabilization mentioned above. Recently, several oxidative processes have been developed that use native lignocellulosic biomass with the aim of depolymerizing the contained lignin. Most of them can be categorized into two subgroups: alkaline and acidic processes.

Alkaline oxidative fractionation processes applied to native lignocellulosic biomass often take place in aqueous sodium hydroxide (NaOH) solution, typically with catalysts added (often Cu-based) under oxygen atmosphere [7–12]. Different possible reaction mechanisms have been discussed in literature and recent articles assume that cleavage occurs by several side chain oxidative steps ending with a retro-aldol reaction [13, 14]. In general, it has been found that high alkalinity and high availability of oxidants are required for such depolymerization reactions [13]. Very high lignin-based yields of aromatic monomers of around 49% were reported by Zhu et al. [10] applying CuO nanoparticles, aqueous NaOH (7.5 wt%) and an O_2 atmosphere (10 bar) for native eucalyptus wood at 160 °C for 1 h. Under similar conditions, also using CuO as catalyst, Hu et al. [7] obtained lignin-based monomer yields of around 26 wt% from native corn stover. By applying CuCl, they could further increase this yield up to around 30 wt% [7]. Schutyser et al. [12] obtained a similar maximum yield of monomers from poplar wood in a comparable alkaline system after shorter reaction times between 0 and 30 min. These yields are remarkably close to the theoretical maximum (based on ether bond content), although these processes do not fully meet the second characteristic of lignin-first processes, the active stabilization of lignin. Reactive sites are transformed by oxidation. But there are still further secondary reactions occurring to the new structures under the applied reaction conditions, recognizable by a rapid decrease in monomer quantities with longer reaction times [7]. Therefore, reaction time is a critical parameter and it was observed that the application of Cu-based catalysts does not increase the maximum yield, but does “expand the operating window in which high product yields are obtainable” [12]. Hu et al. [7] showed that aniline could be added as capping agent to reduce further coupling reactions to a certain extent.

Acidic oxidative fractionation processes applied to native lignocellulosic biomass typically take place in organic solvents (often with water as co-solvent) within an oxygen-rich atmosphere in combination with acidic catalysts; often with longer reaction times (several hours) compared to the alkaline processes [15–20]. Heteropolyacids (HPAs) are one class of acidic catalysts frequently used in such oxidative processes [21–23]. For example, Yang et al. [17, 18] applied phosphomolybdic acid (Keggin structure, $H_3PMo_{12}O_{40}$) in a methanol / water system of around 150 °C and obtained around 38 wt% of aromatic monomers from the lignin contained in birch wood and around 24 wt% from eucalyptus wood. Similar optimal conditions were found by Li et al. [24] for the acidic oxidative fractionation of pine wood, obtaining a maximum monomer yield around 23 wt%. However, they introduced a high mass of catalyst (100–180 wt% of catalyst compared to dry biomass weight) [17, 18, 24] so that the heteropolyacids appear to be a stoichiometric oxidative reagent rather than an oxidative catalyst [25]. Zhou et al. [26] also applied phosphomolybdic acid (Dawson structure, $H_6P_2Mo_{18}O_{62}$) to native biomass achieving a monomer yield of around 13 wt% from pine wood (150 °C, 4 h, 10 bar O_2, methanol/water 8/2 v/v, 1/1 w/w biomass/catalyst). They found that monomer yields could be increased by introducing vanadium as substitution metal for a certain share of molybdenum atoms. A maximum yield of around 24 wt% was achieved for the acid substituted with two vanadium atoms ($H_5PV_2Mo_{10}O_{40}$). The authors explained this finding with the increase of oxidation potential coming along with the increase of the number of vanadium atoms substituted in heteropolyacids [26]. Du et al. [20] developed a two-step, one-pot single-catalyst process also using phosphomolybdic acid (Keggin structure), but in lower amounts (18 wt% based on dry biomass weight). At only 100 °C, they were able to solubilize around 96 wt% of the lignin contained in native poplar wood in a methanol / water mixture and this lignin was furthermore stabilized by methoxylation of its α-OH groups. The obtained lignin- and POM- enriched liquid phase was subjected to a second process step at 140 °C, where the lignin was depolymerized to aromatic monomers with a yield of around 46 wt%. Due to relatively mild conditions (low temperatures) and the protection group effect of the α-methoxylation, sufficient stabilization of the cleavage products is apparently achieved here, so that also the second characteristic of lignin-first processes would be fulfilled in this process to a certain degree.

This overview shows that remarkable amounts of lignin monomers (monomer yields up to 50 wt%) were reported for these oxidative processes, even though most of them lack an active stabilization of the released monomers. However, since different biomass types were used in each study, a direct comparison of these various processes is difficult. The two-step acidic oxidative process by Du et al. [20] in particular was only developed in one laboratory but not yet reproduced by other laboratories in order to prove its general applicability as it is, e.g., the case for the reductive catalytic fractionation, which was applied by many different laboratories (e.g., [27–32]).

In order to increase their scientific significance, the aim of this work is to reproduce and compare the acidic and alkaline oxidative catalytic fractionation procedures presented using the same poplar wood sample in a rigorous lab-to-lab comparison. Therefore, the process conditions of the acidic processes published by Du et al. [20] and Yang et al. [17, 18] and the alkaline processes published by Hu et al. [7] and Zhu et al. [10] were reproduced and applied to poplar wood, with the main difference that a smaller reactor size was used (Table S1 in the Supplementary Information (SI)). Furthermore, for comparison, the poplar wood sample was also treated by reductive catalytic fractionation using the same reactor type and size. Poplar wood was chosen as a typical and often used representative biomass type for such purposes.

In addition to this reproducibility and robustness study, different modifications were investigated: straw digestates as a low-value residual biomass with increased lignin content were used as substrate in such processes for the first time, other heteropolyacids like copper- or vanadium-substituted heteropolyacids were tested and sulfuric acid was examined as an alternative catalyst for oxidative treatment.

Materials and Methods

Materials

Poplar granulate of 2–4 mm was obtained from LASvendi GmbH (Germany).

Straw digestate was obtained from a cereal straw monofermentation biogas plant in Brandenburg (Germany), extensively washed with tap water and repeatedly pressed off using a hydraulic press (40 L, Speidel, Germany) until a fully clear effluent was obtained. Subsequently, the washed material was dried in a convection oven at 45 °C. Further information on the chemicals used is given in section S1.

All biomasses were milled below 1 mm particle size for the biomass analysis methods and further below 0.5 mm particle size for all fractionation processes. Milling was performed in dry state using a cutting mill (MF 10, IKA, Germany) with screening sieves of respective mesh sizes (details about further materials used are specified in section S2).

Treatment Methods

A tenfold parallel reaction system with 32 mL reactors (inner diameter of 23 mm) made of Hastelloy C276, positioned in a heating block and equipped with magnetic stirring (stirrer bar with oval shape, 10 mm long and 5 mm wide) was used to carry out all catalytic experiments (details about the reactor-to-reactor variability are specified in section S7). As a general procedure for every experiment, one reactor was charged with a certain amount of biomass powder and catalyst and 10 mL of solvent (exact amounts are specified in Tables S5, S6 and S7 in the SI for each single experiment). After sealing the reactor, it was flushed with nitrogen three times and again three times with the reaction gas (oxygen or hydrogen). Subsequently, it was flushed with reaction gas and pressurized until the target pressure at room temperature was achieved. The reactor was heated to the reaction temperature with a magnet stirrer set on 300 min^{-1} and, once the temperature was reached, the time measurement was started and the stirrer was set to ca. 600 min^{-1}. After the respective reaction time, the reactor was taken out of the heating block and cooled to room temperature by a flow of compressed air for 30 min. After measuring the final pressure and temperature of the reactor, gas samples were collected in a gas bag and the reactor was opened. Subsequently, the solids and the liquid were separated either by filtration or centrifugation, the liquid phase containing the monomers was partially further purified and then analyzed by GC–MS (further details regarding phase separation and analysis in section S2). In case of a two-step process, the liquid phase obtained after filtration was treated again following the same procedure, but using different process conditions than in the first step.

Many different process variants were reproduced and compared, and the exact process conditions (e.g., amount of biomass, solvent, and catalyst) are specified for each individual experiment together with the results in the SI (Tables S5, S6 and S7).

Analytical Methods and Performance Indicators

The biomass composition including the content w_{ASL} of acid-soluble and w_{AIL} of acid-insoluble lignin (both in g/g) was analyzed by two-step acidic hydrolysis according to [33–35] (further specification in section S2.2). The mass $m_{monomer\ i}$ of the respective lignin monomers (in g) was quantified with the help of a GC/MS system (section S2.2). Monomer yields Y_{AIL} based on only the acid-insoluble lignin and Y_{Lig} based on the total lignin amount contained in the dry biomass weight $m_{biomass,\ dry}$ (in g) introduced into the reactor were calculated in wt% according to Eq. 1 and Eq. 2, respectively.

$$Y_{AIL} = \frac{\sum_i m_{monomer\ i}}{m_{biomass,\ dry} \quad w_{AIL}} 100\ \% \tag{1}$$

$$Y_{Lig} = \frac{\sum_i m_{monomer\ i}}{m_{biomass,\ dry} \quad (w_{AIL} + w_{ASL})} 100\ \% \tag{2}$$

The total biomass solubilization S (in wt%) occurring during the treatment steps was calculated using the dry weights $m_{F,\ empty,\ dry}$ and $m_{F,\ full,\ dry}$ of the empty and used filter or centrifuge tube (both in g) used for the subsequent solid–liquid separation according to Eq. 3.

$$\mathrm{S} = \left(1 - \frac{m_{F,\ full,\ dry} - m_{F,\ empty,\ dry}}{m_{biomass,\ dry}}\right)100\% \tag{3}$$

The gas phase after catalytic treatment was analyzed for the molar amounts n_{CO} of CO and n_{CO_2} of CO_2 (section S2.2). These amounts were referred to the share of carbon ω_C (in g/g) contained in the original biomass and designated as carbon loss in the gas phase L_{gas} calculated in %C according to Eq. 4.

$$L_{gas} = \frac{\left(n_{CO} + n_{CO_2}\right)\ 12 \frac{g}{mol}}{m_{biomass,\ dry} \quad \omega_C} 100\ \% \tag{4}$$

Table 1 Biopolymer composition (mean values and standard deviations calculated from quadruplicates) of poplar wood and straw digestate, determined by two-step acid hydrolysis as described in section S2.2 (SI)

	Poplar wood	Straw digestate
	in wt% based on dry biomass	
Carbohydrate polymers (sum)	64.7 ± 0.2	61.6 ± 0.4
Glucan	48.4 ± 0.2	35.8 ± 0.2
(Arabino-) Xylan	16.3 ± 0.1	25.8 ± 0.4
Acetate	3.1 ± 0.1	0.8 ± 0.1
Lignin	26.0 ± 0.7	21.7 ± 0.3
Acid-soluble (AS)	4.0 ± 0.2	0.9 ± 0.1
Acid-insoluble (AIL)	22.0 ± 0.6	20.8 ± 0.2
Ash content	0.9 ± 0.2	5.7 ± 0.1

Results and Discussion

Substrate Composition

The composition of poplar wood and straw digestate used as substrates within this study is given in Table 1. Poplar wood contains about 20% more lignin compared to the straw digestate sample, especially more acid-soluble lignin based on the method applied (see section S2.2, SI). Compared to typical lignin contents in straw obtained by the same method (e.g., 16 to 21 wt% for wheat straw [36–39]), the lignin content in the straw digestate sample is slightly increased. This can be explained by the fact that lignin is hardly degraded during anaerobic fermentation [40]. Consequently, such straw digestates already existing as industrial residue stream might be more attractive in the context of lignin valorization processes than virgin straw.

Table 2 shows the composition of the substrates used in the reference publications. For their poplar wood sample,

Table 2 Biopolymer composition of biomass samples used in the reference publications, where, however, some of the listed constituents were not further specified (n.s.)

	Poplar wood used by Du et al. [20]	Eucalyptus used by Yang et al. [17]	Corn stover used by Hu et al. [7]	Eucalyptus used by Zhu et al. [10]
	in wt% based on dry biomass			
Carbohydrate polymers (sum)	76.4	59.7	53$^{b)}$	65.4$^{d)}$
Glucan	n.s	41.9	31.7$^{b)}$	46.7$^{d)}$
(Arabino-) Xylan	n.s	17.8	21.3$^{b)}$	18.7$^{d)}$
Lignin	≥ 22.0	25.7	21.9$^{b)}$	≥ 23.8$^{d)}$
Acid-soluble (AS)	n.s	n.s	2.95$^{c)}$	n.s
Acid-insoluble (AIL)	22.0$^{a)}$	n.s	18.15$^{c)}$	23.8$^{a)\ d)}$
Ash content	n.s	n.s	n.s	0.6 $^{d)}$

a) It was not exactly specified in the reference publications whether the values given refer to AS or AIL. Here, it was assumed that the term “Klason lignin” in these publications refers only to acid-insoluble lignin (AIL)

b) The reference publication [7] specifies a lignin content of 21.9 wt% and cites publication [41] with regard to the corn stover. However, that publication gives a slightly different lignin content for corn stover of 21.1 wt% based on the given AS and AIL values. Despite this slight difference, the other values—apart from the specified lignin content—were taken from the cited publication [41]

c) In the reference publication [41], the values for AIL and AS were indicated the other way around. However, it is assumed that this is an error, since the orders of magnitude are typically exactly the opposite and the values were adapted accordingly here

d) All values were apparently based on moist biomass in the reference publication [10]. In this table, the values based on dry biomass were calculated using the moisture content indicated. All other reference publications do not specify, whether the values are based on moist or, as usual, on dry state

Du et al. [20] determined the same content in acid insoluble lignin as was detected for the poplar wood sample in this study, but a significantly higher content in carbohydrate polymers. For all biomasses, detected lignin contents are in a quite narrow range between around 22 and 26 wt%, whereas the contents in carbohydrate polymers vary more strongly (53–76 wt%).

Reductive Catalytic Fractionation

Reductive catalytic fractionation is a method cleaving ether and ester bonds and leading to reduced, stable monomers (Table S2, SI). It can result in monomer yields close to the theoretical maximum based on ether and ester bond content of the lignin [42], was already successfully reproduced in many different laboratories (see introduction) and is discussed as scalable technology for producing aromatics from lignin in native biomass [43]. As the same reactor type and the same biomass samples were used in this study as for the oxidative catalytic fractionation experiments, the achieved results are especially suitable for comparison.

By reductive catalytic fractionation, 10.3 wt% of monomers based on dry biomass corresponding to 47 wt% on acid-insoluble lignin (AIL) basis (Y_{AIL}) and 40 wt% on total lignin basis (Y_{Lig}) were released from poplar wood (Tables 3 and S3). This is similar to the literature values of comparable processes using poplar. As examples, Parsell et al. [44] obtained 40 to 54 wt% of monomers on lignin basis from three different wild type poplar samples and Renders et al. [45] achieved approx. 30 wt% monomers on a lignin basis after a significantly shorter reaction time of 3 h.

Table 3 Amount and type of lignin monomers releasable by reductive catalytic fractionation from poplar wood and straw digestate (values from single determination). For a reductive catalytic fractionation experiment, 10 mL of methanol was mixed with 250 mg of biomass and 50 mg of 5 wt% Pd/C catalyst. The reaction took place at 200 °C with 50 bar H_2 pressure for 24 h. More details regarding the results are given in Table S3 in the SI

	Poplar wood	Straw digestate
	in wt% based on dry biomass	
Total monomers released	10.3	5.6
Among them		
S-Monomers[a]	5.5	2.4
G-Monomers[a]	3.3	1.8
Phenolic acid methyl ester[a]	1.5	1.4
Methyl ester derived from		
Ferulic acid	< 0.1	0.9
p-coumaric acid	< 0.1	0.5
p-hydroxybenzoic acid	1.5	< 0.1

[a] for type and origin of monomers, see Table S2 in the SI

For straw digestates the yields were lower ($Y_{AIL} = 27$ wt% and $Y_{Lig} = 26$ wt%) and comparable with former results from our laboratory with another straw digestate sample [31]. The lower yields on lignin basis from straw digestates indicate a lower lignin depolymerizability compared to poplar, at least by reductive catalytic fractionation. Both substrates contain S- and G-derived monomers (derived from sinapyl or coniferyl alcohol, respectively), whereby S-monomers are released to a greater extent (for individual monomer yields see section S4). Both substrates apparently also contain phenolic acids typically bound by ester-bonds: p-hydroxybenzoic acid was released from the poplar wood and p-coumaric and ferulic acid were released from the straw digestate. This is in accordance with the characteristic incorporation of p-hydroxybenzoate in poplar wood and p-coumarate and ferulate in grasses [28].

Oxidative Catalytic Fractionation

Below, the described published methods for acidic [17, 18, 20] and alkaline [7, 10] oxidative catalytic fractionation (see introduction) are applied to poplar wood as well as straw digestate. Additionally, these methods are modified regarding different parameters. All reactions were downscaled to 10 mL volume of the liquid reaction slurry (reaction conditions of all references processes are summarized in Table S1). Yields and delignification values are given either on acid-insoluble lignin (*AIL*) basis (Y_{AIL}) or on total lignin basis (Y_{Lig}), depending on how it was handled in the respective publication.

Oxidative Catalytic Fractionation in Acidic Environments

Two-Step Procedures Adapted from Du et al. [20], poplar wood was treated with 2.5 mM phosphomolybdic acid in methanol / water (9/1 v/v) at 100 °C for 2 h in a first step to dissolve and α-methoxylate the contained lignin. The obtained lignin-containing liquid was treated in a second step at 140 °C for 4 h to depolymerize the lignin. This way, about 7 wt% of the poplar wood was solubilized, whereby lignin was preferentially dissolved, but only a quarter of acid-insoluble lignin was removed. The monomer yield after the second step was around 2 wt%, with methylparaben accounting for almost half of the monomers (Table 4 and Table S5).

Although it was attempted to replicate the procedure of Du et al. [20] as closely as possible, with the difference that their procedure was scaled down here from 40 to 10 mL, their high delignification of 96 wt% and monomer yield Y_{AIL} around 46 wt% for the optimum could be clearly not achieved (Table 4). Furthermore, in contrast to the results from Du et al. [20], no significantly lower delignification and monomer yield was achieved when nitrogen was used

Table 4 Solubilization S and monomer yields Y achieved with the two-step, one-pot oxidative catalytic fractionation using acidic polyoxometalates developed by Du et al. [20] and comparison to their literature values. Values with a specified variance (standard deviation) are mean values from multiple determinations; the respective number of repetitions varies for the individual values and is indicated in Table S5

Data origin	Reaction conditions	Biomass	Reaction volume	S in wt%	Y_{Lig}	Y_{AIL}
Du et al. [20]	25 mg/mL of substrate in methanol water (9/1 v/v) with 2.5 mmol/L of $H_3PMo_{12}O_{40}$ and 10 bar O_2/N_2 (9/1 v/v) gas atmosphere at 100 °C for 2 h in a first step and at 140 °C and 4 h under otherwise similar conditions with the filtered liquid phase in a second phase. Liquid phase was evaporated and dried residue extracted with DCM	Poplar wood (40 mesh)	40 mL liquid, 60 mL gas	≥ 41.0 $^{a)}$	n.s.	45.9
This study		Poplar wood (35 mesh)	10 mL liquid, 22 mL gas	26.8 ± 9.8	1.8 ± 0.5	2.1 ± 0.6
		Straw digestate (35 mesh)		2 ± 1	0.03	0.03

in the gas phase instead of oxygen, indicating that oxidation catalysis didn't play a decisive role. Similar in tendency compared to Du et al. [20], delignification and monomer yields were lower when sulfuric acid was used instead of phosphomolybdic acid (same pH) and significantly lower when no additive was added at all, indicating that there is an effect of the phosphomolybdic acid on lignin going beyond the effect of the pH value (Table S5). In contrast to Du et al. [20], methylparaben was the main monomer obtained here. Methylparaben can be formed from p-hydroxybenzoic acid, which is typically ester-bound in poplar wood [28] and can thus be released by simple ester bond cleavage and subsequent methylation without the need for ether bond cleavage and further oxidation reactions. The massive deviations observed are further discussed below in section 3.3.3.

The same two-step procedure with phosphomolybdic acid was also applied to straw digestate, where negligible solubilization and monomer yields were observed (Table 4). Apart from phosphomolybdic acid, the commercially available heteropolyacids silicotungstic acid ($H_4SiW_{12}O_{40}$) and phosphotungstic acid ($H_3PW_{12}O_{40}$) were also applied to poplar wood using otherwise similar conditions, which led to similar results (Table S5).

One-Step Procedures Since only a minority of the lignin was apparently dissolved in the first step of the two-step procedure in the scaled-down setup, an attempt was made to apply the conditions of the second step directly to poplar wood and digestate omitting the first step. In this way, the total biomass solubilization increased clearly from around 7 and 2 wt% to 40 and 32 wt% for poplar wood and straw digestate, respectively, whereas the monomer yields increased only slightly to about 4 wt% for poplar wood and 1 wt% for digestate (entries 1 and 2 in Table S6).

Yang et al. [17, 18] used a similar one-step procedure, but applying a tenfold higher mass of phosphomolybdic acid which was used as a stoichiometric reagent and no longer as a catalyst. This process variant was also applied to poplar wood and straw digestate here, achieving monomer yields of around 11 wt% and 4 wt%, respectively (Table 5 and entries 3 and 4 in Table S6). So, by increasing the amount of phosphomolybdic acid, significantly higher monomer yields can be achieved, however, a higher mass of phosphomolybdic acid than biomass is used.

As comparison, clearly higher monomer yields Y_{Lig} on total lignin basis of ca. 38 wt% from birch wood at 150 °C for 2 h [18] and 24 wt% from eucalyptus wood at 140 °C and 2 h [17] were achieved by Yang et al. applying this one-step procedure at two- to four-times higher scale (Table 5).

Applying phosphomolybdic acid at a distinctly longer reaction time of 16 h and a temperature of 160 °C, comparable monomer yields around 10 wt% and 7 wt% were obtained from poplar wood and straw digestate, respectively. However, only at a reduced amount of catalyst compared to that of Yang et al. [17, 18] has been used (entries 5–7 in Table S6).

In similar experiments with phosphomolybdic acid (Dawson structure), Zhou et al. [26] achieved higher yields when molybdenum was partially replaced by vanadium. In a screening of vanadium-substituted phosphomolybdic acids (Keggin structure) [46], the triple-substituted variant showed the highest yield (entries 8–11 in Table S6). However, at all conditions tested here, the triple-substituted phosphomolybdic acid performed worse than the unsubstituted one, so that the hypothesis that vanadium substitution leads to better yields could not be confirmed by the conducted experiments (entries 12–19 in Table S6).

Phosphotungstic acid is more acidic than silicotungstic acid, which again is more acidic than phosphomolybdic acid [47, 48]. Identical molar amounts of these three catalysts were applied for 16 h at 160 °C, whereby the lignin-based monomer yield decreased with a higher acidity of the

Table 5 Monomer yields Y achieved with the one-step oxidative catalytic fractionation using acidic catalysts developed by Yang et al. [17] and comparison to their literature values. The results shown were obtained by single determinations; however, experiments with minor changes in conditions yielded very similar results, as shown in Table S5

Data origin	Reaction conditions	Biomass	Reaction volume	Y_{Lig} in wt%	Y_{AIL}
Yang et al. [17]	25 mg/mL of substrate in methanol water (8/2 v/v) with 25 mM of $H_3PMo_{12}O_{40}$ and 10 bar O_2 gas atmosphere at 140 °C for 4 h. Solids were removed by filtration, methanol evaporated and monomers extracted from aqueous slurry using DCM	Eucalyptus wood (20 mesh)	40 mL liquid, 60 mL gas	24	n.s.
This study		Poplar wood (35 mesh)	10 mL liquid, 22 mL gas	11.2	13.2
		Straw digestate (35 mesh)		3.8	4.0
	Same, but: 62 mM H_2SO_4 instead of 25 mM of $H_3PMo_{12}O_{40}$ (similar pH)	Poplar wood (35 mesh)		11.9	14.1

catalyst (entries 5, 20 and 21 in Table S6). Exactly the same trend has also been observed by other authors [24].

To evaluate the effect of the acidity alone, sulfuric acid was used in place of the polyoxometalates, in a quantity so that a similar pH value was achieved as with the polyoxometalates (Table S6, entries 22 to 27). This enabled higher yields under certain circumstances. The highest measured yield from poplar among the tested acidic processes of around 13 wt% was achieved with 10 mM sulfuric acid at 160 °C and a treatment time of 16 h (entry 24 in Table S6). When sulfuric acid was used instead of phosphomolybdic acid at a similar pH value and otherwise under the same reaction conditions as in Yang et al. [17], a similar monomer yield was obtained (Table 5 and entry 26 in Table S6). This suggests that the acid properties alone are decisive and that the phosphomolybdic acid has no additional effect and can be replaced by the cheaper sulfuric acid. The methanol content in the solvent, on the other hand, is decisive. When the same experiment was carried out using only water, the yield was significantly lower at around 1 wt%, which can be explained by the low solubility of lignin in water (entry 27 in Table S6).

Without any added acid or catalyst (blank experiment), a lignin-based yield around 6 wt% was achieved from poplar wood under similar conditions, showing the yield enhancing effect of a certain acidity (entry 28 in Table S6).

$CuCl_2$, typically used for alkaline oxidative catalytic fractionation processes, was used under the same conditions, leading to a slightly lower yield of around 4 wt% (entry 29 in Table S6). A slightly higher yield around 7 wt% was achieved if the solvent was acidified with sulfuric acid, which was however lower than the acidic reference experiment without $CuCl_2$ (entries 25 and 30 in Table S6). $CuCl_2$ thus had a negative influence on the monomer yield under acidic reaction conditions, whereas the use of the Cu-containing polyoxometalate $(^{n}Bu_4N)_{11}PCu_2Mo_{10}O_{40}$ [49] resulted in an unchanged yield around 6 wt% compared to the blank experiment (entry 31 in Table S6).

Considering the monomers formed in all conducted one-pot acidic catalytic fractionation experiments (Table S6), under comparatively milder conditions (short reaction time, lower acidity), mainly vanillin, syringaldehyde, and methylparaben are obtained. Under harsher conditions, the proportion of vanillin and syringaldehyde is increasingly replaced by methyl vanillate and methyl syringate, which can be formed from vanillin and syringaldehyde through further oxidation. The proportion of syringaldehyde and methyl syringate (S-monomers) becomes very low in some processes. While around 1.7 times more S-monomers than G-monomers are obtained with reductive catalytic fractionation, the S/G-ratio for some of the acidic oxidative catalytic fractionation processes falls below 0.3. As examples, this was observed when using a high amount of phosphomolybdic acid or long reaction times (entries 5–7 in Table S6), when using the more acidic phosphotungstic acid or silicotungstic acid (entries 20 and 21 in Table S6), when using vanadium-substituted phosphomolybdic acid (higher oxidation potential, entries 8 to 19 in Table S6) or in sulfuric acid experiments with long reaction times (entries 24 and 25 in Table S6). Methylparaben, on the other hand, was the most abundant monomer in nearly all experiments with poplar wood, and its proportion within the monomers tends to increase under harsher conditions. Overall, these results indicate that syringaldehyde and methyl syringate have the lowest stability under the process conditions applied, followed by vanillin and methyl vanillate, while methylparaben appears to be the most stable monomer. Interestingly, the higher instability of syringaldehyde was also observed in case of alkaline oxidative fractionation in another study [12]. As discussed above, no ether cleavage or oxidation reaction would be necessary for the release of methylparaben as long as it is derived from p-hydroxybenzoic acid, which would be reasonable considering the methylparaben quantities obtained.

The straw digestates do not contain significant amounts of p-hydroxybenzoic acid and, accordingly, hardly any methylparaben is released there. The individual vanillin,

Table 6 Solubilization *S* and monomer yields *Y* achieved with the alkaline one-step oxidative catalytic fractionation processes published by Hu et al. [7] and Zhu et al. [10] and comparison to their values. Results are from duplicates, where a standard deviation is specified and otherwise from single determinations

Data origin	Reaction conditions	Biomass	Reaction volume	*S* in wt%	Y_{Lig}	Y_{AIL}
Hu et al. [7]	20 mg/mL of substrate in 7.5 wt% NaOH in water with 10 mM of $CuCl_2$ and 10 bar O_2 gas atmosphere at 160 °C for 1 h. Solids were removed by centrifugation, the liquid phase was extracted with ethyl acetate (separation and extraction were n.s. by Hu et al. [7])	Corn stover (size n.s.)	25 mL liquid, 25 mL gas	n.s	28	*n.s.*
This study		Poplar wood (35 mesh)	10 mL liquid, 22 mL gas	41	26.5	31.3
		Straw digestate (35 mesh)		58 ± 7	10.2 ± 0.4	12.0 ± 0.5
Zhu et al. [10]	20 mg/mL of substrate in 7.5 wt% NaOH in water with 50 mM of CuO nanoparticles and 10 bar O_2 gas atmosphere at 160 °C for 1 h. Solids were removed by centrifugation; the liquid phase was extracted with ethyl acetate	Eucalyptus wood (40 mesh)	25 mL liquid, 25 mL gas	~ 30%C	**n.s.**	49
This study		Poplar wood (35 mesh)	10 mL liquid, 22 mL gas	n.m	20.9	24.8
		Straw digestate (35 mesh)		n.m	10.2	12.1

methyl vanillate, syringaldehyde and methyl syringate yields from straw digestates are lower than those from poplar wood in most cases; the total monomer yields are clearly lower in all cases.

Oxidative Catalytic Fractionation in Alkaline Environments

Hu et al. [7] and Zhu et al. [10] treated native lignocellulosic biomass in a 7.5 wt% NaOH solution at 160 °C with different metal compounds under 10 bar O_2 gas atmosphere for 1 h. These conditions were reproduced in a set-up scaled down by factor 2.5 with poplar wood and straw digestate. Using $CuCl_2$ as catalyst, lignin-based yields around 27 wt% and 10 wt% of monomers were obtained from poplar wood and straw digestate, respectively, whereas these yields were slightly lower to similar (21 wt% and 10 wt%) when CuO nanoparticles were applied as catalysts (Table 6 and entries 1, 2 and 4–7 in Table S7). No optimization with regard to reaction time was conducted, however, monomer yields were observed to decrease with longer reaction times, whereby after 16 h hardly any monomers were left (entry 3 in Table S7), showing that the monomers are not stable under the applied alkaline reaction conditions.

Hu et al. [7] obtained maximal yields in a similar range (around 28 wt% from corn stover) considering that they quantified two more monomers (vanillic and syringic acid) and that the kind of biomass used as substrate evidently has an influence. Furthermore, they obtained slightly higher lignin-based yields when using $CuCl_2$ instead of CuO as well. Schutyser et al. [12] also used poplar wood and achieved a maximum monomer yield of around 30 wt% using a slightly different process, involving single heating to 175 °C without maintaining the temperature and using $CuSO_4$ as catalyst. After 60 min reaction time, their yield was reduced by about one third [12]. Hu et al. [7] observed this decrease in yield with longer reaction times as well, however, the reduction only began after the optimal reaction time of approximately 1 h was reached. The comparison of both studies confirms the instability of the monomers under reaction conditions and furthermore shows their high sensitivity with regard to reaction conditions. Zhu et al. [10] also used reaction times of 1 h resulting in comparably higher yields around 32–49 wt% of monomers on acid-insoluble lignin basis obtained from different native biomasses using CuO nanoparticles as catalyst (Table 6).

In order to test further Cu-containing catalysts under such alkaline conditions, the polyoxometalate $(^{n}Bu_4N)_{11}PCu_2Mo_{10}O_{40}$ [49] was furthermore applied (Table S7, entries 8 and 9). With lignin-based yields of around 17 wt%, it gave slightly lower yields than the CuO nanoparticles and $CuCl_2$, however, due to the tetra-n-butylammonium anion, it was also not very soluble in the reaction medium.

Already without any catalyst, lignin-based monomer yields around 13 wt% for poplar wood and 10 wt% for straw digestate were obtained (Table S7; entries 10 and 11), showing the important role that already the alkaline system in combination with the oxygen atmosphere plays. Whereas all applied Cu-containing catalysts led to an increased monomer yield for poplar wood, even an increase of more than 100% in case of $CuCl_2$, their influence was insignificant for the straw digestate.

For all alkaline oxidative catalytic fractionation processes, vanillin (typically 30 to 40%) and syringaldehyde (typically 40 to 60%) were clearly the main monomers obtained. The minor monomers acetovanillone, acetosyringone and especially 4-hydroxy-benzaldehyde had a slightly higher proportion within the total monomers obtained from straw digestate than from wood (Table S7).

Discussion of Observed Deviations from Literature Values

To date, there have been very few attempts to reproduce oxidative catalytic fractionation processes starting from native biomass—and the few that do exist show clear deviations: In two different studies, Yang et al. [17, 18] treated the hardwoods birch and eucalyptus at quite similar conditions, obtaining quite different monomer yields of 24 and 38 wt% (Table S1). Zhu et al. [10] and Hu et al. [7] used comparable conditions with CuO as catalyst to treat corn stalk or corn stover, achieving monomer yields of 38 wt% and 26 wt%, respectively, finding the optimal reaction time to be around 1 h. In contrast, using $CuSO_4$ as catalyst, Schutyser et al. [12] found that just heating to a few minutes of reaction time would be optimal at both 150 °C and 175 °C, followed by a decrease in monomer yield with further reaction time. In our study, as well, partially very high deviations from the reference processes were observed as described in both preceding sections. These will be discussed in the following.

It is only natural that different results are obtained when biomass fractionation is carried out in different laboratories. Different biomass types with different compositions were used, as depicted in Table 2, and the composition as well as the structure certainly have an influence on the fractionation process. Even for the same type of biomass, the composition and polymer structure are influenced by many different factors (e.g., exact subspecies, location, time of harvest) and highly probably varying from sample to sample. Parsell et al. [44] used the same reductive catalytic fractionation method on three different poplar wild types, and the resulting lignin-based monomer yields differed by up to 14 percentage points in absolute terms, which corresponds to a relative deviation of approximately 35%, showing the high expectable variation even within the same type of biomass. Thus, certain deviations compared to Du et al. [20], who also uses poplar, and even more so compared to the other reference publications, which use other types of biomass (Table 2 and Table S1), are expectable.

Furthermore, the calculated lignin-related yield is always based on an analytically determined value, the lignin content, which cannot be determined unequivocally. There are various methods, and each method yields a different lignin content. Especially in case of herbaceous biomass such as straw relative deviations of over 100% were found with regard to the determined lignin content using different methods [50]. All reference publications reproduced above used the same method for lignin content determination standardized by the National Renewable Energy Laboratory in the US [33], which was also used in this study. For the similar predecessor version of this method, a relative deviation of 11% was found in an interlaboratory comparison where 19 different laboratories analyzed the same poplar sample in the same way [51]. Despite the standardization of the methodology, there are obvious deviations in its implementation. For example, it is often not specified whether the acid-insoluble residue has been corrected for its ash and protein content, or at what wavelength and with what extinction coefficient the acid-soluble lignin was quantified photometrically. Furthermore, some treatment steps are carried out with slight modifications. For example, Yang et al. [17] carried out the first hydrolysis step in lignin quantification for two hours instead of one hour and with 20 mL instead of 10 mL of 72 wt% H_2SO_4 per g of biomass. Such deviations can affect the determined lignin content, which in turn influences the calculated yield.

An obvious variation in the oxidative catalytic fractionation compared to the reference publications was the utilization of a different reactor size and stirrer type and especially the downscaling by factor of 2.5–4 (Table S1). Typically, the upscaling of processes is investigated and a decrease in performance is expected due to the lower surface-to-volume ratio, the higher difficulty of homogeneous stirring and consequently a worse mass and heat transfer. Changes in these process characteristics can be particularly detrimental when the final products are unstable and prone to undesirable side and follow-up reactions, as was observed with the oxidized monomers obtained here and in particular with the S-monomers (see sections "Oxidative Catalytic Fractionation in Acidic Environments" and "Oxidative Catalytic Fractionation in Alkaline Environments"). As one example, Kouris et al. [52] observed a reduction in yield by two third when trying to upscale their lignin depolymerization process from 100 mL to 4 L.

With respect to the reproduced oxidative catalytic fractionation processes, the mass transfer is considered as especially critical, as reactants from three different phases must be brought in contact: solid biomass must be brought in contact with the solvent furthermore containing the (in most cases dissolved) catalyst and the oxygen from the gas phase. However, mass transfer properties are not comparable as they are difficult to describe and many details (e.g., about the type of stirrer) are often not provided in the reference publications. A mass transfer that is enhanced too much might also be detrimental if it promotes undesirable degradation reactions, especially as the obtained monomers are unstable under oxidative conditions.

For the same reason of product instability, heat transfer is of great importance. Schutyser et al. [12] showed that, in case of alkaline oxidation, there is only a small window of reaction time where optimal yields are achieved, while yields are rapidly decreasing afterwards. They emphasized that "the heating rate of the reactors could significantly affect results across experimental setups" [12]. This is evident in the literature comparison already raised at the beginning of this section: similar experiments determine very different optima in terms of reaction time. Accordingly, the reproduced reaction time of one hour in case of alkaline oxidation experiments could have been suboptimal for our individual reactor setup and a cause for lower yields. For the acidic oxidation processes, longer reaction times were applied and comparable yields were achieved even after 16 h, so that the heating rate is considered less important in case of these reproduction experiments.

Finally, deviations in the rarely precisely described processes before and after the reaction can lead to differences in the results. For example, there were slight differences in the particle size of the substrate biomass used, and one reference publication did not even specify the particle size precisely (Table S1). Furthermore, none of the reference procedures specified which filter (type and pore size) or, in case of centrifugation, which centripetal acceleration was used to separate solids and liquids after the reaction, which makes an accurate reproduction difficult.

The preceding discussion makes a certain deviation, as observed compared to Hu et al. [7], appear logical, and the high deviations observed compared to Yang et al. [17] and Zhu et al. [10] also appear possible. Still, the discrepancy with the results obtained by Du et al. [20] appears too high to be explained by these reasons. Neither the high lignin solubilization in the first step (27 wt% instead of 96 wt%) nor the efficient conversion of solubilized lignin into monomers in the second step (8 wt% instead of 48 wt% monomer yield based on only the solubilized lignin) could be reproduced. Poplar wood was used in both studies, for which even the same acid-insoluble lignin content of 22 wt% was determined in both studies. Therefore, this process is either extremely sensitive to reaction conditions difficult to reproduce (e.g., mixing), or we may have implemented something incorrectly, for example, steps not described in detail by Du et al. [20] (e.g., the filtration), or a mistake occurred in the process description by the authors. As example, in view of the failure to reproduce already the first solubilization step, a possible explanation might be that lignin oligomers solubilized did not pass through the filter used. Du et al. [20] did not specify the filter type in their publication. However, other authors used a similar filter type and even smaller pore sizes compared to the filter type we used (section S2.1) for allowing solubilized Organosolv lignin to pass through and be separated from insoluble fragments, so this possibility is not considered likely [53]. Further clarification could be provided by other laboratories attempting to reproduce these results, ideally specifying their experimental procedures as precisely as possible.

Consideration of the Overall Processes

The objective of this work is the depolymerization of lignin contained in poplar wood and straw digestates into oxygenated aromatic monomers, which was described and discussed in the previous sections. However, both biomasses contain two to three times more carbohydrate polymers than lignin. With regard to an economically viable and environmentally acceptable process, also these components need to be utilized as completely and efficiently as possible. Therefore, the following section will briefly discuss the recovery of carbohydrates in the remaining solid material, possible losses in the gas phase and some research questions considered relevant for the economy of such processes.

Remaining solids: In some of the experiments conducted, particularly when vanadium-substituted phosphomolybdic acid and/or long reaction times of 16 h were used, very high biomass solubilization rates *S* of up to 90 wt% were observed (e.g., entries 5, 6 and 15 to 18 in Table S6). For the above-mentioned acidic and alkaline processes with the highest monomer yields, the solubilization was lower (40–70 wt%), so that in addition to the increased amount of monomers, a higher amount of solid biomass remained, for which the carbohydrate composition was analyzed in more detail (Table S8).

The lighter color of the residues (Figure S1) from the selected acidic processes already suggested a higher carbohydrate purity than in the residues from the selected alkaline processes, which was confirmed by the compositional analyses. For the selected acid and alkaline processes, the majority of the cellulose (typically around 90 wt%) remains in the residue. The residues from the acidic processes consist of 90 wt% or more of cellulose, while the cellulose content of the residues from the alkaline process described by Hu et al. [7] was slightly below 80 wt%. For the solid residues from the straw digestates, both processes resulted in lower cellulose contents of between 70 and 80 wt%. Hemicellulose accounted for a maximum of 5 wt% of all residues analyzed and is consequently largely solubilized in both processes. The remaining non-carbohydrate gap in the mass balance and the brown coloration of the respective residues suggest that in the case of the alkaline experiments, part of the lignin remains in the solid residue. Thus, all of the solid residues analyzed were more (in case of the acidic processes) or less (in case of the alkaline processes) pure cellulose, which would represent another valuable product. The fate of dissolved carbohydrate and non-monomeric lignin components and was not investigated in this study.

Gas phase losses: Gas phase losses in form of CO and CO_2 were measured and related to the carbon introduced with the biomass. However, theoretically, they could also be produced by degradation reactions of the methanol contained within the solvent. Among the acidic oxidative catalytic fractionation experiments, gas losses were higher than 1%C only when long reaction times of 16 h or the vanadium-substituted phosphomolybdic acid was applied (Table S6). For these experiments, gas losses of up to 10%C or even up to 15%C have been observed, when $CuCl_2$ was used as a catalyst. This indicates a high oxidative effect of vanadium and copper, which, considering the low respective monomer yields, may have been too high under the conditions applied with regard to the goal of lignin monomer recovery.

For all alkaline oxidative catalytic fractionation experiments, no CO or CO_2 gases were detected as both react with NaOH. Therefore, no comparison of the acidic and alkaline process variants can be made with regard to gas phase losses.

Outlook: The process variants examined here enable the recovery of relatively pure cellulose as a solid and dissolved oxygenated aromatics from poplar wood and straw residues. The fate and usability of dissolved, non-monoaromatic products from hemicellulose and lignin would be an interesting topic for follow-up studies. Furthermore, the liquid–solid ratio is regarded as an interesting parameter to vary (to reduce, in particular), as this ratio is an important factor influencing the overall economy and is very high in the reference methods. These use very low solid–liquid ratios between 0.02 and 0.025 kg/L, which are suitable to ensure well mixing and avoiding mass transfer limitations. However, for industrial processes, e.g., for Kraft pulping experiments, solid–liquid ratios are typically much higher (e.g., 0.25 kg/L) [54].

Especial challenges with regard to further scale-up are the possible formation of explosive mixtures, where organic solvents and oxygen are combined and the separation of monomers from the reaction liqueur, in particular for recovering the large quantities of NaOH applied in alkaline treatments. Furthermore, the instability of monomers under reaction conditions, eventually resulting in a low robustness to system changes could be a challenge, which was also emerging as result of this reproducibility study in a downscaled reactor system.

Conclusion

By combining pressurized oxygen or hydrogen gas, a suitable catalyst and a solvent in which lignin can be dissolved, aromatic lignin monomers can be obtained from native poplar wood and from anaerobically digested straw (i.e., straw digestate). This study aimed to reproduce and compare different published oxidative or reductive catalytic fractionation methods using the same reactor type and the same homogenized biomass sample in a rigorous lab-to-lab comparison. Interestingly, in all cases, significantly lower lignin-based yields were obtained from straw digestates than from poplar wood.

The highest monomer yields around 40 wt % and also the highest reproducibility compared to literature results were achieved by reductive catalytic fractionation. This process appears to be particularly robust with regard to changes in the reactor system (e.g., downscaling, different stirring behavior, different heating rates), which can be explained in particular by the stability of the monomers obtained, apparently not undergoing any significant further reactions under the applied reaction conditions [31].

Slightly lower yields approaching 30 wt% were obtained by alkaline oxidative fractionation, also in comparison to literature values. Especially in view of the instability of monomers under reaction conditions and their sensitivity to experimental setups, also observed in literature [12], such deviations can be easily explained. Many further possible reasons were comprehensively discussed in section 3.3.3. Lower yields are to be expected, as no specific optimization was performed on the experimental setup used in this study.

Significantly lower yields were obtained by acidic oxidative fractionation using heteropolyacids, also in comparison to literature values. Slightly more than 10 wt% of monomers were obtained by different variants of one-step processes. With a two-step processes according to Du et al. [20], however, hardly any monomers were obtained and it is concluded that this process is either extremely sensitive with regard to the experimental setup, or there is an error in the process documentation or reproduction that has not been detected within this study. To our knowledge, this process has not yet been repeated in external laboratories.

A comparison of biomass fractionation processes based on published data is of very limited value, as different reactor systems and biomass types are usually used, and even biomass samples of the same type can vary greatly. Against this background, selected, recently developed biomass fractionation processes, including catalytic lignin depolymerization, were reproduced in this comparative study using the same reactor system and the same biomass sample. This allowed the findings summarized above regarding yields, reproducibility, and robustness of the processes to be obtained. However, due to the observed, partly apparently severe influence of the experimental setup, it would be necessary to optimize the individual processes in the new setup for a fair comparison, rather than reproducing published, optimized conditions from other laboratories.

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Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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