Toward a Hydrogen-Free Reductive Catalytic Fractionation of Wheat Straw Biomass**

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The reductive catalytic fractionation (RCF) of lignocellulosic biomass is an attractive method for the conversion of lignin toward valuable low-molecular weight aromatics. A limitation to the upscaling of such technology is represented by the use ofpressurized hydrogen gas. Here, the role of hydrogen gas within the RCF of wheat straw biomass is investigated. The use of H_2 is shown to enhance lignin depolymerization, by virtue of an improved hydrogenolysis and hydrogenation of lignin fragments, with a yield of phenolic monomers that increased from ca. 12 wt% of acid-insoluble lignin in the initial biomass under inert atmosphere to up to ca. 25 wt% under H_2 (in methanol, at 250 °C, with Ru/C). The adoption of methanol, ethanol or isopropanol as hydrogen-donor solvents was also investigated in the absence of H_2. Ethanol was found to give the highest yield of monophenolic compounds (up to ≈20 wt%) owing to a better balance between solvolysis, hydrogenolysis, and hydrogenation of lignin. Nevertheless, a substantial loss of the carbohydrate fraction was observed. The use of a lower temperature (200 °C) in combination with H_3PO_4 resulted in an improved recovery of cellulose in the pulp and in the solubilization of hemicellulose and lignin, with the formation of monosaccharides (≈14 wt% of polysaccharides in the initial biomass) and phenolic monomers (up to 18 wt%, in the absence of H_2). Overall, a tradeoff exists between the removal of H_2 from the process and the production of low-molecular weight phenolics during RCF.

Introduction

Lignin is one of the main components of lignocellulosic biomass, accounting for about 10–30 wt% of lignocellulose.[1,2] It is commonly found in the plant cell wall, where it promotes the transport of nutrients and imparts stiffness and resistance to microbial attack.[3–5] As a biopolymer, it is constituted by alkyl aromatic units, linked together by C–C and ether bonds to form a highly crosslinked network.[6,7] In lignocellulose, lignin is bound to hemicellulose via ether and ester bonds.[8] In turn, hemicellulose is linked to cellulose via hydrogen bonding.[9,10]

Commonly, lignin is separated from (hemi)cellulose during biomass pretreatment, before further processing of the different lignocellulose fractions.[11,12] A primary limitation of many pretreatment strategies is that the valorization of the isolated "technical lignin" fraction is hampered by a high degree of condensation and/or by the presence of impurities.[13] Recently, a new class of so-called "lignin-first" strategies was developed, targeting the chemical passivation of reactive lignin fragments liberated during biomass pretreatment prior to their recondensation.[14–18] Among these methods, the reductive catalytic fractionation of lignocellulose (RCF) is particularly attractive, as it allows to fractionate biomass and to convert lignin into mono- and oligo-phenolics with a single operation.[19–21] Under RCF conditions, lignin fragments are released from the lignocellulose matrix by solvolysis, and further broken down via solvolytic and hydrogenolytic cleavage of labile ether linkages (predominantly β–O–4 bonds),[22] generating reactive (hydroxy)alkenyl-substituted lignin moieties.[23] The latter are ultimately stabilized by catalytic hydrogenation of the C=C bonds in their side chains.[23–25] Scheme S1 summarizes the key steps of RCF.

Previous works on the RCF of hardwood biomass reported that substantial delignification (up to ≈90 wt% of lignin in the initial biomass) and (hemi)cellulose preservation (>90 wt% of polysaccharides in the initial biomass) could be attained, along with a near-theoretical yield of monophenolic compounds (based on the content of β–O–4 linkages in the lignin matrix).[26–29] Importantly, the obtained low-molecular weight lignin fraction was shown to be a potential platform for a variety of industrial applications, including the production of phenols,[30] drop-in-fuels,[31] polymers,[32,33] and inks.[30]

Despite the exceptional advantages offered by RCF in terms of lignin valorization, the frequent adoption of high pressures of hydrogen gas represents a limitation to be addressed for reducing processing costs as well as safety, environmental, and equipment requirements.[34,35] From this point of view, previous works by Rinaldi and coworkers on the treatment of wood

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pellets in the presence of Raney Ni showed that isopropanol could perform as a hydrogen donor solvent, allowing to extract lignin from biomass and to depolymerize it in the absence of hydrogen gas.[31,36–39] Along the same lines, Samec and co-workers reported that, in the presence of Pd/C, soluble products from hemicellulose solvolysis could act as hydrogen donors during the hydrogen-free RCF of woody biomass.[40–42] More recently, Ren *et al.* proposed the RCF biorefining of poplar sawdust carried out under atmospheric pressure, without hydrogen gas.[43] Instead, ethane-1,2-diol) was employed as a hydrogen donor solvent in the process.[43]

While extensive research was carried out investigating the hydrogen-free RCF of woody biomass, the treatment of herbaceous feedstocks received less attention in this sense, due to their typically lower lignin content and to the broader variability of lignin units they comprise,[7] which pose a limitation to the yield and selectivity of lignin derivatives. Moreover, the higher content of minerals in herbaceous biomass may impair the catalytic activity.[44] Shen *et al.* explored the RCF of corn stover over cobalt-supported catalysts in the absence of external H_2.[45] A mixture of isopropanol, water, and formic acid was adopted as a hydrogen donor solvent in the work. The authors reported that, under optimized conditions, a moderately high yield of monophenolic compounds (≈25 wt% of initial lignin) could be obtained from lignin, while hemicellulose and cellulose were hydrolyzed and converted toward furfural and furfuryl alcohol.[45] The adoption of formic acid as a hydrogen donor to replace H_2 within the RCF was illustrated to be effective also for the treatment of hemp hurd, resulting in excellent yields of phenolic monomers (≈40 wt% of initial lignin).[46] Recently, we investigated the adoption of RCF for the valorization of wheat straw, which was found to lead to a moderately large yield of monophenolic compounds (≈25 wt% of initial lignin), for reactions performed in the presence of hydrogen gas.[47]

Clearly, the development of effective hydrogen-free RCF processes for the treatment of herbaceous feedstocks cannot prescind from a thorough understanding of the influence of hydrogen gas and alternative hydrogen donors on the formation of specific lignin and carbohydrate intermediates. In this contribution, the RCF of inexpensive and abundant wheat straw biomass is investigated, exploring the role of the hydrogen gas and of the exogenous gas pressure with respect to the properties of the obtained product streams (Figure 1). The use of different low-boiling alcohols as hydrogen-donor solvents for the catalytic hydrogenolysis and hydrogenation of wheat straw lignin in the absence of H_2 is examined. In addition, the introduction of an acid cocatalyst within the hydrogen-free RCF is studied for enhancing lignin extraction and the formation of phenolic monomers under mildened process conditions. Overall, this study provides insight into the development of a hydrogen-free RCF biorefinery to produce a low-molecular weight lignin oil and processable (hemi)cellulose derivatives from wheat straw biomass.

Results and Discussion

Role of hydrogen gas and gas pressure

To investigate the role of hydrogen gas and the gas pressure with respect to the product distribution from the reductive catalytic fractionation (RCF) of wheat straw, batch RCF experiments were carried out in duplicates treating 3 g of milled wheat straw (*Triticum aestivum*, particle size ≤2 mm,[48] biomass composition reported in Table S1) in 120 mL of methanol, in the presence of 0.3 g of 5 wt% Ru/C and of different amounts of hydrogen or nitrogen gas (10 or 30 bar, measured at room temperature). The experiments were performed at 250 °C, for a duration comprised between 0 and 6 h ("0 h" indicates that the

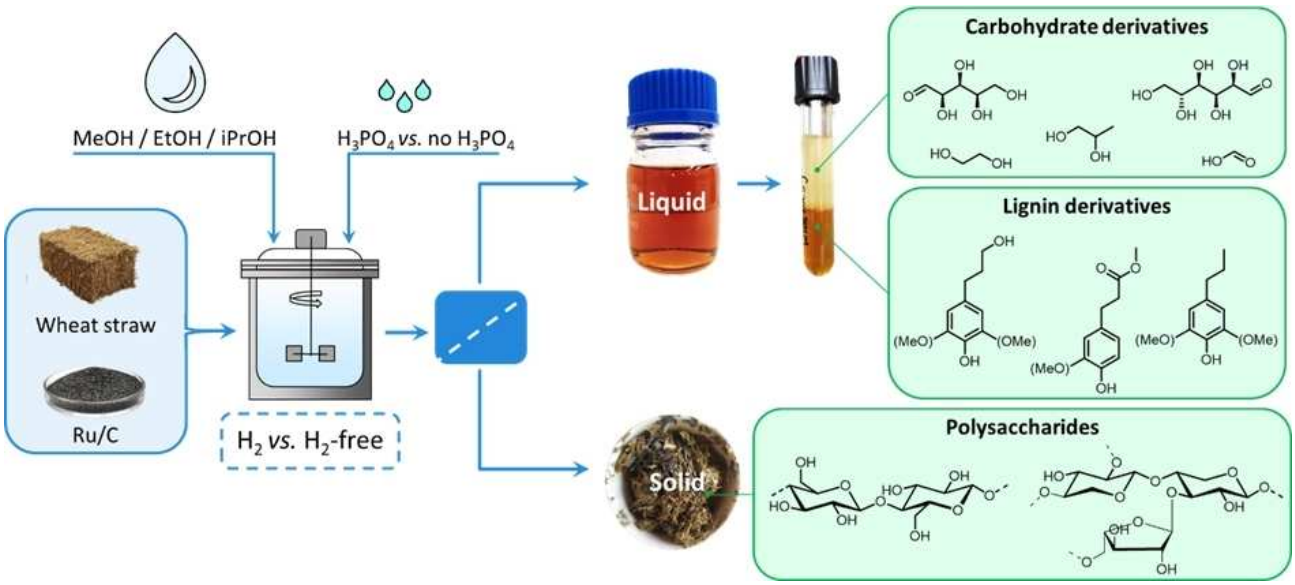


Figure 1. Process outline for the RCF of wheat straw (MeOH: methanol; EtOH: ethanol; iPrOH: isopropanol).

fractionation was halted as soon as the temperature setpoint was reached, typically in ≈40 min). After each experiment, the solid fraction, containing the preserved polysaccharides and the redox catalyst, and the liquid fraction, comprising solubilized lignin and carbohydrate derivatives, were collected, and extensively characterized.

The effects of the presence of hydrogen gas and the applied gas pressure on lignocellulose solvolysis were investigated by assessing the mass balance of organic matter (OM) with respect to the recovered pulp and liquid fractions (Figure S1). The absence of major differences observed for the various explored scenarios indicate that the solubilization of lignin and polysaccharides is independent of these parameters. Overall, the recovery of OM in the pulp decreased from about 70 wt% of OM in the initial biomass at 0 h, to about 30 wt% after 6 h. Concomitantly, the recovery of OM in the liquid increased from ≈15 wt% to ≈27 wt%. The discrepancy between the decrease of OM in the pulp and the increase of soluble OM in the liquid points to a loss of OM that grows with time. This suggests a boost in the formation of volatile products during the treatment (e.g., furans, short organic acids/aldehydes, water, etc.). Further compositional characterization of the isolated pulps showed that the recoveries of C5 and C6 polysaccharides diminished substantially during the fractionation for all scenarios (Table 1), indicating that neither the presence of hydrogen gas nor the exogenous gas pressure affect (hemi)cellulose solvolysis. On the other hand, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analyses highlighted an increasing presence of lignin at the pulp surface for decreasing H_2 pressure (see the discussion presented in the Supporting Information, SI, and Figure S2).

Further inspection of the pulps via X-rays diffraction (XRD) analysis showed that neither the use of H_2, nor the applied pressure affected the cellulose crystallinity index (CI), under the explored conditions (Figure S3). Similarly, subjecting the pulps to enzymatic hydrolysis (20 g L^{-1} of pulp in 0.1 M citrate buffer, pH 4.8, with 15 FPU of Novozymes Cellic Ctec2, at 50 °C, shaking at 150 rpm for 72 h) revealed only minor differences in the digestibility of glucan and xylan for experiments conducted in the presence of H_2 and N_2 (Figure S3). The apparently slight enhancement of the digestibility of polysaccharides observed for the use of H_2 could be related to the modestly lower presence of lignin at the surface of the pulps obtained in this case (as determined by ATR-FTIR analysis).

Evaporating the methanol solvent from the liquid fraction and subjecting the non-volatile residue to liquid-liquid extraction with dichloromethane and water, according to a procedure reported elsewhere,[23,26,49] gave a dichloromethane extract and a water extract. Subsequent evaporation under vacuum of the dichloromethane solvent from the former extract yielded a viscous brown oil, reported to comprise lignin derivatives.[23,26,49] The results in Table 1 show that the yield of oil increased with the reaction time from 30–40 wt% of acid insoluble lignin in the initial biomass at short reaction times (i.e., 0 h), up to about 80 wt% after 6 h, irrespective of the presence of H_2 and of the gas pressure applied, indicating that lignin solvolysis is independent of these factors.[23,50] In order to investigate the molecular weight distribution (MWD) of the produced lignin derivatives, lignin oils were subjected to gel permeation chromatography (GPC) analysis. Figure 2 shows that the presence of H_2 and the H_2 pressure had a positive impact on the formation of phenolic monomers (molecular weight, MW: 100–250 g mol^{-1}) and dimers (MW: ≈400 g mol^{-1}) that became more evident at prolonged reaction times. The less apparent tailing in the region with MW > 600 g mol^{-1}, observed for experiments carried out in the presence of H_2 (particularly evident after 6 h of reaction), highlights a reduced recondensation of lignin fragments, typical of the RCF biorefinery.

Further insight into the yield of monophenolic compounds produced under different conditions was obtained by gas chromatography (GC) coupled with mass spectrometry (MS) or flame ionization detector (FID). Figure 3 and Table 1 illustrate

Table 1. Biomass derivatives isolated in the solid and liquid fractions obtained for the RCF of wheat straw performed under different pressures of H_2 and N_2.

Entry	Experimental conditions[a]			Solid		Liquid		
	Gas	Pressure [bar]	Time [h]	Recovery[b] [wt%]		Yield[c] [wt%]		Yield[d] [wt%]]
				C5	C6	Oil	Phenolic monomers	C5, C6 derivatives
1[e]	H_2	30	0[f]	84 ± 6	85 ± 3	40 ± 6	14.6 ± 3.7	3.3 ± 0.3
2[e]	H_2	30	3	38 ± 3	66 ± 5	71 ± 4	25.2 ± 3.1	4.9 ± 0.2
3[e]	H_2	30	6	27 ± 2	43 ± 1	81 ± 1	27.5 ± 2.6	7.3 ± 0.6
4	H_2	10	0[f]	83 ± 5	83 ± 3	34 ± 3	11.9 ± 2.8	2.9 ± 0.3
5	H_2	10	3	41 ± 4	61 ± 2	73 ± 4	15.7 ± 2.6	3.7 ± 0.3
6	H_2	10	6	28 ± 3	43 ± 2	82 ± 5	20.7 ± 2.4	5.8 ± 0.6
7	N_2	10	0[f]	86 ± 7	82 ± 2	30 ± 3	9.6 ± 1.7	2.6 ± 0.2
8	N_2	10	3	36 ± 4	62 ± 3	76 ± 5	11.0 ± 1.0	3.4 ± 0.2
9	N_2	10	6	27 ± 3	45 ± 1	81 ± 4	12.8 ± 2.6	3.7 ± 0.3
10	N_2	30	0[f]	85 ± 7	86 ± 2	34 ± 5	8.6 ± 1.1	2.4 ± 0.5
11	N_2	30	3	35 ± 4	62 ± 4	68 ± 7	10.4 ± 2.5	3.0 ± 0.2
12	N_2	30	6	26 ± 2	44 ± 2	80 ± 2	12.4 ± 1.2	3.9 ± 0.3

[a] Fractionation experiments were performed in duplicates, treating 3 g of wheat straw biomass (particle size ≤ 2 mm) in 120 mL of MeOH, at 250 °C, under different pressures of H_2 or N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. [b] Recovery of C5 and C6 polysaccharides in the solid fraction, expressed with respect to the weight of C5 and C6 polysaccharides in the initial biomass. [c] Yield of lignin oil and phenolic monomers in the liquid fraction, expressed with respect to the weight of acid-insoluble lignin contained in the initial biomass. [d] Yield of non-condensed carbohydrate derivatives in the liquid fraction, expressed with respect to the total weight of polysaccharides contained in the initial biomass. [e] Experimental conditions explored in our previous work.[47] [f] Fractionation halted immediately after the setpoint temperature was reached.

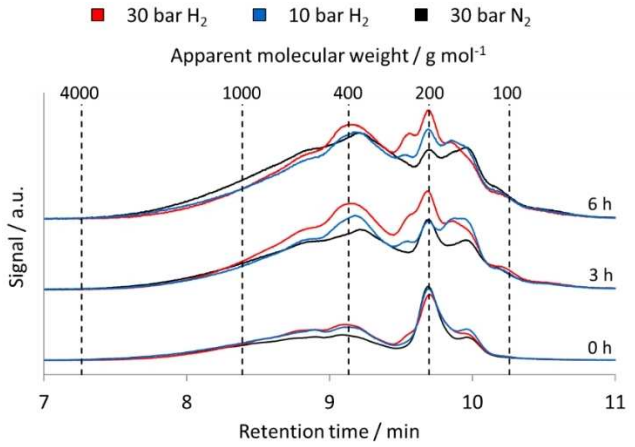


Figure 2. GPC chromatograms showing the MWD of the components of lignin oils obtained from the RCF of wheat straw carried out under different pressures of H_2 or N_2 (measured at room temperature). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, in the presence of 0.3 g of Ru/C, for various durations. The area below each chromatogram was normalized with respect to the yield of lignin oil obtained for the corresponding experiment.

that H_2 influences greatly the kinetics of monomers production. In the presence of 30 bar of H_2 the yield of monophenolic compounds reached a plateau value of ≈25 wt% of acid insoluble lignin in the initial biomass after 3 h of fractionation. On the contrary, the use of an initial H_2 pressure of 10 bar resulted in a slower formation of monomers that continued to increase up to 21 wt% after 6 h. In the absence of H_2, the production of monophenolic compounds was poorer and increased even more slowly with the reaction time (up to ≈12 wt% of acid insoluble lignin in the initial biomass after 6 h). Notably, the N_2 pressure was found not to affect the kinetics of monomers formation. Since no major influence of H_2 and the gas pressure on lignin solvolysis was determined, the differences in the kinetics of monomers production observed for the various scenarios may be attributed to the different effectiveness of catalytic hydrogenolysis and hydrogenation under the explored conditions. Arguably, the catalytic hydrogenolysis and hydrogenation of lignin fragments are more effective for treatments performed under high hydrogen pressure.[28,51] Ferrini and Rinaldi previously reported that a moderately high yield of monomers could be obtained upon solvolysis of labile ether bonds (β–O–4 linkages) in native lignin, which could be increased further by concomitant catalytic hydrogenolysis.[36] Along the same lines, Samec and coworkers recently proposed that only a portion of labile ether bonds (β–O–4 linkages) in lignin structures is cleaved by solvolysis (those located at the extremities of the polymer chain), whereas the breakdown of the remaining portion (non-terminal β–O–4 linkages) is achieved by catalytic hydrogenolysis.[42,52] Other authors suggested instead that β–O–4 linkages in lignin structures are principally broken by solvolysis and not by catalytic hydrogenolysis under RCF conditions.[23,24] Assuming this latter hypothesis holds true and considering the results reported above (Table 1, Figure 3), it follows that the totality of producible monophenolic compounds (i.e., the maximum amount of phenolic monomers that can be formed from the cleavage of inter-unit lignin linkages, which do not undergo subsequent recondensation) would be liberated in solution during the first 3 h of fractionation, as observed in the experiments performed under 30 bar of H_2. At longer reaction times, the yield of monomers would either

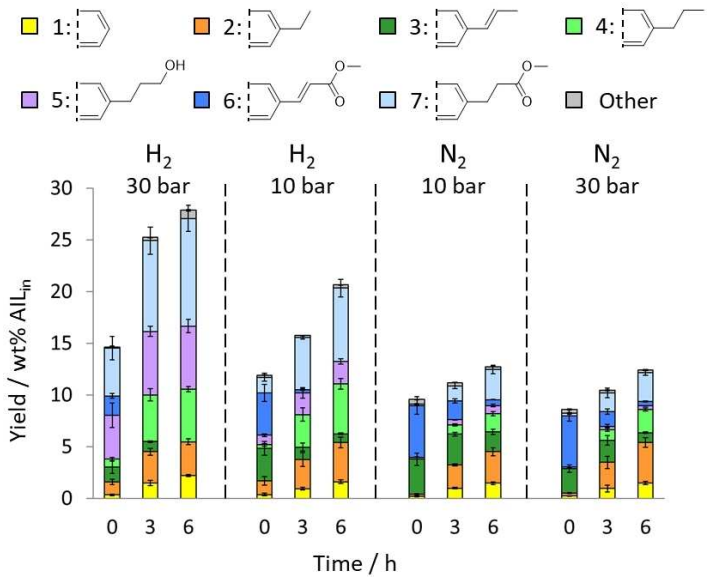


Figure 3. Yield of phenolic monomers as determined by GC analysis of the lignin oils obtained from the RCF of wheat straw carried out under different pressures of H_2 or N_2 (measured at room temperature). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, in the presence of 0.3 g of Ru/C, for various durations. The monomer yield was calculated with respect to the acid insoluble lignin (AIL) content in the initial biomass.

remain constant or decrease, depending on the effectiveness of monomers stabilization against recondensation (via catalytic hydrogenation). The non-negligible increment of the monomer yield observed between 3 and 6 h for a fractionation performed under 10 bar of H_2 disproves the initial hypothesis, suggesting instead that H_2 does as well contribute to the cleavage of lignin inter-unit bonds in the solubilized lignin fragments via catalytic hydrogenolysis.

To better elucidate the role of catalytic hydrogenolysis with respect to the cleavage of lignin inter-unit bonds, 2-phenoxy-1-phenylethanol was selected as a model compound for β–O–4 linkages in lignin,[53,54] and was subjected to RCF conditions, comparing the outcomes achieved for reactions carried out in the presence of Ru/C (for which the model compound can be cleaved both via solvolysis and catalytic hydrogenolysis) and in the absence of a redox catalyst (for which the cleavage of the model compound would predominantly occur via solvolysis). For both conditions an initial hydrogen pressure of only 1 bar was applied to prevent the complete hydrogenation of aromatic rings in the reaction products. The GPC chromatograms in Figure 4a show that, when the catalyst was employed, the peak associated with 2-phenoxy-1-phenylethanol (MW: ≈200 g mol^{-1}) decreased over the course of the reaction and another peak corresponding to monomeric compounds appeared (MW: ≈100 g mol^{-1}). In contrast, for a reaction performed without the catalyst, the dimer peak remained almost unchanged, and no formation of low- or high-MW products was detected. More specifically, GC analysis revealed that a yield of monomers (including phenol, ethylbenzene, and styrene) of nearly 30% (based on carbon content) was obtained in the presence of the redox catalyst, whereas the monomer yield was limited to 2% in its absence (Figure 4b). Such observations demonstrate that solvolysis alone is not sufficient to effectively break down the β–O–4 bond under the applied conditions, thus confirming the essential role of catalytic hydrogenolysis for the cleavage of lignin fragments during RCF. Hydrogenation of the so-formed lignin units is also crucial to promote their preservation against recondensation reactions. Noteworthy, even though the dimer could be seen as representative of terminal β–O–4 bonds, which were reported to be cleaved by solvolysis,[42,52] the applied reaction conditions (absence of water/acid cocatalyst) may be too mild to achieve the bond scission, which would require catalytic hydrogenolysis to occur.

The data reported in Figure 3 reveal also that the presence and the pressure of H_2 considerably affected the fate of the released monomer species (**1**–**7** in Figure 3). Under hydrogen gas, the formation of monomers possessing side chains with C=C bonds, such as 4-propenyl-substituted species (**3**) and 4-methyl coumarate/ferulate (**6**) was detected at short reaction times, but the formation of their reduced counterparts (**4** and **7**, respectively) prevailed after 3 h. In particular, the selectivity toward **3** and **6** was higher at low H_2 pressure, and even larger when N_2 was employed, highlighting a slower catalytic hydrogenation under these conditions.[23,51] In spite of this, the formation of **4** and **7** was detected also under nitrogen gas at prolonged reaction times, suggesting that the solvent or a part of the lignocellulose itself can act as hydrogen donors during RCF, as previously proposed by other authors.[36,41,50] The yield of

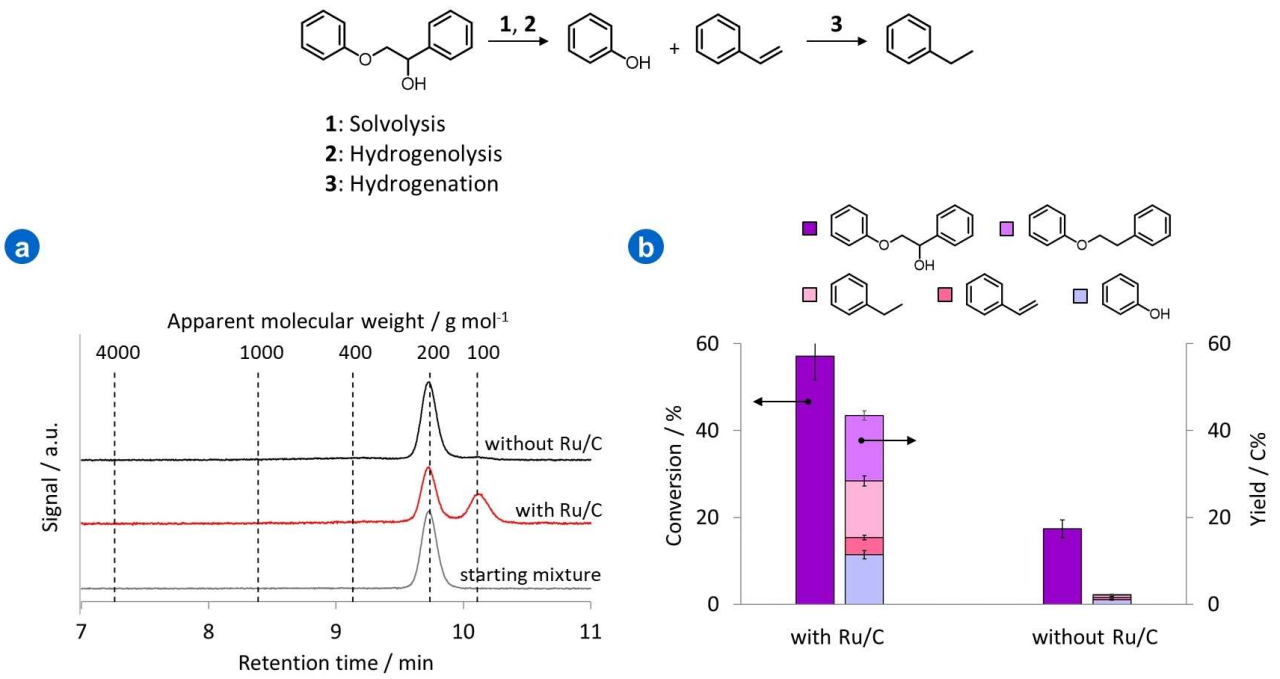


Figure 4. Effect of catalytic hydrogenolysis on the conversion of 2-phenoxy-1-phenylethanol into phenol and styrene/ethylbenzene. (a) MWD of the products as determined by GPC and (b) conversion and yield of monomers as determined by GC–MS/FID. The reactions were performed in duplicates, treating 0.01 g of 2-phenoxy-1-phenylethanol in 120 mL of methanol, in the presence of 0.015 g of Ru/C or in the absence of a redox catalyst, at 250 °C, under 1 bar of H_2 (measured at room temperature), for a duration of 3 h. The arrows in the figure indicate the reference axis.

dealkylated monomers (**1**) was found not to be influenced by the presence and the pressure of H_2, hinting at the independence of dealkylation reactions from hydrogen gas. A similar behavior was determined for the yield of 4-ethyl-substituted monomers (**2**). Conversely, the formation of **5** was scarce in the absence of H_2 and became more important under high pressures of H_2. A similar trend was reported in previous works on the RCF of woody biomass.[23,28] No evident difference in the yields of the various species of monophenolic compounds were observed for experiments performed under different N_2 pressures, indicating that the depolymerization and stabilization of lignin fragments is not affected by inert gas pressure.

The water extract obtained from the liquid-liquid extraction of the non-volatile residue of the liquid fraction was subjected to acid hydrolysis, then it was analyzed via high-performance liquid chromatography (HPLC) to assess the content of non-condensed carbohydrate derivatives produced upon (hemi)cellulose decomposition (e.g., mono- and oligosaccharides, polyols, organic acids, etc.). The yield of non-condensed carbohydrate derivatives was larger in the presence of hydrogen gas and increased at higher H_2 pressure (Figure S4), in view of a more considerable production of ethane-1,2-diol) and propane-1,2-diol. These short diols were reported to be formed during RCF via hydrogenation of retro-aldol condensation intermediates generated from the hydrolysis of (hemi)cellulose.[55–57] On the other hand, the yields of monosaccharides and formic acid did not vary markedly for the different scenarios, suggesting that their formation is independent of hydrogen gas and of the operating pressure.

Using the solvent as a hydrogen donor

With the goal of exploring further the role of the solvent as a hydrogen donor for the replacement of H_2 within the RCF of wheat straw, RCF experiments were performed in methanol, ethanol, and isopropanol, under inert atmosphere (30 bar of N_2, measured at room temperature), and the outcomes were compared.

The analysis of OM in the isolated solid and liquid fractions revealed only few differences deriving from the use of the three solvents (Figure S5). At short reaction times, the use of isopropanol resulted in a slightly higher recovery of OM in the pulp compared to methanol and ethanol and, correspondingly, in a lower recovery of OM in the liquid, pointing to a slower solvolysis in this less polar solvent.[29] After a reaction time of 6 h, the adoption of ethanol as a solvent resulted in a larger recovery of OM in the liquid fraction. Since the OM in the pulp was not lower than that measured for the use of methanol or isopropanol, such observation appears not to be determined by an enhanced solvolysis of lignocellulose in ethanol. On the other hand, the alkylation and esterification of the solubilized lignin and carbohydrate derivatives may be the cause of this behavior.[58,59] Overall, the OM balance decreased from about 85 wt% of OM in the initial biomass at 0 h to 55–60 wt% after 6 h for all scenarios, indicating that a substantial conversion of biomass toward volatiles occurs independently of the solvent that is selected, under the explored reaction conditions.

The compositional analysis of the isolated pulps showed that the (hemi)cellulose decomposition during the treatment is not affected by the type of alcoholic solvent, as the recoveries of polysaccharides followed a similar trend for all scenarios, diminishing from 80–85 wt% at 0 h to 30–35 wt% at 6 h for C5 polysaccharides, and from 80–85 wt% at 0 h to ≈45 wt% at 6 h for C6 polysaccharides (Table 2). Conversely, ATR-FTIR analysis of the pulps suggest that a larger content of lignin is present at the surface of the pulps obtained from RCF performed with less polar alcoholic solvents (see the discussion presented in the SI and Figure S6). Despite this, the Cis of the pulps and the enzymatic digestibility of the preserved glucan and xylan did not vary substantially with the use of different alcoholic solvents (Figure S7).

The yield of lignin oil in the presence of the different solvents was found to follow a similar trend as the yield of liquid OM, with a slower formation of oil observed for the use of isopropanol, which confirms its poorer ability to solvolitically extract lignin (Table 2). The largest yield of oil was observed for the use of ethanol at longer reaction times. Notably, the yield of

Table 2. Biomass derivatives isolated in the solid and liquid fractions obtained for the RCF of wheat straw performed with different alcoholic solvents.

Entry	Experimental conditions[a]		Solid		Liquid		
	Solvent	Time [h]	Recovery[b] [wt%]		Yield[c] [wt%]		Yield[d] [wt%]
			C5	C6	Oil	Phenolic monomers	C5, C6 derivatives
1	MeOH	0[e]	85 ± 7	85 ± 2	34 ± 5	8.6 ± 1.1	2.4 ± 0.5
2	MeOH	3	35 ± 4	62 ± 4	68 ± 7	10.4 ± 2.5	3.0 ± 0.2
3	MeOH	6	26 ± 2	44 ± 2	80 ± 2	12.4 ± 1.2	3.9 ± 0.3
4	EtOH	0[e]	78 ± 6	88 ± 2	35 ± 3	10.8 ± 0.8	2.3 ± 0.1
5	EtOH	3	43 ± 5	60 ± 3	86 ± 7	17.8 ± 2.3	3.0 ± 0.2
6	EtOH	6	35 ± 4	46 ± 1	124 ± 4	19.9 ± 1.5	4.0 ± 0.3
7	iPrOH	0[e]	79 ± 6	86 ± 2	18 ± 4	3.0 ± 0.3	1.9 ± 0.1
8	iPrOH	3	38 ± 4	62 ± 3	56 ± 2	11.6 ± 2.2	3.8 ± 0.3
9	iPrOH	6	36 ± 4	44 ± 1	77 ± 4	14.4 ± 1.5	3.7 ± 0.3

[a] Fractionation experiments were performed in duplicates, treating 3 g of wheat straw biomass (particle size ≤ 2 mm) in 120 mL of methanol, ethanol, or isopropanol, at 250 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. [b] Recovery of C5 and C6 polysaccharides in the solid fraction, expressed with respect to the weight of C5 and C6 polysaccharides in the initial biomass. [c] Yield of lignin oil and phenolic monomers in the liquid fraction, expressed with respect to the weight of acid-insoluble lignin contained in the initial biomass. [d] Yield of non-condensed carbohydrate derivatives in the liquid fraction, expressed with respect to the total weight of polysaccharides contained in the initial biomass. [e] Fractionation halted immediately after the setpoint temperature was reached.

124 wt% of acid insoluble lignin in the initial biomass, determined after 6 h for a reaction performed in the presence of ethanol, indicates the inclusion of non-lignin components in the oil. The incorporation of biomass extractives or humins originating from the condensation of dehydration products formed during (hemi)cellulose decomposition may be partially responsible for this behavior.[60,61] Another explanation could be found in the alkylation and esterification of lignin derivatives by the solvent.[58,59]

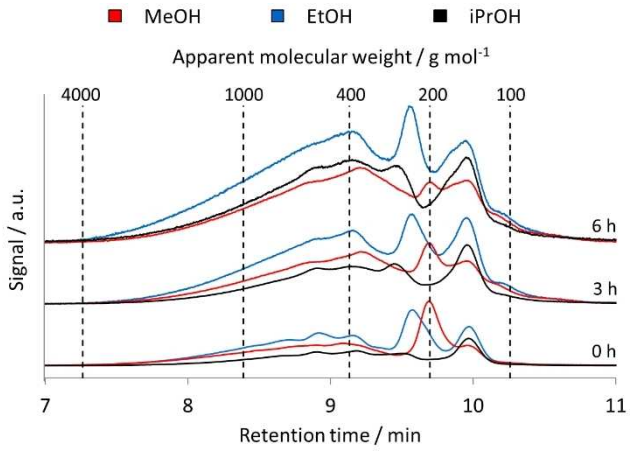


Figure 5. GPC chromatograms showing the MWD of the components of lignin oils obtained from the RCF of wheat straw carried out using different alcoholic solvents. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, ethanol, or isopropanol, at 250 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. The area below each chromatogram was normalized with respect to the yield of lignin oil obtained for the corresponding experiment.

Remarkable differences related to the use of the various alcoholic solvents were observed also in the MWD of the components of the isolated lignin oils (Figure 5). At a short reaction time of 0 h, the use of isopropanol resulted in a low formation of lignin monomers, dimers, and oligomers, consistently with the slower lignin extraction and cleavage with this solvent. On the other hand, the use of methanol and ethanol resulted in a moderate production of lignin monomers. At longer times, while the formation of monophenolic compounds appeared to be hindered in the presence of methanol, a more abundant production of both low- and high-MW lignin derivatives occurred for the use of isopropanol and, more prominently, of ethanol.

The results obtained from GC analysis of lignin oils corroborated the observations made based on GPC (Table 2, Figure 6). At 0 h, the use of isopropanol led to the lowest yield of monomers: 3 wt% of acid insoluble lignin in the initial biomass, which increased to ≈12 wt% after 3 h. In contrast, the use of methanol resulted in a much-reduced increase of the monomer yield over time, which went from ≈9 wt% at 0 h to ≈10 wt% at 3 h. While methanol is more effective for lignin solvolysis,[29] isopropanol is a better hydrogen donor.[39,52] We reason that the marginal increment of the monomer yield observed in methanol compared to isopropanol may be due to the combination of a faster lignin solvolysis and a slower catalytic hydrogenolysis and hydrogenation of lignin moieties in methanol, which could ultimately make the rapidly released fragments more subject to recondensation reactions (Scheme S1). An intermediate outcome was observed for the RCF in ethanol, which resulted in a monomer yield of ≈11 wt% at 0 h and of ≈18 wt% at 3 h, suggesting that the timescales of solvolysis, hydrogenolysis and hydrogenation of lignin are

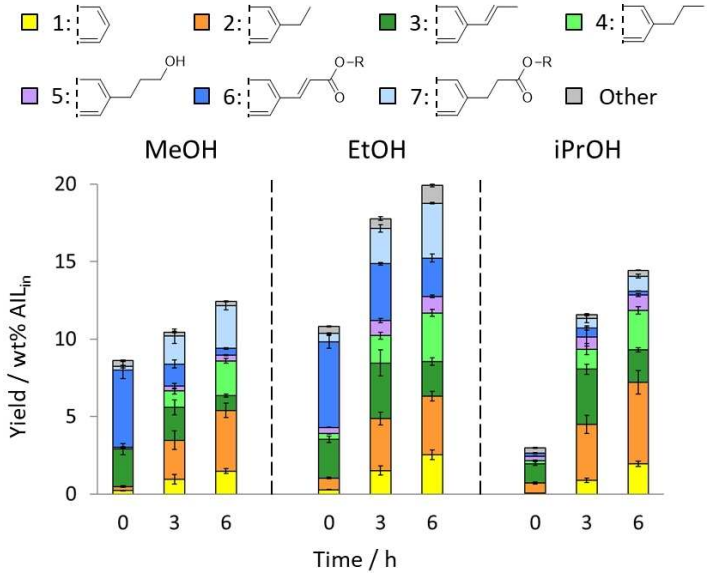


Figure 6. Yield of phenolic monomers as determined by GC analysis of the lignin oils obtained from the RCF of wheat straw carried out using different alcoholic solvents. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, ethanol, or isopropanol, at 250 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. The monomer yield was calculated with respect to the acid insoluble lignin (AIL) content in the initial biomass. Structures **6** and **7** in the legend indicate 4-alkyl coumarate/ferulate and 4-alkyl dihydrocoumarate/ferulate species, wherein the alkyl substituent can be a methyl, ethyl, or isopropyl group.

better with this solvent, under the applied conditions. Remarkably, the use of ethanol allowed to achieve a yield of monophenolic compounds equal to ≈70% of that obtained in the presence of an initial H_2 pressure of 30 bar (Table 1, entry 3).

A qualitative way to gain insight in the lignin depolymerization versus extraction performance in the different solvents may be to consider the ratio between the yield of phenolic monomers (as an indicator of the depolymerization performance) and the yield of lignin oil (as an indicator of the extraction performance). After 6 h of reaction, such ratio would be of 15 wt%, 16 wt%, and 19 wt% for the use of methanol, ethanol, and isopropanol, respectively. This observation suggests that isopropanol provides a better depolymerization performance compared to methanol and ethanol. However, in absolute terms, ethanol appears to be superior thanks to its better ability to extract lignin from the lignocellulose matrix.

The type of alcoholic solvent employed in the process was also found to influence the formation of different monomer species (Figure 6). 4-Methyl-, 4-ethyl- and 4-isopropyl- coumarate/ferulate were produced in the presence of methanol, ethanol, and isopropanol, respectively, confirming the occurrence of lignin esterification by the solvents. The yields of **6** and **7** were lowest for the use of isopropanol. Overall, the yield of monomer species with saturated alkyl chains increased over time at the expense of species possessing unsaturated alkyl chains. A larger yield of unsaturated monomers, such as **3** and **6**, was observed at reaction times equal or greater than 3 h for the use of ethanol and isopropanol as compared to methanol. This may be explained by a slower solvolytic release of lignin fragments in ethanol and isopropanol.[29] Notably, **5**, which is preferentially formed in the presence of H_2 (see above), was observed only for the use of ethanol and isopropanol, highlighting their better hydrogenation performance compared to methanol.[39,52] Conversely, the yield of **1** and **2** did not vary substantially in the presence of different alcoholic solvents.

Table 2 and Figure S8 show that, for the hydrogen-free RCF of wheat straw, the yield of non-condensed carbohydrate derivatives was lower than 4 wt% of polysaccharides in the initial biomass, irrespective of the type of alcoholic solvent used. Nevertheless, the formation of xylose and glucose was highest when methanol was employed and diminished for the adoption of ethanol and even further for the use of isopropanol (Figure S8), possibly due to a poorer solvolytic release of monosaccharides in the presence of less polar alcoholic solvents. In contrast, the yields of ethane-1,2-diol and propane-1,2-diol followed an opposite trend, highlighting the superior performance of isopropanol as a hydrogen donor.[39,52] Another explanation for such behavior may be that methanol is able to perform a better stabilization of sugars in the form of alkyl glycosides compared to ethanol and isopropanol, thus sugar residues would be less available for (de)hydration and retro-aldol condensation reactions in the former solvent.[55,62]

Hydrogen-free RCF at mild temperature with an acid cocatalyst

To overcome the limitations imposed by the extensive decomposition of polysaccharides observed for the RCF of wheat straw in low-boiling alcohols at 250 °C, an alternative hydrogen-free process configuration at milder temperature was investigated. In this framework, an acid cocatalyst was used to promote the cleavage of ester and ether bonds linking lignin to hemicellulose and lignin units with each other (e.g. β-O-4 bonds).[43,49] RCF experiments were performed treating 3 g of milled biomass in 120 mL of methanol, at 200 °C, in the presence of 0.3 g of Ru/C and aqueous H_3PO_4 (800 μL of 85% H_3PO_4, to reach a final concentration in the reaction mixture of 0.1 M), under 30 bar of N_2, for a duration comprised between 0 and 6 h. Analogous blank experiments carried out without adding aqueous H_3PO_4 to the reaction mixture were conducted for comparison. The selection of H_3PO_4 as the acid cocatalyst was based on previous works that demonstrated its successful implementation within RCF systems.[42,49,62]

The mass balance for OM illustrated in Figure S9 shows that the introduction of the acid cocatalyst within RCF resulted in a much larger recovery of OM in the liquid fraction compared to blank experiments and, correspondingly, in a lower recovery of OM in the pulp. A plateau value of ≈46 wt% of OM in the initial biomass was attained for the recovery of OM in the liquid fraction for the use of H_3PO_4 after 3 h of fractionation, whereas a plateau at ≈15 wt% was obtained after the same time in the absence of the acid, demonstrating the substantial enhancement of lignocellulose solvolysis resulting from the use of the acid cocatalyst. Interestingly, in contrast to the observations made above for the RCF conducted at 250 °C, the mass balance for OM did not reveal any substantial loss with the reaction time: the losses remained around 10–15 wt% both in the presence and in the absence of the acid cocatalyst, pointing to a minor conversion of biomass toward volatile components at milder temperature (200 °C).

The influence of H_3PO_4 on the pulp morphology was inspected by field emission gun scanning electron microscopy (FEG-SEM), which showed that the RCF treatment carried out in the presence of the acid cocatalyst resulted in the exposure of disordered slender fibers (Figure 7a). A fibrous structure was evident as well for a blank treatment, but in this case the fibers were packed together and arranged in bundles (Figure 7b), highlighting the effect of the acid with respect to enhancing the disassembly of the lignocellulose structure.

Remarkable differences between the acid-catalyzed treatment and a blank treatment were observed also in terms of the recovery of polysaccharides (Table 3). Consistently with previous works,[43,49,62] the use of the acid cocatalyst led to a considerable removal of hemicellulose from the pulp, with a recovery of C5 polysaccharides that decreased from 68 wt% at 0 h to 10 wt% at 6 h. A much more contained decline from 84 wt% to 70 wt% was observed for blank experiments in the same time range. In contrast, cellulose was well-preserved for both scenarios, with a recovery of about 80 wt% after 6 h of fractionation. Thus, the use of H_3PO_4 resulted in a substantially larger cellulose purity in

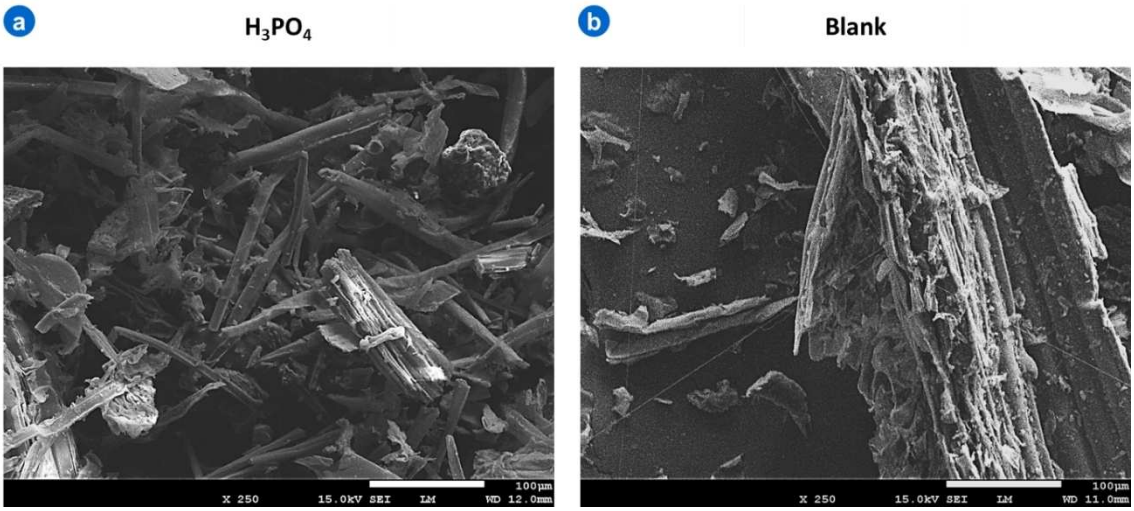


Figure 7. SEM images obtained for the solid fraction isolated after treating 3 g of wheat straw in 120 mL of methanol, at 200 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C. (a) Treatment performed in the presence of aqueous H_3PO_4 (800 µL of 85% H_3PO_4, to reach a final concentration in the reaction mixture of 0.1 M). (b) Treatment performed in the absence of aqueous H_3PO_4, for 3 h. The images were collected using a Jeol FEG-SEM 7600F, operating at 15 keV. The scale bar is 100 µm.

Table 3. Biomass derivatives isolated in the solid and liquid fractions obtained for the H_2-free RCF of wheat straw performed in the presence or in the absence of aqueous H_3PO_4.

Entry	Experimental conditions[a]		Solid Recovery[b] [wt%]		Liquid Yield[c] [wt%]		Yield[d] [wt%]
	Cocatalyst	Time [h]	C5	C6	Oil	Phenolic monomers	C5, C6 derivatives
1	H_3PO_4	0[e]	68±5	88±3	13±1	1.4±0.2	8.2±0.7
2	H_3PO_4	3	16±4	84±2	67±5	15.9±1.5	16.4±2.4
3	H_3PO_4	6	10±2	76±3	83±8	18.2±1.6	15.2±1.1
4	–	0[e]	84±6	92±2	9±1	1.3±0.1	2.1±0.2
5	–	3	79±6	84±3	36±5	10.2±1.0	2.7±0.2
6	–	6	70±5	81±2	41±4	10.7±1.0	2.9±0.2

[a] Fractionation experiments were performed in duplicates, treating 3 g of wheat straw biomass (particle size ≤2 mm) in 120 mL of methanol, at 200 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C and of aqueous H_3PO_4 (800 µL of 85% H_3PO_4, to reach a final concentration in the reaction mixture of 0.1 M), or in the absence of aqueous H_3PO_4, for various durations. [b] Recovery of C5 and C6 polysaccharides in the solid fraction, expressed with respect to the weight of C5 and C6 polysaccharides in the initial biomass. [c] Yield of lignin oil and phenolic monomers in the liquid fraction, expressed with respect to the weight of acid-insoluble lignin contained in the initial biomass. [d] Yield of non-condensed carbohydrate derivatives in the liquid fraction, expressed with respect to the total weight of polysaccharides contained in the initial biomass. [e] Fractionation halted immediately after the setpoint temperature was reached.

the pulp, which reached a maximum of 63 wt% (relative to the OM content of the pulp) after 3 h of fractionation, whereas cellulose purity did not exceed 41 wt% in the absence of the cocatalyst. Notably, the acid hydrolysis of hemicellulose was reported to yield intermediates (e. g. reducing sugars, formic acid) that may serve as hydrogen donors in the concomitant catalytic hydrogenolysis and hydrogenation of lignin.[41,42,63] The ATR-FTIR spectra of the pulps exhibited extensive lignin and hemicellulose removal both in the presence and in the absence of H_3PO_4 (see the discussion presented in the SI and Figure S10). No major differences were observed for the acid-catalyzed and the blank treatments with respect to the CI, which remained around 50% in both cases for durations between 0 and 6 h (Figure S11). On the other hand, a larger enzymatic conversion of glucan and xylan in the pulp was determined at short reaction times in the presence of the acid cocatalyst (Figure S11), possibly due to a faster disassembly of the lignocellulose structure that could make cellulose more accessible to enzymatic attack.[64] At longer times, the enzymatic digestibility of the preserved polysaccharides was slightly larger for a blank treatment, reaching 89% and 92% after 6 h of treatment for glucan and xylan, respectively, compared to a saccharification yield of 80% and 71% achieved in the presence of H_3PO_4. Such difference may be attributed to the higher lignin content at the pulp surface observed via FTIR analysis for acid-catalyzed reactions (see the discussion presented in the SI and Figure S10).[65] Another explanation for this behaviour may be the enhanced formation of enzyme inhibitors (e.g., humins) in the presence of the acid cocatalyst.[64,66]

The formation of lignin oil was also remarkably affected using an acid cocatalyst (Table 3). Blank reactions resulted in yields of oil that increased from 9 wt% of acid insoluble lignin in the initial biomass at 0 h, up to a plateau value of ≈40 wt% after 3 h of fractionation. Larger yields of oil were obtained in

the presence of H_3PO_4, increasing from 13 wt% at 0 h to 83 wt% after 6 h. Such difference points to an enhanced extraction of lignin from biomass by virtue of the action of the acid cocatalyst. Noteworthy, as reported in previous works,[43,49] condensed carbohydrate derivatives arising from the acid-catalyzed repolymerization of intermediates produced upon (hemi)cellulose decomposition (i.e., humins) may be incorporated in lignin oil more substantially in the presence of an acid cocatalyst, thus contributing to its higher yield (see below). The GPC analysis of lignin oils revealed that, for a short reaction time of 0 h, similar MWD profiles were obtained for the use of H_3PO_4 and for a blank treatment. Conversely, at times greater or equal than 3 h the use of the acid cocatalyst resulted in a larger formation of monomers, dimers, and oligomers, compared to the blank reactions (Figure 8). This behavior may be explained by the dual effect of the acid cocatalyst: on the one hand, it promotes the cleavage of ether bonds in lignin structures, thereby liberating higher amounts of short lignin fragments in solution (e.g. monomers and dimers).[49,62] On the other hand, it favors the occurrence of acid-catalyzed recondensation reactions between the formed lignin moieties, yielding more phenolic oligomers.[13] In addition to the peaks attributed to phenolic monomers (MW: 100–250 g mol^{-1}), a peak at MW < 100 g mol^{-1} was observed for the use of H_3PO_4 at 3 h of reaction, which increased after 6 h, possibly associated with the formation of furanic compounds produced upon (hemi)cellulose decomposition.[49]

To shed light on the influence of the acid cocatalyst with respect to the cleavage of lignin inter-unit linkages and on the incorporation of carbohydrate dehydration products in lignin oil, samples of oil obtained from reactions carried out in the presence and in the absence of H_3PO_4 were subjected to ^{1}H-^{13}C

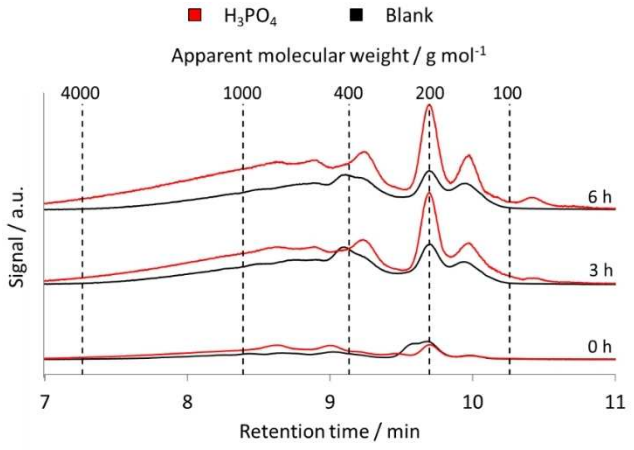


Figure 8. GPC chromatograms showing the MWD of the components of lignin oils obtained from the RCF of wheat straw carried out in the presence of aqueous H_3PO_4 (800 μL of 85% H_3PO_4, to reach a final concentration in the reaction mixture of 0.1 M), or in the absence of aqueous H_3PO_4 (Blank). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. The area below each chromatogram was normalized with respect to the yield of lignin oil obtained for the corresponding experiment.

heteronuclear single quantum coherence (HSQC) NMR analysis. The spectra in panels a and b of Figure S12 show that, for a treatment performed in the presence of the acid cocatalyst, a complete disappearance of the cross signals corresponding to β–O–4 linkages was observed, as opposed to the blank treatment, for which the cross signals were still apparent. Such evidence suggests that H_3PO_4 plays a prominent role with respect to the cleavage of β–O–4 bonds in lignin structures, promoting the release of lignin units during the hydrogen-free RCF of wheat straw at mild temperature. The acid may enhance the breakage of β–O–4 bonds both directly, via acidolysis, and indirectly, via the hydrolysis of hemicellulose and the consequent formation of intermediates that can promote further acidolysis (e.g. organic acids) or that can serve as hydrogen donors for catalytic hydrogenolysis of ether bonds in lignin (e.g. reducing sugars and organic acids).[41,42,63,67] The spectra reported in panels c and d of Figure S12 illustrate that the lignin oil isolated after a reaction performed with the acid cocatalyst comprises furanic structures that are not observed in the absence of H_3PO_4, supporting the idea that the acidic environment promotes dehydration (and condensation) of the intermediates released upon decomposition of (hemi)cellulose from wheat straw and their subsequent incorporation in lignin oil.

Further GC analysis of the lignin oils corroborated the observations made based on GPC. Table 3 shows that the formation of monophenolic compounds was favored by the presence of H_3PO_4, reaching a yield of 18 wt% of acid insoluble lignin in the initial biomass after 6 h of reaction (corresponding to ≈65% of the monomer yield achieved at 250 °C, under H_2, and in the absence of H_3PO_4 - Table 1, entry 3), whereas a plateau value of ≈10 wt% was attained after 3 h for the blank treatment. Interestingly, the presence of the acid cocatalyst was not found to influence the selectivity for different monomer species (Figure 9), which was of about 20 wt% for **3** and 70 wt% for **6** at 0 h, and ≈50 wt% for **3** and 40–45 wt% for **6** at reaction times greater or equal than 3 h. The other monomer species were produced only in marginal amounts, suggesting that the hydrogen-free RCF performed at mild temperature in the presence of an acid cocatalyst may be an attractive method for the selective conversion of wheat straw lignin toward 4-propenyl- and 4-alkylpropenoate-substituted monomers. We surmise that the preferential formation of species possessing unsaturated alkyl chains may be due to the combined effects of a poorer catalytic hydrogenation in the absence of H_2,[23] and of a lower tendency of lignin fragments to undergo recondensation at mild temperature, despite the presence of the acid cocatalyst.[25] Notably, the production of monophenolic compounds possessing side chains with alkene functionalities may be advantageous as these compounds can directly serve as starting materials for various applications, including the manufacture of fine chemicals (e.g. via cross metathesis)[40,68,69] and polymers.[32,70] Finally, consistently with GPC and NMR analyses, GC chromatograms exhibited a more apparent presence of carbohydrate dehydration products for the lignin oil isolated from a reaction performed with H_3PO_4 compared to a blank experiment (Figure S13).

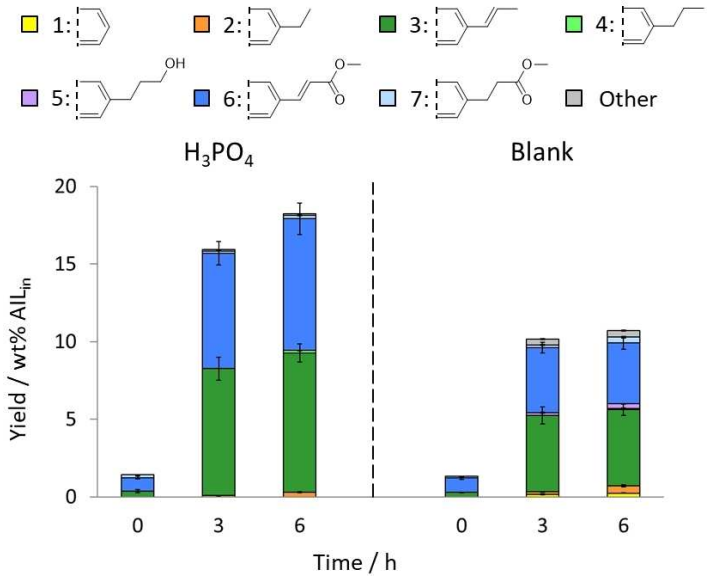


Figure 9. Yield of phenolic monomers as determined by GC analysis of the lignin oils obtained from the RCF of wheat straw carried out in the presence of aqueous H_3PO_4 (800 μL of 85 % H_3PO_4, to reach a final concentration in the reaction mixture of 0.1 M), or in the absence of aqueous H_3PO_4 (Blank). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 200 °C, under 30 bar of N_2 (measured at room temperature), in the presence of 0.3 g of Ru/C, for various durations. The monomer yield was calculated with respect to the acid insoluble lignin (AIL) content in the initial biomass.

The yield of non-condensed carbohydrate derivatives isolated in the water phase obtained from liquid-liquid extraction of the non-volatile residue of the liquid fraction was also greatly influenced by the employment of H_3PO_4 within the RCF process (Table 3). Figure S14 shows that moderately high yields of xylose and glucose (up to a maximum of about 14 wt% of polysaccharides in the initial biomass) were achieved in the presence of the acid cocatalyst. Conversely, negligible amounts of monosaccharides were measured for blank reactions, in line with the less extensive decomposition of hemicellulose observed in this scenario.

To inspect a possible enhancement of the yields of lignin monomers or non-condensed carbohydrate products that could arise from the use of a better hydrogen-donor solvent within the acid-catalyzed process at mild temperature, an additional experiment was conducted subjecting wheat straw to RCF conditions in the presence of ethanol instead of methanol, for a duration of 3 h. In parallel, control reactions were carried out for comparison pressurizing the reactor with 30 bar of H_2, both for the use of methanol and for ethanol. The outcomes of these process configurations are summarized in Tables S2–S4. A remarkable difference observed when ethanol was adopted is the greater yield of lignin oil that was attained, hinting to the possible occurrence of lignin alkylation and esterification by the solvent.[58,59] Under inert atmosphere, the use of ethanol was not found to result in a much larger monomer yield compared to methanol (17 wt% for ethanol vs. 16 wt% for methanol). Nonetheless, the partial formation of 4-propyl-substituted monophenolic compounds measured in ethanol points to an improved hydrogenation of lignin in this solvent (Figure S15). Performing the acid-catalyzed RCF under hydrogen gas resulted in monomer yields that reached ≈22 wt% both for the use of methanol and for ethanol (corresponding to 80% of the monomer yield obtained at 250 °C, in the absence of H_3PO_4 - Table 1, entry 3), with an extensive hydrogenation of the alkyl side chains, and the formation of 4-propanol-substituted monophenolic compounds, which were not observed under N_2 (Figure S17). The yield of non-condensed carbohydrate derivatives did not change markedly in the presence of ethanol or for the use of H_2, and monosaccharides were the main products for all the explored scenarios (Figure S16).

A significant finding is that the drop of the monomer yield associated with the replacement of H_2 with N_2 was considerably more contained for the acid-catalyzed process at mild temperature (from ≈22 wt% to ≈16 wt%) in comparison to that determined for RCF at supercritical conditions (from ≈25 wt% to ≈12 wt%). Thus, we propose that the mild-temperature acid-catalyzed process can represent a promising strategy for the development of a hydrogen-free RCF treatment of wheat straw biomass. The reader is invited to see the simplified economic assessment presented in the SI, which suggests that the acid-catalyzed, hydrogen-free RCF of wheat straw produces revenues per unit weight of biomass comparable to those reported for the RCF of woody biomass,[26,71] and for other lignin-first processes.[17,18]

Conclusions

The reductive catalytic fractionation (RCF) of wheat straw at 250 °C, in the presence of different pressures of hydrogen and nitrogen gas was investigated. The use of methanol, ethanol

and isopropanol as hydrogen-donor solvents within a hydrogen-free RCF was studied. Hydrogen gas was found to play a prominent role in enhancing the yield of phenolic monomers (up to ≈25 wt% of acid insoluble lignin in the initial biomass) and non-condensed carbohydrate derivatives (up to ≈7 wt% of polysaccharides in the initial biomass), boosting the formation of monophenolic compounds with saturated side chains from lignin, and short glycols from (hemi)cellulose. Reactions with biomass and model reactions showed that both solvolysis and hydrogenolysis contribute to the cleavage of labile lignin interunit bonds during RCF. In the absence of H_2, the use of ethanol as a solvent led to the highest yield of phenolic monomers (up to ≈20 wt%), by virtue of a good balance between solvolysis, hydrogenolysis and hydrogenation of lignin. Nevertheless, an extensive (hemi)cellulose decomposition was observed when processing wheat straw at 250 °C that was recognized as a substantial drawback with respect to the valorization of the carbohydrate fraction. The adoption of a lower treatment temperature of 200 °C in combination with aqueous H_3PO_4 was shown to be a convenient way to overcome such limitation, resulting in a high cellulose recovery in the pulp (≥80 wt%), and a considerable solubilization of hemicellulose (with moderate release of monosaccharides in the medium) and lignin. Importantly, the use of H_3PO_4 boosted the formation of monophenolic compounds compared to a treatment without acid cocatalyst, leading to a yield of monomers of up to ca. 18 wt% under inert atmosphere that did not increase drastically in the presence of H_2.

While process conditions should be further optimized to improve the yield of low-MW lignin derivatives in the absence of hydrogen gas, the present study provides insight into the role of H_2 during RCF and outlines a pathway toward the development of a hydrogen-free RCF of lignocellulosic biomass.

Experimental Section

A full list of the materials used in this work and detailed descriptions of the experimental procedures are available in the Supporting Information. In this section, the main experimental procedures adopted in this work are briefly described.

RCF experiments were performed in duplicates in a 300 mL Parr batch reactor (Parr Instrument Company; Figure S17). Therefore, 3 g of milled biomass were introduced in the reactor, with 120 mL of solvent (methanol, ethanol, or isopropanol), 0.3 g of Ru/C, and a chosen amount of aqueous H_3PO_4 (800 μL of 85 % H_3PO_4, or absent). The reactor was sealed, flushed with N_2, then it was flushed and pressurized with H_2 or N_2 (10 or 30 bar). The speed of the stirrer was set to 750 rpm and the reactor was heated at a rate of about 10 °C min^{-1} up to a setpoint of 250 °C (or 200 °C). Once the setpoint was reached, the mixture was left to react at constant temperature for a duration comprised between 0 and 6 h.

After each experiment, the reactor was quickly cooled down to room temperature, depressurized, and its content was collected. A solid and a liquid fraction were separated by centrifugation. The solid fraction was washed with fresh solvent (40 mL) to remove components weakly adsorbed to the pulp. The washing solvent was mixed with the liquid fraction, and the mixture was filtered to eliminate residual solid particles. The filtrate was collected (Figure S18a). The retentate was recovered and added to the solid fraction, which was then dried at 60 °C to a constant weight. Subsequently, the solid fraction was sieved to separate the pulp (Figure S18b) from the spent catalyst (Figure S18c).

The isolated fractions were characterized in terms of dry matter, ash and organic matter contents following well-established protocols.[72,73]

The carbohydrate content of the pulp was determined via acid hydrolysis followed by HPLC of the released monosaccharides. Further characterization of the pulp was performed via ATR-FTIR, XRD, FEG–SEM, and enzymatic saccharification followed by HPLC of the released monosaccharides.

Portions of the liquid fraction were evaporated under N_2 flow to remove the solvent. Then, the dried residues underwent three successive liquid-liquid extractions with dichloromethane and water (recycling the water phase), to isolate lignin derivatives from more polar carbohydrate products. The dichloromethane extracts were mixed, and the solvent was evaporated under vacuum to obtain a viscous brown lignin oil (Figure S18d), which was then analyzed GPC, GC-MS/FID, and 1H-13C HSQC NMR.

The water extract was subjected to dilute acid hydrolysis to convert alkylated sugars back to their parent sugars,[49] before quantification of non-condensed carbohydrate derivatives via HPLC.

Model reactions were performed using an identical set-up as for reactions with biomass. In this case, 0.01 g of 2-phenoxy-1-phenylethanol were introduced in the batch reactor, together with 120 mL of methanol and a chosen amount of Ru/C (0.015 g or absent). The reactor was sealed, flushed with N_2, then it was flushed and pressurized with H_2 (1 bar). The reactions were performed at 250 °C for 3 h. The reactor content was then collected and filtered under vacuum to remove catalyst particles. The reaction products were characterized via GPC and GC–MS/FID.

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Conflict of Interests

The authors declare no competing financial interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Lignocellulose · Biorefinery · Wheat straw · Fractionation · Lignin depolymerization · Heterogeneous catalysis

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