

Reductive catalytic fractionation of wheat straw biomass

*Filippo Brienza,^{a, b} Korneel Van Aelst,^c François Devred,^b Delphine Magnin,^d Bert F. Sels,^c
Patrick Gerin,^a Iwona Cybulska*^a and Damien P. Debecker*^b*

^a Applied Microbiology Division, Earth and Life Institute (ELI), UCLouvain, Croix du Sud 2,
1348 Louvain-La-Neuve, Belgium.

^b Institute of Condensed Matter and Nanoscience (IMCN), UCLouvain, Place Louis Pasteur 1,
1348 Louvain-La-Neuve, Belgium.

^c Centre for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200F, 3001
Leuven, Belgium.

^d Bio- and Soft Matter Division, Institute of Condensed Matter and Nanoscience (IMCN)
UCLouvain, Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium.

ABSTRACT

Reductive catalytic fractionation (RCF) is a promising method for the development of so-called “lignin-first” biorefineries. Apart from the widely investigated virgin woody biomass, it is essential to explore the potential of waste biomass feedstocks. Herein, the RCF of wheat straw is examined, to produce lignin mono-/oligomers along with a processable carbohydrate pulp. The use of different catalysts (Ru/C and Ru/Al₂O₃) and catalyst loadings (0 – 20% w/w_{biomass}) revealed the superior performance of Ru/C, which resulted in the largest yield of phenolic monomers (up to ~25 wt% of initial acid insoluble lignin) and in the lowest formation of high-molecular weight fragments in the extracted lignin oil. Furthermore, the operating temperature was shown to substantially affect both lignin extraction-depolymerization and polysaccharides preservation-processability. For a reaction time of 3 hours, an increase of the temperature from 200 to 250 °C resulted in a > 2-fold boost of the yields of lignin oil and monophenolics, while the recovery of polysaccharides decreased by about 30 wt% (with ~20% lower enzymatic digestibility). An economic assessment highlighted that the high-temperature treatment becomes the most profitable configuration as the market price of lignin products increases. Overall, this work provides insight into the adoption of RCF for the upgrading of lignocellulose from inexpensive and widely available wheat straw biomass.

KEYWORDS

Lignocellulose, Biorefinery, Wheat straw, Fractionation, Lignin depolymerization, Heterogeneous catalysis

INTRODUCTION

Lignin represents the largest source of renewable aromatics available on Earth and, as such, it is considered an alluring platform for the sustainable production of chemicals and materials.¹⁻⁵ Despite its inherent potential, the valorization of the lignin fractions produced by conventional biomass fractionation methods is hampered by the heterogeneity and the high degree of condensation of such technical lignins.⁶⁻⁹ The incumbent need of more efficient strategies for lignin valorization fostered the development of a new class of methods that aim at the active stabilization of lignin derivatives produced during biomass fractionation, thereby preventing lignin condensation.^{10,11} Among these so-called “lignin-first” approaches, the reductive catalytic fractionation (RCF) of lignocellulose is particularly promising, as it was demonstrated to effectively extract lignin from biomass and to convert it toward valuable monophenolics with near-theoretical yields (based on the content of β -O-4 linkages in the lignin matrix), in a single step.^{12,13} RCF relies on the thermal treatment of lignocellulose in an organic solvent, in the presence of a redox catalyst and a source of hydrogen.^{12,13} Under these conditions, lignin is solubilized and labile lignin inter-unit bonds (mainly β -O-4 linkages⁷) are cleaved *via* solvolysis and hydrogenolysis.^{14,15} The resulting (hydroxy)alkenyl-substituted lignin moieties are ultimately stabilized against recondensation by the action of the redox catalyst, which promotes the hydrogenation of C=C bonds in their side chains.^{14,16,17}

The first studies on the catalytic hydrogenolysis and hydrogenation of woody biomass date back to the 1940s, when this method was employed as a means to explore the chemical structure of lignin.^{18,19} However, it was only in the 2010s that the potential of RCF for the development of integrated biorefineries was recognized.²⁰⁻²³ Although several breakthroughs were made since then, paving the way for the industrial application of RCF,^{24,25} the majority of these studies have

been chiefly focused on the treatment of woody biomass, while less attention was given to the fractionation of herbaceous feedstocks. In general, the latter have lower lignin contents and a higher fraction of G- and H-lignin units,⁸ more prone to undergo recondensation,²⁶ which poses a limitation to the formation of low-MW phenolics that can be attained *via* RCF. In spite of this, herbaceous feedstocks represent a considerable fraction of the available biomass supply,²⁷ and the majority of the existing biorefineries in the EU rely on agricultural residues and byproducts, rather than wood, as primary substrates.²⁸ Thus, the development of methods for the effective valorization of herbaceous feedstocks is of paramount importance.

From this point of view, Anderson and coworkers explored the RCF of corn stover, highlighting how Ru and Ni catalysts performed similarly with respect to the depolymerization of lignin toward mono- and oligophenolics.²⁹ In addition, the authors demonstrated that the implementation of an acid co-catalyst within the reaction system boosts lignin extraction and the yield of phenolic monomers, at the expense of the preservation of hemicellulose in the pulp.²⁹ The RCF of corn stover was also investigated by Li *et al.*, who showed that the adoption of unsupported MoS₂ catalysts for the RCF of corn stover leads to a moderately high yield of monophenolics (up to ~20 wt% of the initial lignin content).³⁰ Other biomass feedstocks, such as corncob³¹, bamboo,³² and hemp³³ were found to be particularly prone to undergo RCF, leading to the production of lignin monomers in high yields (~40 wt% of the initial lignin content), along with processable carbohydrate pulps.³² Importantly, the RCF treatment of herbaceous feedstocks was typically found to result in the considerable formation of *p*-hydroxycinnamic esters,²⁹⁻³² which have been recognized as promising platforms for the manufacturing of pharmaceutical products and polymeric materials.³⁴⁻³⁸

In this work, the RCF of wheat straw, which was recognized as the most promising agricultural residue for bioeconomy,³⁹ is inspected. The influence of the catalyst type and loading on the yield and distribution of soluble lignin and carbohydrate derivatives, as well as on the quality of the isolated pulp is examined. Furthermore, the effect of the treatment temperature on the kinetics of lignocellulose disassembly and on the properties of the different product fractions is explored. Finally, the profitability of the process is examined, highlighting the most promising configurations and the limitations to the use of RCF for the pretreatment of wheat straw.

EXPERIMENTAL SECTION

A full list of the materials used in this work and detailed descriptions of the experimental procedures and of the calculations performed are available in the Supporting information. Here, a condensed description of the main experimental process is provided.

Fractionation experiments

RCF experiments were carried out in duplicates using a 300 mL Parr batch reactor (Parr Instrument Company), shown in Figure S1. The lignocellulosic biomass (3 g, particle size ≤ 2 mm⁴⁰) was loaded in the reactor, together with the catalyst (0 – 0.6 g of 5 wt% Ru/C or 5 wt% Ru/Al₂O₃) and 120 mL of methanol. The reactor was sealed, flushed with N₂, then flushed and pressurized with H₂ (30 bar, introduced at ambient temperature). Subsequently, the mixture was stirred (750 rpm) and the temperature was ramped up to a setpoint (200 or 250 °C), at a rate of ~ 10 °C min⁻¹. When the set-point temperature was reached, the mixture was left to react for a duration of 0 – 6 hours at constant temperature.

Products separation and analysis

After each experiment, the reactor was rapidly cooled down to room temperature by a water flow through the cooling coil, and depressurized. The reactor content was collected and centrifuged to separate the solid fraction (containing the pulp and the catalyst) from the liquid fraction. The solid was washed with methanol (40 mL), followed by centrifugation to separate the solid and the washing liquid. The liquid recovered after washing was added to the liquid fraction from the reaction and the mixture was filtered under vacuum to eliminate residual solid particles. The filtrate was collected (Figure S2a). The retentate was recovered and added to the solid fraction. The latter was dried at 60 °C to a constant weight, to evaporate the residual solvent, and sieved to remove the spent catalyst (Figure S2b). Finally, the isolated pulp was collected (Figure S2c).

Dry matter, ash, and organic matter contents were determined for all the isolated fractions.

The pulp (Figure S2c) was characterized *via* a battery of techniques, including acid/enzymatic hydrolysis followed by high-performance liquid chromatography (HPLC) analysis, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray powder diffraction (XRD) analysis, field emission gun scanning electron microscopy (FEG-SEM).

Portions of the liquid fraction were evaporated under nitrogen flow to remove the solvent, then underwent a three-fold liquid-liquid extraction with dichloromethane and water, to isolate lignin derivatives (in dichloromethane) from more polar products (in water). The dichloromethane fractions were mixed, and the dichloromethane solvent was evaporated under vacuum to yield a viscous brown lignin oil (Figure S2d), which was subsequently analyzed *via* FTIR spectroscopy, gel permeation chromatography (GPC), gas chromatography (GC) coupled with a mass

spectrometry (MS) detector and a flame ionization detector (FID), and ^1H - ^{13}C heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR).

The water phase obtained from the liquid-liquid extraction of the non-volatile residue of the liquid fraction was subjected to dilute acid hydrolysis, and was analyzed for non-condensed carbohydrate derivatives by HPLC.

RESULTS AND DISCUSSION

Process outline and product streams composition

As a first attempt to evaluate the potential of RCF for the pretreatment of wheat straw, typical process conditions adopted for processing woody biomass were used.^{14,23,41} Therefore, batch fractionation experiments were performed in duplicates treating 3 g of wheat straw (*Triticum aestivum*, particle size ≤ 2 mm,⁴⁰ biomass composition reported in Table S1) in 120 mL of methanol, at 250 °C, in the presence of 5 wt% Ru/C (loading: 10% w/w_{biomass}) and 30 bar H₂ (introduced at ambient temperature), for a duration of 3 hours. After each experiment, a solid fraction comprising the pulp and the spent catalyst, and a liquid fraction containing solubilized lignin and carbohydrate derivatives were collected, as illustrated in Figure 1.

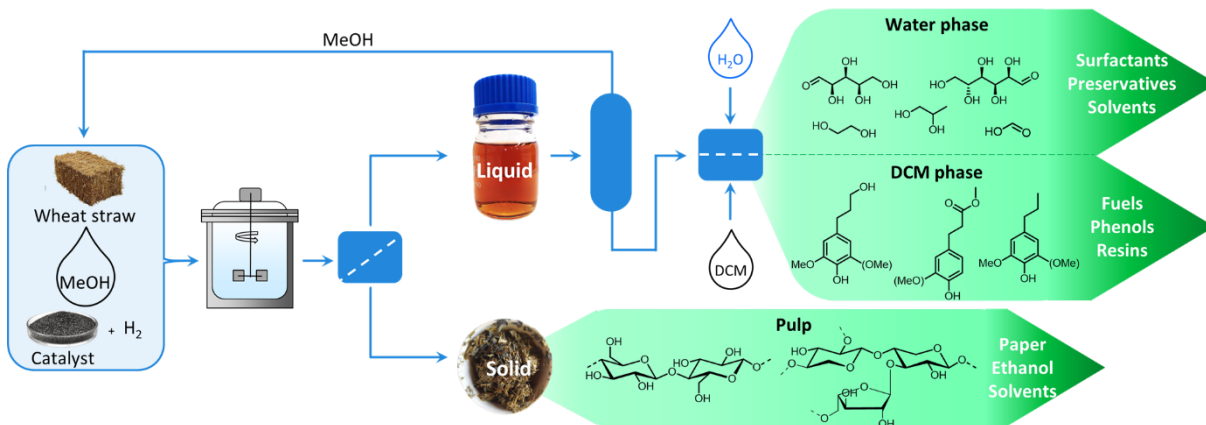


Figure 1 Outline of the RCF of wheat straw, with possible valorization routes for each product stream.

Overall, 42 wt% of the initial biomass organic matter (OM) was recovered in the pulp, while 25 wt% was found in the liquid fraction (Table 1). The loss of 33 wt% in the mass balance for OM suggests that considerable formation of volatiles occurred during the process (*e.g.* furans, short organic acids, etc.). The compositional characterization of the pulp revealed recoveries of 38 wt% and 66 wt% for C5 and C6 polysaccharides, respectively (Table 1), indicating substantial carbohydrate decomposition, consistently with previous findings on the RCF of corn stover under analogous conditions.²⁹

The chemical and structural features of the pulp and of the untreated biomass were inspected *via* ATR-FTIR spectroscopy (Figure S3, band assignments reported in Table S2). The treatment of wheat straw was found to result in the shrinkage of the bands at 1740 cm⁻¹ and 1235 cm⁻¹, assigned to hemicellulose and lignin,^{42,43} and in the diminution of the bands at 1595 cm⁻¹, 1510 cm⁻¹, 1465 cm⁻¹ and 1425 cm⁻¹ assigned to lignin,⁴³⁻⁴⁵ indicating delignification. Additionally, the increase of the band at 900 cm⁻¹ marks the formation of amorphous cellulose.⁴⁶ Further XRD analysis showed that the cellulose crystallinity index (CI) decreased from 56% for untreated biomass to 35% for the pulp (Table 1, Figure S4), likely due to the partial disruption of cellulose crystalline domains.

As expected from previous works on the RCF of woody and herbaceous biomass,^{21,29} the disassembly of lignocellulose structure achieved during the process ultimately led to an increased enzymatic convertibility of polysaccharides in the pulp compared to untreated biomass (Table 1).

Table 1 Characterization of the solid and liquid fractions obtained from the RCF of wheat straw performed under typical conditions^a.

Solid	Recovery (wt%)	OM ^b	42 ± 2
		C5 ^c	38 ± 3
		C6 ^c	66 ± 5
	Saccharification ^d (%)	Glucan	60 ± 0
		Xylan	66 ± 2
	CI ^e (%)		35 ± 3
Liquid	Recovery (wt%)	OM ^b	25 ± 0
	Yield (wt%)	Lignin oil ^f	71 ± 4
		Monophenolics ^f	25.2 ± 3.1
		C5, C6 derivatives ^g	4.9 ± 0.2

^a Treating 3 g of wheat straw (particle size ≤ 2 mm) in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/W_{biomass}), for 3 hours.

^b Expressed with respect to the weight of OM contained in the initial biomass.

^c Expressed with respect to the weight of polysaccharide contained in the initial biomass.

^d Expressed with respect to the amount of polysaccharide recovered in the pulp. The yield of saccharification of glucan and xylan for raw wheat straw were 21% and 16%, respectively.

^e The CI of raw wheat straw was 56%.

^f Expressed with respect to the weight of acid-insoluble lignin contained in the initial biomass.

^g Non-condensed carbohydrate derivatives, expressed with respect to the total weight of polysaccharides contained in the initial biomass.

The methanol solvent in the liquid fraction obtained after RCF was evaporated and the non-volatile residue was subjected to a liquid-liquid extraction with dichloromethane and water to separate lignin derivatives (in dichloromethane) and carbohydrate derivatives (in water), according to a procedure reported elsewhere.^{14,23,29} Evaporating the dichloromethane solvent from the dichloromethane extract gave a viscous brown lignin oil with a yield of 71 wt% of acid insoluble lignin in the initial biomass, indicating considerable extraction of lignin. Further insight into the structural features of the components present in the oil was obtained *via* FTIR analysis (Figure S5,

band assignments reported in Table S2). The strong absorption band at 1740 cm^{-1} as well as the band at 1160 cm^{-1} were assigned to coumarate and ferulate structures,³⁰ typical of lignin from herbaceous biomass.^{29,47} Other bands, characteristic of aryl rings, were apparent, namely at 1595 ,⁴⁴ 1510 ,⁴³ 1425 ,^{44,45} 1270 ,⁴⁸ 1045 ,⁴⁹ and 834 cm^{-1} ,^{30,50} highlighting the dominant presence of lignin derivatives in the oil. Additionally, the bands at 1465 , 1380 , and 1235 cm^{-1} indicate the presence of alkyl and methoxy groups in lignin structures.^{43,44}

The molecular weight distribution (MWD) of the lignin oil was investigated by GPC analysis (Figure S6), which revealed the presence of phenolic monomers (MW: $100 - 250\text{ g mol}^{-1}$), dimers (MW: $\sim 400\text{ g mol}^{-1}$) and oligomers (MW: $> 600\text{ g mol}^{-1}$). Several regions could be distinguished in the chromatogram, corresponding to distinct monomeric structures, including 4-propanol-substituted monomers (MW: $\sim 240\text{ g mol}^{-1}$), methyl esters of coumaric/ferulic acids (MW: $\sim 200\text{ g mol}^{-1}$), 4-propenyl- and 4-propyl-substituted monomers (MW: $\sim 160\text{ g mol}^{-1}$), and dealkylated monomers (MW: $\sim 100\text{ g mol}^{-1}$), suggesting that the RCF of wheat straw leads to a broad distribution of phenolic products, in contrast to the more selective depolymerization of lignin from woody biomass.^{15,21,23}

With the goal of elucidating the phenolic monomers composition, the lignin oil was subjected to gas chromatography (GC-MS/FID) analysis (Figure S7). The large pool of monomeric products, summarized in Table S3, confirms the deductions made based on GPC. The yield of monophenolics was $\sim 25\text{ wt}\%$ of acid insoluble lignin in the initial biomass, with 4-methyl dihydroferulate ($5.9\text{ wt}\%$), 4-propanol syringol ($4.2\text{ wt}\%$), 4-methyl dihydrocoumarate ($2.9\text{ wt}\%$) and 4-propyl syringol ($2.9\text{ wt}\%$) being the most abundant species detected. Methyl esters of ferulic/coumaric acid were reported to be produced during RCF *via* transesterification with the methanol solvent,^{29,30,36} whereas the formation of 4-propanol-(and 4-propenyl-/4-propyl-

)substituted monomers was reported to occur *via* hydrogenation (and a combination of hydrogenolysis and hydrogenation) of 4-propenol-substituted lignin units.⁵¹ On the other hand, the production of 4-ethyl- substituted monomers was explained by: (i) the hydrogenation of 4-vinyl-substituted monophenolics formed *via* decarboxylation of coumarates and ferulates,^{29,30} (ii) the dehydrogenation and subsequent decarbonylation of 4-propanol-substituted monomers,^{52,53} and (iii) the occurrence of dealkylation reactions.⁵⁴ The marginal presence of 4-methyl-substituted monomers and of species lacking alkyl side chains was associated with the occurrence of dealkylation reactions.^{29,54} Scheme S1 illustrates the main reaction pathways that we propose for the formation of monophenolics during the RCF of wheat straw, on the basis of previous works.^{29,30,51,52}

Next to the lignin oil, the water phase obtained after liquid-liquid extraction of the non-volatile residue of the liquid fraction was subjected to acid hydrolysis (4 wt% H₂SO₄, 121 °C for 1 hour) to convert alkylated sugars back to their parent sugars,²⁹ prior to be analyzed by HPLC (Figure S8) to inspect the presence of non-condensed carbohydrate derivatives generated from (hemi)cellulose decomposition (*e.g.* mono- and oligo-saccharides, polyols, organic acids, etc.). Low yields of organic acids (formic acid: 1.9 wt%, levulinic acid: 0.1 wt%), sugars (xylose: 1.1 wt%, glucose: 0.4 wt%) and diols (ethylene glycol: 1.0 wt%, 1,2-propylene glycol: 0.4 wt%) were measured (by total weight of polysaccharides in the initial biomass). These compounds were reported to form during catalytic hydrogenolysis of biomass *via* a combination of hydrolysis, retro-aldol condensation, hydrogenation, (de)hydration and decarbonylation reaction pathways,^{20,55,56} as summarized in Scheme S2. Despite the extensive decomposition of C5 and C6 polysaccharides that was observed (with a loss of about 46 wt% of polysaccharides in the initial biomass), the presence of non-condensed carbohydrate derivatives in the aqueous phase remained minimal (with

a total yield of 4.9 wt% relative to the polysaccharides content of the initial biomass). Volatile species may be partially lost during the evaporation of the solvent from the liquid fraction (*e.g.* formic acid, hydroxymethylfurfural, furfural). Other reasons for this discrepancy may be found in the participation of intermediates from (hemi)cellulose decomposition in condensation reactions to generate humins (also termed pseudolignin),^{57,58} or in their conversion toward gaseous products (*e.g.* CO₂).^{56,59}

Influence of the redox catalyst

To inspect the influence of the redox catalyst on the RCF of wheat straw, fractionation experiments were conducted in the presence of 5 wt% Ru/C (loading: 10% or 20% w/w_{biomass}), 5 wt% Ru/Al₂O₃ (loading: 10% w/w_{biomass}) and in the absence of a redox catalyst (*blank* reaction). These supported Ru catalysts have been previously applied at similar loadings for the RCF of woody,⁵¹ and, more recently, of herbaceous biomass feedstocks.³⁶

In agreement with previous studies,^{14,29} Figure S9 shows that lignocellulose solvolysis is independent of the presence, the type and the catalyst loading. The recovery of OM in the pulp decreased gradually with time. On the contrary, the recovery of OM in the liquid fraction increased for all scenarios from about 16 wt% of OM in the initial biomass at short reaction times to ~27 wt% after 6 hours. Interestingly, the loss of OM balance was not influenced by the catalyst, but became more considerable at longer reaction times, suggesting enhanced fragmentation of the reaction products into volatiles. The recoveries of C5 and C6 polysaccharides in the pulp diminished with time irrespective of the catalyst type and loading (Table 2). On the other hand, ATR-FTIR analyses of the isolated pulps highlighted a slightly larger presence of lignin in the pulp obtained for the *blank* experiment (more apparent bands at 1740, 1595, and 1510 cm⁻¹ in

Figure S10a), compared to the experiments carried out in the presence of redox catalysts (Figure S10a and b). Such observation may be due to the higher tendency of reactive lignin units liberated during solvolysis to undergo condensation reactions in the absence of a catalyst, ultimately redepositing on the pulp in the form of condensed lignin. Notably, the band at 1595 cm^{-1} , associated with lignin, was found to become more visible at prolonged reaction times also in the presence of Ru/C (Figure S11), suggesting a gradually less effective prevention of recondensation reactions. The latter may be due to a slower diffusion in the catalyst pores of the bigger lignin fragments that are typically released from the lignin matrix at longer reaction times.²² Another explanation could be found in the partial deactivation of the catalyst. In this respect, the release of minerals from the herbaceous biomass was reported to favor catalyst sintering, fouling, and poisoning.^{36,60}

Table 2 Biomass derivatives obtained from the RCF of wheat straw performed in the presence of different types and loadings of redox catalysts.

Entry	Experimental conditions ^a			Solid Recovery ^b (wt%)		Liquid Yield ^c (wt%)		
	Catalyst	Loading (wt%) ^c	Time (h)	Yield ^d (wt%)		Oil	Monomers	C5, C6 derivatives
				C5	C6			
1	Ru/C	10	0 ^f	84 ± 6	84 ± 3	40 ± 6	14.6 ± 3.7	3.3 ± 0.3
2	Ru/C	10	3	38 ± 3	66 ± 5	71 ± 4	25.2 ± 3.1	4.9 ± 0.2
3	Ru/C	10	6	27 ± 2	43 ± 1	81 ± 1	27.5 ± 2.6	7.3 ± 0.6
4	Ru/Al ₂ O ₃	10	0 ^f	86 ± 6	82 ± 2	40 ± 3	12.9 ± 0.7	2.9 ± 0.2
5	Ru/Al ₂ O ₃	10	3	40 ± 6	60 ± 2	69 ± 5	15.3 ± 1.0	4.4 ± 0.4
6	Ru/Al ₂ O ₃	10	6	30 ± 4	48 ± 3	79 ± 4	16.4 ± 1.1	5.1 ± 0.4
7	-	0	0 ^f	84 ± 7	84 ± 1	41 ± 5	8.4 ± 0.8	2.8 ± 0.2
8	-	0	3	42 ± 5	62 ± 2	66 ± 7	7.7 ± 0.7	2.7 ± 0.2
9	-	0	6	29 ± 5	41 ± 3	77 ± 6	7.1 ± 0.6	3.2 ± 0.3
10	Ru/C	20	0 ^f	78 ± 6	82 ± 3	39 ± 2	16.7 ± 1.4	3.6 ± 0.2
11	Ru/C	20	3	45 ± 4	62 ± 2	65 ± 6	26.3 ± 2.5	6.1 ± 0.5
12	Ru/C	20	6	32 ± 3	45 ± 1	75 ± 4	30.9 ± 2.1	7.5 ± 0.4

^a Fractionation experiments were performed in duplicates, treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), in the presence (or in the absence) of different catalysts and different loadings 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 Expressed with respect to the weight of biomass introduced in the reactor.

^f Fractionation halted immediately after the setpoint temperature was reached.

XRD analyses of the pulps revealed that the CI is not affected by the type and the loading of the catalyst (Figure 2). Conversely, prolonged treatment times determined a substantial diminution of the CI from 56% for raw wheat straw to about 30% for a pulp obtained after 6 hours of fractionation, pointing to the depletion of crystalline cellulose or to the redeposition of condensed (pseudo)lignin on the pulp.⁶¹ The assessment of the enzymatic digestibility of the pulp showed a similar behavior (Figure 2), with yields of saccharification for glucan and xylan that did not vary with the catalyst type and loading, but decreased sharply with the treatment time, possibly due to a larger presence of aromatic components (*i.e.* redeposited lignin),⁶² as highlighted *via* FTIR analysis. Remarkably, the largest yields of saccharification (~70-75%) were determined at very short reaction times (*i.e.* “0 h” condition).

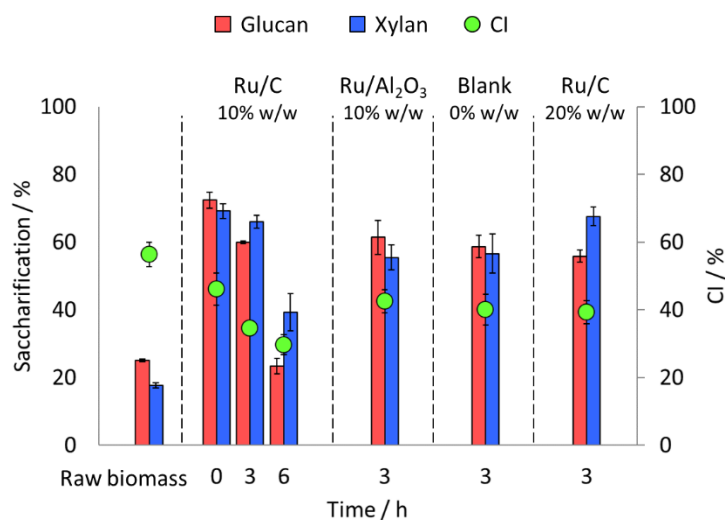


Figure 2 Yields of saccharification of glucan and xylan (red and blue bars) and cellulose crystallinity index (green circles) of the solid fraction obtained from the RCF of wheat straw carried out in the presence (or in the absence: *Blank*) of different catalysts, and in the presence of different loadings of Ru/C (expressed as % w/w_{biomass}). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), for various durations.

In line with previous reports on RCF,^{14,29} the formation of lignin oil was found to be independent of the redox catalyst and the yield of oil increased progressively with the duration of the fractionation experiments from about 40 wt% of acid insoluble lignin in the initial biomass at short reaction times up to ~80 wt% after 6 hours, with the largest amount of oil being extracted in the first 3 hours (Table 2). Conversely, Figure 3 shows marked differences in the MWD of the components of the lignin oils extracted in the presence of different catalysts and catalyst loadings. Figure 3a shows that, at short reaction times, the MWD was rather similar for the use of Ru/C, Ru/Al₂O₃ and for a *blank* experiment. In contrast, for longer durations, Ru/C appeared superior, leading to the highest production of monophenolics. The use of Ru/Al₂O₃ yielded a lignin oil with a fraction of phenolic dimers analogous to that obtained in the presence of Ru/C, but a lower amount of monomers, pointing to a lower stabilization performance of Ru/Al₂O₃.⁶³ With the goal of inspecting whether the different behavior of the two catalysts could be explained by a different

dispersion of the active metal sites, the two redox catalysts were subjected to H₂-chemisorption to determine the proportion of Ru atoms effectively accessible on the surface of each catalyst. A dispersion of 28% was measured for Ru/Al₂O₃, in contrast to a value of 19% measured for Ru/C. These results indicate that the metal dispersion is not the factor limiting the intrinsically lower performance of Ru/Al₂O₃. Some possible explanations for the observed behavior could be (i) a less favorable interaction of lignin fragments with the metal particles supported on Al₂O₃,⁵¹ or (ii) a higher tendency of Al₂O₃-supported catalysts to undergo deactivation.⁶⁴

The GPC profiles for experiments carried out at 3 and 6 hours exhibit tails extending to high MW increasing in the order: Ru/C < Ru/Al₂O₃ < *blank*, highlighting how the use of an effective catalyst (Ru/C) allows to partially avoid lignin repolymerization. The presence and the type of a redox catalyst appeared to play a role also on the distribution of the produced monophenolics, as indicated by the different profiles of the chromatograms in the region between 100 and 250 g mol⁻¹. In particular, the peak corresponding to 4-propanol-substituted monomers (~240 g mol⁻¹) was visible only for catalyzed reactions, whereas only the peaks for methyl coumarate/ferulate (~200 g mol⁻¹), alkyl-substituted monomers (~160 g mol⁻¹) and dealkylated monomers (~100 g mol⁻¹) were apparent for a *blank* reaction. Figure 3b illustrates that the use of a higher loading of Ru/C led to a slightly larger formation of phenolic monomers. The less marked tail in the region with MW > 600 g mol⁻¹ indicates a more effective prevention of lignin recondensation. Importantly, the greatest differences deriving from catalyst loading were observed after 6 hours of treatment, hinting at a possible loss of catalytic activity upon prolonged reactions, which may be overcome at high loading thanks to the presence of larger amounts of catalyst. As mentioned above, catalyst deactivation during RCF may occur through multiple routes, the most frequently recognized being: sintering,^{36,65,66} leaching,³⁶ poisoning,⁶⁷ and fouling.^{36,67,68} From this point of view, we surmise

that the fouling of the active sites may be a prominent deactivation route for the treatment of wheat straw, due to the considerable release of minerals, soluble carbohydrate derivatives and large lignin fragments in the reaction medium (Figure S12).

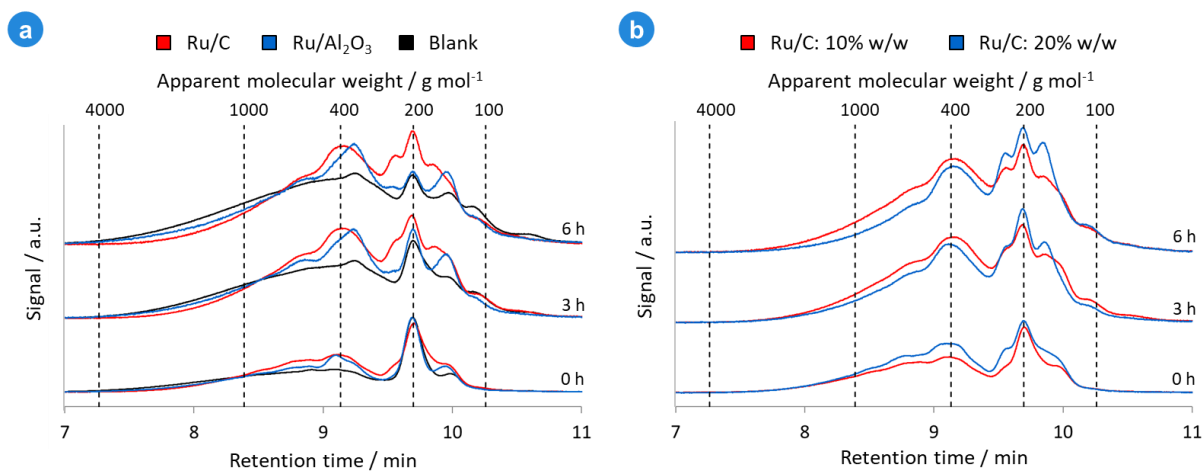


Figure 3 GPC chromatograms showing the MWD of the components of lignin oils obtained from the RCF of wheat straw carried out in the presence (or in the absence: *Blank*) of different catalysts (a), and in the presence of different loadings of Ru/C (expressed as % w/w_{biomass}) (b). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), for various durations. The area underneath each chromatogram was normalized with respect to the yield of lignin oil obtained for the corresponding experiment.

Consistently with GPC results, GC analysis (Figure 4, Table 2) showed that the yield of monophenolics achieved in the presence of different catalysts and for the *blank* experiment was comparable at short reaction times. Conversely, for longer durations it increased in the order: *blank* < Ru/Al₂O₃ < Ru/C. The use of Ru/C led to a considerable boost of the monomer yield during the first 3 hours of reaction, and to a further slight increase at 6 hours. When Ru/Al₂O₃ was adopted, the increment of the monomer yield with the reaction time was moderate, highlighting its poorer performance with respect to the stabilization of monophenolics. On the contrary, a progressively lower monomer yield was determined for the *blank* experiments, hinting to an extensive repolymerization of lignin derivatives.¹⁴ The formation of different monomeric species (Figure 4,

1 – 7) was also found to vary depending on the catalyst type and on the reaction time. The use of Ru/C led to a fast hydrogenation of C=C bonds in the side chains of the produced monophenolics, with the prevalent formation of 4-methyl dihydroferulate/coumarate species (**7**), 4-propanol- (**5**), 4-propyl- (**4**) and 4-ethyl-substituted species (**2**) (Figure 4). A minimal presence of 4-propenyl- (**3**) and methyl ferulate/coumarate (**6**) was observed only at low catalyst loading and very short reaction time. On the other hand, the adoption of Ru/Al₂O₃ resulted in a greater formation of unsaturated species, including **3** and **6**, which disappeared progressively with time, likely due to decarboxylation, hydrogenation and repolymerization reactions (Scheme S1). The highest yield of unsaturated components was observed for *blank* reactions, with a relatively large production of **6**. In this case, the yield of **3** was marginal, indicating that the hydrogenolysis of terminal hydroxyl groups in lignin monomers does not readily occur in the absence of a redox catalyst (Scheme S1). Additionally, a lower yield of **2** was determined for *blank* experiments, probably due to a more substantial recondensation of 4-vinyl-substituted monomers under these conditions (Scheme S1). A gradual boost of the formation of **1** at longer reaction times was measured for all scenarios, which shows that the occurrence of dealkylation reactions is independent of the redox catalyst. Overall, the use of Ru/C with a loading of 20% w/w_{biomass} resulted in slightly larger yields of monophenolics compared to the scenario employing a catalyst loading of 10% w/w_{biomass} (Figure 4). Such a marginal change suggests that, under the explored conditions, the formation of monophenolics was limited by the solvolytic extraction of lignin or by inherent features of wheat straw lignin (*e.g.* content of β-O-4 linkages), rather than by the catalytic hydrogenolysis and hydrogenation of lignin fragments.⁶⁹ Interestingly, a lower yield of **2** was observed at higher catalyst loading, likely due to the preferential hydrogenation of ferulates/coumarates with respect to their decarboxylation under these conditions (Scheme S1).

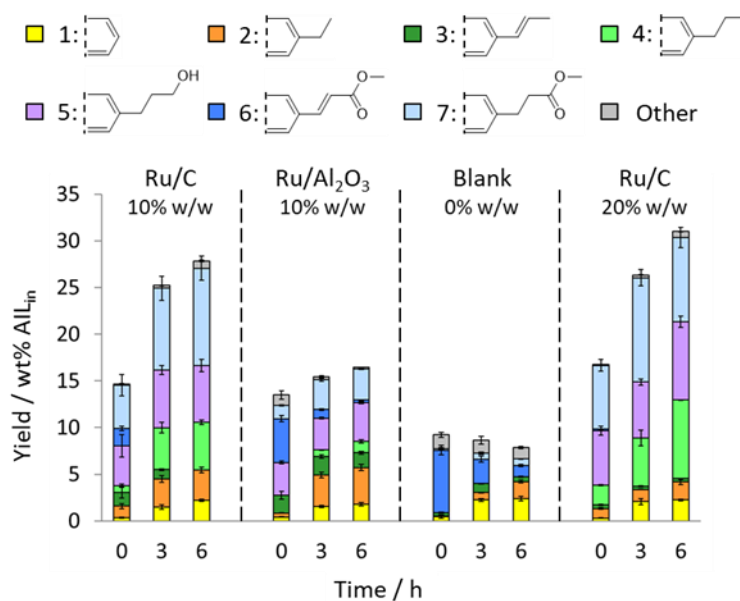


Figure 4 Yield of phenolic monomers as determined by GC analysis of the lignin oils obtained from the RCF of wheat straw carried out in the presence (or in the absence: *Blank*) of different catalysts, and in the presence of different loadings of Ru/C (expressed as % w/w_{biomass}). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), for various durations. The monomer yield was calculated with respect to the acid insoluble lignin (AIL) content in the initial biomass.

With the goal of gaining further insight into the effect of the redox catalyst on the structural features of the aromatic components produced during the RCF of wheat straw, samples of lignin oil extracted in the presence of Ru/C and in the absence of a redox catalyst were subjected to ¹H-¹³C heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) analysis. Table S4 summarizes the structural patterns considered in the analysis of the obtained spectra. Figure S13, Figure S14, and the data in Table S5 show that a low content of residual native lignin linkages (β -O-4, β - β resinol, β -5 phenylcoumaran) was determined after the treatment, both in the absence and in the presence of the redox catalyst, hinting at the occurrence of an extensive cleavage of such linkages for both scenarios. This is consistent with the idea that solvolysis is the main mechanism governing the disruption of inter-unit bonds in lignin chains under the explored conditions, as previously proposed by other authors.¹⁴ In the presence of Ru/C, the depletion of

native inter-unit bonds was accompanied by the formation of new structural motifs, typical of RCF lignin (β -1 ethyl, β -5 ethyl).⁷⁰ Consistently with GPC and GC data, Ru/C was found to boost the formation of 4-(3-alkylpropanoate) end-units (aromatic species containing alkyl esters of coumaric/ferulic acids), 4-propanol, 4-propyl and 4-ethyl end units. On the contrary, only 4-(3-alkylpropenoate) end-units were detected in the lignin oil isolated from the *blank* experiment. The considerably larger fraction of end-units found for the RCF lignin oil (69%, based on total aromatic units) compared to the *blank* lignin oil (7%) constitutes additional indication of the extensive depolymerization and stabilization of wheat straw lignin achieved during the catalytic process. Notably, the larger portion of unassigned spectrum for the *blank* experiment suggests extensive formation of non-native C-C bonds between lignin fragments in this case.⁷⁰ Importantly, the *blank* experiment led to a substantial formation of phenolics containing carbonyl groups in their side chains (22%) and to the formation of ether-linked furfural structures (1.4%) that was instead largely prevented in the presence of Ru/C, highlighting the importance of the redox catalyst in steering the selectivity of the generated lignin and carbohydrate derivatives.

The yield of non-condensed carbohydrate derivatives shown in Figure 5 exhibited a similar dependence on the presence, type and loading of redox catalyst as that of monophenolics. While little variations of the yield of sugars and formic acid were observed for the different scenarios, the presence of short diols (ethylene glycol and 1,2-propylene glycol) was detected only when a redox catalyst was employed. The use of Ru/C led to the largest formation of glycols, pointing out its superior hydrogenation performance (Scheme S2). Once again, the use of a higher loading of Ru/C did not result in larger yields of glycols, suggesting that catalytic hydrogenation is not the limiting step in their formation.

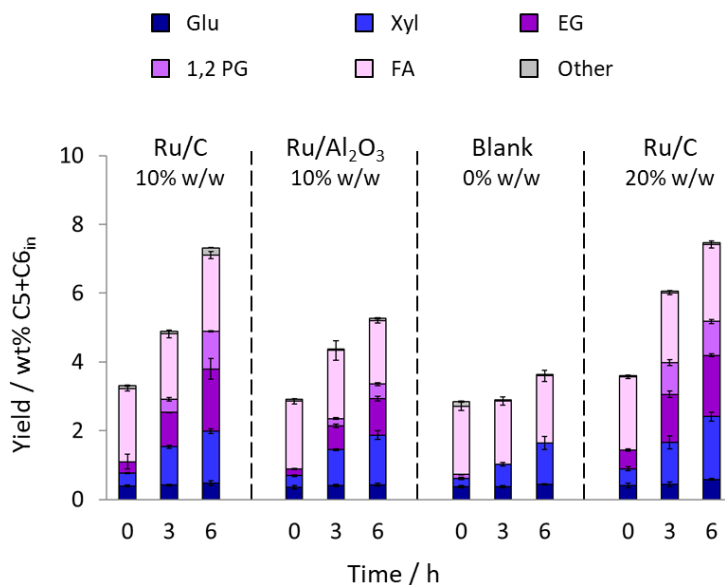


Figure 5 Yield of non-condensed carbohydrate derivatives (Glu: glucose; Xyl: xylose; EG: ethylene glycol; 1,2 PG: 1,2-propylene glycol; FA: formic acid; Other: levulinic acid and furfural) as determined by HPLC analysis of the water phase isolated after liquid-liquid extraction of the non-volatile residue of the liquid fraction obtained from the RCF of wheat straw carried out in the presence (or in the absence: *Blank*) of different catalysts, and in the presence of different loadings of Ru/C (expressed as % w/w_{biomass}). Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, at 250 °C, under 30 bar of H₂ (introduced at ambient temperature), for various durations. The yield of non-condensed carbohydrate derivatives was calculated with respect to the total content of polysaccharides in the initial biomass.

In conclusion, the use of Ru/C appeared to be the preferred choice for the RCF of wheat straw, as it results in a superior lignin depolymerization and in the largest yield of phenolic monomers. Importantly, the adoption of a catalyst loading of 10% w/w_{biomass} appeared to be sufficient for maximizing the reductive stabilization of lignin and carbohydrate derivatives.

Tuning the process temperature

The effect of the process temperature on the RCF of wheat straw was assessed by performing fractionation experiments at 200 °C and 250 °C. In line with previous findings on RCF,^{22,29,71} Figure S15 shows that the adoption of a lower temperature led to a less extensive disassembly of lignocellulose and a lower recovery of OM in the liquid fraction. The loss in the mass balance for

OM was remarkably smaller at 200 °C compared to that observed at 250 °C, and remained below 15 wt% of OM in the initial biomass after 6 hours, indicating a lower conversion of biomass toward volatile components under these conditions.

Table 3 Biomass derivatives isolated in the solid and liquid fractions obtained from the RCF of wheat straw performed at different temperatures.

Entry	Experimental conditions ^a		Solid		Liquid		
	Temperature (°C)	Time (h)	Recovery ^b (wt%)		Yield ^c (wt%)		Yield ^d (wt%)
			C5	C6	Oil	Monomers	C5, C6 derivatives
1	200	0 ^e	91 ± 5	93 ± 2	11 ± 1	1.9 ± 0.3	2.3 ± 0.1
2	200	3	80 ± 6	88 ± 2	32 ± 3	12.4 ± 2.6	3.1 ± 0.2
3	200	6	73 ± 6	80 ± 2	36 ± 5	12.8 ± 1.4	3.2 ± 0.1
4	250	0 ^e	84 ± 6	84 ± 3	40 ± 6	14.6 ± 3.7	3.3 ± 0.3
5	250	3	38 ± 3	66 ± 5	71 ± 4	25.2 ± 3.1	4.9 ± 0.2
6	250	6	27 ± 2	43 ± 1	81 ± 1	27.5 ± 2.6	7.3 ± 0.6

^a Fractionation experiments were performed in duplicates, treating 3 g of biomass in 120 mL of methanol, at different temperatures, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/w_{biomass}), 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 inspection of the raw biomass and of the obtained pulps *via* scanning electron microscopy (SEM) revealed that evident changes in the surface morphology occurred during RCF. While the surface of raw biomass appeared uniform and compact (Figure S16a), both a treatment at 200 °C and at 250 °C resulted in an apparent fibrous structure (Figure S16b and c). At higher temperature the fibers were thinner and more shredded, suggesting a more substantial disruption of lignocellulose structure. The compositional analysis of the pulps showed that the recoveries of C5 and C6 polysaccharides were larger at 200 °C, and diminished slightly from ~90 wt% at a short treatment time (*i.e.* “0 h” condition) to 75 – 80 wt% after 6 hours (Table 3). On the contrary,

polysaccharides underwent remarkable depletion at 250 °C. ATR-FTIR analysis of the pulps isolated at 200 °C revealed a progressive decrease of the band at 1595 cm⁻¹ (Figure S17), assigned to lignin.⁴⁴ Such behavior is opposite to that observed at 250 °C (Figure S11), suggesting that redeposition of condensed lignin on the pulp occurs less extensively at 200 °C. This observation may be explained by a slower release of lignin fragments in the reaction medium at lower temperature, which would likely require a lower redox capacity for their stabilization. Figure 6 illustrates that the CIs were also affected by the operating temperature. The pulps obtained at short reaction times exhibited similar CIs of ~46% both at 200 and at 250 °C. Conversely, longer processing times resulted in a considerably lower decline of the CI at 200 °C, compared to that observed at 250 °C. This difference may be explained by a minor disruption of cellulose crystalline domains or by a lower recondensation and redeposition of (pseudo)lignin on the pulps at milder temperature.^{72,73} The enzymatic digestibility of the polysaccharides recovered in the pulp at 200 °C increased gradually from about 35% at short reaction times, up to over 90% after 6 hours (Figure 6), pointing out the effectiveness of longer pretreatments at mild temperature, as opposed to the trend observed at 250 °C.

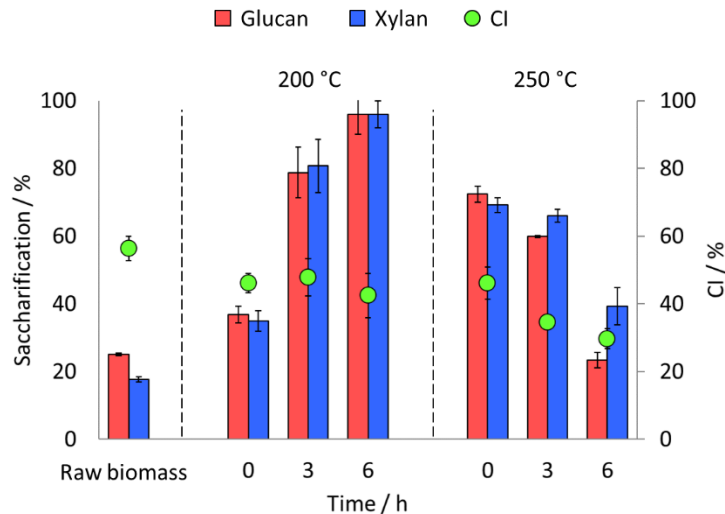


Figure 6 Yields of saccharification of glucan and xylan (red and blue bars) and cellulose crystallinity index (green circles) of the solid fraction obtained from the RCF of wheat straw carried out at different temperatures. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/w_{biomass}), for various durations.

The yield of lignin oil obtained at 200 °C reached a plateau of ~35 wt% of acid insoluble lignin in the initial biomass after 3 hours of fractionation (Table 3). Remarkably, this value is comparable to the yield of 40 wt% determined at a short reaction time for a treatment carried out at 250 °C, highlighting the superior extraction of lignin achieved at high temperature. GPC analysis of the isolated lignin oils showed that treating wheat straw at 200 °C resulted in the extraction of a lignin oil possessing a lower content of phenolic monomers, dimers and oligomers compared to a treatment at 250 °C (Figure 7). Notably, a lower fraction of heavy components appeared to be present in the oil isolated after RCF at 200 °C, as evidenced by the smaller area of the region at $MW \geq 600 \text{ g mol}^{-1}$ relatively to that of the region corresponding to monophenolics ($100 \text{ g mol}^{-1} \leq MW \leq 250 \text{ g mol}^{-1}$). Such finding may be explained by the less effective extraction of large lignin fragments at mild temperature or by the lower tendency of monophenolics to undergo repolymerization at these conditions.^{71,74}

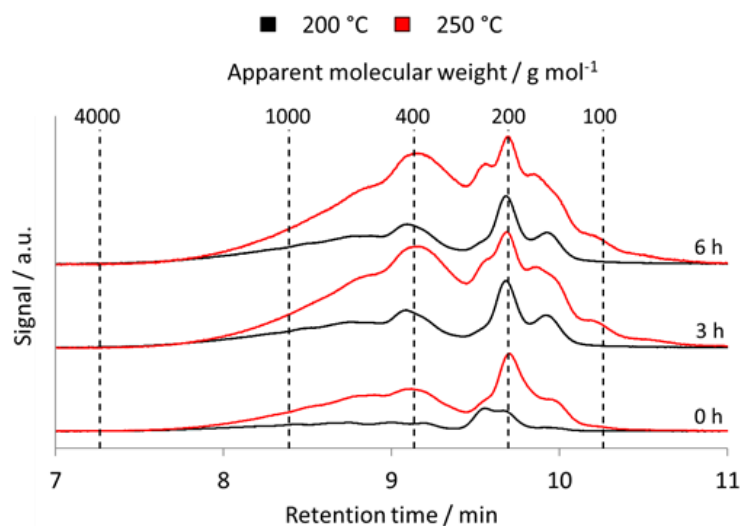


Figure 7 GPC chromatograms showing the MWD of the components of lignin oils obtained from the RCF of wheat straw carried out at different temperatures. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/w_{biomass}), for various durations. The area underneath each chromatogram was normalized with respect to the yield of lignin oil obtained for the corresponding experiment.

GC analysis of lignin oils confirmed the lower formation of phenolic monomers observed at 200 °C *via* GPC (Table 3). After 3 hours of reaction, the yield of monophenolics reached plateaus of ~12 wt% and ~25 wt% of acid insoluble lignin in the initial biomass at 200 °C and 250 °C, respectively. The treatment temperature was also found to affect the selectivity of different monomer species (Figure 8). A larger presence of species possessing C=C bonds in the side chains (**3**, **6**) was detected at 200 °C, which increased between 0 and 3 hours, then decreased at longer reaction times with the concomitant the formation of their saturated counterparts (**4**, **7**), suggesting that the hydrogenation of phenolic monomers proceeds more slowly at lower temperature. Additionally, the formation of **1** was observed only at 250 °C, indicating that dealkylation reactions tend not to occur at milder temperature.

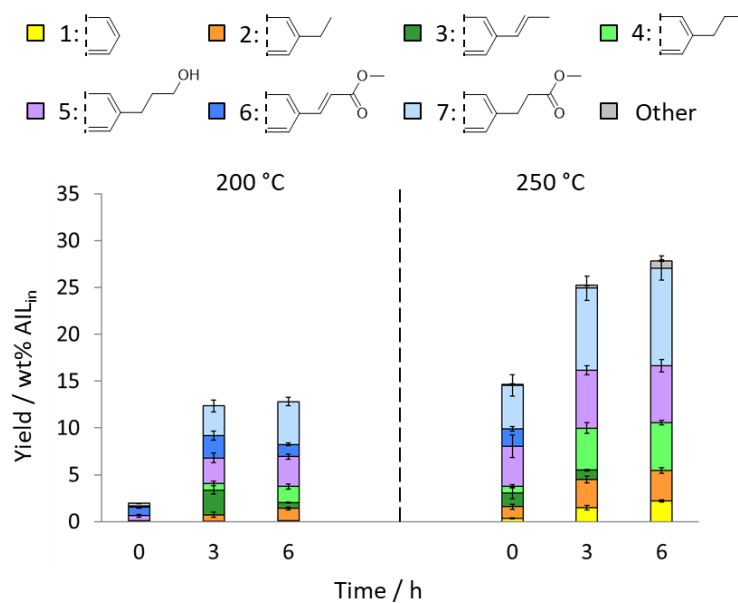


Figure 8 Yield of phenolic monomers as determined by GC analysis of the lignin oils obtained from the RCF of wheat straw carried out at different temperatures. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/w_{biomass}), for various durations. The monomer yield was calculated with respect to the acid insoluble lignin (AIL) content in the initial biomass.

The operating temperature was also found to affect the formation of non-condensed carbohydrate derivatives. For a RCF conducted at 200 °C, only a marginal change of the yield of these products was observed during the 6 hours of reaction, which remained around 3 wt% of polysaccharides in the initial biomass (Table 3). In contrast, a treatment at 250 °C led to an increase of the yield of carbohydrate derivatives from ~3 wt% at short reaction times to ~7 wt% after 6 hours. Figure 9 illustrates that a gradual boost of the yield of xylose, ethylene glycol and 1,2-propylene glycol was measured at high temperature. This trend was not observed under milder conditions. On the one hand, the release of xylose can be correlated with the more extensive solvolysis of hemicellulose observed at 250 °C. On the other hand, the formation of short glycols constitutes further indication of the enhanced catalytic hydrogenation achieved at higher temperature.

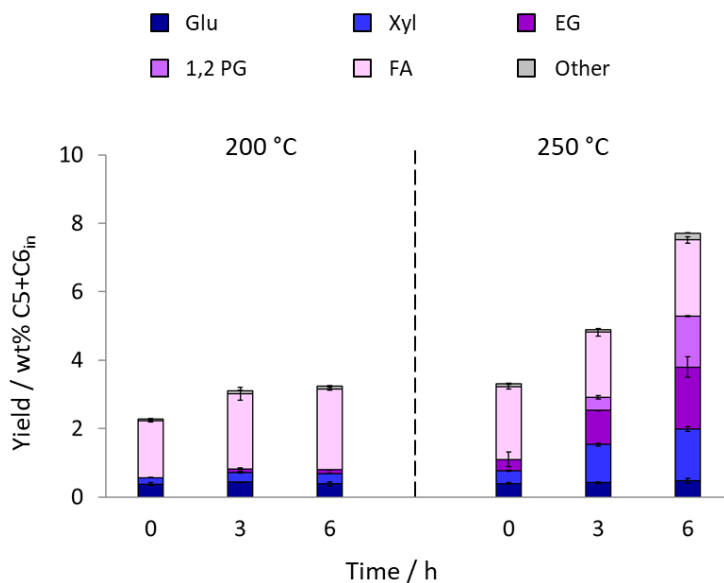


Figure 9 Yield of non-condensed carbohydrate derivatives (Glu: glucose; Xyl: xylose; EG: ethylene glycol; 1,2 PG: 1,2-propylene glycol; FA: formic acid; Other: levulinic acid and furfural) as determined by HPLC analysis of the water phase isolated after liquid-liquid extraction of the non-volatile residue of the liquid fraction obtained from the RCF of wheat straw carried out at different temperatures. Fractionation experiments were performed treating 3 g of biomass in 120 mL of methanol, under 30 bar of H₂ (introduced at ambient temperature), in the presence of Ru/C (loading: 10% w/w_{biomass}), for various durations. The yield of non-condensed carbohydrate derivatives was calculated with respect to the total content of polysaccharides in the initial biomass.

Overall, the adoption of a mild operating temperature of 200 °C was found to yield a processable pulp in high yields, along with moderate yields of lignin oil and phenolic monomers. On the contrary, treating wheat straw at 250 °C resulted in an opposite outcome. The production of non-condensed carbohydrate derivatives was limited for both scenarios. Ultimately, the selection of the best configuration will depend on economic considerations.

Brief economic assessment of the RCF of wheat straw

In order to investigate the profitability of the RCF of wheat straw, an economic assessment of the process was carried out. The techno-economic assessment conducted by Tschulkow *et al.* for the reductive fractionation of woody biomass was adopted as a starting point for the present analysis,

assuming an identical capital expenditure (CAPEX).⁷⁵ In addition, analogous consumptions of hydrogen and nitrogen gases, solvents, and catalyst were assumed for the present analysis.^{2,75} The extraction of phenolic monomers from lignin oil was considered to be realized using cyclohexane, which was reported to be effective for isolating monophenolics from lignin oil derived from herbaceous biomass.³⁶ Figure S18 illustrates the process flow diagram considered for the RCF of wheat straw.

Two process configurations of interest were compared: a treatment at 200 °C for 3 hours and a treatment at 250 °C for 3 hours, corresponding to entries 2 and 5 in Table 3. The outcomes in terms of the yields of pulp, phenolic monomers and phenolic oligomers for each configuration are summarized in Table S6. A capacity of 150 kt y⁻¹ of annual dry wheat straw intake was considered. The operating expenditures (OPEX) and the revenues determined for each process configuration are reported in Table S7 and in Table S8. It is important to remark that considering equal CAPEX and OPEX for the two process configurations is somewhat a strong assumption. For instance, the adoption of a temperature of 200 °C results in a lower operating pressure compared to the configuration at 250 °C (see Supporting information), which would impose less stringent equipment requirements and, ultimately, would lead to a lower cost of the reactor unit. Moreover, the use of a low temperature would require a lower energy input for the reactor unit compared to the high temperature configuration. Conversely, the downstream isolation of lignin oil would require a greater energy input (*i.e.* in the distillation unit) for the process performed at 200 °C, which produces liquid fractions with a lower concentration of lignin components, compared to the treatment at 250 °C. Analogously, the energy requirement for the isolation of phenolic monomers would be larger for the high temperature configuration, which yields a lignin oil with a lower concentration of monomers. In view of such considerations about the variability of the CAPEX

and the OPEX with the process conditions, the results of this economic assessment should be regarded more in terms of the trends that are highlighted, rather than as absolute values.

Assuming that the experimental data is scalable, the net present value (NPV) for the RCF of wheat straw was calculated. Negative NPVs of -29.9 M€ and of -79.8 M€ were determined for a treatment performed at 200 °C and at 250 °C, respectively, indicating that, under the current assumptions, neither process configuration appears to be economically feasible. Notably, negative NPVs in the range from about -19 to -33 M€ were reported by Tschulkow *et al.* for the RCF of common woody feedstocks such as birch, poplar, and pine biomass.⁷⁵ In that work, the authors highlighted that the selling price of lignin derivatives is among the most influential variables with respect to the profitability of the RCF biorefinery.⁷⁵ Thus, a sensitivity analysis was carried out to investigate the effect of the price of lignin monomers and oligomers on the economic feasibility of the RCF of wheat straw. While a large variability exists in the market prices reported in the literature for phenolic monomers (between ~1750 € t⁻¹ and ~12000 € t⁻¹),^{1,23,75} the price of phenolic oligomers is commonly considered to be similar to that of phenol-formaldehyde resins or printing inks (1500 – 2000 € t⁻¹)^{2,23,75}. However, in general, the selling price of lignin derivatives is ultimately related to their potential applications. From this point of view, the lignin oil obtained from the RCF of herbaceous biomass was reported to be a promising material for the manufacturing of biobased antimicrobials,³⁶ and 4-methyl (dihydro)coumarate was recognized as one of the main contributors to the bacteriostatic activity.^{36,37} Such high-value applications of lignin oil and monophenolics suggest that larger market prices may be considered for the lignin derivatives isolated from the RCF of wheat straw, compared to those initially assumed. In line with this, the sensitivity analysis was conducted for selling prices of up to 5000 € t⁻¹.

The results illustrated in Figure 10 show that a treatment conducted at 200 °C would be economically feasible at lower selling prices for phenolic monomers and oligomers compared to a treatment performed at 250 °C, as highlighted by the larger area of the region corresponding to positive NPVs in Figure 10a compared to that in Figure 10b. For instance, fixing the monomer price at 3000 € t⁻¹ would impose a minimum oligomer selling price of about 2700 € t⁻¹ for the mild temperature process (Figure 10a) and of 3200 € t⁻¹ for the high temperature configuration (Figure 10b), in order to achieve a positive NPV. On the other hand, in view of the higher yield of lignin monomers and oligomers achieved at 250 °C, the increase of the revenues with the selling price of lignin derivatives is greater for this process configuration, leading to the largest NPVs at monomer and oligomer prices higher than ~3400 € t⁻¹ (Figure 10b).

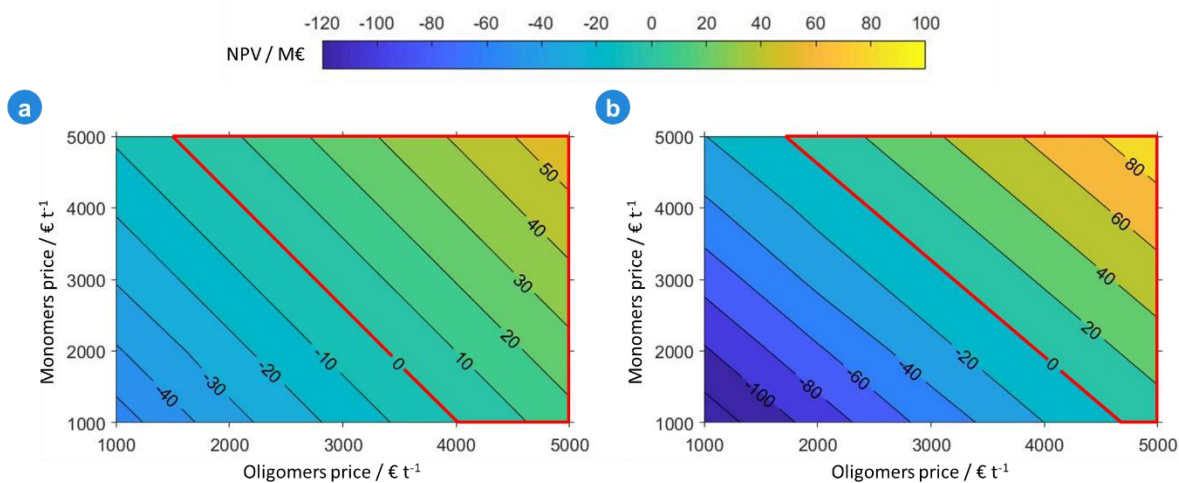


Figure 10 Influence of the market price of phenolic monomers and oligomers on the NPVs calculated for the RCF of wheat straw performed at 200 °C (a) and 250 °C (b), for 3 hours. In each plot, the contours of the region corresponding to positive NPVs are highlighted in red.

Along with the selling price of lignin derivatives, that of the pulp was also recognized to greatly affect the economic performance of RCF.⁷⁵ Thus, a second sensitivity analysis was performed considering a pulp price in a range of 300 to 600 € t⁻¹ (based on the fluctuations of the price of sugar over the last 10 years).⁷⁶ Figure S19 shows that, by virtue of the greater yield of pulp, a

treatment at 200 °C would result in a positive NPV for pulp prices greater than about 470 € t⁻¹, whereas a treatment performed at 250 °C would not be economically feasible in the price range that was considered for the analysis. Importantly, the excellent enzymatic digestibility that was determined for the pulp obtained from a treatment at 200 °C compared to that obtained at 250 °C suggests it could be reasonable to consider a higher pulp selling price for the former scenario.

Overall, these sensitivity analyses indicate that the selection of the operating conditions for the RCF of wheat straw shall not prescind from the market price of lignin and carbohydrate products, with the use of a low treatment temperature leading to the most convenient process configuration for low monomers/oligomers prices and high pulp prices, and the adoption of a high treatment temperature being more profitable at high prices for lignin derivatives and low prices for the carbohydrate pulp.

While, as previously mentioned, the above calculations should be taken with caution in absolute terms, future work should focus on further increasing the process revenues to improve the economic feasibility of the RCF of wheat straw. With this scope, the introduction of water as a co-solvent or of an acid co-catalyst within a process at mild temperature could be explored to enhance the yields of lignin oil and phenolic monomers.^{77,78} In addition, the adoption of a shorter reaction time for a process at high temperature could lead to an increase of the yield of pulp, and an improved profitability even at low prices for lignin derivatives.^{29,30}

CONCLUSIONS

The reductive catalytic fractionation (RCF) of wheat straw in methanol was investigated, targeting the production of low-molecular weight lignin derivatives along with processable polysaccharide pulp. The use of a redox catalyst was shown to enhance the formation of phenolic monomers from

lignin and short diols from (hemi)cellulose, thanks to a more extensive hydrogenation activity. Ru/C was found to exhibit a superior performance compared to Ru/Al₂O₃ and to a non-catalytic treatment, leading to the highest yield of monophenolics of about 25 wt% of acid insoluble lignin in the initial biomass after 3 hours of treatment at 250 °C. A drawback related to the use of such a high temperature was found in the poor preservation of polysaccharides and in the progressively decreasing enzymatic digestibility of the isolated pulp. Conversely, processing wheat straw at 200 °C was shown to afford higher yields of digestible pulp, but a more limited production of lignin oil and phenolic monomers. An economic assessment of the RCF of wheat straw highlighted that, irrespective of the preciseness of the absolute economic parameters, a RCF process performed at 200 °C is more economically feasible at lower selling prices of lignin monomers/oligomers prices, whereas a process conducted at 250 °C is the most favorable configuration for higher prices of lignin derivatives. The present study shows that wheat straw can be an attractive candidate for the sustainable production of valuable light aromatics and processable pulps *via* the RCF technology.

ASSOCIATED CONTENT

Supporting information

The Supporting information is available free of charge. A complete description of the materials used in this work, of the experimental procedures adopted for carrying out fractionation experiments and for the analysis of the obtained product streams is given. Details of the calculations are provided. The supporting figures include pictures of the experimental setup and of the fractionation products, FTIR spectra, XRD profiles, GPC, GC, and HPLC chromatograms, ¹H-¹³C HSQC NMR spectra of lignin oils, SEM images of isolated pulps, OM mass balances, a flow diagram of RCF, and an economic sensitivity analysis. The supporting schemes show the

proposed reaction pathways for the formation of monophenolics and carbohydrate derivatives. The supporting tables provide details about the compositional analysis of wheat straw biomass, ATR-FTIR bands assignments, ¹H-¹³C HSQC NMR cross signals assignments and quantification, and the calculations and the data used for the economic assessment.

AUTHOR INFORMATION

Corresponding Authors

* damien.debecker@uclouvain.be

* iwona.cybulska@uclouvain.be

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was funded by an FSR grant (Fonds spéciaux de recherche) from UCLouvain and by the Innoviris research grant BRIDGE-RE4BRU. D. P. D. thanks the Francqui Foundation for his Francqui Research Professor Chair. The MOCA platform of UCLouvain is acknowledged for its support with analytical techniques. M. Leclercq and T. Nicolay are acknowledged for their help with assembling the experimental setup and with the development of GC-MS/FID methods.

REFERENCES

- (1) Gillet, S.; Aguedo, M.; Petitjean, L.; Morais, A. R. C.; da Costa Lopes, A. M.; Łukasik, R. M.; Anastas, P. T. Lignin Transformations for High Value Applications: Towards Targeted Modifications Using Green Chemistry. *Green Chem.* **2017**, *19* (18), 4200–4233. <https://doi.org/10.1039/C7GC01479A>.
- (2) Liao, Y.; Koelewijn, S.-F.; Van den Bossche, G.; Van Aelst, J.; Van den Bosch, S.; Renders, T.; Navare, K.; Nicolai, T.; Van Aelst, K.; Maesen, M.; Matsushima, H.; Thevelein, J. M.; Van Acker, K.; Lagrain, B.; Verboekend, D.; Sels, B. F. A Sustainable Wood Biorefinery

- for Low-Carbon Footprint Chemicals Production. *Science* **2020**, *367* (6484), 1385–1390. <https://doi.org/10.1126/science.aau1567>.
- (3) Meng, Q.; Yan, J.; Wu, R.; Liu, H.; Sun, Y.; Wu, N.; Xiang, J.; Zheng, L.; Zhang, J.; Han, B. Sustainable Production of Benzene from Lignin. *Nat Commun* **2021**, *12* (1), 4534. <https://doi.org/10.1038/s41467-021-24780-8>.
 - (4) Zhao, S.; Abu-Omar, M. M. Materials Based on Technical Bulk Lignin. *ACS Sustainable Chem. Eng.* **2021**, *9* (4), 1477–1493. <https://doi.org/10.1021/acssuschemeng.0c08882>.
 - (5) Chatterjee, S.; Saito, T. Lignin-Derived Advanced Carbon Materials. *ChemSusChem* **2015**, *8* (23), 3941–3958. <https://doi.org/10.1002/cssc.201500692>.
 - (6) Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S.-F.; Beckham, G. T.; Sels, B. F. Chemicals from Lignin: An Interplay of Lignocellulose Fractionation, Depolymerisation, and Upgrading. *Chem. Soc. Rev.* **2018**, *47* (3), 852–908. <https://doi.org/10.1039/C7CS00566K>.
 - (7) Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110* (6), 3552–3599. <https://doi.org/10.1021/cr900354u>.
 - (8) Galkin, M. V.; Samec, J. S. M. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. *ChemSusChem* **2016**, *9* (13), 1544–1558. <https://doi.org/10.1002/cssc.201600237>.
 - (9) Calvaruso, G.; Clough, M. T.; Rechulski, M. D. K.; Rinaldi, R. On the Meaning and Origins of Lignin Recalcitrance: A Critical Analysis of the Catalytic Upgrading of Lignins Obtained from Mechanocatalytic Biorefining and Organosolv Pulping. *ChemCatChem* **2017**, *9* (14), 2691–2700. <https://doi.org/10.1002/cctc.201700473>.
 - (10) Korányi, T. I.; Fridrich, B.; Pineda, A.; Barta, K. Development of ‘Lignin-First’ Approaches for the Valorization of Lignocellulosic Biomass. *Molecules* **2020**, *25* (12), 2815. <https://doi.org/10.3390/molecules25122815>.
 - (11) Abu-Omar, M. M.; Barta, K.; Beckham, G. T.; Luterbacher, J. S.; Ralph, J.; Rinaldi, R.; Román-Leshkov, Y.; Samec, J. S. M.; Sels, B. F.; Wang, F. Guidelines for Performing Lignin-First Biorefining. *Energy Environ. Sci.* **2021**, 262–292. <https://doi.org/10.1039/D0EE02870C>.
 - (12) Renders, T.; Van den Bossche, G.; Vangeel, T.; Van Aelst, K.; Sels, B. Reductive Catalytic Fractionation: State of the Art of the Lignin-First Biorefinery. *Current Opinion in Biotechnology* **2019**, *56*, 193–201. <https://doi.org/10.1016/j.copbio.2018.12.005>.
 - (13) Renders, T.; Van den Bosch, S.; Koelewijn, S.-F.; Schutyser, W.; Sels, B. F. Lignin-First Biomass Fractionation: The Advent of Active Stabilisation Strategies. *Energy Environ. Sci.* **2017**, *10* (7), 1551–1557. <https://doi.org/10.1039/C7EE01298E>.
 - (14) Van den Bosch, S.; Renders, T.; Kennis, S.; Koelewijn, S.-F.; Van den Bossche, G.; Vangeel, T.; Deneyer, A.; Depuydt, D.; Courtin, C. M.; Thevelein, J. M.; Schutyser, W.; Sels, B. F. Integrating Lignin Valorization and Bio-Ethanol Production: On the Role of Ni-Al₂O₃ Catalyst Pellets during Lignin-First Fractionation. *Green Chem.* **2017**, *19* (14), 3313–3326. <https://doi.org/10.1039/C7GC01324H>.
 - (15) Galkin, M. V.; Samec, J. S. M. Selective Route to 2-Propenyl Aryls Directly from Wood by a Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis. *ChemSusChem* **2014**, *7* (8), 2154–2158. <https://doi.org/10.1002/cssc.201402017>.

- (16) Chen, L.; van Muyden, A. P.; Cui, X.; Fei, Z.; Yan, N.; Laurency, G.; Dyson, P. J. Lignin First: Confirming the Role of the Metal Catalyst in Reductive Fractionation. *JACS Au* **2021**, *1* (6), 729–733. <https://doi.org/10.1021/jacsau.1c00018>.
- (17) Qiu, S.; Wang, M.; Fang, Y.; Tan, T. Reductive Catalytic Fractionation of Lignocellulose: When Should the Catalyst Meet Depolymerized Lignin Fragments? *Sustainable Energy Fuels* **2020**, *4* (11), 5588–5594. <https://doi.org/10.1039/D0SE01118E>.
- (18) Godard, H. P.; McCarthy, J. L.; Hibbert, H. Hydrogenation of Wood. *J. Am. Chem. Soc.* **1940**, *62* (4), 988–988. <https://doi.org/10.1021/ja01861a508>.
- (19) Pepper, J. M.; Hibbert, H. Studies on Lignin and Related Compounds. LXXXVII. High Pressure Hydrogenation of Maple Wood ¹. *J. Am. Chem. Soc.* **1948**, *70* (1), 67–71. <https://doi.org/10.1021/ja01181a021>.
- (20) Li, C.; Zheng, M.; Wang, A.; Zhang, T. One-Pot Catalytic Hydrocracking of Raw Woody Biomass into Chemicals over Supported Carbide Catalysts: Simultaneous Conversion of Cellulose, Hemicellulose and Lignin. *Energy Environ. Sci.* **2012**, *5* (4), 6383–6390. <https://doi.org/10.1039/C1EE02684D>.
- (21) Parsell, T.; Yohe, S.; Degenstein, J.; Jarrell, T.; Klein, I.; Gencer, E.; Hewetson, B.; Hurt, M.; Kim, J. I.; Choudhari, H.; Saha, B.; Meilan, R.; Mosier, N.; Ribeiro, F.; Delgass, W. N.; Chapple, C.; Kenttämaa, H. I.; Agrawal, R.; Abu-Omar, M. M. A Synergistic Biorefinery Based on Catalytic Conversion of Lignin Prior to Cellulose Starting from Lignocellulosic Biomass. *Green Chem.* **2015**, *17* (3), 1492–1499. <https://doi.org/10.1039/C4GC01911C>.
- (22) Ferrini, P.; Rinaldi, R. Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions. *Angew. Chem. Int. Ed.* **2014**, *53* (33), 8634–8639. <https://doi.org/10.1002/anie.201403747>.
- (23) Van den Bosch, S.; Schutyser, W.; Vanholme, R.; Driessen, T.; Koelewijn, S.-F.; Renders, T.; De Meester, B.; Huijgen, W. J. J.; Dehaen, W.; Courtin, C. M.; Lagrain, B.; Boerjan, W.; Sels, B. F. Reductive Lignocellulose Fractionation into Soluble Lignin-Derived Phenolic Monomers and Dimers and Processable Carbohydrate Pulps. *Energy Environ. Sci.* **2015**, *8* (6), 1748–1763. <https://doi.org/10.1039/C5EE00204D>.
- (24) Cooreman, E.; Vangeel, T.; Van Aelst, K.; Van Aelst, J.; Lauwaert, J.; Thybaut, J. W.; Van den Bosch, S.; Sels, B. F. Perspective on Overcoming Scale-Up Hurdles for the Reductive Catalytic Fractionation of Lignocellulose Biomass. *Ind. Eng. Chem. Res.* **2020**, *59* (39), 17035–17045. <https://doi.org/10.1021/acs.iecr.0c02294>.
- (25) Feghali, E.; van de Pas, D. J.; Torr, K. M. Toward Bio-Based Epoxy Thermoset Polymers from Depolymerized Native Lignins Produced at the Pilot Scale. *Biomacromolecules* **2020**, *21* (4), 1548–1559. <https://doi.org/10.1021/acs.biomac.0c00108>.
- (26) Wei Kit Chin, D.; Lim, S.; Pang, Y. L.; Lam, M. K. Fundamental Review of Organosolv Pretreatment and Its Challenges in Emerging Consolidated Bioprocessing. *Biofuels, Bioprod. Bioref.* **2020**, *14* (4), 808–829. <https://doi.org/10.1002/bbb.2096>.
- (27) Searle, S.; Malins, C. *Availability of Cellulosic Residues and Wastes in the EU*; ICCT: Washington DC, USA, 2013.
- (28) European Commission. Joint Research Centre. *Biorefineries Distribution in the EU*; Publications Office: LU, 2018.
- (29) Anderson, E. M.; Katahira, R.; Reed, M.; Resch, M. G.; Karp, E. M.; Beckham, G. T.; Román-Leshkov, Y. Reductive Catalytic Fractionation of Corn Stover Lignin. *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 6940–6950. <https://doi.org/10.1021/acssuschemeng.6b01858>.

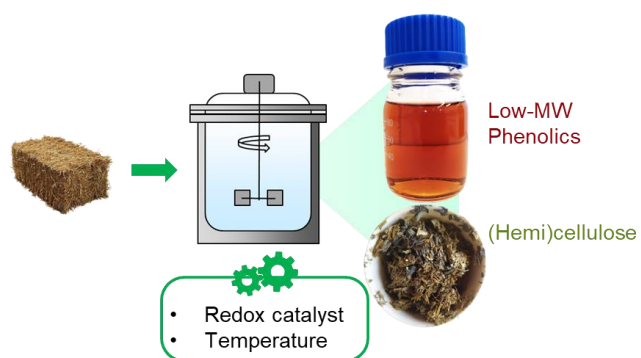
- (30) Li, S.; Li, W.; Zhang, Q.; Shu, R.; Wang, H.; Xin, H.; Ma, L. Lignin-First Depolymerization of Native Corn Stover with an Unsupported MoS₂ Catalyst. *RSC Adv.* **2018**, *8* (3), 1361–1370. <https://doi.org/10.1039/C7RA11947J>.
- (31) Wang, S.; Gao, W.; Li, H.; Xiao, L.; Sun, R.; Song, G. Selective Fragmentation of Biorefinery Corncob Lignin into *p*-Hydroxycinnamic Esters with a Supported Zinc Molybdate Catalyst. *ChemSusChem* **2018**, *11* (13), 2114–2123. <https://doi.org/10.1002/cssc.201800455>.
- (32) Zhang, K.; Li, H.; Xiao, L.-P.; Wang, B.; Sun, R.-C.; Song, G. Sequential Utilization of Bamboo Biomass through Reductive Catalytic Fractionation of Lignin. *Bioresource Technology* **2019**, *285*, 121335. <https://doi.org/10.1016/j.biortech.2019.121335>.
- (33) Muangmeesri, S.; Li, N.; Georgouvelas, D.; Ouagne, P.; Placet, V.; Mathew, A. P.; Samec, J. S. M. Holistic Valorization of Hemp through Reductive Catalytic Fractionation. *ACS Sustainable Chem. Eng.* **2021**, *accsuschemeng.1c06607*. <https://doi.org/10.1021/acssuschemeng.1c06607>.
- (34) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From Lignin-Derived Aromatic Compounds to Novel Biobased Polymers. *Macromol. Rapid Commun.* **2016**, *37* (1), 9–28. <https://doi.org/10.1002/marc.201500474>.
- (35) Beristain, M. F.; Nakamura, M.; Nagai, K.; Ogaw, T. Synthesis and Characterization of Poly[Propargyl(3-Methoxy-4-Propargyloxy)Cinnamate]: A Polymer from a Natural Product. *Designed Monomers and Polymers* **2009**, *12* (3), 257–263. <https://doi.org/10.1163/156855509X436076>.
- (36) Ebikade, O. E.; Samulewicz, N.; Xuan, S.; Sheehan, J. D.; Wu, C.; Vlachos, D. G. Reductive Catalytic Fractionation of Agricultural Residue and Energy Crop Lignin and Application of Lignin Oil in Antimicrobials. *Green Chem.* **2020**, *22* (21), 7435–7447. <https://doi.org/10.1039/D0GC02781B>.
- (37) Pei, K.; Ou, J.; Huang, J.; Ou, S. *P*-Coumaric Acid and Its Conjugates: Dietary Sources, Pharmacokinetic Properties and Biological Activities: *P*-Coumaric Acid and Its Conjugates. *J. Sci. Food Agric.* **2016**, *96* (9), 2952–2962. <https://doi.org/10.1002/jsfa.7578>.
- (38) Taofiq, O.; González-Paramás, A.; Barreiro, M.; Ferreira, I. Hydroxycinnamic Acids and Their Derivatives: Cosmeceutical Significance, Challenges and Future Perspectives, a Review. *Molecules* **2017**, *22* (2), 281. <https://doi.org/10.3390/molecules22020281>.
- (39) Thorenz, A.; Wietschel, L.; Stindt, D.; Tuma, A. Assessment of Agroforestry Residue Potentials for the Bioeconomy in the European Union. *Journal of Cleaner Production* **2018**, *176*, 348–359. <https://doi.org/10.1016/j.jclepro.2017.12.143>.
- (40) Thornburg, N. E.; Pecha, M. B.; Brandner, D. G.; Reed, M. L.; Vermaas, J. V.; Michener, W. E.; Katahira, R.; Vinzant, T. B.; Foust, T. D.; Donohoe, B. S.; Román-Leshkov, Y.; Ciesielski, P. N.; Beckham, G. T. Mesoscale Reaction–Diffusion Phenomena Governing Lignin-First Biomass Fractionation. *ChemSusChem* **2020**, *13* (17), 4495–4509. <https://doi.org/10.1002/cssc.202000558>.
- (41) Huang, Y.; Duan, Y.; Qiu, S.; Wang, M.; Ju, C.; Cao, H.; Fang, Y.; Tan, T. Lignin-First Biorefinery: A Reusable Catalyst for Lignin Depolymerization and Application of Lignin Oil to Jet Fuel Aromatics and Polyurethane Feedstock. *Sustainable Energy Fuels* **2018**, *2* (3), 637–647. <https://doi.org/10.1039/C7SE00535K>.
- (42) Kobayashi, N.; Okada, N.; Hirakawa, A.; Sato, T.; Kobayashi, J.; Hatano, S.; Itaya, Y.; Mori, S. Characteristics of Solid Residues Obtained from Hot-Compressed-Water

- Treatment of Woody Biomass. *Ind. Eng. Chem. Res.* **2009**, *48* (1), 373–379. <https://doi.org/10.1021/ie800870k>.
- (43) Li, C.; Cheng, G.; Balan, V.; Kent, M. S.; Ong, M.; Chundawat, S. P. S.; Sousa, L. daCosta; Melnichenko, Y. B.; Dale, B. E.; Simmons, B. A.; Singh, S. Influence of Physico-Chemical Changes on Enzymatic Digestibility of Ionic Liquid and AFEX Pretreated Corn Stover. *Bioresource Technology* **2011**, *102* (13), 6928–6936. <https://doi.org/10.1016/j.biortech.2011.04.005>.
- (44) Xu, F.; Yu, J.; Tesso, T.; Dowell, F.; Wang, D. Qualitative and Quantitative Analysis of Lignocellulosic Biomass Using Infrared Techniques: A Mini-Review. *Applied Energy* **2013**, *104*, 801–809. <https://doi.org/10.1016/j.apenergy.2012.12.019>.
- (45) Sammons, R. J.; Harper, D. P.; Labbé, N.; Bozell, J. J.; Elder, T.; Rials, T. G. Characterization of Organosolv Lignins Using Thermal and FT-IR Spectroscopic Analysis. *BioResources* **2013**, *8* (2), 2752–2767. <https://doi.org/10.15376/biores.8.2.2752-2767>.
- (46) Liao, Y.; de Beeck, B. O.; Thielemans, K.; Ennaert, T.; Snelders, J.; Dusselier, M.; Courtin, C. M.; Sels, B. F. The Role of Pretreatment in the Catalytic Valorization of Cellulose. *Molecular Catalysis* **2020**, *487*, 110883. <https://doi.org/10.1016/j.mcat.2020.110883>.
- (47) Luo, H.; Klein, I. M.; Jiang, Y.; Zhu, H.; Liu, B.; Kenttämaa, H. I.; Abu-Omar, M. M. Total Utilization of Miscanthus Biomass, Lignin and Carbohydrates, Using Earth Abundant Nickel Catalyst. *ACS Sustainable Chem. Eng.* **2016**, *4* (4), 2316–2322. <https://doi.org/10.1021/acssuschemeng.5b01776>.
- (48) Agarwal, U.; Atalla, R. Vibrational Spectroscopy. In *Lignin and Lignans*; Heitner, C., Dimmel, D., Schmidt, J., Eds.; CRC Press, 2010; pp 103–136. <https://doi.org/10.1201/EBK1574444865-c4>.
- (49) Fang, C.; Schmidt, J. E.; Cybulska, I.; Brudecki, G. P.; Frankær, C. G.; Thomsen, M. H. Hydrothermal Pretreatment of Date Palm (*Phoenix Dactylifera* L.) Leaflets and Rachis to Enhance Enzymatic Digestibility and Bioethanol Potential. *BioMed Research International* **2015**, *2015*, 1–13. <https://doi.org/10.1155/2015/216454>.
- (50) del Río, J. C.; Gutiérrez, A.; Rodríguez, I. M.; Ibarra, D.; Martínez, Á. T. Composition of Non-Woody Plant Lignins and Cinnamic Acids by Py-GC/MS, Py/TMAH and FT-IR. *Journal of Analytical and Applied Pyrolysis* **2007**, *79* (1–2), 39–46. <https://doi.org/10.1016/j.jaap.2006.09.003>.
- (51) Renders, T.; Cooreman, E.; Van den Bosch, S.; Schutyser, W.; Koelewijn, S.-F.; Vangeel, T.; Deneyer, A.; Van den Bossche, G.; Courtin, C. M.; Sels, B. F. Catalytic Lignocellulose Biorefining in *n*-Butanol/Water: A One-Pot Approach toward Phenolics, Polyols, and Cellulose. *Green Chem.* **2018**, *20* (20), 4607–4619. <https://doi.org/10.1039/C8GC01031E>.
- (52) Yamaguchi, S.; Kondo, H.; Uesugi, K.; Sakoda, K.; Jitsukawa, K.; Mitsudome, T.; Mizugaki, T. H₂-Free Selective Dehydroxymethylation of Primary Alcohols over Palladium Nanoparticle Catalysts. *ChemCatChem* **2021**, *13* (4), 1135–1139. <https://doi.org/10.1002/cctc.202001866>.
- (53) Di, L.; Yao, S.; Li, M.; Wu, G.; Dai, W.; Wang, G.; Li, L.; Guan, N. Selective Catalytic Hydrogenolysis of Carbon–Carbon σ Bonds in Primary Aliphatic Alcohols over Supported Metals. *ACS Catal.* **2015**, *5* (12), 7199–7207. <https://doi.org/10.1021/acscatal.5b02180>.
- (54) Song, S.; Zhang, J.; Yan, N. Support Effects in the De-Methoxylation of Lignin Monomer 4-Propylguaiacol over Molybdenum-Based Catalysts. *Fuel Processing Technology* **2020**, *199*, 106224. <https://doi.org/10.1016/j.fuproc.2019.106224>.

- (55) Weingarten, R.; Kim, Y. T.; Tompsett, G. A.; Fernández, A.; Han, K. S.; Hagaman, E. W.; Conner, Wm. C.; Dumesic, J. A.; Huber, G. W. Conversion of Glucose into Levulinic Acid with Solid Metal(IV) Phosphate Catalysts. *Journal of Catalysis* **2013**, *304*, 123–134. <https://doi.org/10.1016/j.jcat.2013.03.023>.
- (56) Paksung, N.; Matsumura, Y. Decomposition of Xylose in Sub- and Supercritical Water. *Ind. Eng. Chem. Res.* **2015**, *54* (31), 7604–7613. <https://doi.org/10.1021/acs.iecr.5b01623>.
- (57) van Zandvoort, I.; Wang, Y.; Rasrendra, C. B.; van Eck, E. R. H.; Bruijninx, P. C. A.; Heeres, H. J.; Weckhuysen, B. M. Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem* **2013**, *6* (9), 1745–1758. <https://doi.org/10.1002/cssc.201300332>.
- (58) Cheng, Z.; Everhart, J. L.; Tsilomelekis, G.; Nikolakis, V.; Saha, B.; Vlachos, D. G. Structural Analysis of Humins Formed in the Brønsted Acid Catalyzed Dehydration of Fructose. *Green Chem.* **2018**, *20* (5), 997–1006. <https://doi.org/10.1039/C7GC03054A>.
- (59) Zhang, J. Catalytic Transfer Hydrogenolysis as an Efficient Route in Cleavage of Lignin and Model Compounds. *Green Energy & Environment* **2018**, *3* (4), 328–334. <https://doi.org/10.1016/j.gee.2018.08.001>.
- (60) Lange, J. Renewable Feedstocks: The Problem of Catalyst Deactivation and Its Mitigation. *Angew. Chem. Int. Ed.* **2015**, *54* (45), 13186–13197. <https://doi.org/10.1002/anie.201503595>.
- (61) Agarwal, U. P.; Reiner, R. R.; Ralph, S. A. Estimation of Cellulose Crystallinity of Lignocelluloses Using Near-IR FT-Raman Spectroscopy and Comparison of the Raman and Segal-WAXS Methods. *J. Agric. Food Chem.* **2013**, *61* (1), 103–113. <https://doi.org/10.1021/jf304465k>.
- (62) Hu, F.; Jung, S.; Ragauskas, A. Pseudo-Lignin Formation and Its Impact on Enzymatic Hydrolysis. *Bioresource Technology* **2012**, *117*, 7–12. <https://doi.org/10.1016/j.biortech.2012.04.037>.
- (63) Deng, W.; Tan, X.; Fang, W.; Zhang, Q.; Wang, Y. Conversion of Cellulose into Sorbitol over Carbon Nanotube-Supported Ruthenium Catalyst. *Catal Lett* **2009**, *133* (1–2), 167–174. <https://doi.org/10.1007/s10562-009-0136-3>.
- (64) Sahebdehfar, S.; Bijani, P. M.; Yaripour, F. Deactivation Kinetics of γ -Al₂O₃ Catalyst in Methanol Dehydration to Dimethyl Ether. *Fuel* **2022**, *310*, 122443. <https://doi.org/10.1016/j.fuel.2021.122443>.
- (65) Anderson, E. M.; Stone, M. L.; Katahira, R.; Reed, M.; Beckham, G. T.; Román-Leshkov, Y. Flowthrough Reductive Catalytic Fractionation of Biomass. *Joule* **2017**, *1* (3), 613–622. <https://doi.org/10.1016/j.joule.2017.10.004>.
- (66) Li, X.; Guo, T.; Xia, Q.; Liu, X.; Wang, Y. One-Pot Catalytic Transformation of Lignocellulosic Biomass into Alkylcyclohexanes and Polyols. *ACS Sustainable Chem. Eng.* **2018**, *6* (3), 4390–4399. <https://doi.org/10.1021/acssuschemeng.8b00012>.
- (67) Van den Bossche, G.; Vangeel, T.; Van Aelst, K.; Arts, W.; Trullemans, L.; Navare, K.; Van den Bosch, S.; Van Acker, K.; Sels, B. F. Reductive Catalytic Fractionation: From Waste Wood to Functional Phenolic Oligomers for Attractive, Value-Added Applications. In *ACS Symposium Series*; Yoo, C. G., Ragauskas, A., Eds.; American Chemical Society: Washington, DC, 2021; Vol. 1377, pp 37–60. <https://doi.org/10.1021/bk-2021-1377.ch003>.
- (68) Chesi, C.; de Castro, I. B. D.; Clough, M. T.; Ferrini, P.; Rinaldi, R. The Influence of Hemicellulose Sugars on Product Distribution of Early-Stage Conversion of Lignin

- Oligomers Catalysed by Raney Nickel. *ChemCatChem* **2016**, *8* (12), 2079–2088. <https://doi.org/10.1002/cctc.201600235>.
- (69) Anderson, E. M.; Stone, M. L.; Hülsey, M. J.; Beckham, G. T.; Román-Leshkov, Y. Kinetic Studies of Lignin Solvolysis and Reduction by Reductive Catalytic Fractionation Decoupled in Flow-Through Reactors. *ACS Sustainable Chem. Eng.* **2018**, *6* (6), 7951–7959. <https://doi.org/10.1021/acssuschemeng.8b01256>.
- (70) Van Aelst, K.; Van Sinay, E.; Vangeel, T.; Cooreman, E.; Van den Bossche, G.; Renders, T.; Van Aelst, J.; Van den Bosch, S.; Sels, B. F. Reductive Catalytic Fractionation of Pine Wood: Elucidating and Quantifying the Molecular Structures in the Lignin Oil. *Chem. Sci.* **2020**, *11* (42), 11498–11508. <https://doi.org/10.1039/D0SC04182C>.
- (71) Ferrini, P.; Rezende, C. A.; Rinaldi, R. Catalytic Upstream Biorefining through Hydrogen Transfer Reactions: Understanding the Process from the Pulp Perspective. *ChemSusChem* **2016**, *9* (22), 3171–3180. <https://doi.org/10.1002/cssc.201601121>.
- (72) Shinde, S. D.; Meng, X.; Kumar, R.; Ragauskas, A. J. Recent Advances in Understanding the Pseudo-Lignin Formation in a Lignocellulosic Biorefinery. *Green Chem.* **2018**, *20* (10), 2192–2205. <https://doi.org/10.1039/C8GC00353J>.
- (73) Karimi, K.; Taherzadeh, M. J. A Critical Review of Analytical Methods in Pretreatment of Lignocelluloses: Composition, Imaging, and Crystallinity. *Bioresource Technology* **2016**, *200*, 1008–1018. <https://doi.org/10.1016/j.biortech.2015.11.022>.
- (74) Shu, R.; Zhang, Q.; Ma, L.; Xu, Y.; Chen, P.; Wang, C.; Wang, T. Insight into the Solvent, Temperature and Time Effects on the Hydrogenolysis of Hydrolyzed Lignin. *Bioresource Technology* **2016**, *221*, 568–575. <https://doi.org/10.1016/j.biortech.2016.09.043>.
- (75) Tschulkow, M.; Compennolle, T.; Van den Bosch, S.; Van Aelst, J.; Storms, I.; Van Dael, M.; Van den Bossche, G.; Sels, B.; Van Passel, S. Integrated Techno-Economic Assessment of a Biorefinery Process: The High-End Valorization of the Lignocellulosic Fraction in Wood Streams. *Journal of Cleaner Production* **2020**, *266*, 122022. <https://doi.org/10.1016/j.jclepro.2020.122022>.
- (76) European Commisison. *Sugar Market Situation AGRI E 4 - Expert Group Common Market Organisation on Arable Crops*; 2022.
- (77) Renders, T.; Van den Bosch, S.; Vangeel, T.; Ennaert, T.; Koelewijn, S.-F.; Van den Bossche, G.; Courtin, C. M.; Schutyser, W.; Sels, B. F. Synergetic Effects of Alcohol/Water Mixing on the Catalytic Reductive Fractionation of Poplar Wood. *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 6894–6904. <https://doi.org/10.1021/acssuschemeng.6b01844>.
- (78) Renders, T.; Schutyser, W.; Van den Bosch, S.; Koelewijn, S.-F.; Vangeel, T.; Courtin, C. M.; Sels, B. F. Influence of Acidic (H₃PO₄) and Alkaline (NaOH) Additives on the Catalytic Reductive Fractionation of Lignocellulose. *ACS Catal.* **2016**, *6* (3), 2055–2066. <https://doi.org/10.1021/acscatal.5b02906>.

GRAPHICAL ABSTRACT



SYNOPSIS

The reductive catalytic fractionation of wheat straw allows to produce low-molecular weight aromatics from lignin and processable polysaccharide pulp.