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Efficient Depolymerization of Lignin to Biobased Chemicals Using a Two-Step Approach Involving Ozonation in a Continuous Flow Microreactor Followed by Catalytic Hydrotreatment

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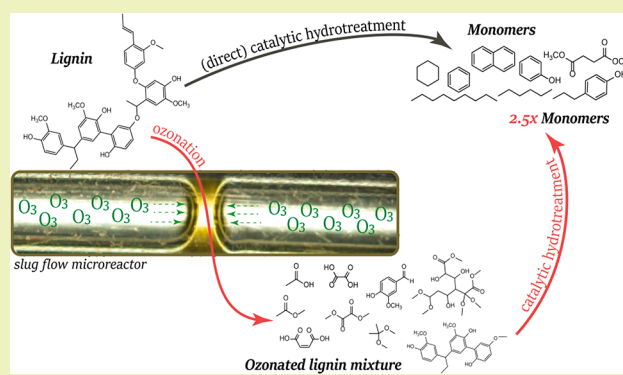
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Supporting Information

ABSTRACT: Lignin is a promising feedstock for the replacement of conventional carbon sources for the production of chemicals and fuels. In this paper, results are reported for the depolymerization of various residual lignins in the absence of a catalyst by utilizing ozone. Reactions were performed in a microreactor setup ensuring high gas–liquid mass transfer rates, a low inventory of ozone, and straightforward scale-up possibilities. The ozonation is demonstrated using a representative model compound (vanillin) and various lignins (pyrolytic and organosolv) dissolved in methanol (2.5 wt %). Experiments were performed under ambient conditions, at gas–liquid flow ratios ranging from 30 to 90 and short residence times on the order of 12–24 s. Analyses of the products after methanol removal revealed the presence of (di)carboxylic acids, methyl esters, and acetals. Extensive depolymerization was achieved (i.e., up to 30% for pyrolytic lignin and 70% for organosolv lignins). Furthermore, a two-step approach in which the ozonated lignin is further hydrotreated (350–400 °C, 100 bar H₂, 4 h, Pd/C as catalyst) showed a substantial increase in depolymerization efficiency, yielding a 2.5-fold increased monomer yield in the product oil compared to a hydrotreatment step only.

KEYWORDS: Lignin, Ozone, Oxidation, Microreactor, Hydrotreatment



INTRODUCTION

Sustainable replacement of conventional carbon sources within the (petro)chemical industry, in particular by biomass resources, has been widely researched. Lignin, one of the three main lignocellulosic biomass fractions, is an aromatic biopolymer with great potential for the production of (intermediate) chemicals and fuels.¹ In typical processes developed to fractionate lignin from biomass, significant structural changes occur to the native material.² Often, condensed and complex aromatic oligomers are formed with typical molecular weights of 1000 to 10 000 Da.³ Despite their wide availability of around 50 million tons/year,⁴ creation of an efficient valorization process to convert lignins into low molecular weight compounds is extremely challenging. A first step requires an efficient depolymerization reaction. Accordingly, (catalytic) methodologies able to break down lignin by both reductive (e.g., catalytic hydrotreatment^{5–9}) and oxidative routes^{1,3,10,11} have been investigated. The direct depolymerization of lignins via catalytic hydrotreatment is reportedly limited by the high amount of stable C–C linkages and competitive repolymerization pathways.^{6,12}

Lignin oxidation has been carried out extensively with the use of oxygen, air, and hydrogen peroxide as oxidants. A broad range of catalytic systems is reported, in which homogeneous catalysts are most often employed, e.g., TEMPO,^{13–15} oxovanadium complexes,^{16–19} metallosalen complexes,^{20,21} and POMs.^{22,23} Heterogeneous catalysts (e.g., chalcopryrite,²⁴ metal supported,^{25–27} metal oxides^{28–30}) and innovative approaches using biomimetic catalysts,^{31–33} DDO,^{34,35} and ionic liquids^{36–38} have been studied as well. Products derived from lignin oxidation include aromatic acids and aldehydes, phenolic building blocks, quinones, and dicarboxylic acids (DCAs) with several potential applications. An oxidation system based on hydrogen peroxide was also used as pretreatment to ultimately obtain hydrocarbons of transportation fuel quality through a subsequent hydrodeoxygenation of the intermediate oxidized lignin oils.^{39–41}

Ozone is relatively less explored as an oxidant for lignin valorization, despite its uses in wastewater treatment as a

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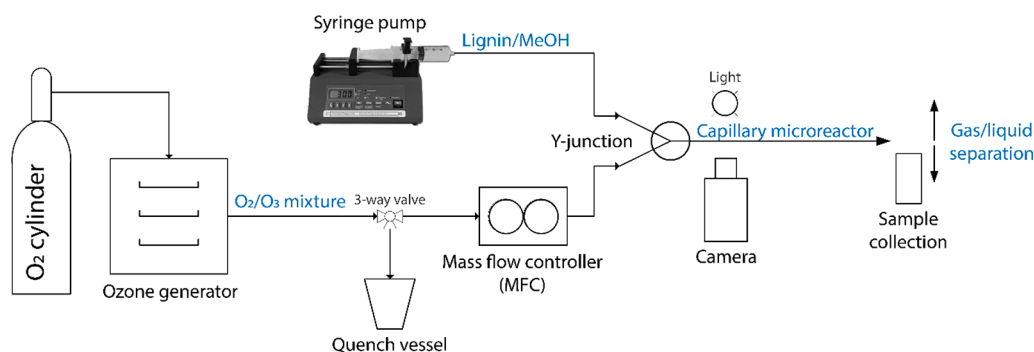


Figure 1. Microreactor setup used for the ozonation experiments

disinfectant,⁴² in the paper and pulp industry as a bleaching agent,¹⁰ and as a pretreatment to improve the enzymatic hydrolysis of biomass.⁴³ Ozone has a high reactivity toward both phenolic and other functionalities under mild conditions, and neither chemical additives nor catalysts are needed.⁴⁴ It can be easily generated in situ, either from oxygen or dry air, and ozone generation technologies are well-established and available at all scales. Furthermore, ozone has a short half-life; thus, any residual ozone in the system quickly decomposes to O₂, providing an overall green conversion reaction with no need of extra separation steps.⁴⁵ Previous works showed that ozonated biomass solutions contain a range of aromatic aldehydes, quinones, and carboxylic acids derived from the lignin fraction.^{46,47} An investigation of alkali lignin ozonation reported that the produced esters are suitable for applications as fuel additives.⁴⁵ A recent publication from our group showed the potential of ozonation for the production of biobased DCAs and esters from pyrolytic lignin (PL).⁴⁸

One important drawback related to the use of ozone is related to safety, as unstable intermediates (e.g., peroxides) can be formed during the process. In this context, continuous processes in microreactors are very attractive, as much smaller volumes are used and a superior control over the reaction can be achieved. Microreactor technology is considered a sustainable solution from both safety and energy-saving aspects, as it offers a substantial process intensification due to the enhanced mass and heat transfer rates, as well as the ease of upscaling by numbering-up.^{49,50} Ozonation of a range of alkenes, aromatics, and amines was successfully performed in such devices.^{51–55} For lignin, the development of valorization processes in continuous flow microreactors is still in its infancy, and no reports for ozonation exist. Promising results were reported on the photocatalytic degradation of lignin model substrates,⁵⁶ ultrafast hydrothermal⁵⁷ and copper chloride-mediated oxidative⁵⁸ depolymerization of Kraft lignin, and supercritical extraction of Kraft lignin oxidation products.⁵⁹

Here we report the ozonation of lignins in a continuous flow microreactor under ambient conditions. The process intensification approach was first tested with vanillin as a representative pyrolytic lignin model. Ozonation experimental studies were continued using lignins (dissolved in methanol, 2.5 wt %), at various gas to liquid (G/L) ratios and residence times. Products after methanol removal were analyzed in detail via chromatographic and spectroscopic techniques. Finally, a two-step approach in which the ozonated lignin is further hydrotreated in the presence of a catalyst was demonstrated, and a substantial increase in the final monomer yields and level

of depolymerization was observed for the samples pretreated with ozone.

■ MATERIALS AND METHODS

Chemicals. Pyrolytic lignin (PL, with an average molecular weight (MW_{av}) = 786 g/mol) was supplied by Biomass Technology Group (BTG, Enschede, The Netherlands). It was obtained by adding water to pine-derived pyrolysis liquids, in an oil to water ratio of 2:1. The two liquid layers were separated and the water-insoluble bottom layer (PL-enriched, typical yield of 25–30 wt %) was used for the experiments.

Organosolv lignins were extracted from walnut shells using an acid-catalyzed alcohol-based organosolv process. The organosolv procedure and lignin isolation methods are reported elsewhere;^{60,61} see the [Supporting Information](#) (SI) for details. Two different organosolv lignins were used in this research, i.e., an ethanosolv (MW_{av} = 2947 g/mol) and a butanosolv (MW_{av} = 4464 g/mol).

Pd/C (5 wt %) was used as catalyst in powder form, purchased from Sigma-Aldrich. Oxygen and hydrogen (>99.99% purity) were purchased from Linde. Tetrahydrofuran (THF), toluene, vanillin, 1,1'-bicyclohexyl, potassium iodide (KI), sodium thiosulfate (Na₂S₂O₃), 30% hydrochloric acid (HCl), methanol (MeOH), deuterated dimethyl sulfoxide (DMSO-*d*₆), and di-*n*-butyl ether (DBE) were purchased from Sigma-Aldrich. All chemicals in this study were used as received.

Ozonation Experiments. All ozonation experiments were performed under ambient conditions (i.e., room temperature and atmospheric pressure). Ozone must be handled with care due to its high reactivity and possible formation of unstable ozonides. The setup is schematically presented in [Figure 1](#). Oxygen was fed from a cylinder to the ozone generator (model LAB2B, Ozonia). The ozone concentration as a function of the oxygen flow was determined by a titration procedure (see the [Supporting Information](#)).

A minimum oxygen flow of 2 L/min was chosen to ensure a stable ozone production rate. Since lower gas flow rates are required in the ozonation step, the oxygen/ozone flow from the generator was split, and a mass flow controller (MFC, Bronkhorst, model F-201D) was used to control the flow into the microreactor, while the remainder was quenched into an aqueous solution of KI. The mass flow controller was calibrated with a digital bubble flow meter. The inlet gas flow to the microreactor was 15.3 mL/min for all experiments, with an ozone concentration of 25 mg/L. The liquid solution, consisting of lignin or vanillin dissolved in MeOH, was fed by a syringe pump (Landgraf Laborsysteme, model LA-30) operating at flow rates of 0.150–4 mL/min. Gas and liquid streams were mixed by a polyether ether ketone (PEEK) Y-junction (inner diameter of 0.5 mm) in order to generate gas–liquid slug flows in the microreactor. The microreactor consists of a tube made from perfluoroalkoxy alkane (PFA) with an internal diameter of 1.6 mm. The total microreactor length was varied between 1.5 to 4 m, in order to obtain residence times between 11.7 to 23.6 s. The gas–liquid flow behavior was visualized and registered by a digital camera (Nikon D3300, equipped

with AF-S 60 mm lens) with a LED backlight (Dolan-Jenner Fiber-Lite Mi-LED A2 illuminator).

In all experiments, samples were taken once a stable gas–liquid slug flow was achieved in the microreactor (i.e., after a minimum of 3 times the residence time). Samples were obtained in duplicate for each evaluated condition. Their average value is reported with an average error within 3%. Oxidized vanillin and lignin samples were directly analyzed by GC-FID and GC–MS. Moreover, MeOH was removed from the oxidized lignin samples by a rotary evaporator (40 °C, 350 mbar, 30 min), and the product was then analyzed by GPC, HPLC, and HSQC NMR (vide infra).

Catalytic Hydrotreatment Experiments. The (ozonated) lignins were hydrotreated in a small batch setup (2 mL); see Figure 2. A T-type particulate filter from Swagelok was used as reactor for the

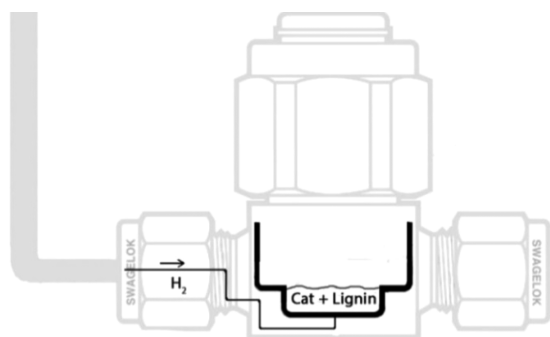


Figure 2. Batch reactor used for the hydrotreatment reaction.

(ozonated) lignin and catalyst. A fluidized sand bed was used for heating the reactor to the desired temperature. The reactor loaded with catalyst [1 g of (ozonated) lignin + 0.05 g of Pd/C] was weighted before hydrogen admission (100 bar at room temperature). After the hydrotreatment, gases were released and the reactor was weighted again to determine the mass balance. The experiments were conducted for 4 h and were performed at two temperatures (350 and 400 °C). The reactor was cooled to room temperature and the organic phase was collected and filtered by a 0.2 μm filter to remove any catalyst particles before analyses.

Liquid Product Analyses. GPC analyses of the feed and products were performed using an Agilent HPLC 1100 system equipped with a refractive index detector. Three columns in series of MIXED type E (length 300 mm, i.d. 7.5 mm) were used. Polystyrene standards were used for calibration. The sample (0.05 g) was dissolved in THF (4 mL) together with 2 drops of toluene as the external reference and filtered (filter pore size 0.45 μm) before injection.

GC×GC-FID analyses were performed on a trace GC×GC system from Interscience equipped with a cryogenic trap and two capillary columns, i.e., an RTX-1701 capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) connected by a Melfit to a Rxi-5Sil MS

column (120 cm × 0.15 mm i.d. and 0.15 μm film thickness) and a flame ionization detector (FID). The injector temperature was set to 280 °C. A dual jet modulator was applied using carbon dioxide to trap the samples after passing through the first column. Helium was used as the carrier gas (flow rate of 0.8 mL/min). The oven temperature was kept for 5 min at 40 °C and then increased to 250 °C at a rate of 3 °C min⁻¹. The pressure was set at 0.7 bar at 40 °C and the modulation time was of 6 s. Quantification of the main functional groups in GC×GC (e.g., aromatics, alkanes, alkylphenolics) was performed by using an average relative response factor (RRF) per component group in relation to an internal standard (di-*n*-butyl ether, DBE). Details are given in ref 7. All samples were diluted around 25 times with THF containing 500 ppm DBE.

Gas chromatography (GC-FID) analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with an RTX-1701 capillary column (60 m × 0.25 mm i.d. and 0.25 μm film thickness). Helium was used as the carrier gas (flow rate of 2 mL/min). The injector and FID temperature were set to 280 °C. For the samples from vanillin experiments, the oven temperature was kept at 60 °C for 5 min and then increased to 250 °C at a rate of 15 °C min⁻¹ and held at 250 °C for 10 min. For the samples from lignin experiments, the oven temperature was kept at 40 °C for 5 min and then increased to 250 °C at a rate of 3 °C min⁻¹ and held at 250 °C for 5 min. All samples were diluted 5 or 10 times with MeOH containing 500 ppm of bicyclohexyl (internal standard). For vanillin quantification, a calibration curve was obtained from solutions of known concentrations and an internal standard (see Figure S4, SI). For ozonated lignin samples, relative response factors of chemical groups were calculated on the basis of calibration curves of representative molecules from each group. This allowed for the concentration estimation of the identified groups of monomers.

Gas chromatography/mass spectrometry (GC–MS) analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with an RTX-1701 capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) and a Quadrupole Hewlett-Packard 6890 MSD selective detector attached. Helium was used as carrier gas (flow rate of 2 mL/min). The injector temperature was set to 280 °C. The oven temperature was kept at 40 °C for 5 min and then increased to 250 °C at a rate of 3 °C min⁻¹ and held at 250 °C for 5 min. All samples were diluted 5 or 10 times with MeOH containing 500 ppm of bicyclohexyl (internal standard).

The HPLC used for carboxylic acids identification and quantification consisted of an Agilent 1200 pump, a Bio-Rad organic acids column Aminex HPX-87H, a Waters 410 differential refractive index detector, and a UV detector. Aqueous sulfuric acid (5 mM) at a flow rate of 0.55 mL/min was used as the mobile phase. The HPLC column was operated at 60 °C. Since the products after ozonation are not fully soluble in water, a water extraction step (proportion of 1:1 of products and water) was performed, and the aqueous phase was further analyzed. Calibration curves of the targeted acids were prepared for accurate quantification and were based on a minimum of four data points with an excellent linear fit (i.e., $R^2 > 0.99$).

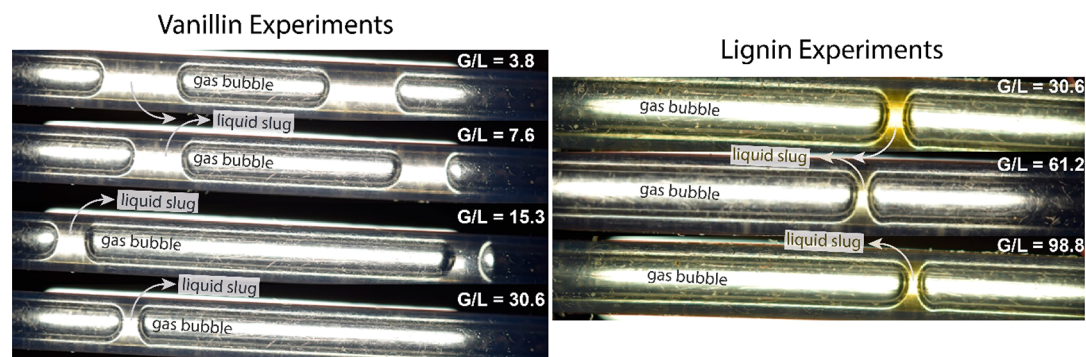


Figure 3. Visual observations of slug flow during the ozonation of vanillin and lignin in the microreactor (perfluoroalkoxyalkane tubing, inner diameter of 1.6 mm).

Heteronuclear single quantum coherence (HSQC) NMR spectra were acquired on a Bruker NMR spectrometer (600 MHz) with the following parameters: 11 ppm sweep width in the F2 domain (^1H), 220 ppm sweep width in the F1 domain (^{13}C), 8 scans, 512 increments, and a total acquisition time of around 1 h. Sample preparation involved the dissolution of 0.05 g of sample in 0.7 g of DMSO- d_6 ; see the Supporting Information for spectra-processing details.

RESULTS AND DISCUSSION

Flow Characteristics in the Microreactor. In the initial phase of experimentation, the flow pattern in the microreactor was investigated to ensure that all experiments were performed in the slug flow regime. This regime, characterized by slugs of liquid alternated with gas bubbles, is known to benefit from high mass and heat transfer rates.⁶² All of the experiments were performed under ambient conditions, first using vanillin and then pyrolytic/organosolv lignins as feedstocks (dissolved in methanol).

The effect of the G/L ratio on the flow pattern was determined by using a constant liquid flow rate (methanol with either vanillin or lignin) and varying the gas inlet flow (ozone with oxygen). The flow patterns were similar for all conditions (i.e., all slug flow); see Figure 3 for examples of photos taken during experiments with vanillin and lignin.

Vanillin Ozonation in a Microreactor. Vanillin was chosen as a representative pyrolytic lignin model compound to evaluate the ozonation performance in the microreactor. Besides validating the process intensification potential in the microreactor setup, the results from vanillin ozonation were also used to obtain a good set of experimental conditions for the subsequent experiments with lignin. Table 1 shows the conditions used for the experiments with vanillin.

Table 1. Experimental Conditions for the Ozonation of Vanillin

| inlet vanillin conc. (ppm) | G/Lratio ^a | ozone/vanillin molar ratio | residence time (s) |
|----------------------------|-----------------------|----------------------------|--------------------|
| 500 | 3.8; 7.6; 15.3; 30.6 | 0.75; 1.5; 3.0; 6.0 | 15.7; 19.7; 23.6 |
| 2500 | 3.8; 7.6; 15.3; 30.6 | 0.15; 0.3; 0.6; 1.2 | 15.7; 19.7; 23.6 |
| 5000 | 3.8; 7.6; 15.3; 30.6 | 0.07; 0.15; 0.3; 0.6 | 15.7; 19.7; 23.6 |

^aOn the basis of inlet flow rates (weight basis).

Figure 4 shows the effect of the different G/L ratios and residence times on the conversion of vanillin (inlet concentration of 500 ppm). Of interest is the observation that the conversion remains constant when increasing the residence time (especially at higher G/L ratios). This is not expected and suggests that insufficient ozone is fed to the microreactor to convert the available vanillin. The same trend was observed for inlet concentrations of 2500 and 5000 ppm (see Figure S6, SI). In addition, higher conversions are achieved with higher G/L ratios at each residence time evaluated. Increasing the G/L ratio leads to larger gas bubbles compared to the liquid slugs (visual observations; see Figure 3), resulting in a higher ozone/vanillin ratio in the reactor. Moreover, the interfacial area is increased, leading to overall higher mass transfer rates, which is beneficial when the reaction in the liquid phase is fast compared to mass transfer of ozone from the gas to liquid phase.^{49,62}

Full conversion of vanillin is not achieved in any of the experiments performed, even at high ozone/vanillin molar ratios, i.e., higher than the stoichiometric coefficient of 2.⁶³ This is likely due to the occurrence of faster secondary reactions involving intermediate products, e.g., ring-opened products from vanillin (muconic acid or related compounds^{64,65}), which lead to ozone depletion before all of the vanillin has been converted. These muconic acid derivatives are known to be very susceptible to further oxidation by ozone due to the presence of unsaturated C–C bonds.⁶⁶ A representative qualitative GC analysis of ozonized vanillin confirms overoxidation, and low molecular weight compounds such as dimethyl oxalate and glyoxylic acid were identified (see Figure S7, SI).

A rough comparison between vanillin ozonation (with an initial vanillin concentration of around 5000 ppm) in a semibatch reactor (previously reported,⁴⁸ 45 wt % conversion after 1.87 min) and in the microreactor setup (53 wt % conversion after 0.26 min; see Figure S6, SI) indeed shows better results for the latter, likely due to improved mass transfer rates of ozone to the liquid phase in the microreactor. The vanillin results show a high reactivity of ozone for low molecular weight model compounds of lignins, as well as the advantages of a microreactor system and ease of operation compared to batch.

Lignin Ozonation in a Microreactor. Following the investigation of vanillin, ozonation experiments with three different lignins (i.e., PL, ethanosolv, and butanosolv) were conducted. PL was chosen for a first evaluation due to its high solubility in methanol, lower MW_{av} and promising results recently reported in a semibatch setup.⁴⁸ Thus, a solution of PL was exposed to ozone in the microreactor, and the products were characterized in detail. PL was diluted in MeOH (2.5 wt %) to facilitate flow operation by lowering the liquid-phase viscosity. Furthermore, MeOH is known to quench reactive radicals, preventing the repolymerization of PL fragments into char.⁶⁷ The low lignin concentration in MeOH was necessary to achieve reasonable ozone/lignin (O/L) weight ratios and thus to allow significant conversion of lignin by ozone, also given the possibility of ozone depletion in the reactor (vide supra). Four microreactor lengths were used (1.5, 2, 2.5, and 3 m), corresponding to four different residence times (11.7, 15.7, 19.7, and 23.6 s). The G/L ratios applied were of 30.6, 61.2, and 98.8, corresponding to O/L weight ratios of 0.04, 0.08, and 0.12, respectively.

All experiments were successfully executed, and stable slug flow operation was achieved for run times up to 120 min. In all experiments, samples were taken (in duplicate) once a stable gas–liquid slug flow was achieved in the microreactor (i.e., after a minimum of 3 times the residence time). The effect of residence times on product composition was determined using GPC and GC analyses. GPC analysis [see Figure 5 and Table S1 (SI)] shows that significant depolymerization already occurs at the shortest residence time (11.7 s), but the extent of depolymerization is constant for longer residence times. Similar to vanillin, ozone depletion may be the main reason.

The effect of residence time and O/L ratio on the amount of monomers after ozonation that can be detected by GC analysis is presented in Figure 6 (a representative chromatogram is shown in Figure S8, SI). The amount of these monomers decreases when increasing the O/L weight ratio, as many of the products are subject to further conversions (e.g., to gas-phase components) or are not identifiable by the FID

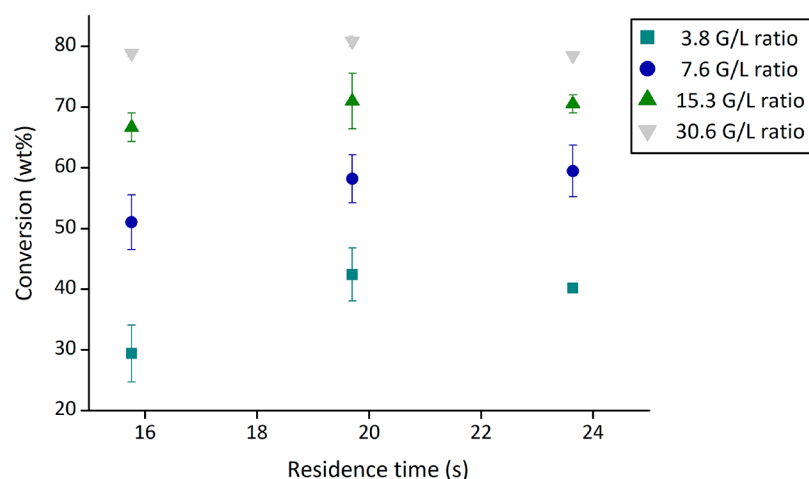


Figure 4. Effect of G/L ratios and residence times on vanillin conversion by ozonation (initial vanillin concentration of 500 ppm).

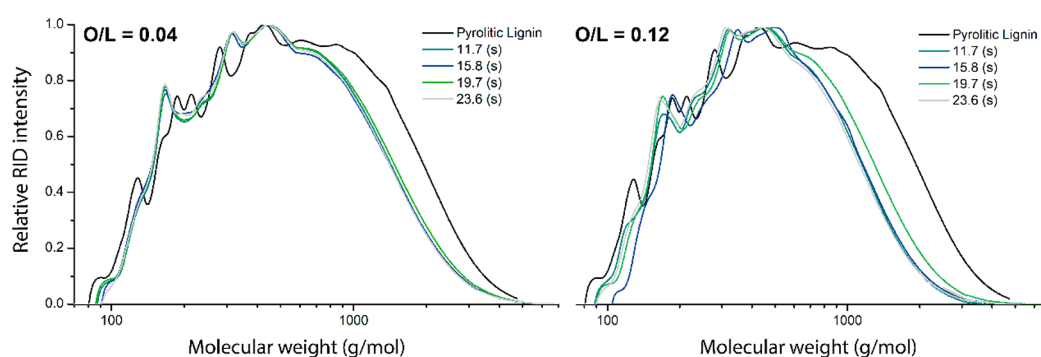


Figure 5. GPC results for PL and its products at different residence times and O/L ratios.

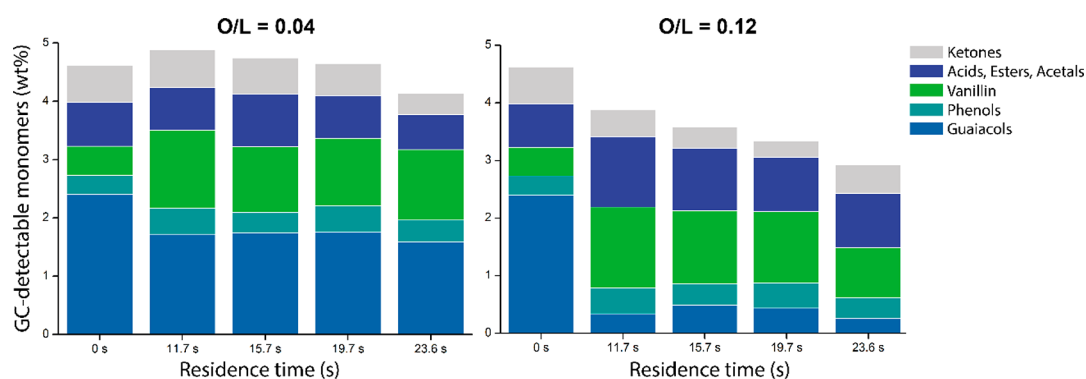


Figure 6. Monomer distribution (GC) of PL and ozonated PL versus residence time and O/L ratio in the microreactor.

detector.⁴⁸ The quantification of the monomers also showed very similar results for all residence times at each O/L ratio applied. From the small fraction of detectable components (<5 wt %), the amount of guaiacols decreased, while vanillin, esters, acids, and acetals increased with ozonation time.

Ozone depletion was further confirmed by an experiment in which the initial concentration of PL in MeOH was lowered from 2.5 to 1 wt %, while the highest G/L ratio and residence times (i.e., 30.6 and 23.6 s, respectively) were applied. Accordingly, the MW_{av} decreased to 470 g/mol, compared to 550 g/mol using the 2.5 wt % PL under the same conditions (see Figure 7), indeed confirming that ozone depletion plays a role.

The experiments with a fixed initial PL concentration (2.5 wt %) and residence time (23.6 s) but increasing O/L ratios

showed a clear color change when increasing the O/L ratio, viz., from dark brown to orange (see Figure 8). In line with that, GPC analyses show a lower molecular weight when the O/L ratio is increased (see Figure 9). For instance, the MW_{av} decreased by 29% with an O/L ratio of 0.12 (see Table S2, SI).

2D-NMR HSQC analyses provided further insights on the structural changes occurring during ozonation (see Figure 10). Most signals in the PL spectrum were identified on the basis of model compounds' spectra and related literature.^{48,68} New methoxy signals (δ_{13C}/δ_{1H} 50–55/3–4 ppm) appeared after ozonation, being related to the formation of dimethyl acetals (the signals of which were also observed in the δ_{13C}/δ_{1H} 90–105/4–5 ppm range) and methyl esters. These compounds were also observed in the GC spectra (vide supra, Figure 6). In addition, the areas related to methoxyphenols (i.e., guaiacols)

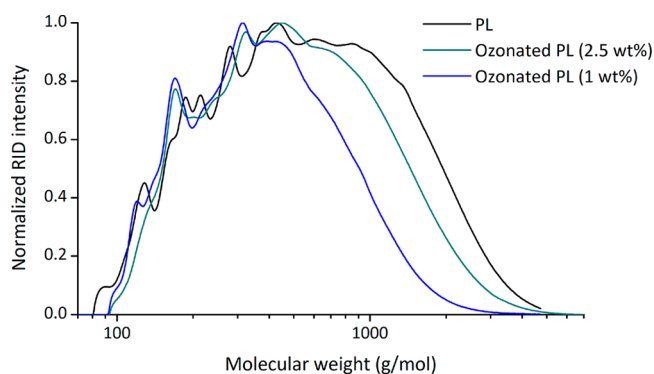


Figure 7. Molecular weight distribution of the products for different initial PL concentrations in the microreactor ($G/L = 30.6$ and residence time of 23.6 s).

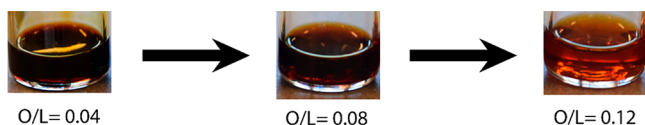


Figure 8. Color change after PL ozonation experiments with increasing O/L ratios.

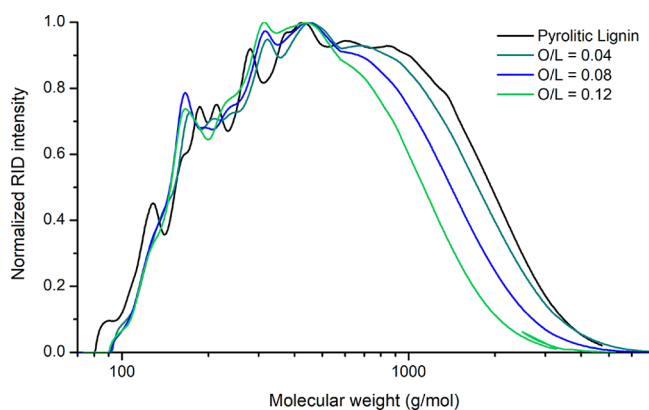


Figure 9. Molecular weight distribution of the products after ozonation versus O/L ratios.

decreased significantly, and signals related to vanillin were identified, also being in line with GC results. Levoglucosan (i.e., a residual sugar present in PL) appears to be resistant to

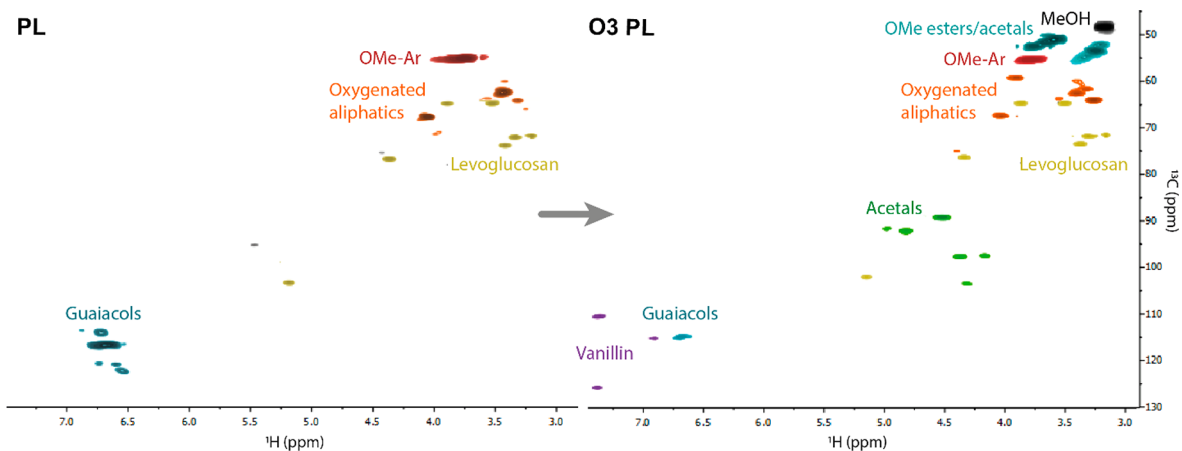


Figure 10. NMR HSQC spectra of PL and ozonated product ($O/L = 0.12$).

ozone attack, and this was also observed in studies of model compounds that we have previously reported.⁴⁸

To overcome GC limitations, HPLC analyses under hydrolysis conditions were performed with the water-soluble fractions of the ozonated lignins. When using these settings, only organic acids and not the corresponding esters were detected. Results show that a range of (di)carboxylic acids/esters were formed during PL ozonation in the microreactor. When applying higher O/L ratios, more (di)acids/esters were formed (see Figure 11), and up to 18.6 wt % of the ozonated oil (at $O/L = 0.12$) consisted of such molecules.

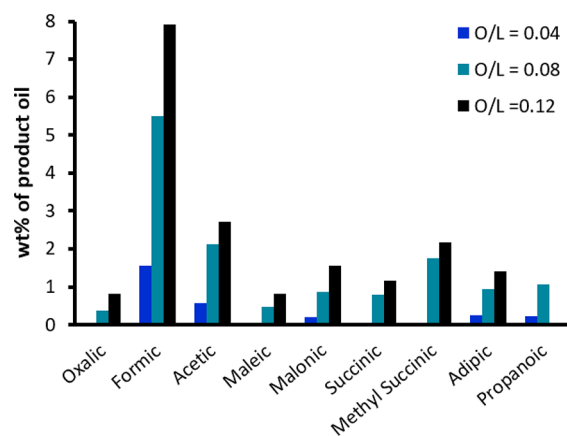


Figure 11. (Di)acids identified in the ozonated products by HPLC under hydrolysis conditions

The structural changes observed are in accordance with the literature. For instance, ozone reacts with phenolic motifs via ring-opening mechanisms, forming unsaturated (di)carboxyl groups (e.g., muconic acid) and the respective esters.^{43,69} As aliphatic C–C unsaturated bonds are easily attacked by ozone,⁷⁰ such primary products are rapidly converted into smaller saturated molecules, such as the ones identified with GC and HPLC analyses (vide supra). Furthermore, the acidic environment and presence of MeOH leads to the formation of methyl esters via esterification reactions.⁴⁸ Figure 12 shows a product overview of the ozonation process.

By using the extent of depolymerization (indicated by the MW_{av} from GPC results) as reference, the ozonation of PL in a microreactor was compared to previous results from our group

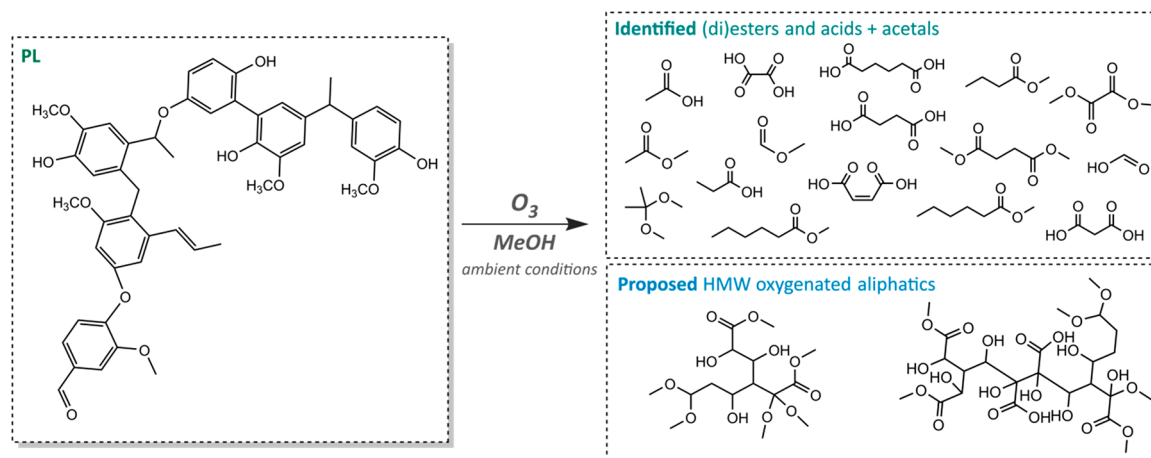


Figure 12. Reaction network for PL ozonation. Adapted from ref 48.

in a semibatch setup.⁴⁸ For instance, the MW_{av} of PL decreased by 29% with an O/L ratio of 0.12 in the microreactor (already at the lowest residence time of 12 s, vide supra). Previous semibatch studies achieved the same depolymerization level with an O/L ratio of 0.3, corresponding to 2 h of reaction time under the conditions applied.⁴⁸ By comparing the two systems, the microreactor is clearly advantageous, by more effectively consuming the ozone present at (much) lower residence times due to an increase in the gas to liquid mass transfer rates of ozone. In addition, the chemoselectivity also differs for both reactor setups (see Figure 13). The lower residence time in the microreactor setup likely suppresses the formation of secondary reaction products like small (di)acids (e.g., oxalic and acetic acid).

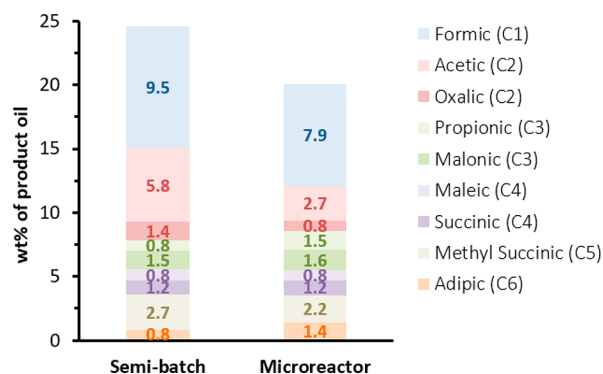


Figure 13. (Di)acids identified (HPLC) for ozonated products in a semibatch reactor⁴⁸ and the continuous microreactor (this work, O/L = 0.12) at similar depolymerization degrees.

Ozonation of Organosolv Lignins in a Microreactor.

To show the versatility of ozonation with respect to the lignin feed, the ozonation of two other lignin types was evaluated as well. These lignins were isolated using typical mild organosolv procedures^{60,61} with ethanol and butanol as solvent and walnut shells as the biomass feed. When compared with PL, in which the structure changed considerably due to the harsh pyrolysis conditions, the structures of these organosolv lignins are closer to native lignin.⁷¹ Because of that, β -O-4, β' -O-4, β - β , and β -5 linkages are present, and their relative ratios can be quantified via 2D-NMR HSQC.⁶⁰ As the organosolvs are more comparable with native lignin, their MW_{av} is higher compared

to that of PL, as well as the amount of C–O bonds (rather than C–C bonds).

Microreactor experiments with organosolv lignins (initial concentration of 2.5 wt %) were conducted at the highest O/L ratio (0.12) and a residence time of 23.6 s in order to minimize ozone depletion. Similar to PL, visual changes in the solutions before/after ozonation were observed (see Figure S11, SI), and the MW_{av} of the ozonated products were substantially lower than the original lignin feed [see Table 2 and Figure S12 (SI)].

Table 2. Average Molecular Weight of Different Lignins before and after Ozonation

| lignin type | MW_{av} | | |
|-------------|------------------|-----------------|--------------|
| | before ozonation | after ozonation | decrease (%) |
| pyrolytic | 786 | 555 | 29 |
| ethanosolv | 2947 | 854 | 71 |
| butanosolv | 4464 | 1426 | 68 |

The MW decrease was much higher than for PL, likely due to the already high extent of depolymerization of PL combined with differences in types of linkages between the aromatic rings. These results clearly show that different lignin types are also depolymerized fast and at ambient conditions by ozone.

The 2D-NMR HSQC analyses before and after ozonation showed similar trends for the organosolv lignins (see Figures S13 and S14, SI). Overall, the aliphatic areas increased, while aromatic units decreased substantially. New methoxy areas (related to acetals and methyl esters) were formed, while the original linkages present within the structure showed a decline. The ethanosolv lignin showed the largest structural change and decrease in aromatics (see Table 3). This might be due to the higher initial MW in the case of butanosolv lignin⁶⁰ and the fact that such (larger) fragments may be more resistant to ozone attack, as they contain lower amounts of reactive phenolic end groups.⁴⁸ In both organosolv lignins, the S-units were shown to be more reactive. The higher reactivity of this motif is expected due to its higher degree of methoxylation, which leads to a higher reactivity toward ozone.^{43,48}

Catalytic Hydrotreatment of (Oxidized) PL. In the previous sections, the high activity of ozone in the depolymerization of lignins is demonstrated. Promising results were achieved under ambient conditions, even with the evidence of ozone depletion in the system, which gives room

Table 3. Aromatic Composition of Organosolv Lignins As Integrated from Their NMR Spectra

| lignin type | before ozonation | | after ozonation | |
|-------------|----------------------|------------------------------------------------------------------------|----------------------|------------------------|
| | aromatic composition | linkages | aromatic composition | aromatics decrease (%) |
| ethanosolv | 62:32:6 S/G/H | 30 β -O-4, 32 β' -O-4, 11 β - β , 4 β -5 | 46:37:17 S/G/H | 83 |
| butanosolv | 67:28:5 S/G/H | 16 β -O-4, 46 β' -O-4, 9 β - β , 4 β -5 | 59:32:9 S/G/H | 45 |

for future optimization studies. The oxidized products are rich in (di)carboxylic acids (DCAs), which are interesting for various applications in the polymer and food industries.^{72,73} Nevertheless, when focusing on hydrocarbons and deoxygenated mixtures as the final product, a second reductive step may be applied to remove oxygen and achieve products with lower oxygen level and even lower molecular weight. Such mixtures could be of interest in applications such as biobased fuels and/or additives, for example.⁴¹ Accordingly, a two-step approach with ozonation as a pretreatment to increase the accessibility of reactants on the lignin structure, decreasing its inherent recalcitrance, followed by a catalytic hydrotreatment may be beneficial to obtain a higher monomer yield consisting of (mainly) hydrocarbons. A solvent-free catalytic hydrotreatment approach was selected as a second step to prove this concept, as extensive literature on lignin depolymerization via such methodology is available.^{5,74,75}

On the basis of previous studies,^{6,76,77} Pd/C was used as the catalyst (5 wt % based on PL intake), and temperatures of 350–400 °C, 100 bar of H₂ pressure, and a reaction time of 4 h were applied. Both the PL feed and oxidized PL (after methanol removal) were used as feed. Due to the small amounts of products generated in the initial ozonation step, hydrotreatment experiments were performed in a small batch setup (1 g of total intake). A drawback of such a small scale was the impossibility of analyzing the gas-phase after the reaction. Moreover, the aqueous phase formed after hydrotreatment could not be quantified accurately, which excludes precise mass balance calculations. It was possible, however, to collect the oil phase after the reaction for further GPC and GC×GC analyses. Table 4 shows the conditions used during

Table 4. Hydrotreatment Conditions and Mass Balances

| expt no. | substrate | hydrotreatment temperature (°C) | reaction time (h) | total mass difference ^a (wt %) |
|----------|--------------|---------------------------------|-------------------|-------------------------------------------|
| 1 | PL–low T | 350 | 4 | 6.0 |
| 2 | PL–high T | 400 | 4 | 6.7 |
| 3 | O3 PL–low T | 350 | 4 | 25.7 |
| 4 | O3 PL–high T | 400/350 ^b | 2/2 ^b | 22.7 |

^aDifference = (reactor + PL + catalyst) before adding hydrogen – (reactor + products + catalyst) after gas release. ^bDue to the pressure limitations of the setup, the temperature had to be decreased.

the hydrotreatment of lignins (“PL”, expts 1 and 2) and ozonated lignins (“O3 PL”, expts 3 and 4), at 350 and 400 °C (“low T”, expts 1 and 3, and “high T”, expts 2 and 4). In the last experiment (i.e., expt 4) the hydrotreatment of ozonated PL at 400 °C reached too high pressures, and the temperature had to be lowered to 350 °C when the reaction time reached 2 h.

The experiments with ozonated PL (i.e., expts 3 and 4) resulted in extensive gas-phase formation during hydrotreatment, as is evident from the large mass loss. A possible explanation is the presence of methoxy groups in the ozonated sample (in the form of acetals and esters), which may be

converted to methane during hydrotreatment.^{6,7} Furthermore, the presence of carbonyl groups (such as in acids and esters) in the ozonated feeds can lead to the formation of significant amounts of CO and CO₂ during hydrotreatment.

GPC analyses of the product oils provided insights on the degree of PL depolymerization (see Figure 14). It is clear that

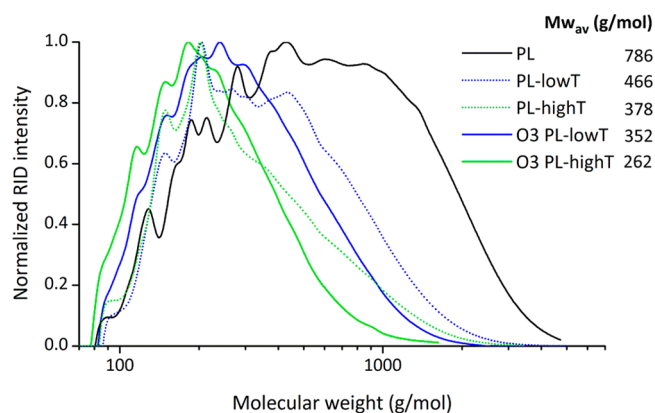


Figure 14. MW distributions of PL and its hydrotreated products (with and without the ozone pretreatment).

the ozone pretreatment has a strong influence on the MW distribution. In addition, the reaction temperature also plays an important role in MW reduction, as hydrocracking rates are intensified at higher temperatures.⁶ In comparison with the PL hydrotreated without prior ozonation, the MW_{av} of the product oils obtained from the ozonated samples is substantially lower (i.e., 25% and 30% lower at 350 and 400 °C, respectively). These results confirm the potential of ozonation as a simple pretreatment to enhance lignin depolymerization.

The monomer yields were detected by GC×GC-FID^{6,7} (see Figure 15). The highest amounts of monomers were obtained when using the ozonated PL samples and conducting the

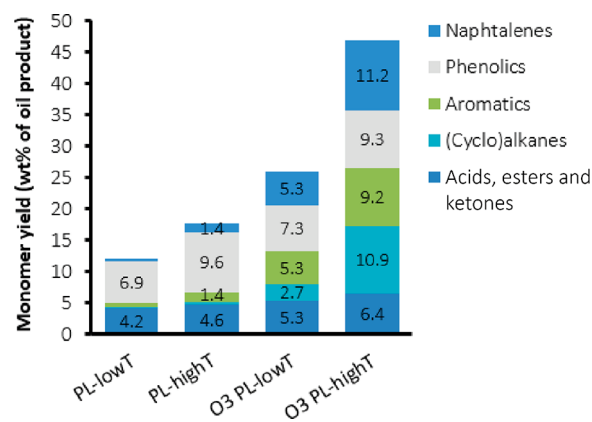


Figure 15. Monomer yields as identified and quantified by GC×GC-FID

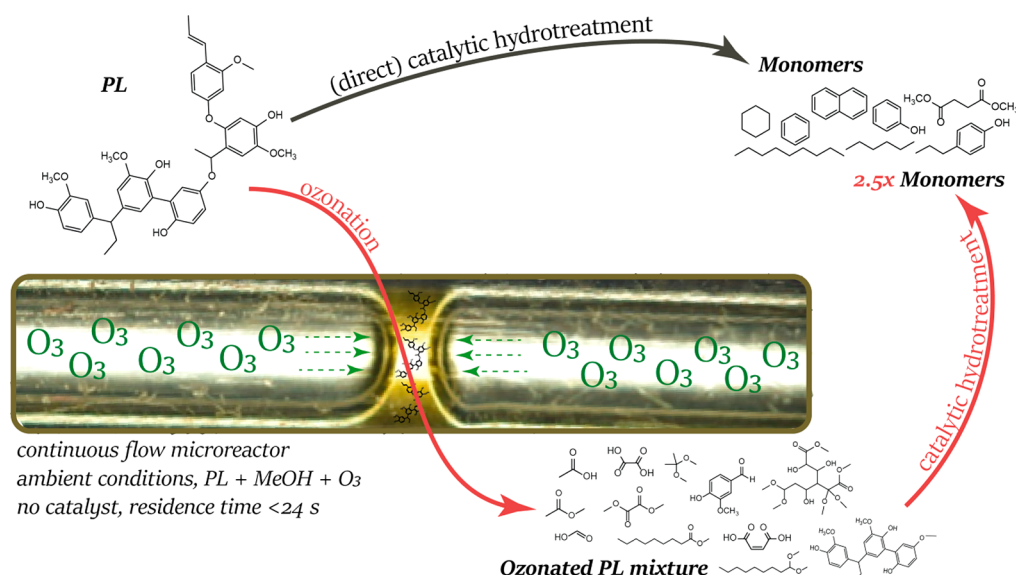


Figure 16. Graphical representation of the combined oxidative–reductive system for PL depolymerization.

experiment at the highest temperature selected in the range, yielding an oil that contained an impressive 47 wt % of monomers. This was more than double that in the experiments with untreated PL (for both low and high temperatures). The identified monomers are mainly comprised of aromatics and phenolics. As such, we can conclude that ozonation can indeed serve as a pretreatment, making the structure more accessible to further processing and ultimately favoring the formation of monomers in a subsequent catalytic hydrotreatment. Further investigations at a larger scale are recommended to determine mass balance closures and to quantify the monomer yields based on lignin intake.

A graphical representation of the two steps is provided in Figure 16. For instance, the direct hydrotreatment of PL yields a range of monomers with different chemical functionalities [e.g., phenolics, aromatics, and (cyclo)alkanes], as well as oligomers not identifiable by GC×GC-FID.^{6,7} By performing the ozonation of PL under ambient conditions in a microreactor, aliphatic polar compounds [e.g., (di)acids, (di)esters and acetals], oxidized aromatics, and lignin fragments with a higher accessibility for further processing are formed. The hydrotreatment of such a mixture leads to a substantial increase in the final monomeric fraction of the product oil, with large amounts of aromatics, naphthalenes, and phenolics.

CONCLUSIONS

A novel methodology for the highly efficient and mild depolymerization of lignin is proposed involving the use of ozone in a continuous flow microreactor. The system is easily operated under ambient conditions without the need of catalysts. The ozonation of vanillin (i.e., a representative lignin model compound) and three different lignins (pyrolytic, butanosolv, and ethanosolv) in methanol showed an overall high reactivity of the feeds upon ozone exposure. Ozonation leads to rapid depolymerization (seconds time scale) of the recalcitrant and often condensed lignin structures (MW_{av} decrease of 29% for PL and 70% for organosolv lignins), generating a range of (di)carboxylic acids and esters (up to 19 wt % for PL) and acetals via oxidative ring-opening, esterification, and acetal formation pathways. Additional

studies regarding a two-step approach involving initial ozonation followed by a subsequent catalytic hydrotreatment resulted in (25–30%) higher levels of PL depolymerization and higher amounts of identified monomers in the product oil (2.5-fold increase) compared to hydrotreatment experiments without prior ozonation of the lignin. The results here presented are promising and show that there is great potential for future research in the use of ozone and optimized microreactor and multistep systems, aiming for high yields of valuable monomers from lignins. The use of microreactor technology has several advantages compared to stirred-tank reactors, such as safer handling of ozone (lower inventories in the reactor), faster removal of the heat generated by the exothermic reactions with ozone (due to high heat transfer coefficients and larger surface to volume ratios), and ease of upscaling by numbering-up.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b04020.

Detailed procedures regarding the microreactor setup and analytical methods, as well as results of additional analyses of the ozonated oils (PDF)

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Notes

The authors declare no competing financial interest.

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