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Oxidative fractionation of biomass to produce phenolic monomers and processable carbohydrate pulp†

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A lignin-first biorefinery based on oxidative fractionation of lignocellulose is presented for the first time. Red oak was successfully delignified through alkaline oxidation yielding carbohydrate pulp and phenolic monomer-rich lignin oil. Process conditions for optimizing phenolic monomer yield, glucan retention in the pulp, and delignification were explored. The effect of temperature, oxygen partial pressure, time, catalyst, and sodium hydroxide concentration were assessed using a response surface statistical method. Two different operating windows were proposed to get the optimum results. Temperature and time were the most significant explanatory variables for all the response models. The presence of $CuSO_4$ catalyst was of slight significance in the production of monomers if reaction time was short. Under optimum reaction conditions, the lignin oil consisted of around 40% phenolic monomers (mainly syringaldehyde and vanillin). The structural features of the lignin oil were further analyzed by GC/MS, GPC, and 2D HSQC NMR techniques. The isolated carbohydrate pulp retained approximately 97 wt% of the cellulose under optimum reaction conditions. Powder X-ray diffraction of the isolated carbohydrate pulp showed that the cellulose was of crystalline structure, indicating its potential for paper production. Enzymatic hydrolysis of the carbohydrate pulp converted 85% of the cellulose to glucose within 120 h, illustrating the potential of cellulosic ethanol production *via* this lignin-first strategy.

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Introduction

Growing concern over global climate change and societal dependence on fossil fuels have increased interest in biorefining to produce fuels, chemicals, and materials. Lignocellulose, as a sustainable and highly abundant resource, is a promising feedstock for biorefining. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin. Numerous approaches to lignocellulosic biomass processing have been developed with the goal of efficiently utilizing all components of the biomass.[1]

Many biorefinery approaches focus on conversion of lignocellulosic biomass to specific chemical products rather than converting the whole plant to bio-oil, which contains hundreds of different compounds. These approaches encourage fractionation of lignocellulose to its various components to reduce the complexity of downstream processing. The primary focus of most of these biorefineries is harvesting valuable products from carbohydrates, with lignin a subordinate constituent that is often treated as a by-product. This typically involves removing lignin from lignocellulose in the first stages of fractionation to facilitate carbohydrate recovery.[2,3] Current delignification methods employ harsh reaction conditions to efficiently remove lignin. Under severe reaction conditions, lignin undergoes irreversible condensation reactions, producing recalcitrant lignin known as technical lignin.[4] Technical lignin is used in low-value applications such as boiler fuels for heat and power generation.

Lignin is the only component of biomass that consists of aromatic structures, making it an attractive feedstock for production of aromatic compounds.[5] Second-generation biorefineries are expected to increase the supply of extracted lignin.[6–8] Technoeconomic and life cycle analysis of lignocellulosic biorefineries show that their economic viability and environmental sustainability will require lignin utilization.[6] Unfortunately, due to the highly condensed structure of conventional biorefinery lignins (*e.g.*, soda, kraft, sulfite), depolymerization of lignin to valuable chemicals and fuels is hampered.[4] To retain the intrinsic values of native lignin, biorefineries will have to implement alternative methods to protect the native structure of lignin. Innovative depolymerization methods such as ammonia-based

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fractionation,[9] γ-valerolactone-assisted hydrolysis,[10] and mild organosolv techniques[11] can substantially retain the native structure of lignin. In these methods, mild reaction conditions preserve lignin ether bonds, decreasing the extent of subsequent condensation reactions to less useful products. However, this can also result in low yields of isolated lignin. Harsher reaction conditions are required to increase the extent of delignification. Thus, there is a dichotomy between delignification yield and lignin product value.[4]

Unlike lignin, cellulose is less prone to depolymerization because of its crystalline structure. Therefore, it can be more easily recovered in later steps of the biorefinery. As a result, a "lignin-first" strategy has emerged for biorefineries in which the biomass is first processed to remove valuable lignin-derived molecules while carbohydrate remains in the biomass for later stages of processing.

Reductive catalytic fractionation (RCF) is a well-known lignin-first strategy. Lignin is thermally depolymerized in a solvent with reactive intermediate products immediately converted into stable phenolic monomers.[12,13] Formaldehyde-assisted fractionation is another lignin-first strategy introduced by Luterbacher *et al.*[14] to preserve the native structure of lignin during the acid-catalyzed delignification. Formaldehyde forms stable acetals with lignin reactive side-chains, which prevents lignin depolymerization and subsequent condensation reactions.

Most RCF methods use external hydrogen or hydrogen donor molecules to stabilize deconstruction products, which is a relatively expensive approach to recovering stable products.[5] Moreover, separating the heterogeneous catalyst used in the process from carbohydrates is challenging. Van den Bosch *et al.*[15] recommended using catalyst pellets in a basket to make catalyst separation easier. However, physical solid–solid contact between catalyst and reactants is problematic.[16,17]

Lignin isolation and depolymerization *via* oxidation is an intriguing alternative to reductive approaches to recovering lignin from biomass and producing processable carbohydrate pulp. Lignin oxidation produces a range of functionalized aromatic chemicals including carboxylic acids and aldehydes with significant economic value. Lignin oxidation has been performed under acidic and alkaline reaction conditions. Acidic solutions such as concentrated acetic acid,[18] organic solvents,[19] and inorganic acids[20,21] have been successfully used to depolymerize technical lignin such as kraft and organosolv to valuable chemicals like vanillin, methyl vanillate, vanillic acid, and syringaldehyde. Alkaline oxidation of lignin using molecular oxygen can selectively produce valuable chemicals such as vanillin and syringaldehyde in high yields. The vast majority of studies on alkaline lignin oxidation focus on technical lignin. Lignosulfonates,[22–24] kraft lignin,[25,26] and steam explosion lignin are among the most studied condensed lignin substrates. Phenolic monomer yields from these processes are generally low, ranging from 1.5 wt% to around 20 wt%.[24]

Although one-step oxidation of biomass to phenolic monomers and cellulose is an intriguing approach from both economic and environmental standpoints, it has received less attention. Processing the lignin portion of biomass into aromatic aldehydes while preserving carbohydrates under alkaline oxidation conditions is challenging since there is a trade-off between delignification and carbohydrate retention in the pulp.[27] Traditional oxidation of biomass is performed in nitrobenzene[28] under strongly alkaline conditions and high temperatures with reaction times of 2–4 hours. Such harsh reaction conditions achieve complete conversion and solubilization of the biomass. More recently, Tarabanko *et al.*[29] studied the alkaline oxidation of pine wood. They obtained around 18 wt% phenolic monomer yield at 160 °C in the presence of 1 M NaOH at 0.3 MPa oxygen after 25 min. The cellulose yield of the remaining solid was modest (63.9% of the initial wood's cellulose), which is either related to the reaction condition or the very long heating and cooling time of the reactor (heating time: 20–53 min; cooling time: 50–105 min). Beckham *et al.*[30] studied the alkaline oxidation of native poplar with the goal of increasing phenolic monomer yield. They obtained around 30 wt% phenolic monomer yield (including about 7 wt% non-oxidative products such as *p*-coumaric acid) in 2 M NaOH at 175 °C and 5 bar oxygen with 10 mg $LaMn_{0.8}Cu_{0.2}O_3$ catalyst after 30 min. Although phenolic monomer yield was relatively high, other aspects such as carbohydrate retention in the pulp, delignification, and further processing opportunities of the solid pulp were not described.

This paper explores an approach to oxidative fractionation of lignocellulose that selectively converts lignin to valuable chemicals while achieving efficient delignification and high glucan retention in the remaining pulp. In this study, $CuSO_4$ was used as a catalyst. Compared to other copper complexes, $CuSO_4$ is an excellent choice of catalyst form due to its good solubility in water, allowing water to be used as a reaction solvent.[31] Additionally, $CuSO_4$ can be separated from low molecular weight products and reused through simple extraction after the depolymerization reaction.[31] A schematic diagram of the proposed lignin-first biorefinery is illustrated in Fig. 1. This study is a comprehensive investigation of reaction conditions affecting yields of desired products. A central composite response surface statistical model was used to evaluate selected explanatory variables and find the optimum reaction conditions.

Materials and methods

Chemicals and materials

Pyridine (anhydrous, 99%), pyridine-d_5 (99.5 atom% D), dimethyl sulfoxide-d_6 (99.5 atom% D) *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% TMCS, vanillin (99%), syringaldehyde (+98%), vanillic acid (+97%), syringic acid (+95%), syringol (+99%), benzyl phenyl ether (98%), T. Reesei ATCC 26921 cellulase enzymes, and sodium citrate dihydrate were purchased from Sigma-Aldrich. Sodium hydroxide pellets (+98%), copper(II) sulfate pentahydrate (+>98%), hydrochloric acid solution 6N, acetone (+99%), tetrahydrofuran (HPLC

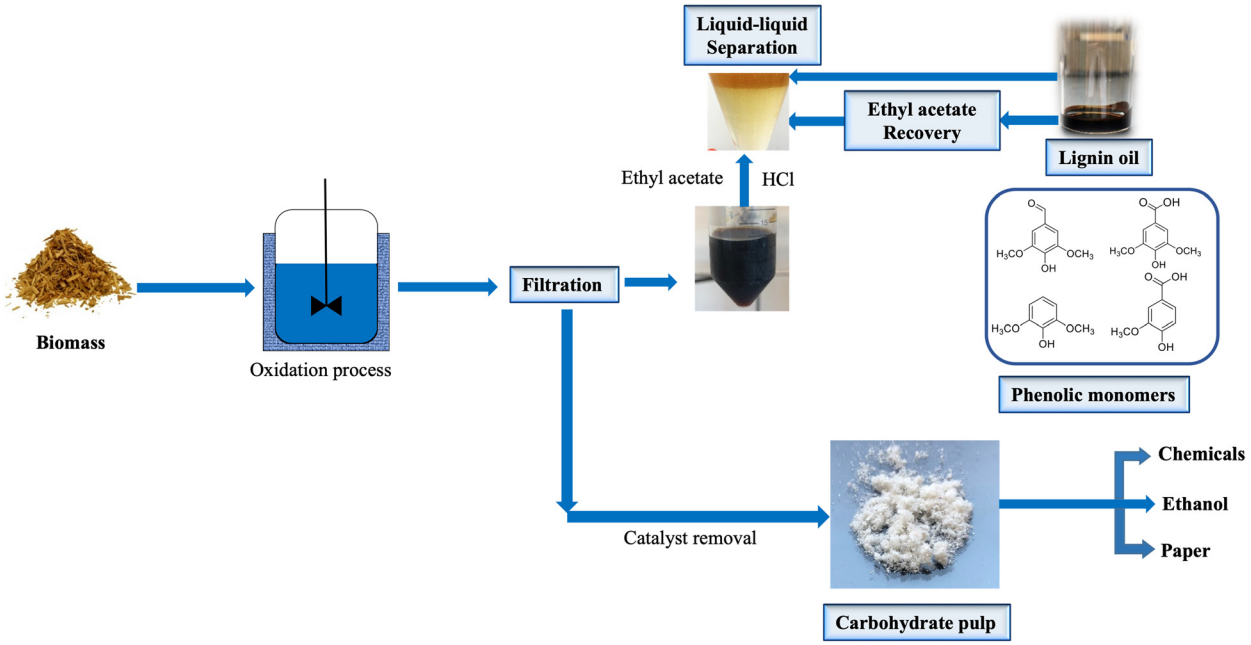

Fig. 1 Schematic diagram of the proposed integrated biorefinery process.

grade), ethyl acetate (+99%), dextrose (D-glucose) anhydrous, and ampicillin were purchased from Fischer Scientific. Sulfuric acid 72% w/w aqueous solution was purchased from Alfa Aesar. D(+)-Xylose (+99%) was purchased from Acros Organics. Citirc acid monohydrate was purchased from Research Product International. Red oak wood with a particle size of less than 300 μm was obtained from Iowa State University's BioCentury Research Farm (BCRF). The total lignin content of the extractive-free red oak was 27 wt%.

Oxidation experiments

Alkaline oxidation of biomass was performed in a 12 ml reactor made of 316 stainless steel tubing (i.d. 0.75″) and Swagelok fittings. The reactor was connected to an oxygen tank by 1/8″ tubing and a pressure relief valve. Extractive-free red oak (130 mg), copper sulphate ($CuSO_4$) catalyst, and NaOH aqueous solution (8 ml) were added to the reactor. The reactor was sealed, and the contents were stirred at 750 rpm using a magnetic stir bar. Next, the reactor was purged with nitrogen five times and then pressurized with oxygen to the desired partial pressure followed by addition of nitrogen gas to achieve a total pressure of 300 psi. The reactor was submerged in a preheated Thermo-Scientific silicon-oil bath. At the end of the desired reaction time, the reactor was removed from the oil bath and quenched in cold water. The timer was started once the temperature reached the target temperature for each experiment.

The solid residue was separated from the liquid product by centrifuge (AccuSpin1, Fisher Scientific). The liquid was then neutralized with concentrated HCl to pH < 2 and extracted with ethyl acetate (3 × 5 ml). A rotovap was used to remove ethyl acetate. The recovered lignin oil was collected for analysis. The solid residue was mixed with DI water and acidified with concentrated HCl to dissolve the catalyst. The solid residue was washed with fresh DI water and dried at 105 ± 3 °C until a constant weight was achieved. Although not performed in this study, the $CuSO_4$ catalyst could be recovered through acidification with sulfuric acid and precipitation.

The compositional analysis of biomass (red oak) and the solid residues obtained after the reaction was carried out using the NREL procedure which is briefly described in the ESI.†

Design of experiment and statistical modelling

Response surface methodology was used to evaluate the optimum reaction conditions. A central composite design with uniform precision was used as a statistical model to assess explanatory variables of interest in this process. Central composite design always considers several axial points that allow estimation of curvature. If the distance from the center of the design space to a cube point is ±1 unit from each explanatory variable, the distance from the center of the design to the axial points is $|\alpha| > 1$. Five explanatory variables were selected for this study. The inscribed central composite design space is depicted in Fig. 2. Preliminary experiments helped to select the range for each explanatory variable. The combination of explanatory variable and levels for this process are shown in Table 1, which includes 18 cube points, 8 factorial points, and 6 center points to determine the system variability.

The influence of each explanatory variable on phenolic monomer yield, delignification, and glucan retention in the pulp was evaluated with the goal of maximizing these response variables. Although delignification is expected to be

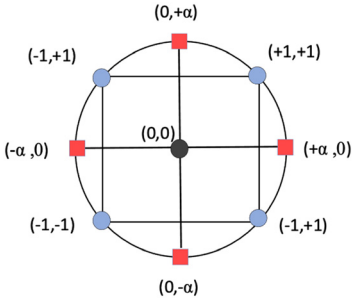

Fig. 2 Inscribed central composite design space. Levels are coded as follows: 0 for center points, −1/+1 for cube points, and $-\alpha$, $+\alpha$ for axial points.

Table 1 Factor-level combinations for central composite design of experiments (red oak weight was constant for all experiment = 130 mg)

Explanatory variable	$-\alpha$	−1	0	$+\alpha$	+1
Temperature (°C)	120	145	170	195	220
Time (min)	4	18	32	46	60
O_2 pressure (psi)	40	80	120	160	200
NaOH (M)	0.5	0.87	1.25	1.62	1.94
Catalyst (wt%)	0	9.6	19.2	28.8	38.5

maximized when phenolic monomer yield is maximized, it was included in the model as a response variable.

JMP 15 Pro was used for data analysis and regression fitting. Response variables were fitted with a regression curve including quadratic terms, linear terms, interaction terms and an intercept. Although the full model with all the combinations showed a good fit with the data, a reduced model was applied to remove some insignificant terms (p-value >0.3) to improve R^2 and adjusted R^2. Residuals *versus* actual data plots and residual *versus* predicted plots showed random scatter (Fig. S1–S6†). The experiment at 220 °C (α, 0, 0, 0, 0) did not produce enough solid residue to do the compositional analysis on it, so it was ultimately removed from the model.

Analytical methods

Prior to GC analysis, lignin oil was derivatized *via* silylation to improve the volatility of products like syringic acid and vanillic acid. Ten milligrams of lignin oil were dissolved in 500 µl pyridine in a small reaction vial to which 100 µl BSTFA (with 1% TMCS) was added. The vial was well mixed, capped tightly, and heated to 60 °C for 15 min. After that, an internal standard was added to the sample and it was then filtered and transferred to a GC vial. A gas chromatograph with mass spectrometer and flame ionization detector (Agilent 7890A GC-MS/FID) was used to analyze samples. The GC was equipped with two identical Agilent J&W capillary columns for the separation of the products. One of the columns was connected to the FID, while the other was connected to the MS. The GC oven temperature was ramped from 35 °C to 280 °C at a heating rate of 5 °C min^{-1}. FID back detector and the injection port in the GC were both held constant at 280 °C. Response factors of the compounds were obtained by calibration with commercial standards. Yields were calculated by the following equation:

$$\text{Yield} = \frac{\text{mass of product}}{\text{mass of lignin in substrate}} \times 100\ \text{wt\%} \quad (1)$$

The HPLC system used for sugar analysis was a Dionex Ultimate 3000 LC system (Sunnyvale, CA, USA) with a quaternary analytical pump and a Shodex refractive index (RI) detector (New York, NY, USA). The analytical columns used were a 300 mm × 7.7 mm i.d, 8 µm, HyperRez XP Carbohydrate (Thermo Fisher Scientific). The guard column was a Carbohydrate H+ cartridge with a guard holder (Thermo Fisher Scientific). The guard columns were used to eliminate possible interferences caused by anions and cations. The instrument parameters were as follows: The mobile phase was ultrapure 18.2 MΩ deionized water with a flow rate of 0.2 mL min^{-1}, and the column temperature was set at 55 °C. See the supplementary information for details on sugar analysis.

GPC analysis was performed to assess the molecular weight distribution of lignin oil. Ten milligrams of lignin oil were dissolved in 5 ml tetrahydrofuran and filtered with a glass microfiber syringe filter (0.45 µm) before transferring to the GPC vial. GPC analysis was performed using a Dionex Ultimate 3000 (Sunnyvale, CA) HPLC system, equipped with a Shodex refractive index (RI). Two Agilent columns, PLgel 3 µm 100 Å 300 × 7.5 mm (p/n PL1110-6320) and one Mesopore 300 × 7.5 mm (p/n PL1113-6325) column were used. Tetrahydrofuran was used as an eluent, and the instrument was calibrated from 162–45 120 g mol^{-1}. The software used to control the instrument and evaluate the samples was Dionex Chromeleon version 6.8.

NMR analysis was performed with a Bruker Biospin NEO 400 MHz spectrometers equipped with liquid-nitrogen cooled 5 mm Prodigy Probe with typical geometry (broadband coil closest to the sample). Bruker's Topspin 3.5 software was used to process spectra. The central solvent peak was used as the internal reference (δ_H/δ_C: DMSO-d_6, 2.49/39.50). For the HSQC NMR experiment, 20 mg lignin oil was dissolved in a 500 mL solution of DMSO-d_6 and pyridine-d_5 (4 : 1, v/v). The Bruker standard pulse sequence 'hsqcedetgpsisp2.2' was used with the following parameters: 12 ppm sweep width in F2 (1H), centered at 5.5 ppm, acquiring 3366 data points, 220 ppm sweep width centered at 105 ppm in F1 (13C) acquiring 620 increments, 20 scans per increment, a 1.0 s relaxation delay, and with the evolution time set for a 1-bond 1H–13C coupling constant of 145 Hz, with a total acquisition time of ~5 h. Peak assignment was performed according to the literature.[32]

Enzymatic hydrolysis of the cellulose product was performed according to the NREL LAP Low Solids Enzymatic Saccharification of Lignocellulosic Biomass, with only slight modification.[33] Cellulase enzymes from T. Reesei ATCC 26921

Table 2 Summary of RSM fit and ANOVA statistics for the response variables (phenolic monomer yield, glucan retention, and delignification)

	Summary of fit			ANOVA		
Response	Mean	RSME	R squared	p-Value	F-Ratio	Significant
Phenolic monomer yield	23.86	4.6	0.86	0.0012	5.55	YES
Glucan retention	84.99	6.23	0.82	0.0027	4.59	YES
Delignification	89.2	3.53	0.98	<0.001	39.04	YES

(Sigma-Aldrich) with cellulase activity of 210 FPU mL^{-1} based on the NREL standard cellulase activity assay for filter paper units were used for enzymatic hydrolysis.[34] In short, biomass loadings were set at 1% (w/v) in 0.1 M sodium citrate buffer (pH 4.8) supplemented with 0.1 mg L^{-1} ampicillin to further minimize bacterial fermentation. Enzyme loading was kept at 30 FPU g^{-1} biomas.[35] Incubation and hydrolysis were performed in an Innova 4000 Incubator Shaker (New Brunswick Scientific) set at 50 °C and 200 RPM for 5 days. Samples for glucose analysis were taken approximately every 24 hours, with subsequent centrifugation, filtration, and preservation at −20 °C prior to analysis. Glucose analysis was performed using the Thermo Fisher Scientific/Dionex Ultimate 3000 HPLC. Further details on this method can be found in a previous study.[33]

Results and discussion

Effect of explanatory variables on response variables

The results of all 32 tests used in the Response Surface Methodology (RSM) and Analysis of Variance (ANOVA) are reported in the ESI† (Table S1). A summary of the RSM fit and ANOVA statistics are summarized in Table 2. All responses showed a good fit with the data, and the models were significant at the 95% confidence interval.

As shown in Fig. 3, reaction temperature was a significant factor for all of the response variables when all other explanatory variables were at the center point (time: 32 min, O_2 pressure: 120 psi, catalyst present: 19 wt%, NaOH: 1.25 M). Phenolic monomer yield, glucan retention, and delignification all showed quadratic relationships with temperature. The optimum temperature for maximum phenolic monomer yield, glucan retention, and delignification were 175 °C, 140 °C, and 200 °C, respectively. It is not surprising that glucan retention reached its maximum at lower temperatures: alkaline oxidation at high temperatures readily decomposes carbohydrate when other explanatory variables are not optimized.

Reaction time was the second most important explanatory variable for all the response variables. The univariate effect of time on all response variables is depicted in Fig. 4. While phenolic monomer yield and delignification showed quadratic relations with time, glucan retention had a negative linear correlation. A shorter reaction time preserved more cellulose which is consistent with the alkaline pulping process.[36] When wood chips are exposed to high temperature and alkaline conditions, a shorter reaction time can produce stronger pulp.[36] Phenolic monomer yield and delignification reached their maximum extent at around 33 min and 43 min, respectively, when other explanatory variables were kept constant at their center point (temperature: 170 °C, O_2 pressure: 120 psi, catalyst: 19 wt%, NaOH: 1.25 M).

The interaction effect between reaction time and temperature was a significant explanatory variable for all three response variables, which shows the importance of decreasing the reaction time as reaction temperature increases. As shown in Fig. 5, at 120 °C the no monomers were produced for the first 20 min of reaction before increasing to its maximum yield at about 45 min. At 150 °C and 170 °C, monomers yield reached maximum yield after 32 min and 23 min, respectively, indicating the need for longer reaction times as temperature decreases. The decrease in

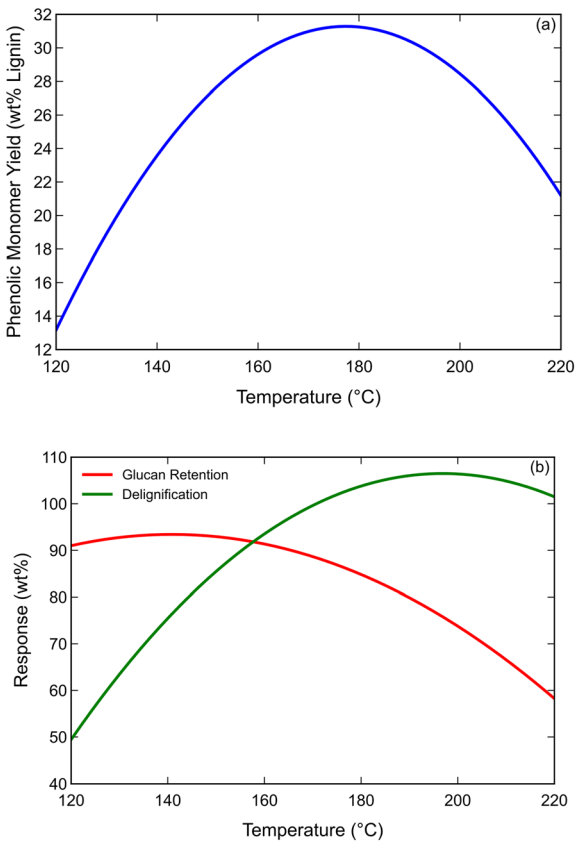

Fig. 3 Modelled univariate effect of reaction temperature on (a) phenolic monomer yield (b) glucan retention and delignification where other explanatory variables were constant at their center points (time: 32 min, O_2 pressure: 120 psi, catalyst: 19 wt%, NaOH: 1.25 M). Glucan retention is calculated based on the initial cellulose content of the biomass.

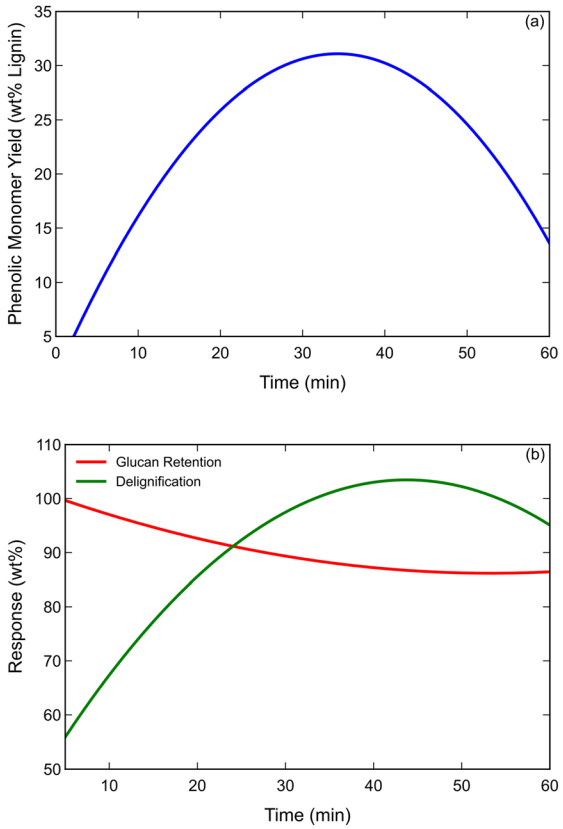

Fig. 4 Modelled univariate effect of reaction time on (a) phenolic monomer yield (b) glucan retention and delignification, where other explanatory variables were kept constant at their center points (temperature: 170 °C, O_2 pressure: 120 psi, catalyst: 19 wt%, NaOH: 1.25 M). Glucan retention is calculated based on the initial cellulose content of the biomass.

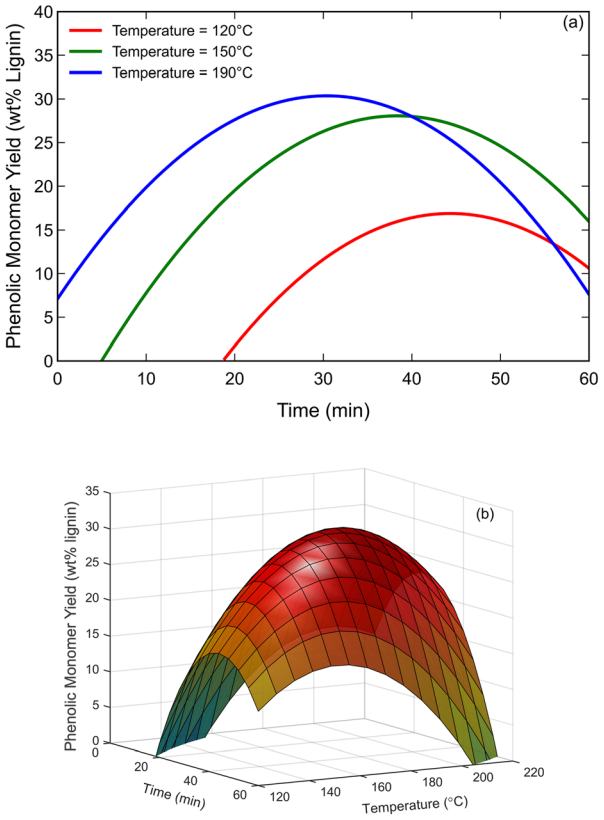

Fig. 5 (a) The interaction effect of temperature and time on phenolic monomer yield for three randomly selected temperatures. (b) Response surface plot for phenolic monomer yield showing the effect of time and temperature over the entire range of this study. Regression models were generated while other explanatory variables were constant at their center point (O_2 pressure: 120 psi, catalyst: 19 wt%, NaOH: 1.25 M).

phenolic monomer yield with longer reaction times is probably the result of monomers being oxidized to CO_2, H_2O, and CO.[5]

Fig. 6 illustrates the interaction of reaction time and temperature on glucan retention while other explanatory variables were kept constant at their center point. As shown in Fig. 6a, there is a negative correlation with time for all three temperatures, which means longer reaction times solubilize more carbohydrate. At 120 °C, glucan retention was still around 100 wt% after 15 min, but it was around 95 wt% and 60 wt% at 170 °C and 220 °C, respectively. As shown in the response surface plot (Fig. 6b), the same negative correlation was observed for all the other temperatures in the studied range.

Oxygen pressure was only statistically significant for phenolic monomer yield and glucan retention, but this term was included in all models in order to improve the overall fit with the data. The univariate model of the oxygen pressure on each response is shown in Fig. 7. Both phenolic monomer yield and glucan retention showed a negative linear correlation with oxygen pressure.

Increasing the oxygen pressure accelerates both product formation and degradation. It has been shown that oxidation products can experience deeper oxidation to light gases including H_2O, CO_2, and CO under oxidative conditions depending on the reaction conditions.[5] Increasing oxygen concentration under alkaline reaction conditions could also destroy cellulose if other reaction conditions are not optimized. According to these data, it seems like oxygen has a negative effect on the response, but it is probably because of the high oxygen pressure range explored in this study.

Catalysts are thought to facilitate lignin oxidation by electron abstraction of the phenolate group to phenoxy radicals.[37,38] Metal salts or metal oxides and noble metal catalysts are often used for the alkaline oxidation of lignin. Some studies show that catalyst accelerates product formation and increases the phenolic monomer yield,[39,40] while other studies do not report any increase in the phenolic monomer yield.[41] This inconsistency could be related to various reaction conditions applied in the alkaline oxidation process. In this study, $CuSO_4$, the most common and one of the most effective catalyst for alkaline oxidation of lignin, was studied over a wide range of temperature, time, oxygen pressure, and NaOH concentration. As shown in Fig. 8, the catalyst was not a very significant explanatory variable for any

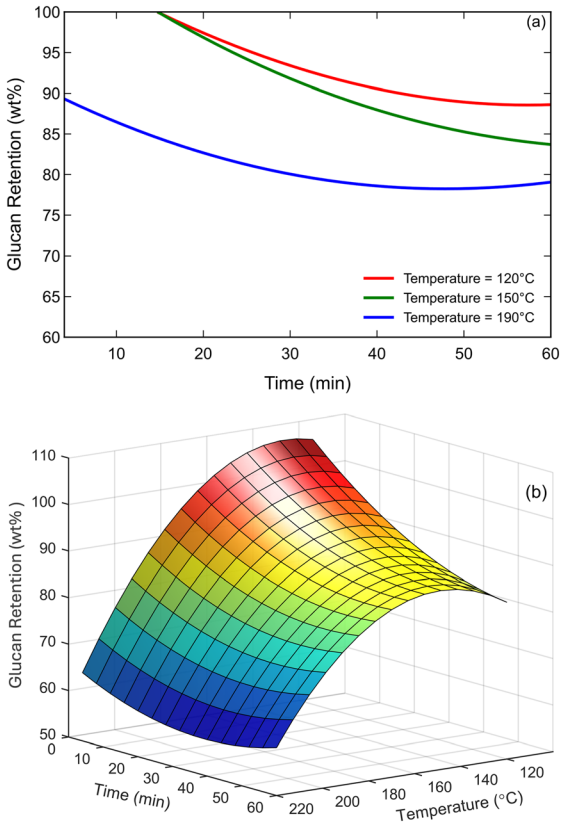

Fig. 6 (a) The interaction effect of temperature and time on glucan retention for three randomly selected temperatures. (b) The response surface plot of glucan retention showing the effect of time and temperature over the entire range of this study. Regression models were generated while other explanatory variables were constant at their center point (O_2 pressure: 120 psi, catalyst: 19 wt%, NaOH: 1.25 M).

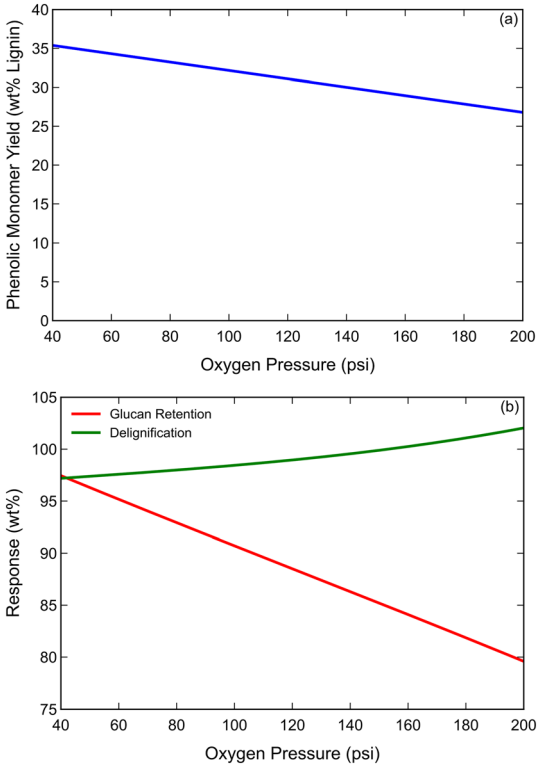

Fig. 7 Modelled univariate effect of oxygen pressure on (a) phenolic monomer yield (b) glucan retention and delignification, where other explanatory variables were constant at their center points (temperature: 170 °C, time: 32 min, catalyst: 19 wt%, NaOH: 1.25 M). Glucan retention is calculated based on the initial cellulose content of the biomass.

of the responses when the rest of the explanatory variables were constant at their center point (temperature: 170 °C, time: 32 min, O_2 pressure: 120 psi, NaOH: 1.25 M). Phenolic monomer yield and glucan retention showed minimal changes with catalyst concentration. There was a slightly positive relationship between catalyst and phenolic monomer yield, increasing the yield from 28 at zero level for the catalyst to 33 for 50 mg catalyst. Glucan retention showed a quadratic correlation with catalyst with a maximum of around 19 wt% catalyst loading. However, the changes are not that significant, and delignification rate did not show any significant change with catalyst concentration. Although the catalyst did not prove a significant explanatory variable, the interaction effect of catalyst and time showed that catalyst might increase phenolic monomer yield under certain reaction conditions. For instance, at a short reaction time, the catalyst showed a significant impact on phenolic monomer yield, increasing from 9 wt% to 24 wt% when it increases from 0 to 50 mg. On the other hand, at longer reaction time, the amount of catalyst did not affect phenolic monomer yield. These results are consistent with other studies that found the use of a catalyst accelerates the reaction and eventually increases phenolic monomer yield.[34,35] Therefore, adding catalyst is beneficial for shorter reaction times, but the same yield can be achieved at longer reaction time without catalyst (Fig. 9).

However, it should be noted that at high temperatures, phenolic monomers are rapidly produced but also quickly decompose through oxidative degradation.[30] Therefore, the time of the reaction is a critical explanatory variable to preserve produced monomers. Under these circumstances, adding catalyst is the best way to increase the phenolic monomer yield.

NaOH was a significant explanatory variable for phenolic monomer yield and glucan retention. The univariate effect of NaOH on the phenolic monomer yield and glucan retention is illustrated in Fig. 10. They both showed quadratic relationships with a maximum around 1.25 M NaOH while keeping other explanatory variables constant at their center points (temperature: 170 °C, time: 32 min, O_2 pressure: 120 psi, catalyst: 19 wt%). NaOH provides a key role in oxidative depolymerization of lignin. It ionizes the hydroxyl group of lignin, allowing oxygen to attack the hydroxyl group and promote oxidation.[32]

Optimizing reaction conditions

In order to find the optimum reaction conditions, the desired ranges for all three response variables were defined. Since

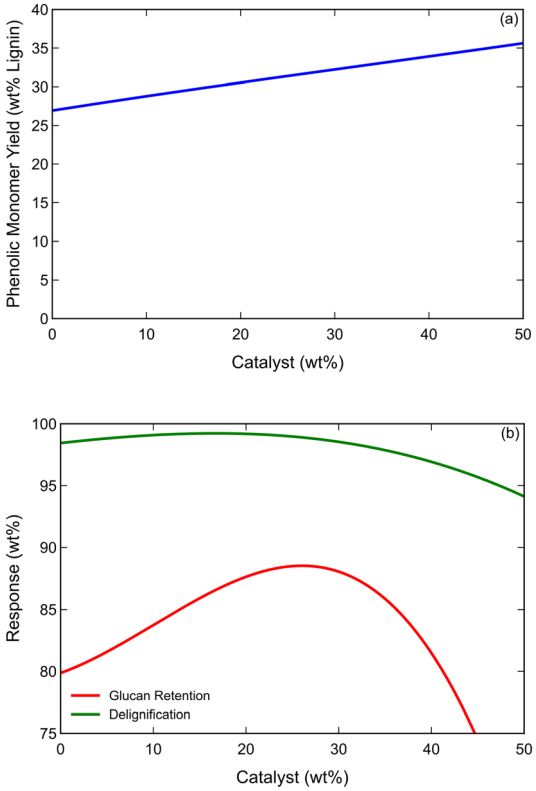

Fig. 8 Modelled univariate effect of catalyst on (a) phenolic monomer yield (b) glucan retention and delignification, where other explanatory variables were constant at their center points (temperature: 170 °C, time: 32 min, O_2 pressure: 120 psi, NaOH: 1.25 M). Glucan retention is calculated based on the initial cellulose content of the biomass.

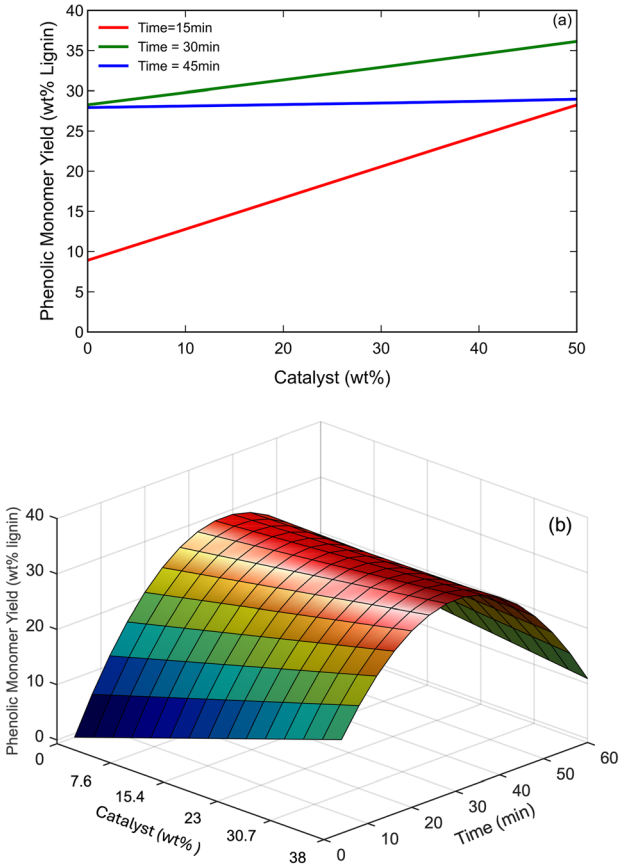

Fig. 9 The interaction effect of catalyst and time on phenolic monomer yield (a) two-dimensional (b) three-dimensional (response surface). Regression models were produced while keeping other explanatory variables constant at their center point (temperature: 170 °C, O_2 pressure: 120 psi, NaOH: 1.25 M).

the goal is to maximize phenolic monomer yield, the highest phenolic monomer yield was set to 50 wt%. Delignification and glucan retention were selected to match a target between 95–100%. Optimization was performed by JMP, and two different reaction areas were proposed for approaching the desired response variables. Fig. 11 and 12 show the contour profiles for two different areas where all the conditions are met. When the amounts of NaOH and catalyst were held constant at the middle point (1.25 M and 19 wt%, respectively) and oxygen pressure was held constant at 40 psi, the optimum reaction conditions were found between 160 °C and 180 °C and 33 and 45 min (white area in Fig. 11). In this reaction space, phenolic monomer yield, glucan retention, and delignification are more than 35 wt%, 97 wt%, and 95 wt%, respectively, as long as the combination of explanatory variables is in the white area of the contour profiler. For instance, for reaction conditions of 170 °C, 30 min, 40 psi oxygen, 19 wt% catalyst, and 1.25 M NaOH, the phenolic monomer yield, glucan retention, and delignification are 36 wt%, 97.24 wt%, and 97.35 wt%, respectively. One of the actual experiments was performed at these conditions (Table S1,† pattern 0 0 a 0 0), allowing a test of this model. Phenolic monomer yield, glucan retention, and delignification were 39 wt%, 96%, 99%, respectively, for this experiment, which is very close to model predictions.

If lower temperatures and longer reaction times are preferred, additional NaOH must be employed, but adding catalyst is unnecessary (as discussed earlier). When NaOH and oxygen pressure are held constant at 40 psi and 2 M, the white area includes the optimum reaction conditions.

Characterization of the lignin oil and isolated pulp

Fig. 13 shows the gas chromatogram of the oil and the yield of monomers for reaction conditions given in Table 3. Vanillin and syringaldehyde are the main compounds found in all experiments. Besides vanillin and syringaldehyde, other monomers include vanillic acid, syringic acid, methylhydroquinone, and acetovanillone. As shown in this figure, the highest phenolic monomer yield (39 wt%) was achieved at 170 °C, 40 psi oxygen pressure, 19 wt% catalyst, and 1.25 M NaOH after 32 min of the reaction (entry 4). Syringaldehyde showed the highest phenolic monomer yield in all of the experiments, in line with lignin composition of red oak as a hardwood.

GPC profile of lignin oil produced under optimum reaction conditions is depicted in Fig. 14. It shows two peaks

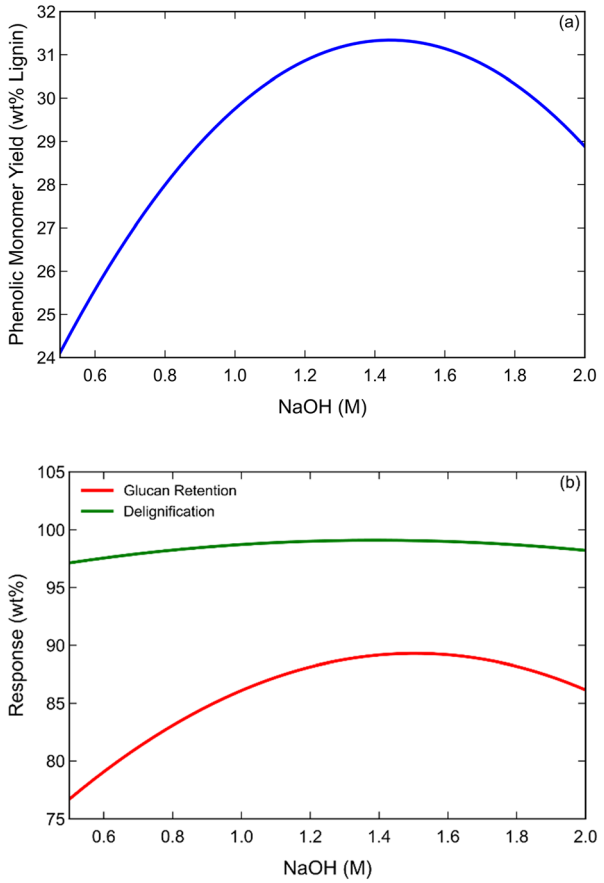

Fig. 10 Modelled univariate effect of NaOH on (a) phenolic monomer yield (b) glucan retention and delignification, while other explanatory variables were constant at their center points (temperature: 170 °C, time: 32 min, O_2 pressure: 120 psi, catalyst: 19 wt%). Glucan retention was calculated based on the initial cellulose content of the biomass.

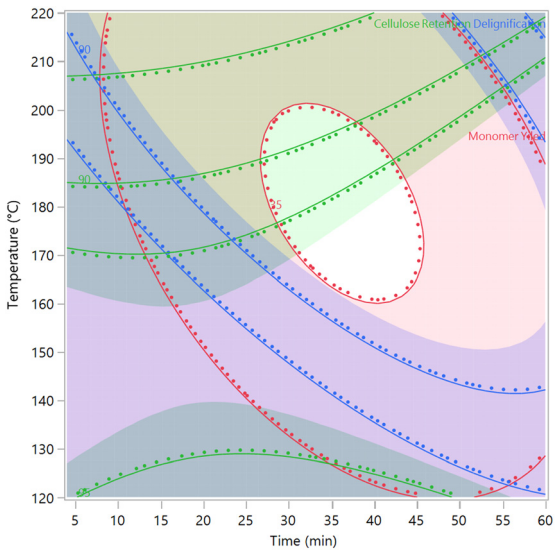

Fig. 11 Contour profiler of the optimum reaction conditions when shorter reaction time is preferred. Reaction conditions: T = 160–180 °C, t = 35–44 min, O_2 (psi) = 40, catalyst = 19 wt%, NaOH = 1.25 M mg, yield >35 wt%, glucan retention >97 wt%, delignification = 95 wt%.

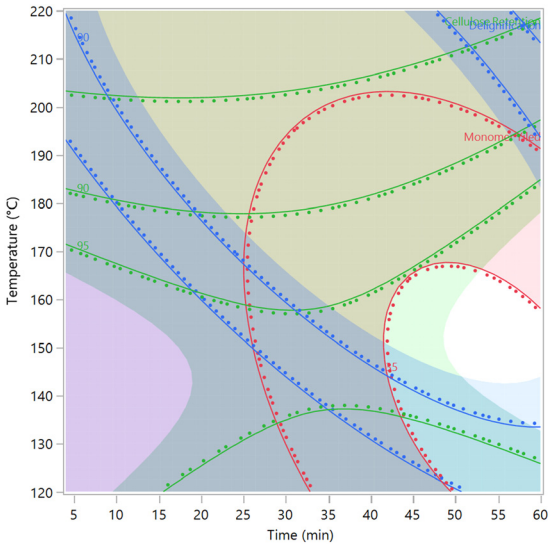

Fig. 12 Contour profiler of the optimum reaction conditions when longer reaction time is preferred. Reaction conditions: T = 140–160 °C, t = 50–60 min, O_2 (psi) = 40 psi, catalyst = 0 mg, NaOH = 1.43 M, yield >35 wt%, glucan retention >97 wt%, delignification = 95 wt%.

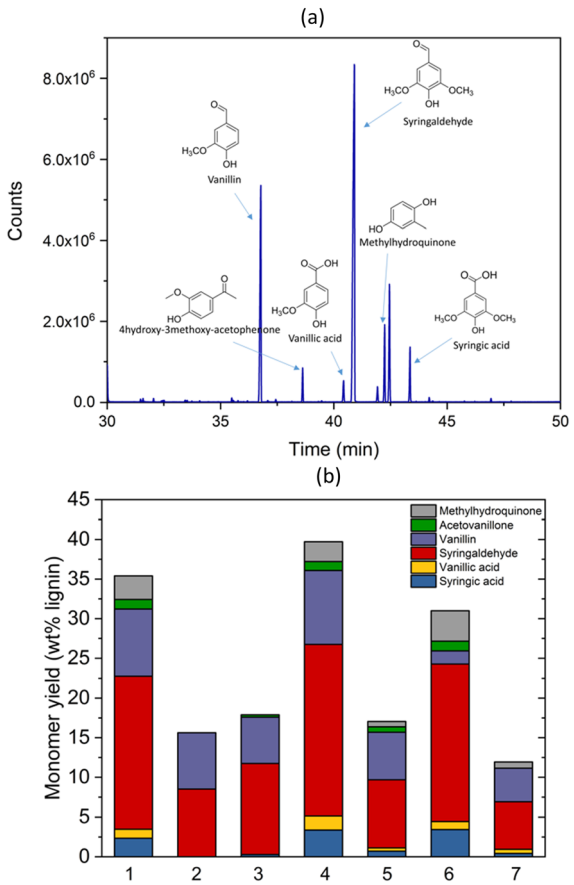

Fig. 13 Gas chromatogram and phenolic monomer yield of the lignin-oil produced from alkaline oxidation of red oak. (a): Reaction conditions 170 °C, 40 psi oxygen, 19.2 wt% catalyst, 1.25 M NaOH, 32 min, (b): reaction conditions are summarized in Table 3.

Table 3 Reaction condition for Fig. 13

Entry	T (°C)	T (min)	O_2 (psi)	Cat (wt%)	NaOH (M)
1	195	18	80	28.8	0.875
2	195	46	160	28.8	0.875
3	170	60	120	19.2	1.25
4	170	32	40	19.2	1.25
5	145	18	160	28.8	0.875
6	145	46	80	9.6	1.625
7	120	32	120	19.2	1.25

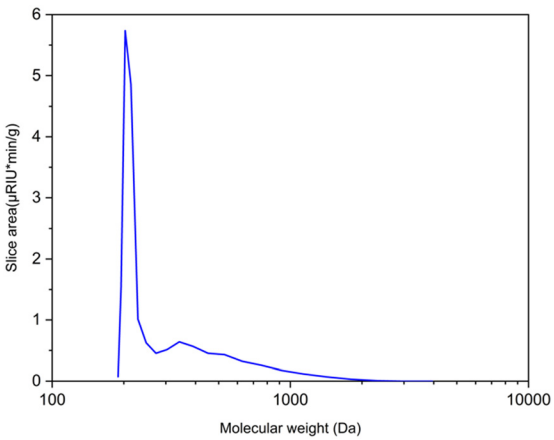

Fig. 14 Molecular weight distribution of lignin oil produced from red oak under oxidation conditions. Reaction conditions: 170 °C, 40 psi oxygen, 19.2 wt% catalyst, 1.25 M NaOH, 32 min.

near 200 Da and 350 Da, suggesting successful depolymerization to mostly monomers and dimers. The sharp signal at 200 Da corresponds to benzaldehydes (vanillin and syringaldehyde), as confirmed by authentic samples.

The lignin oil was further characterized by two-dimensional (2D) heteronuclear single quantum coherence (HSQC) NMR. The aromatic region of the HSQC spectra (Fig. 15a) shows signals of guaiacyl and syringyl groups. Oxidized guaiacyl and syringyl groups ($S'_{2/6}$ and G'_2) are more prominent due to the formation of benzaldehydes in high yield (vanillin and syringaldehyde), which is consistent with the GC results (Fig. 13). As shown in Fig. 15b, δ_H/δ_C in the ranges 3.5–5.5 ppm and 70–90 ppm does not show any peaks, indicating that most of the ether bonds in the resinol, β-O-4, and phenylcoumaran structures have been broken. Fig. 15a also displays the aldehyde region (side-chain part of the spectrum) for δ_H/δ_C in the ranges of 9–10.2 ppm and 188–195 ppm.

Powder X-ray diffraction patterns were recorded at room temperature by using a Rigaku Ultima IV X-ray diffractometer. The X-ray diffraction patterns of the original red oak and isolated carbohydrate pulps after the oxidation process are depicted in Fig. 16. The results indicate the presence of crystalline cellulose before and after the process. These results suggest that isolated carbohydrates are suitable for paper production.

The enzymatic hydrolysis of the original red oak and the isolated carbohydrate pulp after the oxidation reaction (170 °C, 40 psi oxygen, 219.2 wt% catalyst, 1.25 M NaOH) was performed according to NREL procedure with minor modifications. As shown in Fig. 17 recalcitrance of the cellulose in the pulp was drastically reduced after the pretreatment. Glucose yield of the pretreated red oak was around 85% after 120 h of hydrolysis while it was only around 5 wt% for untreated red oak. This

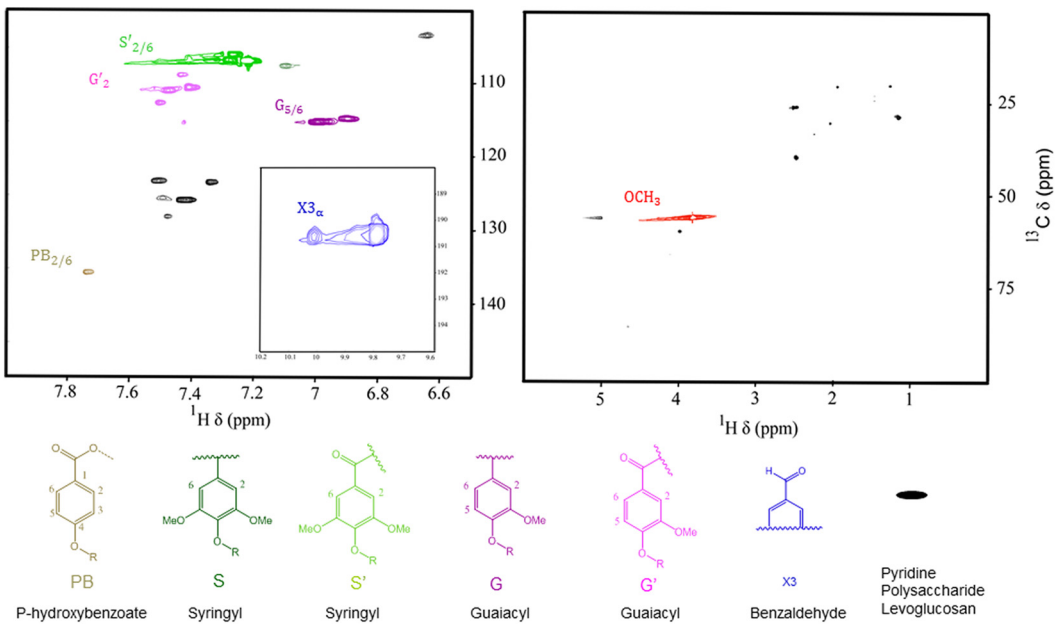

Fig. 15 HSQC NMR spectra of lignin oils obtained under alkaline oxidation conditions. Reaction conditions: 170 °C, 40 psi oxygen, 19.2 wt% catalyst, 1.25 M NaOH, 32 min.

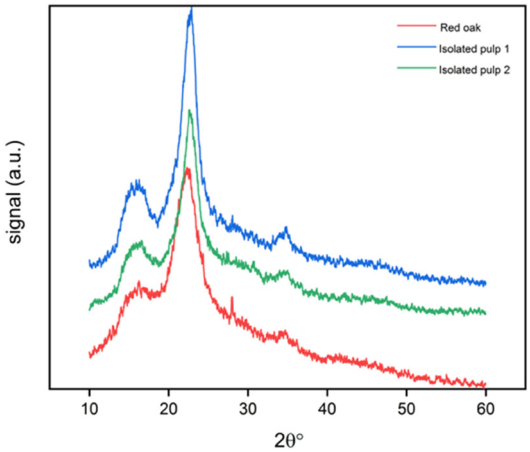

Fig. 16 X-ray diffractometer patterns of red oak and the isolated carbohydrate pulp after oxidation process. Reaction conditions for isolated pulp 1: 150 °C, 40 psi oxygen, no catalyst, 2 M NaOH, 55 min. Reaction conditions for isolated pulp 2: 170 °C, 40 psi oxygen, 19.2 wt% catalyst, 1.25 M NaOH.

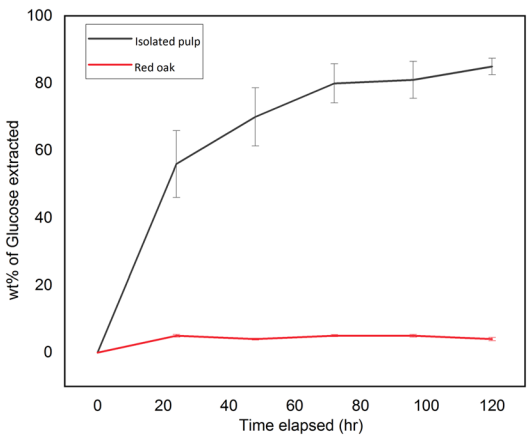

Fig. 17 Cellulose saccharification efficiency for isolated pulp collected after the pretreatment (reaction condition: 170 °C, 40 psi oxygen, 19.2 wt% catalyst, 1.25 M NaOH) and unreacted red oak.

shows the possibility of producing fermentable sugars from isolated carbohydrate pulp obtained from this pretreatment process.

Conclusions

This study presents an effective lignin-first oxidative fractionation strategy for red oak biomass, yielding high-value phenolic monomers and a cellulose-rich pulp suitable for further processing. Using a central composite statistical design and JMP optimization, two distinct sets of reaction conditions were identified to satisfy varying process priorities.

For balanced performance—maximizing phenolic monomer yield while retaining cellulose and achieving high delignification—optimum conditions were found between 160–180 °C and 33–45 minutes, with 1.25 M NaOH, $CuSO_4$ catalyst at 25 mg, and oxygen pressure at 40 psi. In this reaction space, modeled outcomes predicted monomer yields of >35 wt%, glucan retention >97 wt%, and delignification >95%. These predictions were validated experimentally, yielding 39 wt% phenolic monomers, 96% glucan retention, and 99% delignification at 170 °C, 30 min. This confirms that high lignin depolymerization and cellulose recovery can be simultaneously achieved without excessive degradation of the carbohydrate fraction.

Alternatively, if lower temperatures and longer residence times are preferred—*e.g.*, for energy savings or thermal sensitivity—similar performance can be reached by increasing NaOH dosage (*e.g.*, to 2 M), even in the absence of a catalyst. In this condition space, glucan retention and monomer yields remain high, though reaction efficiency may be slightly reduced.

The resulting carbohydrate pulp retained crystalline cellulose structure, as confirmed by powder X-ray diffraction, and achieved 85% glucose conversion *via* enzymatic hydrolysis within 120 hours. These findings underscore the flexibility and potential of this oxidative lignin-first approach for integrated production of aromatic monomers, paper-grade pulp, or bioethanol feedstocks.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

P. H.: conceptualization; investigation; methodology; writing (original draft). E. R.: investigation; methodology; writing (original draft). R. C. B.: conceptualization; funding acquisition; project administration; writing (review & editing).

Conflicts of interest

There are no conflicts to declare.

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References

1 G. W. Huber, S. Iborra and A. Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, *Chem. Rev.*, 2006, **106**(9), 4044–4098, DOI: **10.1021/cr068360d**.

2 D. A. Laird, R. C. Brown, J. E. Amonette and J. Lehmann, Review of the Pyrolysis Platform for Coproducing Bio-Oil and Biochar, *Biofuels, Bioprod. Biorefin.*, 2009, **3**(5), 547–562, DOI: **10.1002/BBB.169**.

3 C. Liu, H. Wang, A. M. Karim, J. Sun and Y. Wang, Catalytic Fast Pyrolysis of Lignocellulosic Biomass, *Chem. Soc. Rev.*, 2014, **43**(22), 7594–7623, DOI: **10.1039/c3cs60414d**.

4 T. Renders, S. Van Den Bosch, S. F. Koelewijn, W. Schutyser and B. F. Sels, Lignin-First Biomass Fractionation: The Advent of Active Stabilisation Strategies, *Energy Environ. Sci.*, 2017, **10**(7), 1551–1557, DOI: **10.1039/c7ee01298e**.

5 P. Hafezisefat, J. K. Lindstrom, R. C. Brown and L. Qi, Non-Catalytic Oxidative Depolymerization of Lignin in Perfluorodecalin to Produce Phenolic Monomers, *Green Chem.*, 2020, **22**(19), 6567–6578, DOI: **10.1039/d0gc02505d**.

6 S. Van Den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, Reductive Lignocellulose Fractionation into Soluble Lignin-Derived Phenolic Monomers and Dimers and Processable Carbohydrate Pulps, *Energy Environ. Sci.*, 2015, **8**(6), 1748–1763, DOI: **10.1039/c5ee00204d**.

7 R. J. A. Gosselink, E. De Jong, B. Guran and A. Abächerli, Co-Ordination Network for Lignin - Standardisation, Production and Applications Adapted to Market Requirements (EUROLIGNIN), *Ind. Crops Prod.*, 2004, **20**(2), 121–129, DOI: **10.1016/j.indcrop.2004.04.015**.

8 M. Balat and H. Balat, Recent Trends in Global Production and Utilization of Bio-Ethanol Fuel, *Appl. Energy*, 2009, **86**(11), 2273–2282, DOI: **10.1016/j.apenergy.2009.03.015**.

9 A. Mittal, R. Katahira, B. S. Donohoe, S. Pattathil, S. Kandemkavil, M. L. Reed, M. J. Biddy and G. T. Beckham, Ammonia Pretreatment of Corn Stover Enables Facile Lignin Extraction, *ACS Sustainable Chem. Eng.*, 2017, **5**(3), 2544–2561, DOI: **10.1021/acssuschemeng.6b02892**.

10 J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger and J. A. Dumesic, Nonenzymatic Sugar Production from Biomass Using Biomass-Derived γ-Valerolactone, *Science*, 2014, 277–280, DOI: **10.1126/science.1246748**.

11 C. S. Lancefield, I. Panovic, P. J. Deuss, K. Barta and N. J. Westwood, Pre-Treatment of Lignocellulosic Feedstocks Using Biorenewable Alcohols: Towards Complete Biomass Valorisation, *Green Chem.*, 2017, **19**(1), 202–214, DOI: **10.1039/c6gc02739c**.

12 E. M. Anderson, R. Katahira, M. Reed, M. G. Resch, E. M. Karp, G. T. Beckham and Y. Román-Leshkov, Reductive Catalytic Fractionation of Corn Stover Lignin, *ACS Sustainable Chem. Eng.*, 2016, **4**(12), 6940–6950, DOI: **10.1021/acssuschemeng.6b01858**.

13 J. Wildschut, A. T. Smit, J. H. Reith and W. J. J. Huijgen, Ethanol-Based Organosolv Fractionation of Wheat Straw for the Production of Lignin and Enzymatically Digestible Cellulose, *Bioresour. Technol.*, 2013, **135**, 58–66, DOI: **10.1016/j.biortech.2012.10.050**.

14 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, Formaldehyde Stabilization Facilitates Lignin Monomer Production during Biomass Depolymerization, *Science*, 2016, **354**(6310), 329–334.

15 T. Renders, W. Schutyser, G. Van den Bossche, J. M. Thevelein, D. Depuydt, S. Van den Bosch, B. F. Sels, T. Vangeel, C. M. Courtin, S.-F. Koelewijn, S. Kennis and A. Deneyer, Integrating Lignin Valorization and Bio-Ethanol Production: On the Role of Ni-Al 2 O 3 Catalyst Pellets during Lignin-First Fractionation, *Green Chem.*, 2017, **19**(14), 3313–3326, DOI: **10.1039/c7gc01324h**.

16 B. Ma, C. Zhao, S. R. Agrawal and M. Abu-Omar, A Synergistic Biorefinery Based on Catalytic Conversion of Lignin Prior to Cellulose Starting from Lignocellulosic Biomass, *Green Chem.*, 2015, **17**, 1492–1499, DOI: **10.1039/c4gc01911c**.

17 M. V. Galkin and J. S. M. Samec, Selective Route to 2-Propenyl Aryls Directly from Wood by a Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis, *ChemSusChem*, 2014, **7**(8), 2154–2158, DOI: **10.1002/cssc.201402017**.

18 W. Partenheimer, The Aerobic Oxidative Cleavage of Lignin to Produce Hydroxyaromatic Benzaldehydes and Carboxylic Acids via Metal/Bromide Catalysts in Acetic Acid/Water Mixtures, *Adv. Synth. Catal.*, 2009, **351**(3), 456–466, DOI: **10.1002/adsc.200800614**.

19 J. Mottweiler, M. Puche, C. Räuber, T. Schmidt, P. Concepción, A. Corma and C. Bolm, Copper- and Vanadium-Catalyzed Oxidative Cleavage of Lignin Using Dioxygen, *ChemSusChem*, 2015, **8**(12), 2106–2113, DOI: **10.1002/CSSC.201500131**.

20 T. Voitl and P. R. Von Rohr, Oxidation of Lignin Using Aqueous Polyoxometalates in the Presence of Alcohols, *ChemSusChem*, 2008, **1**(8–9), 763–769, DOI: **10.1002/cssc.200800050**.

21 H. Werhan, J. M. Mir, T. Voitl and P. R. Von Rohr, Acidic Oxidation of Kraft Lignin into Aromatic Monomers Catalyzed by Transition Metal Salts, *Holzforschung*, 2011, **65**(5), 703–709, DOI: **10.1515/HF.2011.071**.

22 H. R. Bjørsvik and L. Liguori, Organic Processes to Pharmaceutical Chemicals Based on Fine Chemicals from Lignosulfonates, *Org. Process Res. Dev.*, 2002, **6**(3), 279–290, DOI: **10.1021/op010087o**.

23 A. W. Pacek, P. Ding, M. Garrett, G. Sheldrake and A. W. Nienow, Catalytic Conversion of Sodium Lignosulfonate to Vanillin: Engineering Aspects. Part 1. Effects of Processing Conditions on Vanillin Yield and Selectivity, *Ind. Eng. Chem. Res.*, 2013, **52**(25), 8361–8372, DOI: **10.1021/ie4007744**.

24 V. E. Tarabanko and N. Tarabanko, Catalytic Oxidation of Lignins into the Aromatic Aldehydes: General Process Trends and Development Prospects, *Int. J. Mol. Sci.*, 2017, **18**(11), 2421–2439, DOI: **10.3390/ijms18112421**.

25 P. C. Rodrigues Pinto, E. A. Borges Da Silva and A. E. Rodrigues, Insights into Oxidative Conversion of Lignin to High-Added-Value Phenolic Aldehydes, *Ind. Eng. Chem. Res.*, 2011, **50**(2), 741–748, DOI: **10.1021/ie102132a**.

26 A. E. Rodrigues, Production of Vanillin by Oxidation of Pine Kraft Lignins with Oxygen, *Holzforschung*, 1995, **49**(3), 273–278, DOI: **10.1515/hfsg.1995.49.3.273**.

27 W. Guoxiong, M. Heitz and E. Chornet, Improved Alkaline Oxidation Process for the Production of Aldehydes (Vanillin

and Syringaldehyde) from Steam-Explosion Hardwood Lignin, *Ind. Eng. Chem. Res.*, 1994, **33**(3), 718–723, DOI: **10.1021/ie00027a034**.

28 D. Min, Z. Xiang, J. Liu, H. Jameel, V. Chiang, Y. Jin and H. M. Chang, Improved Protocol for Alkaline Nitrobenzene Oxidation of Woody and Non-Woody Biomass, *J. Wood Chem. Technol.*, 2014, **35**(1), 52–61, DOI: **10.1080/02773813.2014.902965**.

29 V. E. Tarabanko, K. L. Kaygorodov, E. A. Skiba, N. Tarabanko, Y. V. Chelbina, O. V. Baybakova, B. N. Kuznetsov and L. Djakovitch, Processing Pine Wood into Vanillin and Glucose by Sequential Catalytic Oxidation and Enzymatic Hydrolysis, *J. Wood Chem. Technol.*, 2017, **37**(1), 43–51, DOI: **10.1080/02773813.2016.1235583**.

30 W. Schutyser, J. S. Kruger, A. M. Robinson, R. Katahira, D. G. Brandner, N. S. Cleveland, A. Mittal, D. J. Peterson, R. Meilan, Y. Román-Leshkov and G. T. Beckham, Revisiting Alkaline Aerobic Lignin Oxidation, *Green Chem.*, 2018, **20**(16), 3828–3844, DOI: **10.1039/c8gc00502h**.

31 J. Dai, G. N. Styles, A. F. Patti and K. Saito, $CuSO_4/H_2O_2$-catalyzed lignin depolymerization under the irradiation of microwaves, *ACS Omega*, 2018, **3**(9), 10433–10441, DOI: **10.1021/acsomega.8b01567**.

32 D. J. McClelland, A. H. Motagamwala, Y. Li, M. R. Rover, A. M. Wittrig, C. Wu, J. S. Buchanan, R. C. Brown, J. Ralph, J. A. Dumesic and G. W. Huber, Functionality and Molecular Weight Distribution of Red Oak Lignin before and after Pyrolysis and Hydrogenation, *Green Chem.*, 2017, **19**(5), 1378–1389, DOI: **10.1039/c6gc03515a**.

33 M. G. Resch, J. O. Baker and S. R. Decker, Low Solids Enzymatic Saccharification of Lignocellulosic Biomass, *Tech. Rep. NREL/TP-5100-63351*, 2015, pp. 1–9.

34 B. Adney and J. Baker, *Measurement of Cellulase Activities: Laboratory Analytical Procedure (LAP)*, Issue Date: 08/12/1996, 2008.

35 P. A. Johnston, H. Zhou, A. Aui, M. M. Wright, Z. Wen and R. C. Brown, A Lignin-First Strategy to Recover Hydroxycinnamic Acids and Improve Cellulosic Ethanol Production from Corn Stover, *Biomass Bioenergy*, 2020, **138**, 1–20, DOI: **10.1016/j.biombioe.2020.105579**.

36 A. J. Ragauskas and L. A. Lucia, High Selectivity Oxygen Delignification, *OSTI Technical Report*, 2005, DOI: **10.1017/CBO9781107415324.004**.

37 R. B. Santos, E. A. Capanema, M. Y. Balakshin, H.-M. Chang and H. Jameel, Lignin Structural Variation in Hardwood Species, *J. Agric. Food Chem.*, 2012, **60**(19), 4923–4930, DOI: **10.1021/jf301276a**.

38 G. Wu and M. Heitz, Catalytic Mechanism of Cu2+ and Fe3+ in Alkaline O2 Oxidation of Lignin, *J. Wood Chem. Technol.*, 1995, **15**(2), 189–202, DOI: **10.1080/02773819508009507**.

39 Q. Xiang and Y. Y. Lee, Production of Oxychemicals from Precipitated Hardwood Lignin, *Appl. Biochem. Biotechnol.*, 2001, **91–93**, 71–80, DOI: **10.1385/ABAB:91-93:1-9:71**.

40 F. G. Sales, L. C. A. Maranhão, N. M. Lima Filho and C. A. M. Abreu, Kinetic Evaluation and Modeling of Lignin Catalytic Wet Oxidation to Selective Production of Aromatic Aldehydes, *Ind. Eng. Chem. Res.*, 2006, **45**(20), 6627–6631, DOI: **10.1021/ie0601697**.

41 J. C. Villar, A. Caperos and F. García-Ochoa, Oxidation of Hardwood Kraft-Lignin to Phenolic Derivatives with Oxygen as Oxidant, *Wood Sci. Technol.*, 2001, **35**(3), 245–255, DOI: **10.1007/s002260100089**.