**Lignin deconstruction**

Reactive distillation reductive catalytic deconstruction (RD-RCD) oil characterization

Gas chromatography-mass spectrometry (GC-MS) chromatograms were analyzed using an automated procedure in OpenChrom version 1.4.0. All chromatograms were denoised, baselined, and normalized, and peaks were chosen with a first derivative method. Peaks were integrated using a trapezoidal approach and filtered to remove those making up less than 0.25% of total peak area. Selectivities were calculated relative to the areas of all identified phenolic compounds. Overall phenolic monomer yields were determined from the fraction of the bio-oil consisting of phenolic compounds (by peak area) and the washed distillate mass (i.e., gravimetric yields were corrected according to phenolic content). A list of analyzed samples in order of increasing deconstruction yield is shown in Table 1 in the main text.

Retention times for identified phenolic products and solvent reforming by-products are shown in Table S1. A set of pure compounds (guaiacol, methylguaiacol, ethylguaiacol, propylguaiacol, syringol, and methyleclopentenone; all purchased from Sigma-Aldrich and used as received) were employed as references for product identification to supplement the National Institute of Standards and Technology (NIST) mass spectrum library. By-products included methyl-substituted cyclopentenones, dioxolanes, and solketal; however, it was not possible to identify conclusively many of the non-phenolic peaks as the mass spectra were not an exact match to any compounds in the NIST database or the reference compounds. The fragmentation patterns were similar in many cases, and there were low probability matches to NIST library entries, indicating that the unidentified species likely are in the same family of compounds. A GC-MS chromatogram for the reference compounds is shown in Figure S1, and chromatograms for the 6 lignin bio-oils are shown in Figures S2-S7 in order of deconstruction yield (see main text Figure 2).
Table S1: Retention times for identified RD-RCD compounds using GC-MS.

| Compound          | Retention time (min) |
|-------------------|----------------------|
| A 4-ethylphenol   | 11.19                |
| B Guaiacol        | 9.43                 |
| C 4-methylguaiacol| 11.02                |
| D 4-ethylguaiacol | 12.27                |
| E 4-propylguaiacol| 13.49                |
| F Isoleugenol     | 14.06, 14.61         |
| G 4-vinylguaiacol | 12.88                |
| H Syringol        | 13.46                |
| I 4-methylsyringol| 14.67                |
| J 4-ethylsyringol | 15.65                |
| K 4-propylsyringol| 16.63                |
| L 4-propenylsyringol| 17.79              |

References for by-products

| Compound          | Retention time (min) |
|-------------------|----------------------|
| M Catechol        | 12.63                |
| N 3-methyl-2-cyclopentenone | 7.65 |
| O Dihydroxyacetone| 7.58                 |
| P Solketal        | 6.95                 |
| Q Glycerin        | 8.75                 |
**Figure S1:** GC-MS chromatograms of pure reference compounds. Standards include guaiacol, methylguaiacol, ethylguaiacol, propylguaiacol, syringol, catechol, methylcyclopentenone, dihydroxyacetone, solketal, and glycerin. Co-eluting compounds are offset vertically for clarity.

**Figure S2:** GC-MS chromatogram for KHA1 RD-RCD oil.
Figure S3: GC-MS chromatogram for KSA RD-RCD oil.

Figure S4: GC-MS chromatogram for SNWA RD-RCD oil.
Figure S5: GC-MS chromatogram for KHA2 RD-RCD oil.

Figure S6: GC-MS chromatogram for OHP RD-RCD oil.
Figure S7: GC-MS chromatogram for BHF RD-RCD oil.

Additionally, the determination of RD-RCD bio-oil composition by GC-MS was validated with a model bio-oil prepared from known compounds. The composition of the bio-oil is shown in Table S2, and a plot of the known composition vs. the normalized mass selective detector (MSD) peak area is shown in Figure S8. The $R^2$ value for a linear fit was 0.99, suggesting that this method can be used to accurately quantify product distributions.

Table S2: Model bio-oil composition by weight and GC-MS peak area.

| Compound                | Mass (%) | MSD Area (%) |
|-------------------------|----------|---------------|
| 4-vinylguaiacol         | 2.1      | 0.8           |
| Creosol                 | 3.1      | 2.9           |
| 2,5-dimethylphenol      | 4.1      | 5.1           |
| Phenol                  | 4.1      | 4.3           |
| Propylguaiacol          | 5.2      | 6.5           |
| Syringol                | 20.6     | 18.6          |
| 4-ethylguaiacol         | 28.8     | 32.0          |
| Guaiacol                | 31.9     | 29.7          |
Figure S8: Validation of GC-MS method for determining RD-RCD bio-oil compositions with a model bio-oil.

Mass balances

As a representative example, a full mass balance was carried out for KSA deconstructed via RD-RCD. First, the bottoms of the reaction were diluted with a 1 M sodium hydroxide solution to reduce the viscosity of the mixture and keep the lignin residue in solution. Then, the mixture was vacuum filtered with a Grade 4 Whatman filter paper and a Buchner funnel to remove the solid catalyst and any biochar that formed in the reaction. The mass balance accounted for 99.5% of starting mass, with the individual components shown in Table S3.

Table S3: Full mass balance for sample KSA.

| Component                  | Mass (g) | % of starting mass |
|----------------------------|----------|--------------------|
|                            |          | % of sub-category mass |
| Lignin                     | 3.98     |                    |
| Glycerin                   | 138.78   |                    |
| Ru/C                       | 0.67     |                    |
| **Total inputs**           | **143.43** |                  |
| **Distillate**             |          |                    |
| Ethyl acetate extract      | 2.54     | 31.9%              |
| *Phenolics (corrected by GC-MS area)* | 0.19 | 7.6% (4.9% yield on starting lignin basis) |
| Ethyl acetate insoluble    | 2.87     | 36.0%              |
| **Filtered solids**        | **0.91** | **0.6%**           |
| Catalyst                   | 0.67     | 73.6% (assuming full recovery) |
| Bio-char                   | 0.24     | 26.4% (6% on starting lignin basis) |
| **Filtrate**               | **133.82** | **93.3%**         |
| Precipitated residual lignin | 1.00    | 0.7% (25.1% on starting lignin basis) |
| **Total mass balance**     | **142.70** | **99.5%**         |

Residual lignin was further isolated from the filtrate via precipitation in acidic water. The pH of the filtrate was adjusted to ~1-2 with 1 M hydrochloric acid, and a light brown solid precipitated (Figure S9). The solid was filtered off and dried under vacuum at 100 °C. Once dry,
the material was redissolved in 1 M sodium hydroxide and methanol prior to reprecipitation with 1 M hydrochloric acid. Again, the solid residue was dried under vacuum at 100 °C until a constant weight was achieved. In total, 1.00 g of solid lignin residue was recovered (~25 wt.% of initial lignin feedstock); however, the material was a fine powder, and some was lost at each purification step, so this mass is not the true yield. Rather, this isolation procedure is intended to demonstrate that the oligomeric lignin can be recovered for further upgrading.

Figure S9: Photo of recovered lignin residue after precipitation and drying.

Catalyst-free RD-RCD

Samples KSA, OHP, and BHF were deconstructed using RD-RCD for 15 h at 250 °C without catalyst as a control experiment. The phenolic product yields were significantly lower than for RD-RCD with Ru/C as shown in Table S4. Specifically, the yields without catalyst were reduced by 70%, 74%, and 82% for KSA, OHP, and BHF, respectively, relative to the ‘with catalyst’ cases.

Table S4: Catalyst-free RD-RCD results.

| Sample | Catalyst-free yield (wt.% on a lignin basis) | Yield with Ru/C (wt.% on a lignin basis) |
|--------|---------------------------------------------|----------------------------------------|
| KSA    | 2.8                                         | 9.2                                    |
| OHP    | 4.2                                         | 16.0                                   |
| BHF    | 5.8                                         | 31.7                                   |
Glycerin reforming products

Glycerin reforming was studied via a control experiment in which RD-RCD was conducted without lignin (i.e., with only glycerin and catalyst). The GC-MS chromatogram for the distillate is shown in Figure S10 with the chromatogram for KSA bio-oil for reference. The analogous peaks in the KSA bio-oil chromatogram make up ~70% of the unidentified products by peak area. Distillate mass corresponded to 4.5% of the starting glycerin, and the bottoms were almost entirely glycerin. The overall mass balance was 99.1%, indicating that little, if any, gaseous products were generated in the reaction. Note that these two samples were characterized on a different GC-MS system (Shimadzu QP2020 NX equipped with an AOC-20i autosampler and RTX-5MS column using helium as the carrier gas), and retention times for known compounds are not the same as those listed in Table S1. For these samples, the injection temperature was 300 °C, and the initial column temperature was 50 °C. The column temperature was held at 50 °C for 1 min and then ramped to 315 °C at 15 °C/min.

Figure S10: Control experiment GC-MS chromatograms. (Top) KSA bio-oil and (bottom) glycerin control experiment. Peak labels above the top chromatogram correspond to the compounds in Table S1 (guaiacol, creosol, ethylguaiacol, propylguaiacol and isoeugenol).
3D printing

A biobased stereolithography (SLA) 3D-printing resin was prepared from acrylated SNWA bio-oil (50 wt.%), vanillyl alcohol diacrylate (45 wt.%), and Irgacure TPO-L (5 wt.%). The resin was printed with a Peopoly Moai 200 SLA printer as described in the main text. The printed material was soaked in isopropanol and subsequently cured under ultraviolet light for 10 min. The final material became flaky, and the print broke because of shrinkage upon curing as shown in Figure S11.

Figure S11: 3D-printed resin that exhibited shrinkage upon curing. The object immediately after curing is shown on the left, and the print after several hours is shown on the right.
**Technoeconomic analysis (TEA)**

Physical property estimation

The critical properties of the bio-oil products were estimated using a group contribution method by Nannoolal et al. (63) Expected products from RCD/RD-RCD, mostly substituted phenols, guaiacols, and syringols, were broken down into their respective group contribution components. For compounds with known boiling points, the experimental values were employed, and estimates from the group contribution method outlined below were used for cases in which no experimental data were found. The equations for the estimation of the critical temperature ($T_c$) are shown below, and an example of the estimation method for guaiacyl methacrylate is shown in Table S5.

$$T_c = T_b \left( b + \frac{1}{a + (\Sigma_i N_i C_i + GI)^c} \right) \quad (\text{eqn. 1})$$

$$GI = \frac{1}{n} \sum_{i=1}^{m} \sum_{j=1}^{m} \frac{c_{i,j}}{m-1} \quad (\text{eqn. 2})$$

Parameters for critical temperature ($T_c$; eqn. 1) estimation with the Nanooolal method (63) are the normal boiling point ($T_b$), number of groups of type $i$ ($N_i$), contribution for group $i$ ($C_i$), and total group interaction contribution ($GI$). Fixed coefficients are $a$, $b$, and $c$. $GI$ (eqn. 2) is dependent on the number of atoms excluding hydrogen ($n$), the group interactions between groups $i$ and $j$ ($C_{i,j}$), and the total number of interaction groups per molecule ($m$).
Table S5: Example of group contribution breakdown for critical temperature estimation for guaiacyl methacrylate by the Nanoolal method.

| Number of atoms                                      | Frequency | Contribution | Total     |
|------------------------------------------------------|-----------|--------------|-----------|
| >COO-                                                | 1         | 0.0757089    | 0.075709  |
| >C-O-C<                                              | 1         | 0.0125082    | 0.012508  |
| CH₃- not connected to N, O, F, or Cl                 | 2         | 0.0418682    | 0.083736  |
| Aromatic =C< connected to O, N, Cl, or F             | 2         | 0.0681923    | 0.136385  |
| Aromatic =CH<                                       | 4         | 0.0161154    | 0.064462  |
| H₂C=C<                                               | 1         | 0.0454406    | 0.045441  |
| Group interactions                                   |           |              |           |
| >C=O connected to sp² carbon                         | 1         | -0.0356113   | -0.03561  |
| Ortho position—counted only once and only if there   | 1         | 0.0012823    | 0.001282  |
| are no meta or para pairs                            |           |              |           |
| **Total**                                            |           |              | **0.3839113** |
| Estimated boiling point (K)                          | 411       |              |           |
| a                                                     |           | 0.989        |           |
| b                                                     |           | 0.669        |           |
| c                                                     |           | 0.861        |           |
| **Critical Temperature (K)**                         |           |              | **562**   |

The normal boiling points of the functionalized methacrylates were needed for the Nanoolal group contribution method to estimate the critical properties. A least squares regression was constructed to estimate the boiling points of these phenolic methacrylates from those of the corresponding phenolic alcohols. The correlation consisted of the experimental boiling points of methacrylate monomers and their respective alcohols reported in literature (64). Aromatic and cycloaliphatic compounds were preferred for the correlation because of their structural similarities to the lignin-based phenolics, but additional non-cycloaliphatic/aromatic monomers and alcohols were added to create a more robust correlation. The compounds with known boiling points were phenol, phenyl methacrylate, lauryl alcohol, lauryl methacrylate, 2-ethylhexanol, 2-ethylhexyl methacrylate, cyclohexanol, cyclohexyl methacrylate, 2-phenylethanol, and 2-phenylethyl methacrylate. The correlation is shown in Figure S12 and has an R² value of 0.90.
Figure. S12: Boiling point prediction correlation. Linear regression relating the boiling points of methacrylate compounds to those of their corresponding alcohols. This correlation was leveraged to predict the boiling point of phenolic methacrylates from experimental boiling point data for the starting phenolic compounds.

For compounds not in the Aspen database, the boiling point, critical temperature, critical volume, critical pressure, and chemical structure were added into Aspen Plus V11, and vapor pressure as a function of temperature was determined using a combination of experimental data and estimated boiling point/critical point. Coefficients for the Wagner 25 liquid vapor pressure equation were fit to the data with Microsoft Excel’s solver tool (64-67). Vapor pressure is particularly important for modeling the RD-RCD process, and manually fitting of the data resulted in a more accurate and physically realistic model. Unknown or missing physical properties were estimated with the Aspen Plus Property Constant Estimation System (PCES).

Simulation

Process flowsheets of RCD, RD-RCD, monomer functionalization, and polymerization are shown in Figures S13-S15. Aspen Plus V11 was used to simulate the production of the pressure-sensitive adhesive (PSA) polymer from lignin. Most of the components involved in the reactions were selected from the Aspen database. Lignins were defined with the structures and physical properties reported by the National Renewable Energy Laboratory (NREL) (61). For other compounds that were not in the database, missing parameters were estimated as described above. The heat capacity of poly(syringyl methacrylate) at a number average molecular weight (Mₙ) ~20,000 g/mol was measured experimentally using differential scanning calorimetry and fit to the Design Institute for Physical Properties (DIPPR) equation as a surrogate for the block polymer heat capacity. Because the block polymer was relatively high in molecular weight (6), the majority of the heat of reaction for polymerization comes from the propagation reaction. Thus, the heat of reaction was estimated from the phenolic monomer’s heat of polymerization (68). The process operating conditions and reaction yields were taken either from the experimental data or literature (6, 69). It was assumed that these lab-scale yields also will hold for industrial-scale production. The overall monomer and by-product yields for RCD and RD-RCD are listed in Table S6, and the product selectivities are shown in the main text (see Figure 3). Other components in the lignin
sample were assumed to be inert during the reaction, and they were modeled as solid xylose and glucose with the experimentally determined compositions.

Figure S13: Process diagram for RCD lignin deconstruction.

Figure S14: Process diagram for RD-RCD lignin deconstruction.

Figure S15: Process diagram for phenolic monomer functionalization and polymerization.
Table S6: Monomer and by-product yields of RCD and RD-RCD reaction for different lignin samples.

| Samples                          | OHP  | KSA  | BHF  |
|---------------------------------|------|------|------|
| Lignin content (wt.%)           | 93.7 | 100  | 65.1 |
| RD-RCD 15 h monomer yield       | 16.0 | 9.2  | 31.7 |
| (wt.% on a lignin basis)        |      |      |      |
| RD-RCD 15 h by-product yield    | 51.4 | 11.9 | 89.8 |
| (wt.% on a lignin basis)        |      |      |      |
| RCD 15 h monomer yield          | 18.0 | 4.7  | 45.6 |
| (wt% on a lignin basis)         |      |      |      |

Assumptions

Aspen Process Economic Analyzer V11 was used to perform the technoeconomic analysis (TEA) for PSA production. Some additional assumptions were necessary to perform the economic analysis as outlined below:

1. All equipment and operating costs were estimated in Aspen Process Economic Analyzer V11 with Q1 2018 as the cost basis.
2. The plant capacity of the base scenario was assumed as 18,144 t of lignin annually. Sensitivity analysis then was conducted to explore the range of 5,000 t/y to 30,000 t/y.
3. The PSA plant was assumed to be operated for 8000 h/y. The economic life of the project was assumed to be 20 y, and the recovery period was set as 10 y. The internal rate of return on investment was 15%, and a 35% corporate tax was imposed on the profits. The straight-line method for depreciation was applied, and a 10% salvage value relative to the original capital cost after 20 y was assumed. Discounted cash flow analysis was conducted to calculate the minimum selling price (MSP) – the product’s selling price when the net present value is zero.
4. The prices for three lignin feedstocks were taken from the Pulp and Paper Technical Association of Canada — CanmetENERGY webinar (18):
   - Kraft lignin (KSA): $750/t
   - Ethanol-based organosolv lignin (OHP): $1,000/t
   - Integrated thermomechanical biorefinery lignin (BHF): $900/t ($800–$1,500/t for sensitivity analysis)
5. The market price of methanol was $330/t (70), and that of glycerin was $175/t (71). A sensitivity analysis also considered the extreme case of using high purity, refined glycerin with a price of $700/t (71).
6. The cost of hexane was assumed as $687/t (71). Hydrogen was bought at $1,570/t (72), methacrylic anhydride (MAAH) at $10,240/t (73), and butyl acrylate (BA) at $1,412/t (74).
7. The purchase price of CaO (quicklime) was assumed to be $120/t (75), and that of 4-dimethylaminopyridine (DMAP) was $13,870/t (76). The prices of anisole and
azobisisobutyronitrile (AIBN) were estimated to be $3,500/t and $7,000/t, respectively, from reference prices on Alibaba, a worldwide e-commerce platform (77).

8. The catalyst cost for lignin deconstruction was estimated as the precious metal cost plus $11/kg for the supported catalyst manufacturing (78). The unit price of Ruthenium was taken as $6,430/kg for 2018 Q1 (79). Ru/C catalyst consists of 5 wt.% Ru, leading to a final catalyst price of $103,800/t. The catalyst life was taken to be 6 months, and it was assumed that the catalyst manufacturer recovered 99% of the precious metal in the spent catalyst. Therefore, after every 6 months, only the costs of the catalyst support, makeup metals, and manufacturing were incurred.

9. Most chain transfer agents (CTAs) used in laboratory-scale experiments are not produced at large scales, and data for this analysis could not be found. Due to the complex molecular structure, a lack of physical property data, and its small mass flow in the polymer product, the CTA was not modeled explicitly in this simulation. However, its cost was added to the final raw material costs for the TEA. The CTA was estimated to be $20,000/t as the sum of operating costs using the work of Yang and Rosentrater (80).

10. Utilities were assumed to be purchased from a third-party vendor, and the cost was estimated with Aspen Process Economic Analyzer. The wastewater treatment plants were not modeled explicitly in the simulation. Instead, it was assumed that wastewater was treated by a third party at a fixed price ($0.33/kg of organic contaminant) (81).

11. From experimental measurements, substituted cyclopentenones were the main by-product in RD-RCD, and this class of compounds could be converted to diesel and jet fuel (82-84). The price of bioethanol was taken as a reference, and the by-product was assumed to be sold at $1.96/gallon ($0.66/kg) (85).

RCD process description

Lignin was dissolved in the methanol (5 wt.% lignin loaded), heated to 250 °C (H-1), and fed into the deconstruction reactor (R-1) that contained Ru/C (5 wt.% Ru) catalyst and 40 bar hydrogen gas. The reactor then operated at a pressure of 80 bar for 15 h. Because continuous operation is challenging at high pressures, especially for large-volume reactors, two sets of the same reaction equipment were assumed to operate in parallel batch processes so that one reactor system could run the deconstruction as the other cools to enable higher throughput. After this reaction, the product stream was fed to a flash drum (F-1) to separate and recycle the excess hydrogen and methanol from the phenolic monomers. The products were cooled (COOL-1) and extracted with hexane, and the unreacted waste was filtered (FIL-1). Then, hexane was distilled and recycled in a distillation column (C-1) to isolate the phenolic monomer mixture.
**RD-RCD process description**

Lignin was mixed with glycerin (5 wt.% lignin loading), heated (H-1), and fed into a deconstruction reactor (R-1) that contained the Ru/C (5 wt.% Ru) catalyst. The deconstruction reaction was assumed to run for 15 h at 250 °C and ambient pressure. After deconstruction, the product stream was sent to the vacuum distillation (0.2 bar) column (C-1) to separate monomers and the by-product from glycerin and residual lignin. The glycerin was recycled while the distillate was cooled (COOL-2) and extracted with hexane (E-1), and residual lignin was treated as waste. The hexane phase then underwent two consecutive distillations to recycle the hexane (C-2) and separate the by-product from phenolic monomer products (C-3).

**Monomer synthesis and polymerization process description**

The phenolic monomers were mixed with 2 wt.% DMAP and 1.05 stoichiometric equivalents of MAAH. Because of the high reactivity of MAAH, the functionalization reaction was conducted at 45 °C for 3 h until full conversion of phenolics (R-2). Then, excess MAAH and by-product methacrylic acid were neutralized by CaO in the reactor (R-3), where anisole then was introduced to extract functionalized monomers. Next, the reversible addition-fragmentation chain-transfer (RAFT) polymerization was performed at 70 °C in 2 steps. BA was first polymerized with AIBN as the initiator for 5 h. Then, the mixture of lignin-based monomers was added to react for another 5 h to synthesize the final triblock polymer (R-4). The polymer was dried in a flash drum (F-3) to recycle the anisole solvent and obtain the final polymer product.

**Summary of capital and operational costs**

The annual PSA productions in the RCD process were 4,740 t, 28,360 t, and 16,240 t for KSA, BHF, and OHP lignin samples, respectively. RD-RCD plants produced 9,620 t, 19,820 t, and 14,760 t PSA when using KSA, BHF, and OHP lignin samples, respectively. Capital investments and operating costs of each process are listed below in Tables S7-S12:
Table S7: Summary of the capital and operating costs of the RCD process (KSA lignin).

| Item                              | Cost (Million $) | Item                              | Annual cost (Million $/y) |
|-----------------------------------|------------------|-----------------------------------|---------------------------|
| Purchased Equipment               | 69.85            | Total Catalyst Cost               | 1.54                      |
| Other                             | 46.96            | Total Raw Materials Cost          | 40.44                     |
| General and Administrative Overhead| 3.27             | Total Utilities Cost              | 6.09                      |
| Contract Fee                      | 3.50             | Operating Labor Cost              | 1.08                      |
| Contingencies                     | 11.68            | Maintenance Cost                  | 5.24                      |
| Working Capital                   | 6.76             | Operating Charges                 | 0.27                      |
| **Total Capital Cost**            | **142.04**       | **Plant Overhead**                |                           |
|                                   |                  | **General and Administrative Cost**|                           |
|                                   |                  | **Total Operating Cost**          | **61.20**                 |

Table S8: Summary of the capital and operating costs of the RD-RCD process (KSA lignin).

| Item                              | Cost (Million $) | Item                              | Annual cost (Million $/y) |
|-----------------------------------|------------------|-----------------------------------|---------------------------|
| Purchased Equipment               | 24.22            | Total Catalyst Cost               | 1.54                      |
| Other                             | 25.55            | Total Raw Materials Cost          | 49.27                     |
| General and Administrative Overhead| 1.39             | Total Utilities Cost              | 2.76                      |
| Contract Fee                      | 1.49             | Operating Labor Cost              | 0.92                      |
| Contingencies                     | 4.98             | Maintenance Cost                  | 1.47                      |
| Working Capital                   | 2.88             | Operating Charges                 | 0.23                      |
| **Total Capital Cost**            | **60.52**        | **Plant Overhead**                |                           |
|                                   |                  | **General and Administrative Cost**|                           |
|                                   |                  | **Total Operating Cost**          | **61.64**                 |

Table S9: Summary of the capital and operating costs of the RCD process (BHF lignin).

| Item                              | Cost (Million $) | Item                              | Annual cost (Million $/y) |
|-----------------------------------|------------------|-----------------------------------|---------------------------|
| Purchased Equipment               | 71.51            | Total Catalyst Cost               | 1.54                      |
| Other                             | 49.46            | Total Raw Materials Cost          | 116.37                    |
| General and Administrative Overhead| 3.39             | Total Utilities Cost              | 6.54                      |
| Contract Fee                      | 3.63             | Operating Labor Cost              | 1.08                      |
| Contingencies                     | 12.10            | Maintenance Cost                  | 5.36                      |
| Working Capital                   | 7.00             | Operating Charges                 | 0.27                      |
| **Total Capital Cost**            | **147.09**       | **Plant Overhead**                |                           |
|                                   |                  | **General and Administrative Cost**|                           |
|                                   |                  | **Total Operating Cost**          | **144.32**                |
Table S10: Summary of the capital and operating costs of the RD-RCD process (BHF lignin).

| Item                               | Cost (Million $) | Item                               | Annual cost (Million $/y) |
|------------------------------------|------------------|------------------------------------|---------------------------|
| Purchased Equipment                | 35.10            | Total Catalyst Cost                | 1.54                      |
| Other                              | 33.80            | Total Raw Materials Cost           | 90.17                     |
| General and Administrative Overhead| 1.93             | Total Utilities Cost               | 3.59                      |
| Contract Fee                       | 2.07             | Operating Labor Cost               | 0.92                      |
| Contingencies                      | 6.89             | Maintenance Cost                   | 2.11                      |
| Working Capital                    | 3.99             | Operating Charges                  | 0.23                      |
| **Total Capital Cost**             | **83.78**        | **Plant Overhead**                 | 1.52                      |
|                                    |                  | **General and Administrative Cost**| 7.17                      |
|                                    |                  | **Total Operating Cost**           | 107.25                    |

Table S11: Summary of the capital and operating costs of the RCD process (OHP lignin).

| Item                               | Cost (Million $) | Item                               | Annual cost (Million $/y) |
|------------------------------------|------------------|------------------------------------|---------------------------|
| Purchased Equipment                | 70.60            | Total Catalyst Cost                | 1.54                      |
| Other                              | 47.40            | Total Raw Materials Cost           | 80.31                     |
| General and Administrative Overhead| 3.30             | Total Utilities Cost               | 6.49                      |
| Contract Fee                       | 3.54             | Operating Labor Cost               | 1.08                      |
| Contingencies                      | 11.80            | Maintenance Cost                   | 5.25                      |
| Working Capital                    | 6.83             | Operating Charges                  | 0.27                      |
| **Total Capital Cost**             | **143.48**       | **Plant Overhead**                 | 3.17                      |
|                                    |                  | **General and Administrative Cost**| 7.00                      |
|                                    |                  | **Total Operating Cost**           | 105.11                    |

Table S12: Summary of the capital and operating costs of the RD-RCD process (OHP lignin).

| Item                               | Cost (Million $) | Item                               | Annual cost (Million $/y) |
|------------------------------------|------------------|------------------------------------|---------------------------|
| Purchased Equipment                | 30.94            | Total Catalyst Cost                | 1.54                      |
| Other                              | 30.82            | Total Raw Materials Cost           | 75.24                     |
| General and Administrative Overhead| 1.73             | Total Utilities Cost               | 3.08                      |
| Contract Fee                       | 1.85             | Operating Labor Cost               | 0.92                      |
| Contingencies                      | 6.18             | Maintenance Cost                   | 1.92                      |
| Working Capital                    | 3.58             | Operating Charges                  | 0.23                      |
| **Total Capital Cost**             | **75.09**        | **Plant Overhead**                 | 1.42                      |
|                                    |                  | **General and Administrative Cost**| 6.08                      |
|                                    |                  | **Total Operating Cost**           | 90.43                     |
Contributions to the MSP were broken down for RCD and RD-RCD for OHP lignin as shown in Figures S16 and S17. A similar analysis for the other two lignin feedstocks is shown in Figure 5 in the main text.

Figure S16: MSP ($/t PSA) breakdown of the RCD process with OHP lignin. Note: WWT = wastewater treatment.

Figure S17: MSP ($/t PSA) breakdown of the RD-RCD process with OHP lignin. Note: WWT = wastewater treatment.
Finally, sensitivity analyses were performed on the RCD and RD-RCD processes using the BHF lignin sample to demonstrate how the MSP will change in response to uncertainty from different sources as shown in Figure S18 (RCD) and Figure S19 (RD-RCD). Capital investment and the costs of BA, MAAH, and lignin were considered.

![RCD (BHF) sensitivity analysis](image)

**Figure S18: Sensitivity of the MSP of PSA to selected RCD process parameters.** Parameters were varied ±10% relative to the base case design, except for the lignin cost. Blue indicates the low parameter value, and orange indicates the high parameter value. The solid black line shows the baseline cost.
Figure S19: Sensitivity of the MSP of PSA to select RD-RCD process parameters. Parameters were varied ±10% relative to the base case design, except for the glycerin and lignin costs. Blue indicates the low parameter value, and orange indicates the high parameter value. The solid black line shows the baseline cost.

**Lignin screening method**  
**Thermogravimetric Analysis (TGA)**

The TGA method was similar to the Canadian Standards Association published method titled: “Kraft lignin — Determination of thermal stability by thermogravimetry” (86), and is described as follows. Samples (as received from lignin producers) were batched, dried at 105 °C, and placed in sealed glass tubes for storage in a room temperature desiccator. TGA instruments were calibrated prior to use. For sample analysis, 5 ± 2 mg of each sample was added into a clean 100 μL pan. TGA pans were not filled to the top. Subsequently, each specimen was heated at a 10 °C/min to 550 °C and then held isothermally for 30 min. After the hold, the temperature was ramped at 10 °C/min to 700 °C. All heating was performed under a 40 mL/min flow of nitrogen. A TGA Q500 (TA Instruments) was used for lignins OHP and SNWA, whereas a TGA 5500 (TA Instruments) was used for samples KHA1, KHA2, KSA, and BHF. Before commencing analysis with the TGA 5500, the similarity of thermogravimetric curves was validated using Indulin® AT as a reference lignin sample. The temperature at which 40% of the mass loss (T40%) occurs (corresponding to 60% residual mass) was determined by analysis of the raw data. The TGA curves for all screened samples are presented in Figures S20-S25, in order of increasing deconstruction yields.
Figure S20: TGA curve for KHA1 lignin with $T_{40\%}$ at 434 °C.

Figure S21: TGA curve for KSA lignin with $T_{40\%}$ at 470 °C.
Figure S22: TGA curve for SNWA lignin with $T_{40\%}$ at 361 °C.

Figure S23: TGA curve for KHA2 lignin with $T_{40\%}$ at 381 °C.
Figure S24: TGA curve for OHP lignin with $T_{40\%}$ at 367 °C.

Figure S25: TGA curve for BHF lignin with $T_{40\%}$ at 332 °C.
**P nuclear magnetic resonance (NMR) spectroscopy**

**Materials**

Hydroxyl quantification using $^{31}$P NMR spectroscopy was conducted using the method described in previous work by Cateto et al., Hoareau et al., and Hu et al. (87-89) The technical lignin samples were used as received from producers. 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, chromium (III) acetylacetonate (Cr(acac)$_3$), and cholesterol (95% purity) were purchased from Sigma-Aldrich (Canada) and used as received. Deuterated chloroform (CDCl$_3$) from Cambridge Isotopes Laboratory (United States) was dried over A4 molecular sieves prior to use. Reagent grade pyridine (ACP) with a boiling point of 115.4 °C was refluxed over potassium hydroxide for a few hours and then distilled to remove water. Subsequently, it was stored over calcium hydride prior to use.

**Method**

A solvent mixture of pyridine and CDCl$_3$ in 1.6:1 v/v ratio was freshly prepared prior to each batch of sample preparation. The mixture was used to prepare two stock solutions serving as a relaxation agent (5.6 mg/mL of Cr(acac)$_3$) and a reference quantitation standard (5.6 mg/mL cholesterol), respectively. For each NMR spectroscopy experiment, about 40 mg of lignin was dissolved in 0.5 mL solvent mixture in a 1-dram vial. Then, 0.2 mL of cholesterol stock solution and 0.05 mL of Cr(acac)$_3$ stock solution were added, and the mixture was sonicated for about 5 s to ensure full mixing. Finally, 0.1 mL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was introduced with a syringe.

NMR spectra were acquired on a Bruker 500 MHz spectrometer operating at 202.50 MHz for $^{31}$P using a 5-mm BBFO+ SmartProbe. 256 scans of each sample were acquired with a 250 ppm (51,000 Hz) spectral width, a 1.8 s acquisition period, and a 5 s recycle delay. Proton decoupling was performed during acquisition only. Spectra were referenced according to Cateto et al. (87), and the sharp peak arising from the reaction of water and the phosphitylation agent was at 132.2 ppm. Spectra were processed with Bruker TopSpin 4.0 patch level 5 using 1.5 Hz of exponential line-broadening and a 5th-order baseline correction after phasing.

The different lignin hydroxyl groups were quantified by integrating the spectral regions of interest as reported by Cateto et al. (87) and comparing with the integral of the cholesteryl derivative signal to obtain concentrations of lignin hydroxyls, taking into account the 95% purity of the cholesterol employed and the reported ash content for each sample. The integration regions are provided in Table S13.

| Structure                          | $^{31}$P NMR Spectroscopy Integration Region (ppm) |
|------------------------------------|---------------------------------------------------|
| Aliphatic hydroxyls               | 149.0 – 146.0                                     |
| Syringyl phenolic hydroxyls       | 143.0 – 142.0                                     |
| Guaiacyl phenolic hydroxyls       | 140.0 – 139.0                                     |
| $p$-hydroxyphenyl phenolic hydroxyls | 138.5 – 137.5                                   |
| Carboxylic hydroxyl units         | 135.5 – 134.0                                     |
The quantification of condensed phenol units resulted from the difference between the integrals of the peaks at 144–140 ppm and those at 143–142 ppm (syringyl phenolic hydroxyls). The $^{31}$P NMR spectroscopy integration regions for all samples are shown in Figures S26-S31, in order of deconstruction yields.

Figure S26: $^{31}$P NMR spectrum for KHA1 lignin.
Figure S27: $^{31}$P NMR spectrum for KSA lignin.

Figure S28: $^{31}$P NMR spectrum for SNWA lignin.
Figure S29: $^{31}$P NMR spectrum for KHA2 lignin.

Figure S30: $^{31}$P NMR spectrum for OHP lignin.
Figure S31: $^{31}$P NMR spectrum for BHF lignin.
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