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## Supplementary Information

Table S1. Lignin fraction carbon yields of 15 and 30 min from SCM-DHDO experiments with maple wood and GVL extracted lignin. Dimer and trimer yields were estimated for the 15 min time-point using a high-temperature GC-FID.

| Feed | Carbon yield from lignin fraction (\%) |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Maple Wood | GVL extracted lignin | Maple Wood | GVL extracted lignin |
| By compound | 15 min | 15 min | 30 min | 30 min |
| Guaiacol | 0.8 | 0.1 | 0.9 | 0.2 |
| 4-Ethylphenol | 1.5 | 0.1 | 1.4 | 0.3 |
| 4-Methylguaiacol | 1.5 | 0.2 | 1.4 | 0.5 |
| 4-Ethylguaiacol | 1.4 | 0.5 | 1.2 | 0.9 |
| 4-Propylphenol | 1.4 | 0.0 | 1.2 | 0.0 |
| 4-Propylguaiacol | 6.3 | 0.8 | 5.7 | 1.3 |
| 4-Methylsyringol | 0.8 | 0.2 | 0.8 | 0.4 |
| 4-Ethylsyringol | 0.8 | 0.3 | 0.9 | 0.5 |
| 4-Propylsyringol | 0.8 | 1.1 | 1.3 | 0.9 |
| By type |  |  |  |  |
| Syringols | 2.4 | 1.6 | 3.1 | 1.8 |
| Guaiacols | 10.1 | 1.7 | 9.2 | 3.0 |
| Phenols | 2.9 | 0.1 | 2.6 | 0.3 |
| By alkyl tail length |  |  |  |  |
| No tail ( $\mathrm{C}_{0}$ ) | 0.8 | 0.1 | 0.9 | 0.2 |


| Methyl tail $\left(\mathrm{C}_{1}\right)$ | 2.3 | 0.4 | 2.2 | 0.9 |  |
| :--- | ---: | ---: | ---: | ---: | ---: |
| Ethyl tail $\left(\mathrm{C}_{2}\right)$ | 3.7 | 1.0 | 3.6 | 1.7 |  |
| Propyl tail $\left(\mathrm{C}_{3}\right)$ | 8.6 | 1.9 | 8.2 | 2.2 |  |
| Unidentified aromatics | 0 | 0.6 | 0 | 3.0 |  |
| Unidentified cyclohexanols | 0 | 0.0 | 0 | 0.0 |  |
| Total monomers | 15.4 | 4.1 | 15.0 | 8.1 |  |
| $\mathrm{~S} / \mathrm{G} / \mathrm{P}$ ratio | $1.0 / 4.2 / 1.2$ | $1.0 / 1.0 / 0.1$ | $1.0 / 2.9 / 0.8$ | $1.0 / 1.6 / 0.2$ |  |
| Alkyl tail length ratio $\mathrm{C}_{0} / \mathrm{C}_{1} / \mathrm{C}_{2} / \mathrm{C}_{3}$ | $0.1 / 0.3 / 0.4 / 1.0$ | $0.1 / 0.2 / 0.5 / 1.0$ | $0.1 / 0.3 / 0.4 / 1.0$ | $0.1 / 0.4 / 0.8 / 1.0$ |  |
| Estimated dimer yield | 0.0 |  | 2.3 | Not measured | Not measured |
| Estimated trimer yield | 0.0 | 0.0 | Not measured | Not measured |  |

Table S2. Carbon yields from 4 h SCM-DHDO experiments with various feedstocks. Base reaction conditions: 100 mg feed, 100 mg CuMgAlOx catalyst, $2.4 \mathrm{~g} \mathrm{MeOH}, 5 \mathrm{psig}$ initial He pressure, $300^{\circ} \mathrm{C}$ reaction temperature, and 4 h reaction time. *PA products are not deconvoluted from the lignin products.

| Lignin Fraction Carbon Yields (\%) |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Feed: | 100 mg GVL <br> extracted lignin (unreduced catalyst) | $\begin{gathered} 100 \mathrm{mg} \\ \text { GVL } \\ \text { extracted } \\ \text { lignin } \end{gathered}$ | 100 mg <br> Maple Wood | 25 mg GVL <br> extracted lignin | 100 mg GVL extracted lignin (150 mg catalyst) | 25 mg <br> extracted <br> lignin + <br> 75 mg <br> Cellulose | $\begin{gathered} 100 \mathrm{mg} \\ \text { GVL } \\ \text { extracted } \\ \text { lignin + } \\ 100 \mathrm{mg} \mathrm{PA}^{*} \end{gathered}$ | 100 mg GVL extracted lignin + 25 mg PA* | $\begin{gathered} 100 \mathrm{mg} \\ \text { Maple } \\ \text { Enzyme } \\ \text { Lignin (EL) } \end{gathered}$ | 100 mg <br> MeOH insoluble GVL extracted lignin |
| 4-Ethylcyclohexanol | 0.9 (0.03) | 1.6 (0.13) | 2.8 | 1.4 (0.12) | 1.5 (0.16) | 3.3 (0.08) | 2.3 (0.04) | 1.9 (0.15) | 1.6 (0.03) | 1.3 |
| 4-Propylcyclohexanol | 1.5 (0.06) | 2.7 (0.32) | 9.3 | 1.8 (0.14) | 2.3 (0.13) | 2.6 (0.15) | 3.2 (0.01) | 2.7 (0.18) | 4.8 (0.07) | 2.2 |
| 4-Propylphenol | 1.1 (0.04) | 0.7 (0.08) | ND | 0.3 (0.05) | 0.4 (0.03) | ND | 0.7 (0.04) | 0.6 (0.04) | 0.7 (0.01) | 0.6 |
| Unidentified Aromatics | 10.9 (0.74) | 7.7 (1.18) | 12.7 | 7.5 (1.46) | 6.5 (1.33) | 4.8 (1.06) | 11.3 (1.68) | 9.3 (1.32) | 7.0 (0.71) | 5.8 |
| Unidentified Cyclohexanols | 6.3 (0.40) | 7.6 (0.42) | 18.5 | 10.6 (0.87) | 8.4 (1.50) | 7.0 (0.39) | 10.3 (0.96) | 8.3 (0.91) | 10.3 (0.33) | 6.8 |
| Total aromatics | 11.9 (0.78) | 8.4 (1.24) | 12.7 | 7.9 (1.51) | 6.9 (1.36) | 4.8 (1.06) | 12.1 (1.72) | 9.8 (1.36) | 7.7 (0.70) | 6.4 |
| Total cyclohexanols | 8.7 (0.49) | 11.9 (0.59) | 30.5 | 13.8 (1.12) | 12.2 (1.79) | 12.9 (0.61) | 15.8 (1.00) | 13.0 (1.24) | 16.7 (0.23) | 10.4 |
| Total monomer yield | 20.7 (1.27) | 20.3 (1.81) | 43.1 | 21.7 (2.63) | 19.1 (3.16) | 17.7 (1.68) | 27.8 (2.73) | 22.8 (2.60) | 24.4 (0.47) | 16.8 |
| Aromatic/cyclohexanol ratio ( $\mathrm{A} / \mathrm{C}$ ratio) | 1.37 | 0.70 | 0.42 | 0.57 | 0.56 | 0.37 | 0.77 | 0.75 | 0.46 | 0.62 |
| Estimated dimer yield | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | 57 | 54 | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ |
| Estimated trimer yield | Not measured | 7 | 6 | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \mathrm{Not} \\ \text { measured } \end{array}$ | Not measured | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ | $\begin{array}{r} \text { Not } \\ \text { measured } \end{array}$ |

