Supporting information for

Efficient conversion of lignin into a water-soluble polymer by a chelator-mediated Fenton reaction: optimization of H₂O₂ use and performance as a dispersant

Michael S. Kent,^{†,§,*} Jijiao Zeng,^{†,§} Nadeya Rader,[§] Isaac C. Avina,[§] Casey T. Simoes,[§] Christopher K. Brenden,[§] Michael L. Busse,[§] John Watt,[§] Nicholas H. Giron,[§] Todd M Alam,[§] Mark D. Allendorf,[§] Blake A. Simmons,^{†,**} Nelson S. Bell[§] and Kenneth L. Sale^{†,§}

† Joint BioEnergy Institute, Emeryville, CA 94608

§ Sandia National Laboratories, Livermore, CA and Albuquerque, NM 87185

**Lawrence Berkeley National Laboratory, Berkeley, CA 94720

*To whom correspondence should be addressed: <u>mskent@sandia.gov</u>

Michael S. Kent (<u>mskent@sandia.gov)*</u>, Jijao Zeng (zengjijiao@gmail.com); Nadeya Rader (nadeyarader@gmail.com); Isaac C. Avina (icavina@sandia.gov); Casey T. Simoes (ctsimoes@live.com), Christopher K. Brenden (ckbrend@sandia.gov), Michael L. Busse (mlbusse@sandia.gov); John Watt (jdwatt@sandia.gov), Nicholas H. Giron (nhgiron@sandia.gov); Todd M. Alam (tmalam@sandia.gov), Mark D. Allendorf (mdallen@sandia.gov), Nelson S. Bell (nsbell@sandia.gov), Blake A. Simmons (<u>basimmons@lbl.gov</u>); Kenneth L. Sale (<u>klsale@sandia.gov</u>)

*To whom correspondence should be addressed: <u>mskent@sandia.gov</u>



Fig. S1. Images of OS lignin-coated silicon wafers post-reaction for a). FEN and b) CMF. In both cases the final column on the wafer was used as a control for $[H_2O_2]_0 = 0\%$. For the FEN reaction a leak occurred in the well corresponding to the spot at the bottom of the final column and that reaction was disregarded in the analysis. In both cases it is visually evident that the mass loss from the film passes through a maximum with either reactant concentration. Also, it is evident that more mass loss occurs at lower $[H_2O_2]_0$ in CMF than in FEN.



Fig. S2. a). Decrease in film thickness as a function of $[H_2O_2]_0$ for FEN with $[FeCl_2]_0$ ranging from 0 mM to 2.5 mM. b). Decrease in film thickness as a function of $[FeCl_2]_0$ for $[H_2O_2]_0$ ranging from 1 wt % to 15 wt%.



Fig. S3. Data of Figure 2a of the main text replotted versus pH for each lignin loading.



Fig. S4. OS lignin mass solubilized by CMF reactions for different chelators at initial pH of 6.



Fig. S5. The effect of bubbling 100% O_2 on the yield of solubilized lignin. Reactions were performed using 100 mg of OS lignin in 8 mls and $[FeCl_3]_0 = [DHB]_0 = 4 \text{ mM}$ at initial pH of 6.

Fig. S6. The yield of water-soluble products for KRAFT, DMR-EH, IL, and OS lignins for CMF reaction with $[FeCl_3]_o = [DHB]_o = 4 \text{ mM}$ and $[H_2O_2]_o = 0.5\%$ with an initial pH of 6 and a lignin loading of 50 mg in 8 ml. The data points are the means of triplicate trials and the error bars are the standard deviations.

Fig. S7. FTIR spectra of water-soluble material from CMF reaction with $[FeCl_3]_o = [DHB]_o = 4 \text{ mM}$ and $[H_2O_2]_o = 0.5\%$ with an OS lignin loading of 100 mg in 8 ml and an initial pH ranging from 4 to 10.

Fig. S8. FTIR spectra of water-soluble products for CMF reaction at $[FeCl_3]_o = [DHB]_o = 4 \text{ mM}$ and $[H_2O_2]_o = 0.5\%$ with an initial pH of 8 and an OS lignin loading ranging from 25 mg in 8 ml to 400 mg in 8 ml.

Fig. S9. FTIR spectra of water-soluble products for KRAFT, DMR-EH, IL, and OS lignins for CMF reaction with $[FeCl_3]_o = [DHB]_o = 4 \text{ mM}$ and $[H_2O_2]_o = 0.5\%$ with an initial pH of 6 and a lignin loading of 50 mg in 8 ml. The dashed curve is the spectrum for the original KRAFT lignin sample.

Fig. S10. C13 NMR spectra of original OS lignin and water-soluble products for CMF reaction at $[FeCl_3]_o = [DHB]_o = 4 \text{ mM}$ and $[H_2O_2]_o = 0.5\%$ with an initial pH of 6 and a lignin loading of 100 mg in 8 ml. Also shown is the spectrum for polyacrylic acid.