Supporting Information

for

Catalytic Conversion of High S-Lignin to a Sustainable Tri-epoxide Polymer Precursor

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References

Table S-1. Summary of organosolv treatments

Method[a]	Organosolv Treatment Condition
OPL	150 g high-S poplar biomass, 1 L methanol, 3 mL HCl (37% w/w), 70 °C, 14 days
FPL	9 g high-S poplar biomass, 10 mL formaldehyde, 50 mL p-dioxane, 4.2 mL HCl (37% w/w), 95 °C, 3.5 h
FA/AA	10 g high-S poplar biomass, FA/AA 70:30 (v/v), heat to boil and hold 2 h
H_2O/HCl	10 g high-S poplar biomass, 40 mL H_2O, 4 mL HCl (37% w/w), 80 °C, 5 h
H_2O/H_2SO_4	10 g high-S poplar biomass, 40 mL H_2O, 4 mL 37 wt% H_2SO_4, 80 °C, 5 h

[a]Lignin was extracted into liquid phase after each organosolv treatment. The liquid phase was collected by filtration. Then the organosolv lignin precipitated into solid phase after the solvent (or organic solvent) was replaced by water. The solid organosolv lignin was collected by filtration and dried under vacuum for 24 h prior to analysis and reactions.

Table S-2. Comparison of isolated lignin from different organosolv treatments

Entry #	Organosolv treatment	Isolated Lignin yield[a] (%)	Heating Duration (h)	M_w (kg/mol)	M_n (kg/mol)	G unit (%)	S unit (%)
1	Intact high-S poplar	n/a[b]	-	-	-	16	82
2	OPL	25	336	3.9	1.1	35	62
3	FPL	125[c]	3.5	-	-	19	80
4	FA/AA	37	2	2.5	0.5	21	79
5	H_2O/HCl	20	5	1.2	0.4	28	72
6	H_2O/H_2SO_4	13	5	1.6	0.8	33	67

[a]Isolated lignin yield (%) = [Isolated lignin (g) / Theoretical lignin (g)] x 100%

[b]The lignin content is 22% by weight of the high-S poplar woody biomass. Lignin content in native high-S poplar biomass includes acid soluble lignin and acid insoluble lignin which is determined by standard NREL procedures: NREL/TP-510-42618 and NREL/TP-510-42623.

[c]Due to mass gain from reaction of the protection agent formaldehyde with the lignin framework, the isolated FPL shows weight gain.

Table S-3. Lignin monomer selectivity and yield (%) from intact high-S poplar biomass with different Pd:Zn ratio

Entry #	Pd:Zn ratio	Selectivity (%)				Total Yield[e] (%)
		DHE[a]	DMPP[b]	DHE-OH[c]	DMPP-OH[d]	
1	1:0	-	5	21	74	56
2	1:3	12	51	25	12	51
3	1:5	8	69	5	18	61
4	1:10	10	71	6	13	61

[a]DHE selectivity (%) = [DHE (g) / Total monomers (g)] x 100%
[b]DMPP selectivity (%) = [DMPP (g) / Total monomers (g)] x 100%
[c]DHE-OH selectivity (%) = [DHE-OH (g) / Total monomers (g)] x 100%
[d]DMPP-OH selectivity (%) = [DMPP-OH (g) / Total monomers (g)] x 100%
[e] Total yield (%) = [Total monomers (g) / Total lignin substrate (g)] x 100%, Total monomers = DHE + DHE-OH + DMPP + DMPP-OH. In case of using intact poplar biomass, the total lignin substrate was 0.223 g (1 g biomass x 22.3% lignin content).
Reaction condition: 1 g intact high-S poplar biomass, 10 wt% Pd-Zn/C (100 mg) catalyst, 30 mL methanol, 36 bar H_2 (gauge pressure measured at room temperature), 225 $^{\circ}$C, 12 hours.

Table S-4. Illustration of lignin monomers selectivity and yield (%) with different types of isolated lignin

Entry #	Isolated Lignin	Selectivity (%)				Total Yield[e] (%)
		DHE[a]	DMPP[b]	DHE-OH[c]	DMPP-OH[d]	
1	OPL	15.6	56	15.6	12.8	32
2	FPL	6	26	33	35	22.2
3	FA/AA	8	92	-	-	3.6
4	H_2O/HCl	12	49	18	21	33
5	H_2O/H_2SO_4	7	93	-	-	9.7

[a]DHE selectivity (%) = [DHE (g) / Total monomers (g)] x 100%
[b]DMPP selectivity (%) = [DMPP (g) / Total monomers (g)] x 100%
[c]DHE-OH selectivity (%) = [DHE-OH (g) / Total monomers (g)] x 100%
[d]DMPP-OH selectivity (%) = [DMPP-OH (g) / Total monomers (g)] x 100%
[e] Total yield (%) = [Total monomers (g) / Total lignin substrate (g)] x 100%, Total monomers = DHE + DHE-OH + DMPP + DMPP-OH.
Reaction condition: 500 mg lignin substrate, 10 wt% Pd-Zn/C (Pd:Zn 1:10) catalyst, 30 mL methanol, 36 bar H_2 (gauge pressure measured at room temperature), 225 °C, 12 hours.

Table S-5. Illustration of lignin monomers selectivity and yield (%) with improved reaction condition from OPL, FPL, and H_2O/HCl lignin.

Entry #	Isolated Lignin	Selectivity (%)				Total Yield[e] (%)
		DHE[a]	DMPP[b]	DHE-OH[c]	DMPP-OH[d]	
1	OPL[f]	9	36	24	31	50
2	FPL[f]	4	26	28	42	35
3	H_2O/HCl[f]	2	18	32	48	45

[a]DHE selectivity (%) = [DHE (g) / Total monomers (g)] x 100%
[b]DMPP selectivity (%) = [DMPP (g) / Total monomers (g)] x 100%
[c]DHE-OH selectivity (%) = [DHE-OH (g) / Total monomers (g)] x 100%
[d]DMPP-OH selectivity (%) = [DMPP-OH (g) / Total monomers (g)] x 100%
[e] Total yield (%) = [Total monomers (g) / Total lignin substrate (g)] x 100%, Total monomers = DHE + DHE-OH + DMPP + DMPP-OH.
[f] Entries with 30 wt% of Pd-Zn/C (Pd:Zn = 1:10) catalyst loading
Reaction condition: 500 mg lignin substrate, Pd-Zn/C, catalyst, 30 mL methanol, 36 bar H_2 (gauge pressure measured at room temperature), 225 $^\circ$C, 12 h.

Table S-6. Illustration of lignin monomers selectivity and yield (%) with different catalyst loading and reaction time

Entry #	Isolated Lignin	Selectivity (%)				Total Yield[e] (%)
		DHE[a]	DMPP[b]	DHE-OH[c]	DMPP-OH[d]	
1	OPL[f]	16.5	53	12.5	18	39.5
2	OPL[f-18]	9	40	22	29	48
3	OPL[g-18]	5	36.5	24	31	50
4	FPL[f]	3.5	26	26	44.5	31
5	H$_2$O/HCl[f]	8	33	29.5	29.5	43

[a]DHE selectivity (%) = [DHE (g) / Total monomers (g)] x 100%
[b]DMPP selectivity (%) = [DMPP (g) / Total monomers (g)] x 100%
[c]DHE-OH selectivity (%) = [DHE-OH (g) / Total monomers (g)] x 100%
[d]DMPP-OH selectivity (%) = [DMPP-OH (g) / Total monomers (g)] x 100%
[e] Total yield (%) = [Total monomers (g) / Total lignin substrate (g)] x 100%, Total monomers = DHE + DHE-OH + DMPP + DMPP-OH.
[f] Entries with 20 wt% of Pd-Zn/C (Pd:Zn = 1:10) catalyst loading, [f-18] indicates entry with 20 wt% catalyst but 18h reactions.
[g-18] indicates the entry with 30 wt% catalyst but 18h reactions.
Reaction condition: 500 mg lignin substrate, Pd-Zn/C (Pd:Zn 1:10) catalyst, 30 mL methanol, 36 bar H$_2$ (gauge pressure measured at room temperature), 225 $^\circ$C, 12 h.

Table S-7. Illustration of economic efficiency of converting 2300 kilo ton poplar biomass into DMPPO to displace BPA market

	Plantation yield	**Land occupation**	**Agricultural cost**
Input	7 dry ton/acre	1% of Iowa state	$58 – 138 million
	DMPPO yield	**Market size**	**Product value**
Output	300 kilo ton	3.75% of BPA market	$600 million
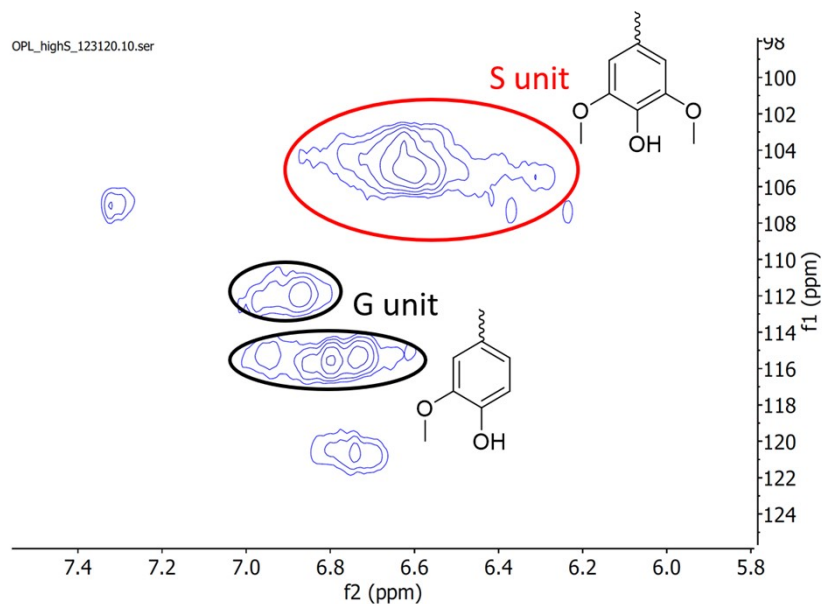
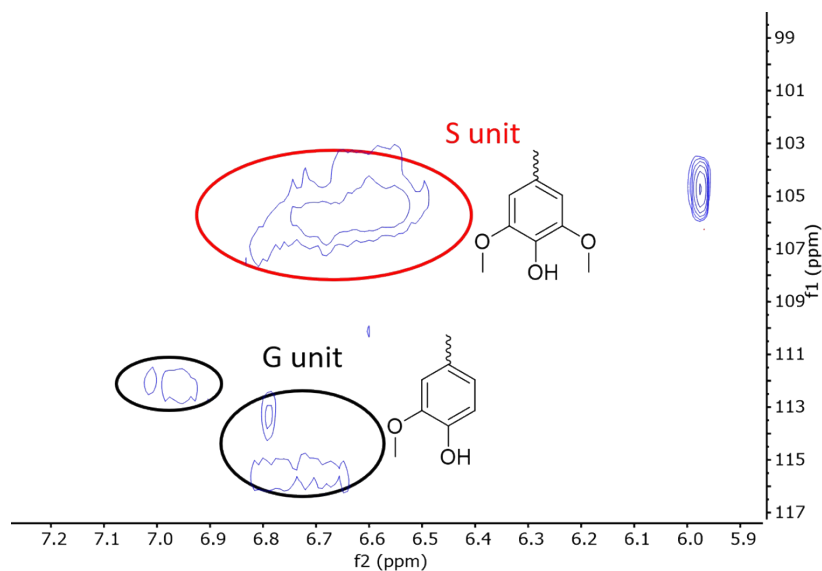**Figure S-1-a**. 2D HSQC NMR of the aromatic region on OPL lignin.

Figure S-1-b. 2D HSQC NMR of the aromatic region on FPL lignin.

Figures S-1-a and S-1-b illustrate the aromatic region of 2D HSQC NMR of OPL and FPL lignins which indicate the specific carbon-proton corrections of G and S units. The content of each lignin unit was calculated according to a method described on literature which uses the integration of the contour signals of the G and S units.[1] For instance, the percentage of G and S

content X% can be calculated as: $X\% = X/(S_{2/6} + S'_{2/6} + G_2 + G_5 + G_6)$, where $X = S_{2/6} + S'_{2/6}$ when calculating the S unit content, while $X = G_2 + G_5 + G_6$ for G unit. The carbon-proton ($^{13}C/^{1}H$) correlations were assigned according to literature.[2] By which, $S_{2/6}$: 103.0-104.0 ppm/6.6-6.8 ppm, $S'_{2/6}$: 105.0-106.0 ppm/7.3-7.4 ppm, G_2: 110.0-111.0 ppm/7.0-7.1 ppm, G_5: 114.0-115.0 ppm/6.7-6.9 ppm, and G_6: 118.0-119.0 ppm/6.8-6.9 ppm.
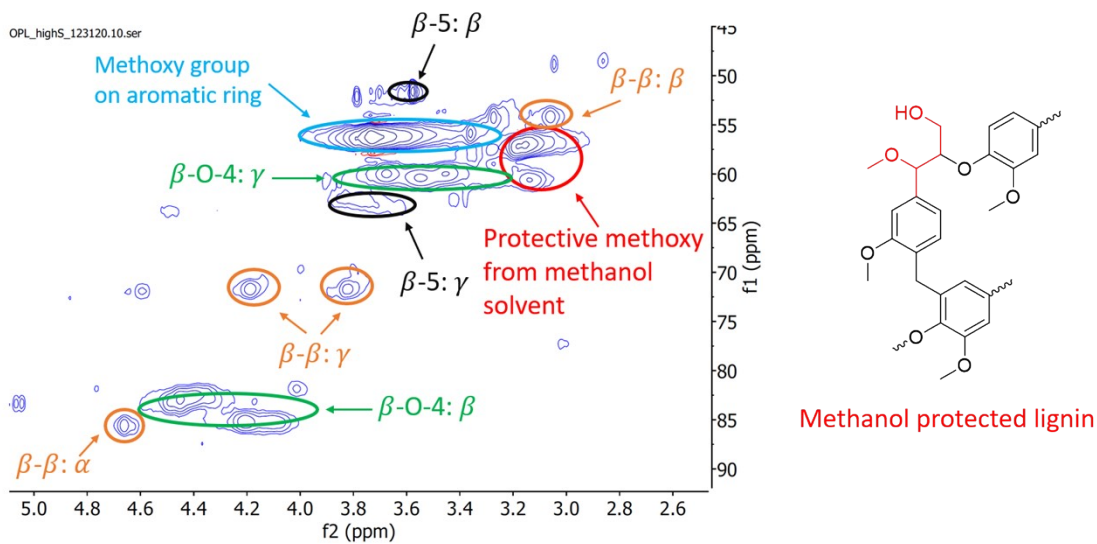
Figure S-2. 2D HSQC NMR of the aliphatic region for OPL lignin

Figure S-2 illustrates the 2D HSQC NMR detection of the aliphatic region on OPL lignin. By which, the protective methoxy group attached to the lignin structure was observed (labeled in red). The source of additional methoxy group was the methanol solvent which was used for lignin extraction during OPL organosolv treatment.
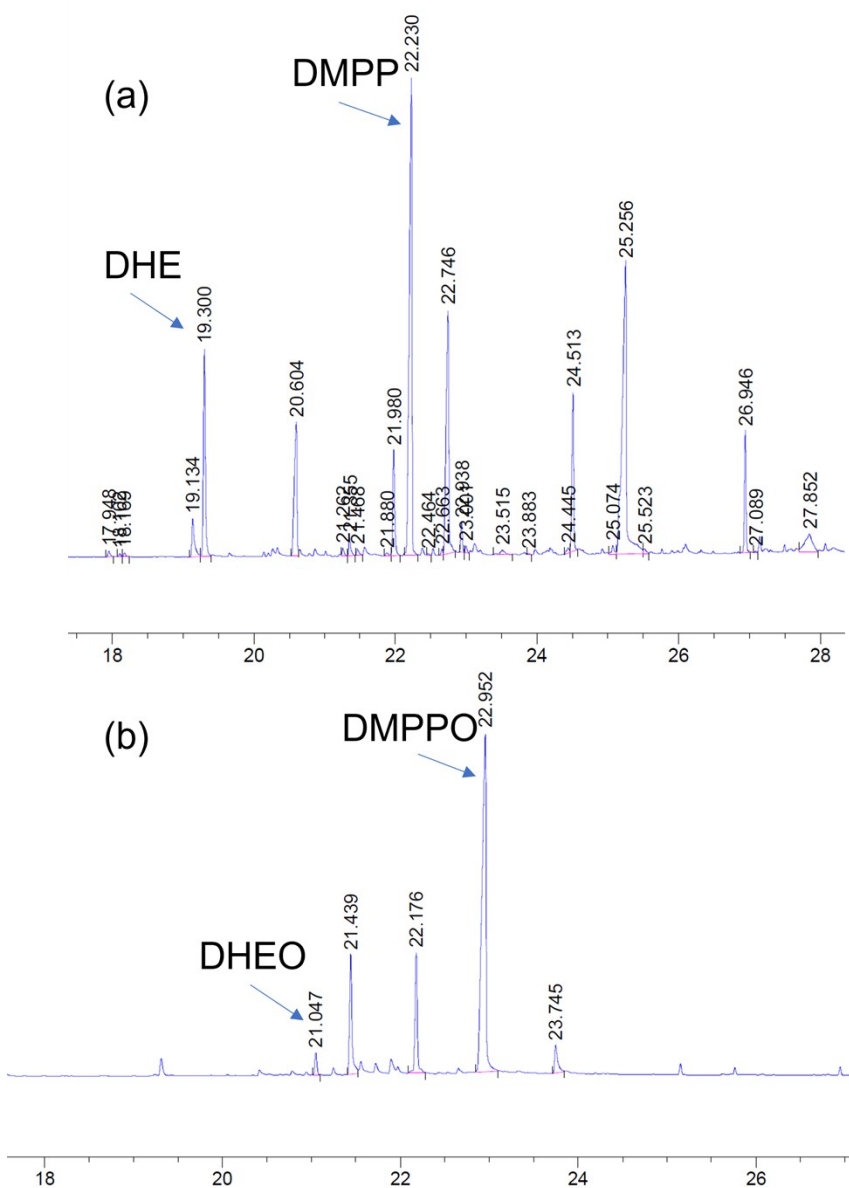
Figure S-3. GC-FID spectrum of (a) DMPP oil obtained from lignin depolymerization reaction and (b) DMPPO product made from the DMPP oil display in spectrum Figure S-3 (a) over Nb_2O_5 catalyst.

Figure S-3 (a) displays the GC-FID result of DMPP (22.230 min) oil derived from high-S poplar lignin which shows the peak of DMPP as the major product and many other GC peaks as by-products and unidentified species. The commercial clean standard DMPP is transparent with slightly yellow coloured oil. However, the DMPP oil made from lignin depolymerizations was in dark brown colour. This phenomenon also indicates the DMPP oil in (a) was impure. Similarly, the DMPPO made from such dark brown DMPP oil also contained by-products and impurities as displayed in (b). This result suggests our Nb_2O_5 catalyst was tolerant to the by-products and impurities which still converted DMPP in the dark brown oil into DMPPO. However, the GC

peaks (Figure S-3 (b)) of by-products and impurities were reduced in the DMPPO product after the Nb_2O_5 reaction. This could because the by-products and impurities were adsorbed to the Nb_2O_5 and caused the catalyst had colour change from white (fresh Nb_2O_5) to grayish brown (used Nb_2O_5). By which, this change to the Nb_2O_5 may also cause the deactivation after the third run of recycling test (Figure 7).
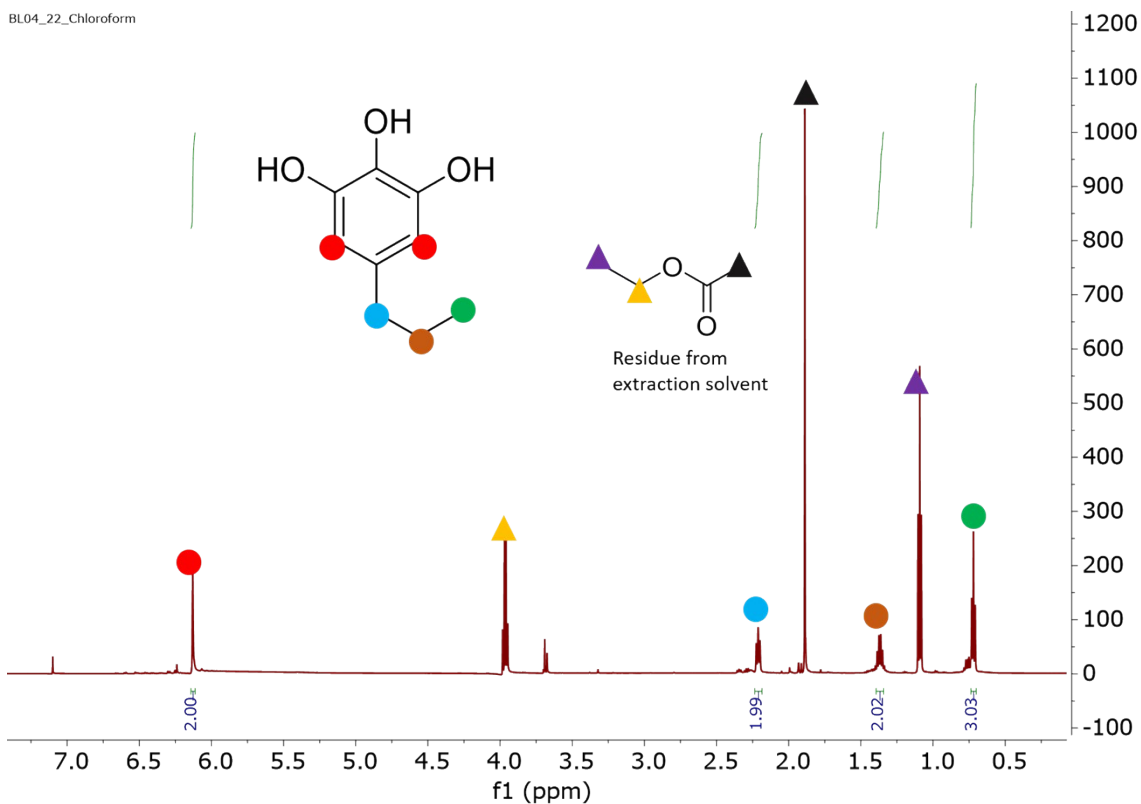
Figure S-4. ^{1}H NMR of DMPPO obtained from the Nb$_2$O$_5$ catalyzed reaction mixture.

Figure S-4 illustrates the proton signal of DMPPO molecule made from DMPP over Nb$_2$O$_5$ catalyst. The assignment of proton signals on spectrum by DMPPO was labeled with the colored circles. The signals labeled with triangles were due to the ethyl acetate residue because the DMPPO was produced in reaction water medium and after reaction it was extracted by ethyl acetate into organic layer and thus some ethyl acetate remained with DMPPO after product extraction.
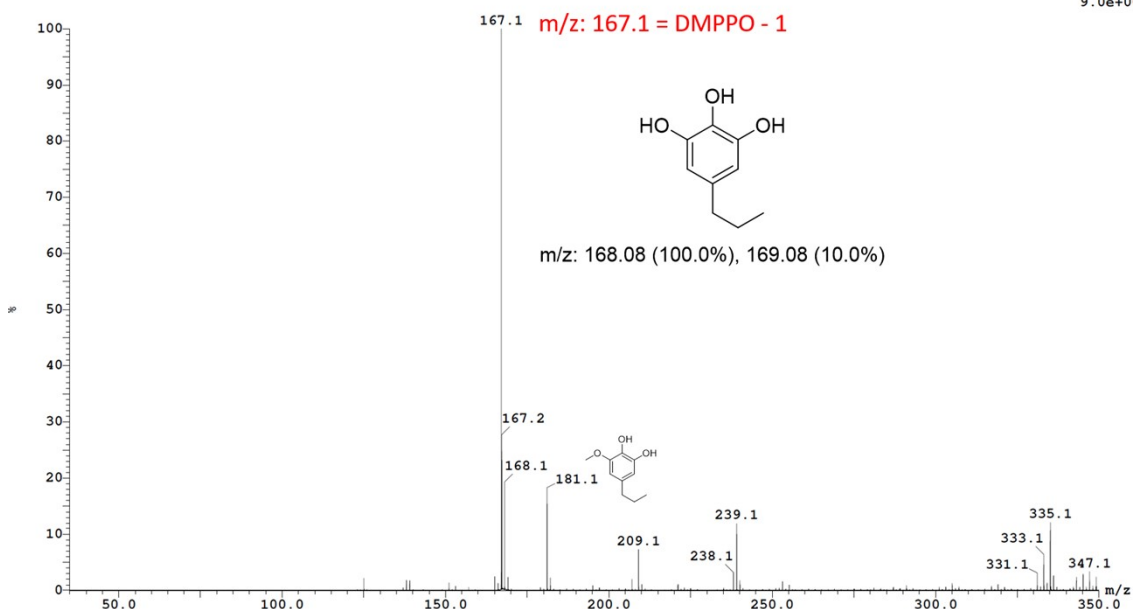
Figure S-5. ES- mass spectroscopy of DMPPO obtained from the Nb_2O_5 catalyzed reaction mixture.

ES- mass spectroscopy was also used to confirm the production of DMPPO. According to the chemical structure of DMPPO which contains three phenolic hydroxyl groups, ES- mass spectroscopy was selectively performed for the detection. The DMPPO was ionized in the negative ion mode by giving off a proton and the detected mass of DMPPO was the molecular weight of DMPPO – 1. The molecular weight of DMPPO is 168.08 g/mol, and thus the detected 167.1 m/Z on the spectrum indicates the presence of DMPPO. On the other hand, the by-product MeO-DHEO which molecular weight is 182.08 was also observed on the ES- detection at the detected m/Z of 181.1. The other small signals such as 209.1, 239.1, and 335.1 were from the instrument background.
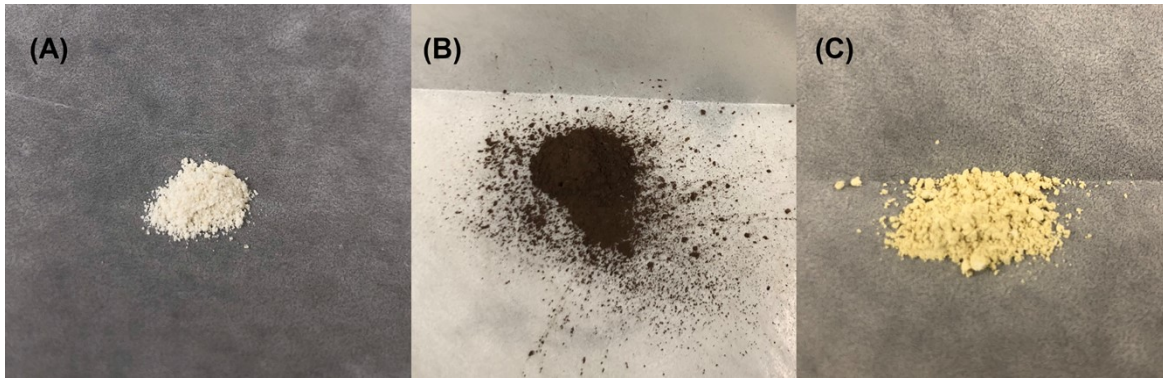
Figure S-6. Illustration of colour on (A) fresh Nb_2O_5, (B) used Nb_2O_5 after 3rd recycle reaction, and (C) the regenerated Nb_2O_5 after calcination at 450 $^\circ$C.
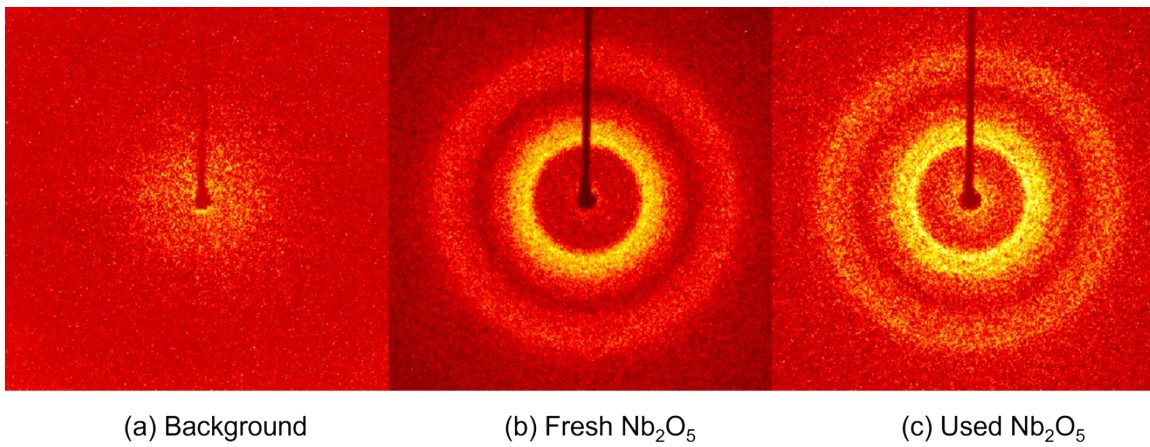

(a) Background   (b) Fresh Nb_2O_5 (c) Used Nb_2O_5

Figure S-7. Comparison of XRD between (a) background, (b) fresh Nb_2O_5, and (c) Used Nb_2O_5. The Used Nb_2O_5 was obtained after the 3rd recycle reaction.
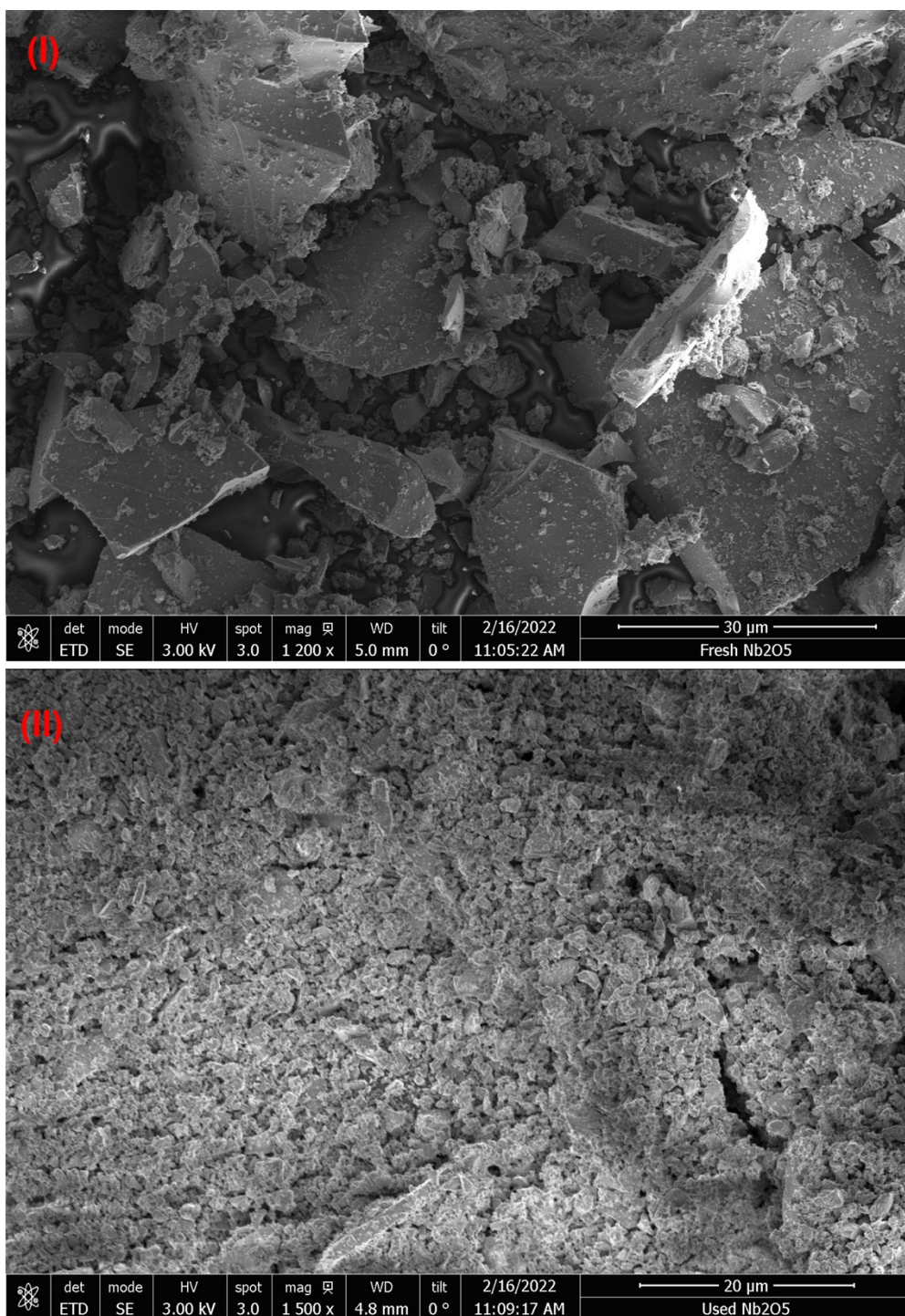
(I)

det	mode	HV	spot	mag ⊡	WD	tilt	2/16/2022	30 µm
ETD	SE	3.00 kV	3.0	1 200 x	5.0 mm	0 °	11:05:22 AM	Fresh Nb2O5

(II)

det	mode	HV	spot	mag ⊡	WD	tilt	2/16/2022	20 µm
ETD	SE	3.00 kV	3.0	1 500 x	4.8 mm	0 °	11:09:17 AM	Used Nb2O5

Figure S-8. SEM of (I) fresh Nb_2O_5 and (II) used Nb_2O_5. The Used Nb_2O_5 was obtained after the 3rd recycle reaction.
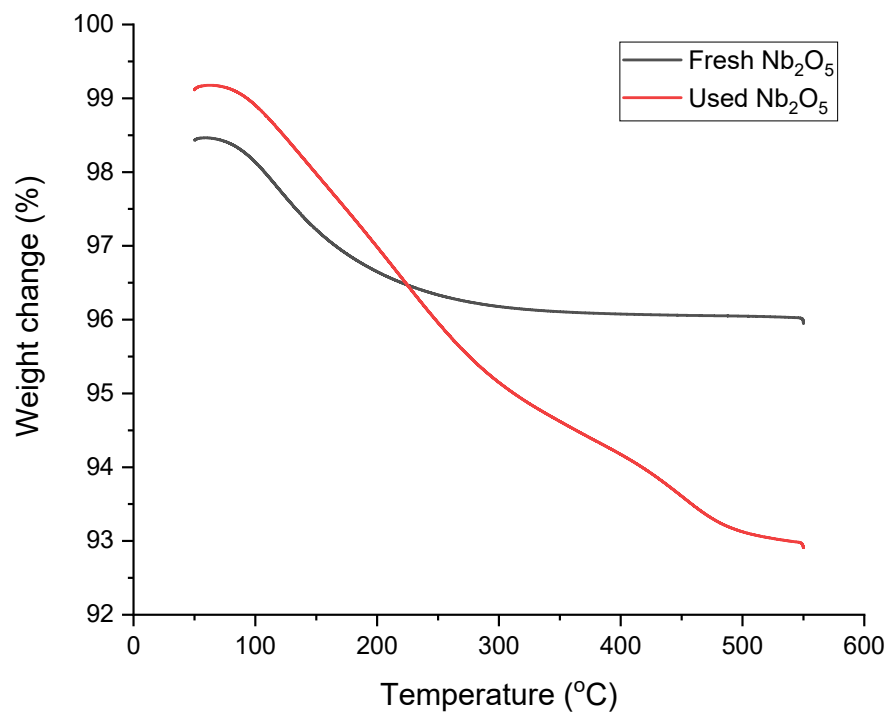
Figure S-9. Comparison between fresh Nb_2O_5 and used Nb_2O_5 by TGA analysis. The Used Nb_2O_5 was obtained after the 3rd recycle reaction.
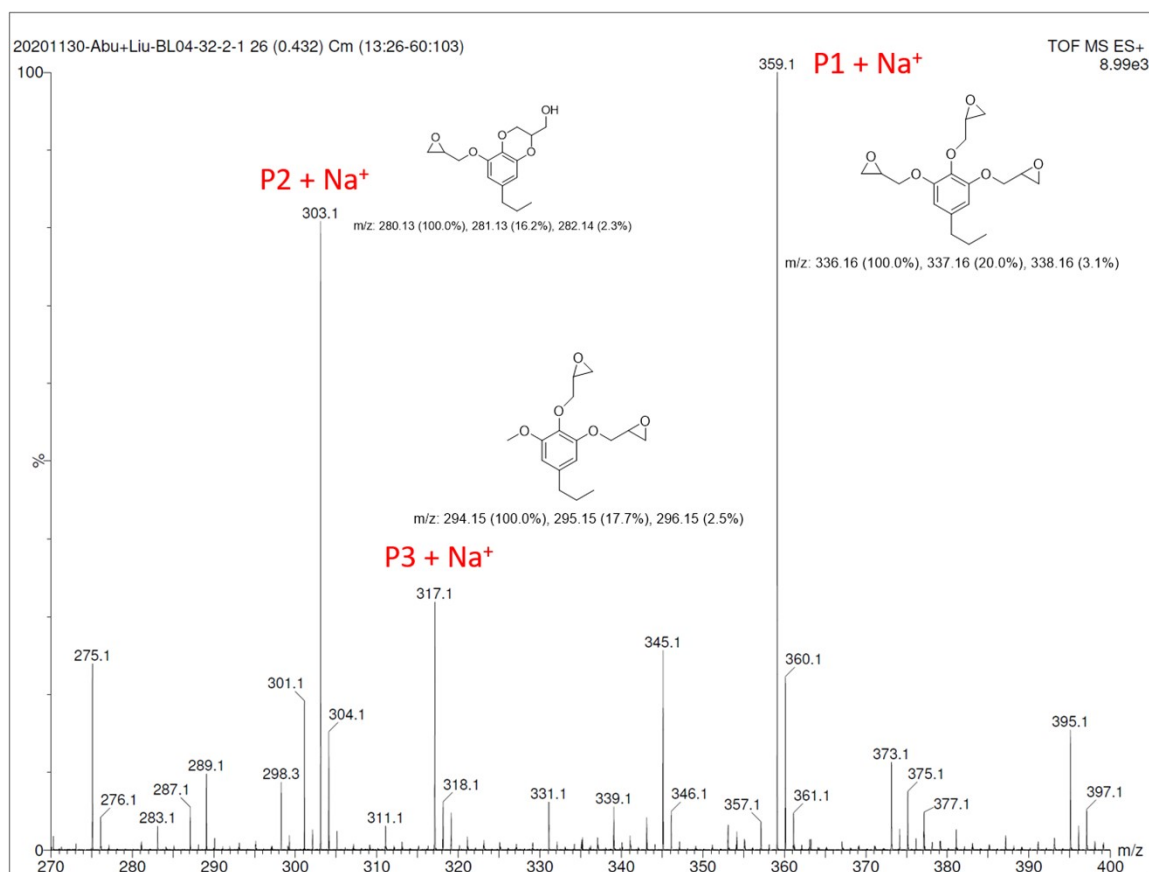
Figure S-10. ES+ mass spectroscopy of epoxides made from the lignin derived DMPPO.

ES+ mass spectroscopy was used for the detection of epoxides made from lignin derived DMPPO. Due to the chemical structures of the epoxides, they are hardly ionized in the negative ionization mode. Therefore, the positively charged adducts were added to the epoxide molecules during the measurement. The detection in Figure S-5 shows the mass spectroscopy detection of the epoxides with sodium ion adducts (Na$^+$) which the detected m/Z was the molecular weight of epoxide + 23. P1 is the tri-epoxides made from DMPPO which has molecular weight 336.16 g/mol and thus the 359.1 signal indicated the formation of P1. Similarly, the detected m/Z of 303.1 represented the byproduct P2 formed during the reaction of DMPPO with epichlorohydrin. According to the literature, the product distribution between the epoxides (P1) and ring-opening byproduct (P2) was around 1:1.[3] Thus the detection of P2 was also significant on ES+ mass spectroscopy. The di-epoxides product P3 was also observed at the detected m/Z of 317.1. The formation of P3 was because the byproduct MeO-DHEO made from DMPP over Nb$_2$O$_5$ and further reacted with epichlorohydrin.
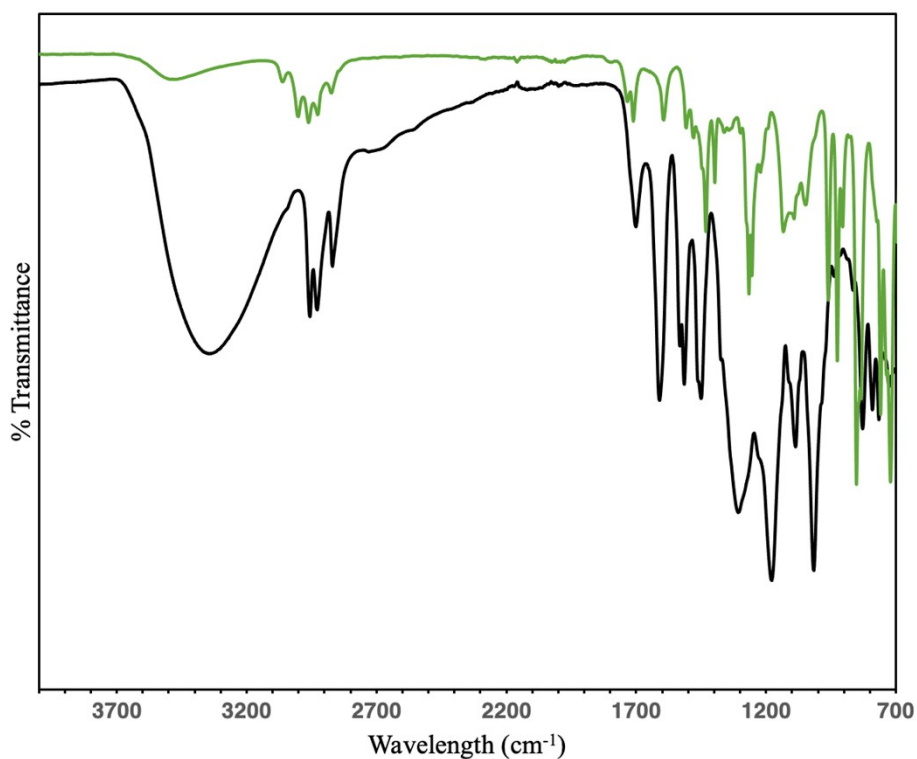
Figure S-11. FT-IR spectra of DMPPO mixture (black coloured) and epoxy monomers (green coloured).

Before epoxidation of the DMPPO mixture, peaks appear at around 3331 cm^{-1} for O−H stretching, 2867, 2950 and 2957 cm^{-1} for alkyl C−H stretch, and 1610, 1515 and 1448 cm^{-1} aromatic C−C bond. After the epoxidation of the phenols with epichlorohydrin, an epoxy ring band at 927 cm^{-1} and a C−O−C ether linkage at 1015 cm^{-1} are observed. The O-H bands of the glycidyl ethers significantly decreased after epoxidation, indicating the hydroxyl groups are consumed but with some benzodioxane side product O-H present.
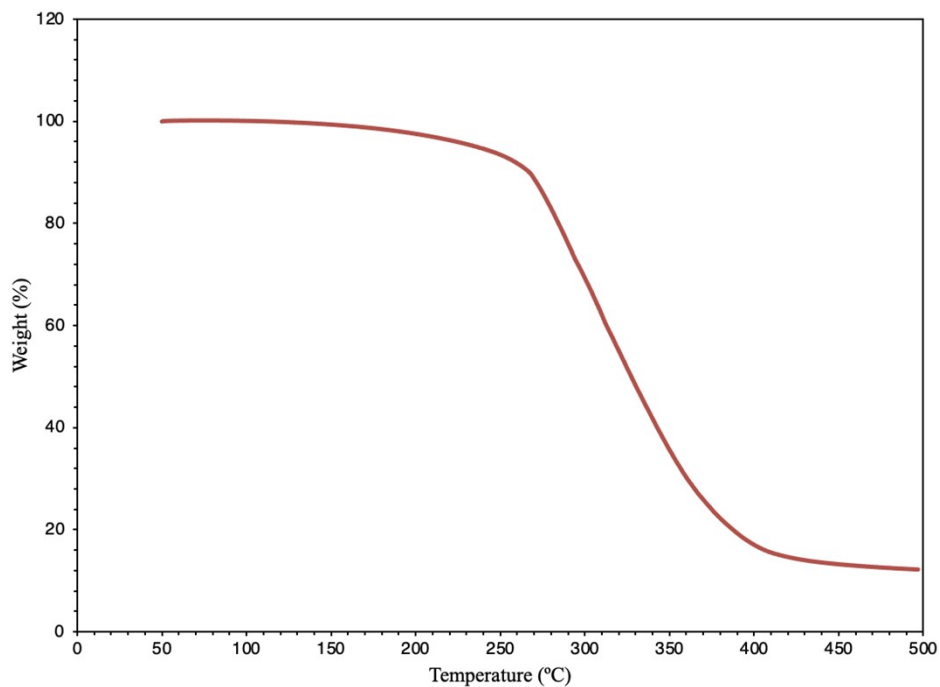
Figure S-12. TGA analysis thermogram of DMPPO based epoxy network as a function of temperature.

Thermogravimetric analysis (TGA) thermograms show a one-step degradation profile, which is attributed to the decomposition of cross-linked polymer network. The onset degradation temperature (T_{d5}, temperature at 5% weight loss) was 252 $^{\circ}$C.

References

1.	Cheng, C. B.; Truong, J.; Barrett, J. A.; Shen, D. K.; Abu-Omar, M. M.; Ford, P. C., Hydrogenolysis of Organosolv Lignin in Ethanol/Isopropanol Media without Added Transition-Metal Catalyst. *Acs Sustain Chem Eng* **2020,** *8* (2), 1023-1030.

2.	Luo, H.; Abu-Omar, M. M., Lignin extraction and catalytic upgrading from genetically modified poplar. *Green Chem* **2018,** *20* (3), 745-753.

3.	Zhao, S.; Abu-Omar, M. M., Biobased Epoxy Nanocomposites Derived from Lignin-Based Monomers. *Biomacromolecules* **2015,** *16* (7), 2025-2031.