Room Temperature Depolymerization of Lignin using a Protic and Metal Based-Ionic Liquid System: An Efficient Method of Catalytic Conversion and Value Addition

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Table of contents

1) NMR spectra of EAN

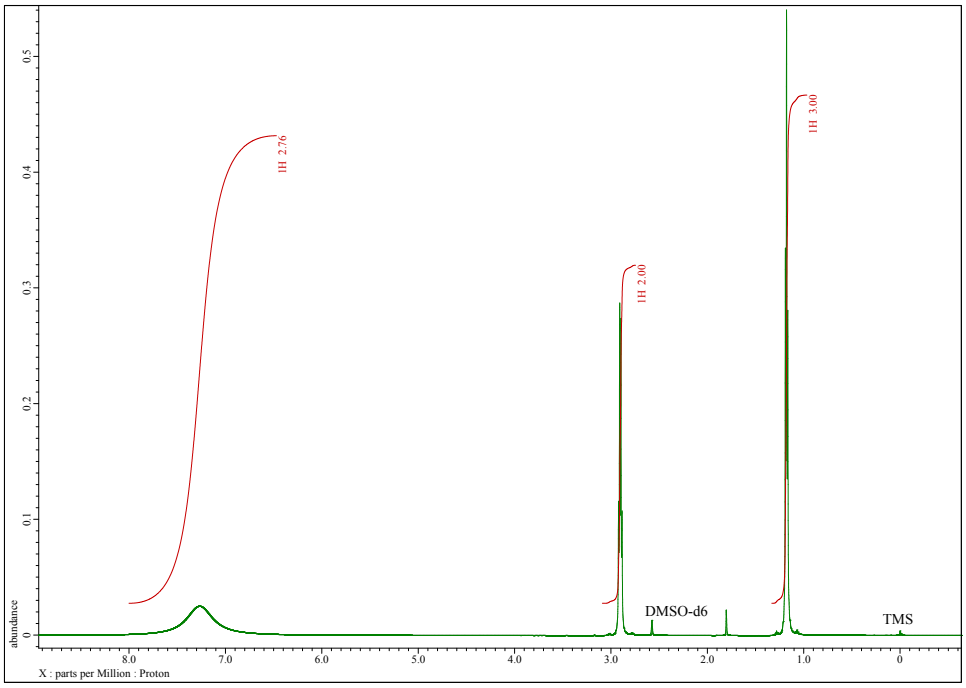

Figure S1. ^{1}H NMR spectra of ethylammonium nitrate.

2) Raman analysis of $[Bmim]_2[MnCl_4]$ and $[Pro]_2[MnCl_4]$

The tetrahedral manganese based ionic liquid complex $[MnCl_4]^{2-}$ has been confirmed using the Raman spectra. The characteristic peak at 251cm^{-1} due to the Mn –Cl bond in $[MnCl_4]^{2-}$ counter anion.

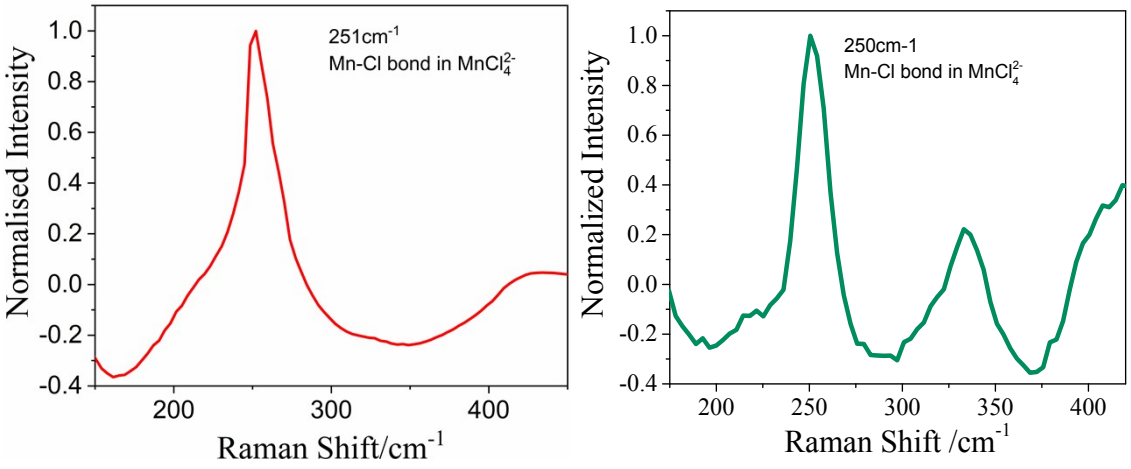

Figure S2. Raman spectra of $[Bmim]_2[MnCl_4]$, and $[Pro]_2[MnCl_4]$.

3) UV, LC-MS, Elemental and EPR analysis of $[Bmim]_2[MnCl_4]$, and $[Pro]_2[MnCl_4]$

The UV spectra show the three peaks of the $[MnCl_4]^{2-}$ complex at 353nm, 432nm, and 445nm which confirm the tetrahedral structure of the $[MnCl_4]^{2-}$.

The EPR spectra has been used to confirm the Mn(II) in the $[Bmim]_2[MnCl_4]$, and $[Pro]_2[MnCl_4]$. The tetrahedral Mn(II) complex of $[MnCl_4]^{2-}$ show six hyperfine splitting lines which is corresponding to the Ms= +5/2, +3/2, +1/2, –1/2, –3/2, –5/2 d5 system.The six lines shows due to unpaired electron in Mn(II) counter ion.

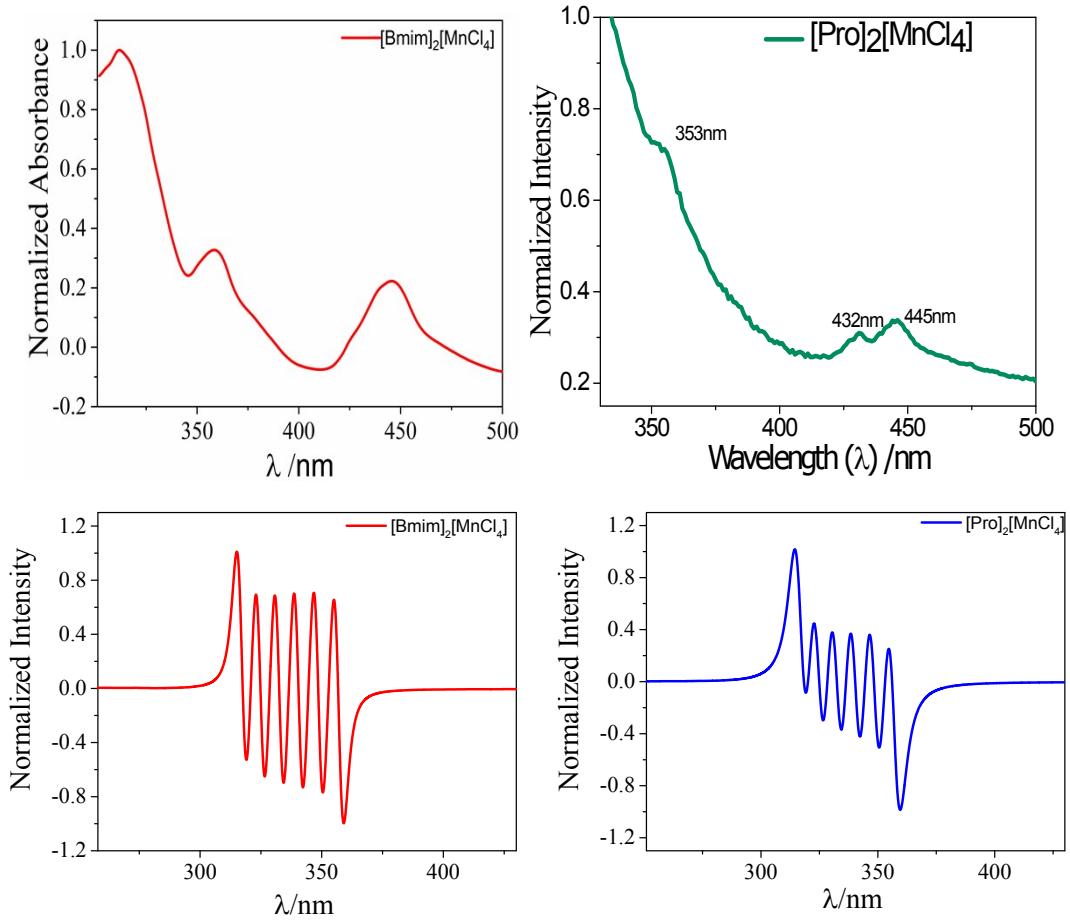

Figure S3. Raman and UV analysis of $[Bmim]_2[MnCl_4]$, and $[Pro]_2[MnCl_4]$.

LC-MS

$[Pro]_2[MnCl_4]$: ESI + 116.07 ESI - 197.80

$[Bmim]_2[MnCl_4]$: ESI + 139.12 ESI - 197.80

Elemental Composition

	%C	%H	%N
$[Bmim]_2[MnCl_4]$	39.12	5.91	10.19
$[Pro]_2[MnCl_4]$	27.56	4.22	6.36

4) GC-MS chromatogram of EAN (5 wt% lignin) Table 1, Entry 1

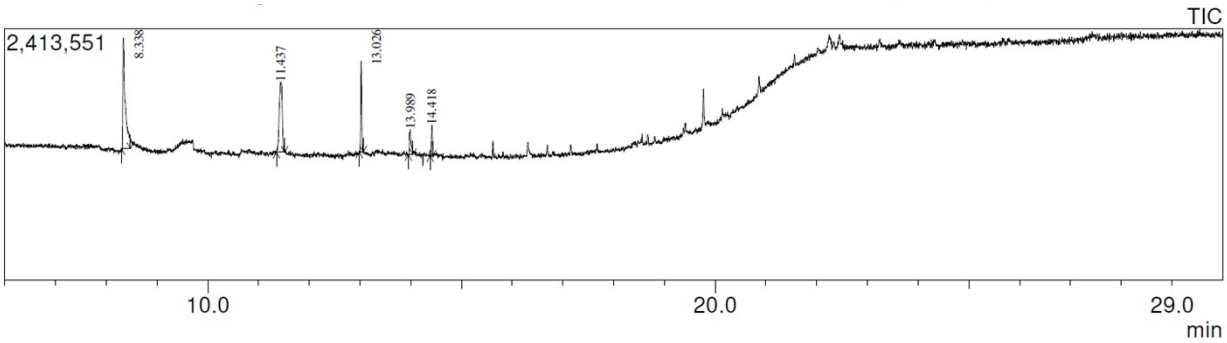

Figure S4. GC-MS chromatogram of EAN (5 wt% lignin) Table 1, Entry 1.

5) GC-MS chromatogram of EAN + $[Bmim]_2[MnCl_4]$ (9.8g:0.2g) (5 wt% lignin) Table 1, Entry 2

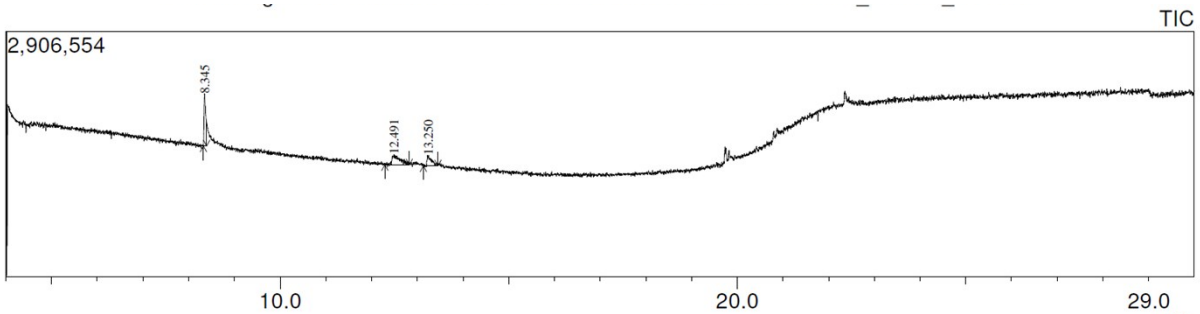

Figure S5. GC-MS chromatogram of EAN + $[Bmim]_2[MnCl_4]$ (9.8g:0.2g) (5 wt% lignin) Table 1, Entry 2.

6) GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$(9.8g:0.2g) (5 wt% lignin) Table 1, Entry 3

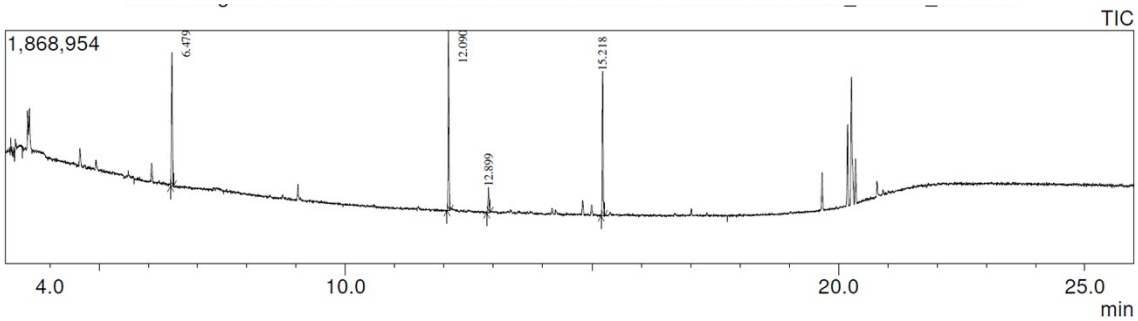

Figure S6. GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$(9.8g:0.2g) (5 wt% lignin) Table 1, Entry 3

7) GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 4

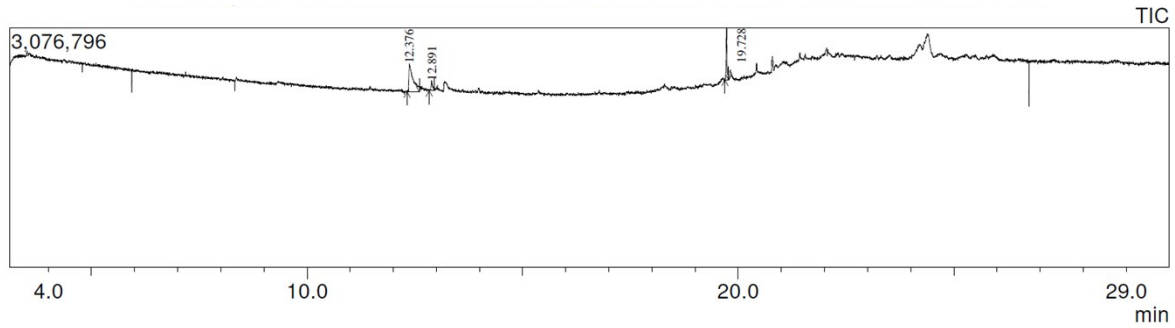

Figure S7. GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 4

8) GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 5

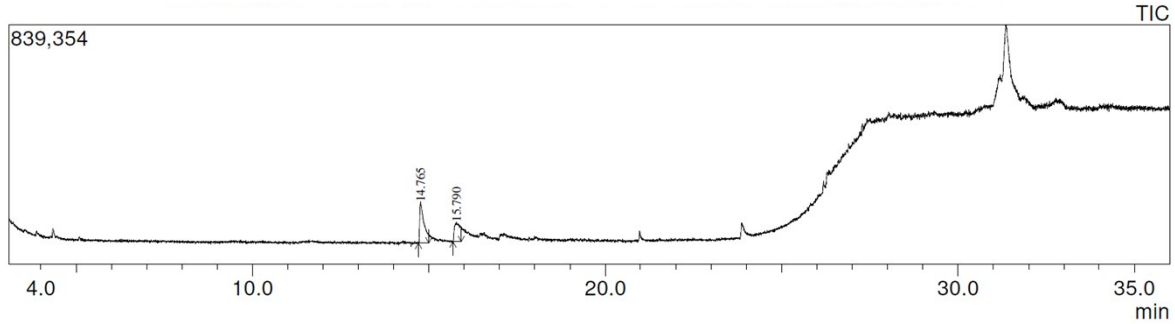

Figure S8. GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 5

9) GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 6

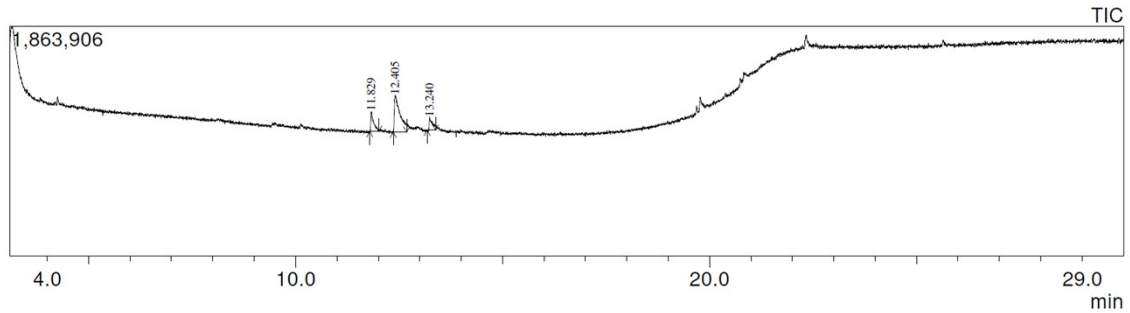

Figure S9. GC-MS chromatogram of EAN + $[Pro]_2[MnCl_4]$ (9.6g:0.4g) (5 wt% lignin) Table 1, Entry 6.

10) NMR spectra of DSIL: Fresh and after 5th cycle

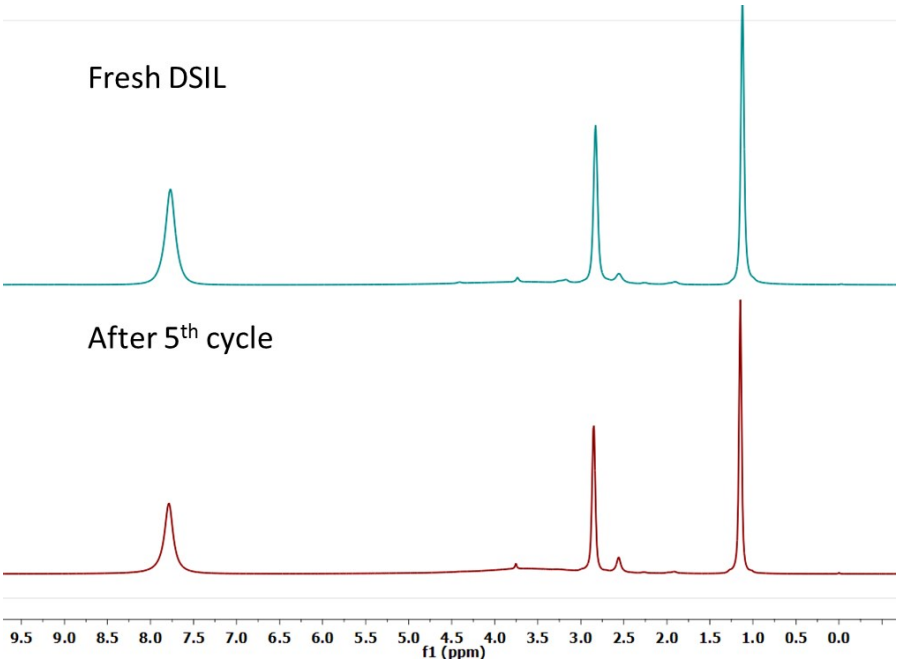

Figure S10. NMR spectra of fresh (up) and after 5th (down) DSIL.

11) FE-SEM micrographs of prepared films

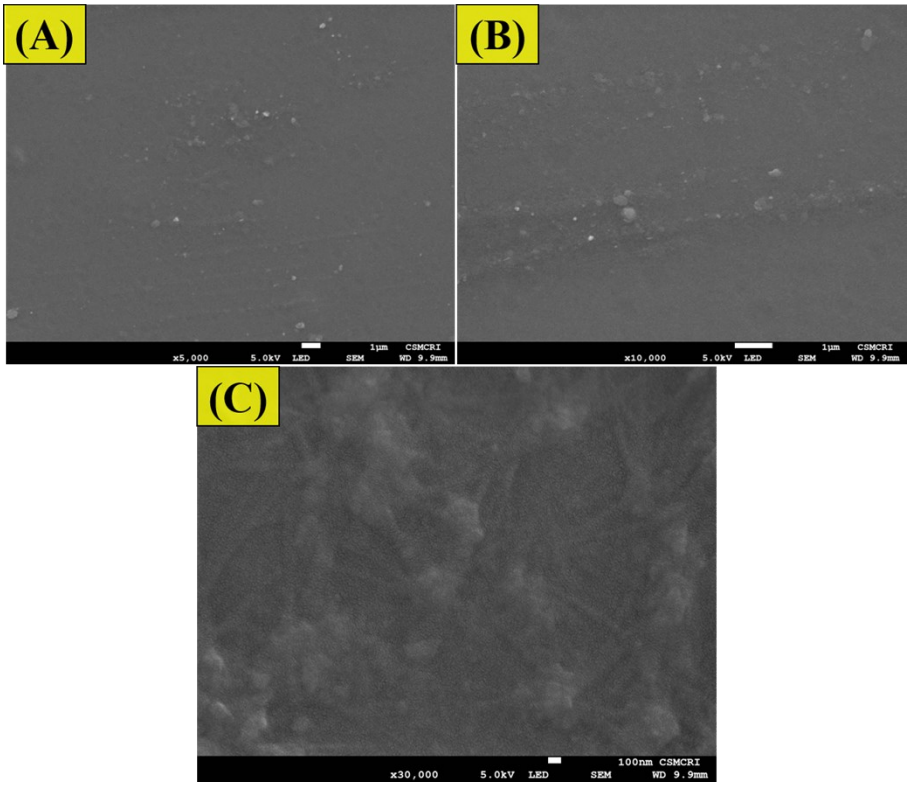

Figure S11. FE-SEM micrographs of lignin-chitosan films.

12) 2D HSQC NMR of pure and depolymerised lignin

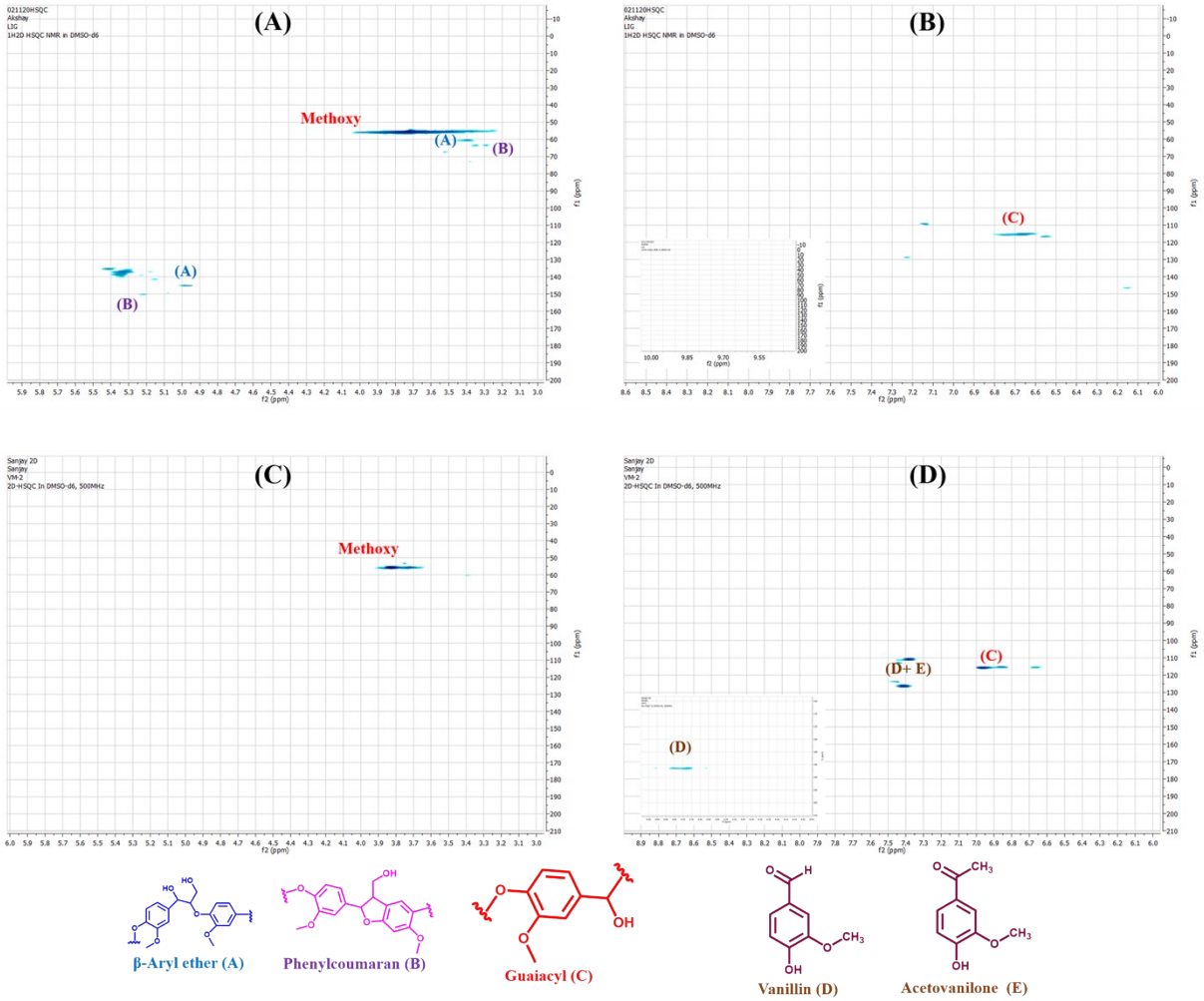

Figure S12. 2D-HSQC NMR spectra of the pure lignin (A, B) and the depolymerized lignin (C, D).

13) Purification of vanillin from extracted EtOAc phase

The isolation and quantification of vanillin have also been confirmed by using methods described by Liu et. al.[3] In brief, the depolymerized lignin was completely dissolved in the NaOH solution during the oxidation reaction. After being diluting to 100 mL, a 5.0 mL aliquot of the product mixture was transferred to a 50 mL centrifuge tube and acidified to pH 1.5 with 3 M HCl. The sample was then extracted with 5 × 20 mL of ethyl acetate (EtOAc). The organic fraction was filtered, dried with sodium sulfate, and solvent was removed using rotary evaporator. The dried extract was weighed and dissolved in 4.0 mL of acetone followed by gas chromatography coupled to mass spectrometry (GC-MS) analysis. The yield of pure vanillin which was found to be **16%** in yield.

Vanillin yield calculation

The yield of vanillin has been calculated by using equation mentioned below.

$$Vanillin\ yield\ (\%) = \frac{Concentration\ (M)\ X\ M.W.\ of\ Vanillin\ X\ Volume\ of\ sample(ml)\ X\ D.F.}{weight\ of\ lignin\ (g)}\ X\ 100$$

The table mentioned below shows the area under the curve for each system studied.

No.	IL/DSIL	Lignin (%)	Time (h)	Area under the curve	Vanillin Yield (%)
1	EAN+$[bmim]_2[MnCl4]_2$(5%)	5	6	1350649	8-10%
2	EAN+$[Pro]_2[MnCl4]_2$(5%)	5	6	1874831	9-12%
3	EAN+$[Pro]_2[MnCl4]_2$(5%)	5	4	2795066	16-19%
4	EAN+$[Pro]_2[MnCl4]_2$(4%)	5	4	2423303	15-17%
5	EAN+$[Pro]_2[MnCl4]_2$(3%)	5	4	1843068	11-14%
6	EAN+$[Pro]_2[MnCl4]_2$(2%)	5	4	1229800	5-9%
7	EAN+$[Pro]_2[MnCl4]_2$(5%)	20	4	3022921	18-20%

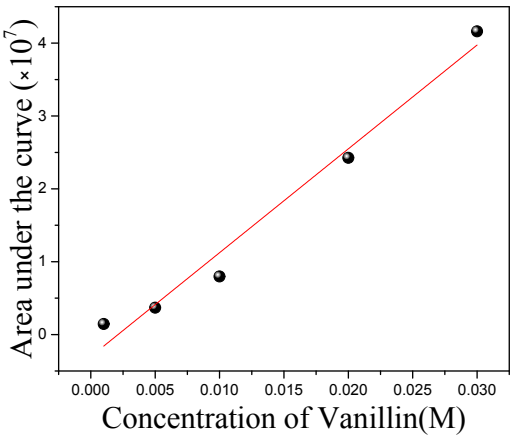

Figure S13. Calibration curve for vanillin.

References

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2. B. T. Allen, The Journal of Chemical Physics 1965, **43**(11), 3820–3826.
3. Liu, S.; Das, L.; Blauch, D. N.; Veronee, C.; Dou, C.; Gladden, J.; Sun, N.; Socha, A. M., Statistical design of experiments for production and purification of vanillin and aminophenols from commercial lignin. *Green Chemistry* **2020,** *22* (12), 3917-3926.