Electronic Supplementary Material (ESI) for Green Chemistry.

***Supplementary data (15 pages)***

# Isolation of phenolic monomers from kraft lignin using magnetically recyclable TEMPO nanocatalyst

Saurabh C Patankar,[a] Liyang Liu,[a] Lun Ji,[a] Sonal Ayakar,[b] Vikramaditya Yadav,[b] and Scott Renneckar[a*]

[a]*Department of Wood Science, The University of British Columbia, 2424 Main Mall, Vancouver, British Columbia, Canada V6T1Z4.*

[b]*Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, British Columbia, Canada V6T1Z3.*

* *E-mail: scott.renneckar@ubc.ca*

Table of Contents

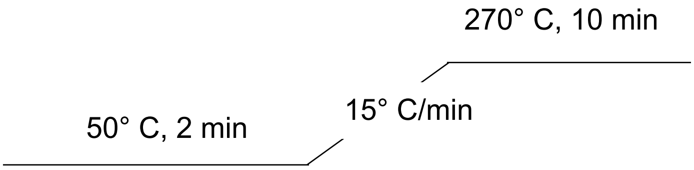
| **Sr No.** | **Content** | **Page No.** |
|---|---|---|
| 1 | Chemicals | 02 |
| 2 | Separation and analysis of phenolic monomers and polymeric lignin | 02 |
| 3 | Characterization of lignin and Fe@MagTEMPO catalyst | 03 |
| 4 | Preparation of acid washed, acetone soluble (ASKL) and acetone insoluble (AIKL) kraft lignin | 03 |
| 5 | Fe@MagTEMPO catalyst recovery and reuse procedure | 04 |
| 6 | Details of NMR analysis | 05 |
| 7 | Details of GPC analysis | 05 |
| 8 | Details of ICP analysis | 05 |
| 9 | Table S1: Comparison of vanillin yield derived through oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst with values in literature | 06 |
| 10 | Table S2: Effect of pH on vanillin selectivity and phenolic monomer yield during oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst | 07 |
| 11 | Table S3: ICP analysis of reaction mixtures, post oxidation reaction | 07 |
| 12 | Table S4: Semi quantitative analysis of ASKL and Oxidized ASKL after oxidative depolymerization using Fe@MagTEMPO catalyst (per 100 Ar) | 07 |
| 13 | Table S5: Molecular weight analysis of ASKL and oxidized ASKL | 07 |
| 14 | Table S6: EDX analysis of Fe@MagTEMPO, Indulin AT, Oxidized Indulin AT and oxidized ASKL | 08 |
| 15 | Figure S1: Schematic representation of Fe@MagTEMPO catalyst | 08 |
| 16 | Figure S2: Variation in zeta potential with respect to pH in Fe@MagTEMPO catalyst | 08 |
| 17 | Figure S3: GCMS spectra of monomers obtained from different starting lignins during oxidative depolymerization using Fe@MagTEMPO catalyst | 09-12 |
| 18 | Figure S4: Parity plot for vanillin yield calculated by mass balance of solids and by extrapolating calibration curve for vanillin concentration using flame ionization detector | 12 |
| 19 | Figure S5: Effect of catalyst loading on oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst | 13 |
| 20 | Figure S6: TEM image of fresh and used Fe@MagTEMPO catalyst used for oxidative depolymerization of kraft lignin | 13 |
| 21 | Figure S7: $^{31}$P NMR spectrum of ASKL and oxidized ASKL after oxidative depolymerization using Fe@MagTEMPO catalyst | 14 |
| 22 | Figure S8: GPC chromatogram for ASKL and oxidized ASKL (4 h sample) using Fe@MagTEMPO catalyst | 14 |
| 23 | Figure S9: Atomic force microscopy images of Fe@MagTEMPO nanocatalyst | 15 |
| 24 | Nomenclature | 16 |
| 25 | References | 16 |

## Chemicals

Iron (II) chloride tetrahydrate ($FeCl_2$. $4H_2O$), sodium hypochlorite solution (NaClO with 10-15% available chlorine), tetraethyl orthosilicate ($C_8H_{20}O_4Si$, TEOS), (3-Aminopropyl) triethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$, APTS), 4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy ($C_9H_{16}NO_2$, 4-Oxo-TEMPO), 5-Ethyl-2-methylpyridine borane complex ($C_8H_{14}BN$), hydrochloric acid (HCl, 37%) ammonium hydroxide ($NH_4OH$, 28-30% $NH_3$ basis), toluene ($C_6H_5CH_3$, anhydrous 99.8%), ethyl acetate ($C_4H_8O_2$, anhydrous 99.8%), ethanol ($C_2H_5OH$, anhydrous), pyridine ($C_5H_5N$, anhydrous), acetic anhydride ($C_4H_6O_3$), acetone ($C_3H_6O$), dimethyl sulfoxide-d$_6$ ($C_2D_6OS$), cyclohexanol ($C_6H_{12}O$), chromium (III) acetylacetone ($C_{15}H_{21}CrO_6$) and tetrahydrofuran ($C_4H_8O$, HPLC grade) were procured from Sigma-Aldrich Canada Co., Oakville, Ontario. Iron (III) chloride ($FeCl_3$, anhydrous), sodium bromide (NaBr) and sodium hydroxide (NaOH) were procured from Fischer Scientific Company, Ottawa, Canada. All the procured chemicals were ACS reagent grade except otherwise stated. Distilled water was produced in laboratory using Barnstead Mega Pure system. Three technical softwood kraft lignins were used. Indulin AT was procured from West Rock, BioChoice lignin was procured from Lignoboost process of Domtar and Lignoforce lignin was procured from West Fraser.

## Separation and analysis of phenolic monomers and polymeric lignin after oxidative depolymerization of lignin using Fe@MagTEMPO catalyst [1,2]

The reaction mixture was then acidified to pH 1.9 using 37% (w/w) HCl solution. The acid insoluble precipitated lignin was separated using centrifuge at 5000 rpm for 20 min. The separated solid fraction was then lyophilized at -53° C under 0.016 mbar vacuum for 48 h using Labconco Freezone 4.5 freeze drier. 80 cm$^3$ acid soluble fraction was then vigorously mixed with 20 cm$^3$ ethyl acetate in a separation funnel. The organic fraction was separated and analyzed using Clarus 680 Perkin Elmer gas chromatograph (GC) equipped with Clarus SQ8T mass spectrometer (MS). The GCMS chromatograms were integrated using TurboMass software (version 6.1.0.1963). Following temperature program was used for the GC oven:



The monomer yield was calculated as follows:

$$Monomer\ yield(\%) = \frac{(Mass\ of\ lignin\ at\ start\ of\ oxidation - Mass\ of\ recovered\ lignin\ after\ oxidation)}{Mass\ of\ lignin\ at\ start\ of\ oxidation} \times 100$$

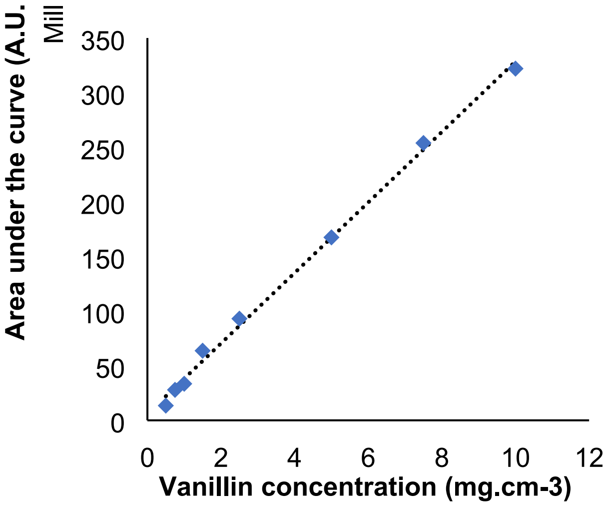
The vanillin selectivity was calculated from gas chromatogram as follows:

$$Vanillin\ selectivity\ (\%) = \frac{Area\ under\ the\ curve\ of\ vanillin\ peak}{Sum\ of\ area\ under\ the\ curve\ of\ all\ peaks\ in\ chromatogram} \times 100$$

The vanillin yield was quantified by two methods. The first method involved using monomer yield value from mass balance of solids post oxidation and vanillin selectivity as follows:

$$Vanillin\ yield\ (\%) = Monomer\ yield(\%) \times \frac{Vanillin\ selectivity\ (\%)}{100}$$

The second method involved generating calibration curve in GC for different vanillin concentration (mg.cm$^{-3}$) in ethyl acetate using FID detector.



This calibration curve was then used to estimate vanillin concentration in monomer mixture after oxidative depolymerization of lignin samples using Fe@MagTEMPO catalyst and vanillin yield was derived by assuming 100% extraction efficiency of vanillin in ethyl acetate from aqueous phase. The parity plot indicated that the vanillin yield value derived from both the methods was in consonance (**Fig. S4**).

## Characterization of lignin and Fe@MagTEMPO catalyst

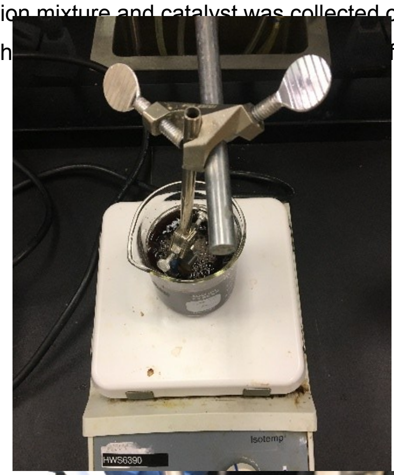
Energy dispersive X-ray spectroscopy (EDX) analysis was carried out using Hitachi S3000N variable pressure SEM equipped with backscatter detector and EDX analysis system. The lignin sample to be analyzed was attached to SEM sample stub using two sided adhesive carbon tape. The sample was sputter coated with gold to prevent charring during analysis. Transmission electron microscopy (TEM) images were captured with Hitachi H7600 TEM equipped with AMT XR50 CCD camera. 20 mg catalyst sample was dispersed in ethanol and few drops of suspension were put on 400-mesh, 3.5 mm copper grid. Atomic force microscopy (AFM) images were captured using Veeco multimode 8 system and RTESPA-150 cantilever tip with force constant of 5 N.m$^{-1}$ and resonant frequency of 150 kHz. A drop of 0.01% (w/w) suspension of Fe@MagTEMPO catalyst in water was put on freshly cleaved mica sheet and dried in vacuum at 40° C before AFM analysis.

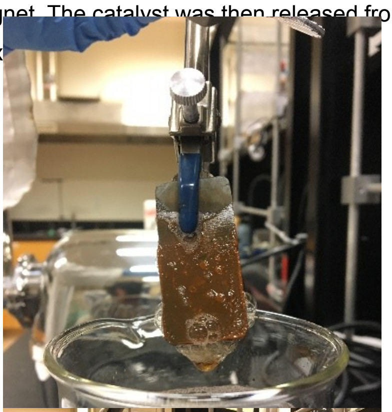
## Preparation of acid washed, acetone soluble (ASKL) and acetone insoluble (AIKL) kraft lignin

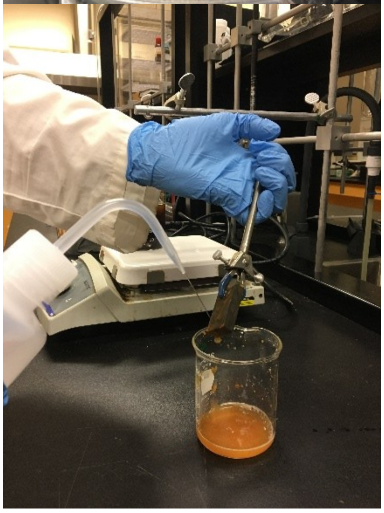
Prior to fractionation, Indulin AT was stirred for 8 h with 1 L of 0.01M hydrochloric acid such that the concentration of lignin was 0.1 g.cm$^{-3}$. The precipitated lignin was separated out by filtration under vacuum and dried in vacuum oven. This fraction was used as acid wash Indulin AT. This dried lignin (100 g) was then incrementally dispersed into 500 cm$^3$ acetone and stirred for 6 hours at 25° C. The acetone insoluble part was isolated through vacuum filtration using 11 µm pore size filter paper and used as AIKL. The supernatant fraction was air dried until acetone evaporated, and the solid fraction was further dried in vacuum oven and was used as ASKL.

## Fe@MagTEMPO catalyst recovery and reuse procedure

The pictures below depict how the catalyst was separated from reaction mixture after oxidation. The external magnet was exposed to reaction mixture and catalyst was collected over the magnet. The catalyst was then released from the surface of magnet using a water jet. Th for further ox







## Details of NMR analysis

The $^{31}$P and 2D HSQC NMR spectrum was acquired on a Bruker Avance 300 MHz spectrometer with a BBI probe at 25 °C.

### $^{31}$P NMR spectrum analysis

20 mg of lignin sample was accurately weighed in a 1.5 cm$^3$ vial, followed by addition of 400 µL deuterated solvent (Chloroform-D/Pyridine=1.6/1). After thorough mixing, 100 µL of 10 mg.cm$^{-3}$ cyclohexanol and 40 µL of 5.6 mg.cm$^{-3}$ chromium (III) acetylacetonate solution were added as internal standard and relaxation reagent respectively. Under vigorous stirring, the hydroxyl groups on lignin including aliphatic hydroxyl, aromatic hydroxyl, and carboxylic acid were modified by the addition of 50µL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The proton decoupled $^{31}$P NMR procedures were adopted to obtain quantitative results for hydroxyl groups. Specifically, five second relation delay time and 1.40 s acquisition time were adopted for the acquiring the spectrum with 800 scans.

### 2D HSQC NMR analysis

Typically, the $^{13}$C-$^{1}$H spectrum was acquired using bruker "hsqcetgpsisp 2.2 pulse program with following parameters: matrices of 2048 data points for the $^{1}$H and 256 data points for $^{13}$C were collected with an interscan delay (D1) of 750 ms, 2000 scans, and spectral width from 12.67 to -3.30 ppm for $^{1}$H and 210 to -30 ppm for $^{13}$C. The total acquisition time was about 5 days 20 hrs. The obtained spectrum was calibrated using the DMSO-d$_6$ signal (2.50/39.5 ppm). Topspin 3.5 software was adopted to process the spectrum including Fourier transform, baseline correction, and calibration. A semi quantitative analysis of HSQC spectrum was performed based on the previous works.[3,4] Specifically, part of aromatic compounds were integrated and defined as the internal standard. For this softwood kraft lignin, the area of G2 was integrated and the value was set to 100 aromatic units (100Ar). All linkages were calculated relative to 100 Ar.

## Details of GPC analysis

### Acetylation of lignin for GPC analysis

300 mg of lignin sample was mixed with 12 cm$^3$ of deuterated solution (acetic anhydride/pyridine=1:1) under magnetic stirring for 48 h at 25° C. The reaction mixture was then poured into 200 cm$^3$ of 0.01 M hydrochloric acid solution, filtered by 0.45 µm nylon membrane, and washed with 400 cm$^3$ of 0.01 M hydrochloric acid solution and 600 cm$^3$ distilled water. Obtained acetylated lignin solids were dried in vacuum oven at 50 °C and stored in the desiccator for further GPC analysis.

Molecular weight analysis using GPC

The dried acetylated lignin sample was dissolved into THF such that its concentration was 2 mg.cm$^{-3}$. The solution was then stabilized for 48 h at 25° C prior to filtration over 0.45 µm filter. 100 µL lignin solution was injected and analyzed at a time. The system temperature was maintained at 35°C and THF (HPLC grade, Fisher Scientific) was used as elutes. GPC analysis was performed using Agilent 1100 GPC equipment (USA). The GPC system equipped with Agilent 1260 ISO pump, Styragel columns HR 4, HR 3, and HR 1 (Waters, Milford, MA), 1260 VWDVL UV (Agilent), WYATT 323-V2 viscostar, WYATT 477-TREX optilab T-rex, WYATT 800-H2HC MALLS. Light scattering and RI detection was done at 785nm. Polystyrene (Mw 1300, 2000, 2500, 5780, 17500, 30000, 200000) received from Pressure Chemical Company was used for calibration. The sample analysis was performed using RI intensity.

## Details of ICP analysis

About 10 mg of catalyst samples and around 3 cm$^3$ of reaction mixtures were aliquoted and treated with 5 cm$^3$ of 15 N sub boiled nitric acid, refluxed, and capped at 120° C for two days to break down most of the organics. Samples were dried down overnight and treated with 3 cm$^3$ of 28 N ultrapure hydrofluoric acid and 2 cm$^3$ of 15 N sub boiled nitric acid and refluxed for two days to break down silicates. After dry down, 5 cm$^3$ of 6 N sub boiled hydrochloric acid was added and heated to ensure complete sample dissolution. Samples were dried down again and treated with few drops of nitric acid to drive off hydrochloric acid and then taken up in 0.3 N nitric acid for analysis by ICP-MS. In addition to the samples, a laboratory blank was prepared along with the samples. A suite of trace elements was analysed by an Agilent 7700x quadrupole ICP-MS using a five- point calibration between 0 ppb and 100 ppb. Standard solutions were made from a commercial multi-element standard solution (IV 71A, Inorganic Ventures Inc.) in 0.3 N nitric acid. A solution of 10 ppb was fed through the system alongside the samples for internal drift correction. Most elements were analysed using both modes with and without He in the collision cell to minimize effects from interferences. All data is corrected for dilution factors and indicated in ppb.

| Lignin type | Reaction Conditions | Vanillin yield (%) | E factor | Ref. |
|---|---|---|---|---|
| Kraft lignin<br>WestVaco Co.<br>(Pinus Spp.) | 60 g.L$^{-1}$ lignin, 2N NaOH aq. solution,<br>9 bar with $pO_2$ being 3 bar, 130° C, 35 min | 10.8 | 20.60 | 5 |
| Lignosulfonate $LS_{1200}$ | 110.6 g $LS_{1200}$, NaOH solution (18 g NaOH in 16 cm$^3$ water),<br>Preheated at 15 bar $O_2$, 190° C for 15 min<br>1.08 g $CuSO_4$. $5H_2O$ catalyst, 2 cm$^3$ Nitrobenzene<br>12 bar $O_2$, 190° C, Upto 30 min | 5.9 | 19.14 | 6 |
| Kraft lignin<br>(Pinus spp.)<br>LWest from<br>WestVaco Co. | 30 mg LWest, 7 cm$^3$ of 2M NaOH aq. solution<br>0.45 cm$^3$ Nitrobenzene, 170° C, 4 h | 12.14 | 273.59 | 7 |
| Sodium Lignosulfonate<br>NaLS | 220 g.L$^{-1}$ NaLS, 3M NaOH aq. solution (pH 14)<br>4.6 g.L$^{-1}$ copper sulfate ($Cu^{2+}$), 11.5 bar with $pO_2$ being 1.3 bar, Air flowrate of 4.5x10$^{-3}$ m$^3$.min$^{-1}$<br>140-160° C | 7 | 21.38 | 8 |
| Spruce kraft lignin | 140 mg lignin, 30 cm$^3$ of 2 M NaOH aq. solution<br>10 mg $LaMn_{0.8}Cu_{0.2}O_3$ catalyst, 5 bar $O_2$ + 15 bar He<br>175° C, 10 min | 17.3 | 217.73 | 9 |
| Indulin AT<br>from West Rock | 1% (w/w) Lignin sample, 200 cm$^3$ *water as solvent*<br>0.175 mg.cm$^{-3}$ Fe@MagTEMPO *recyclable catalyst*<br>0.2 mmol NaBr, 5 mmol.g$^{-1}$ NaClO, *25° C,* 4 h | *15* | *7.75* | This study |
| Acetone soluble Indulin AT<br>(ASKL) | | *21* | *5.25* | |
| Acid wash Indulin AT | | *19.7* | *5.66* | |

**Table S1: Comparison of vanillin yield derived through oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst with values in literature**

**Sample E factor calculations** (solvent is not considered as waste in E fcator calulations as it is usually recycled)

Kraft lignin (WestVaco Co.) using $O_2$ as primary oxidant

Basis: 1 L solvent

60 g lignin and 80 g NaOH are used. $O_2$ is not included in E factor calculation as even unreacted $O_2$ cannot be considered as waste.

Yield of vanillin is 10.8% so 6.48 g vanillin is isolated from 60 g lignin.

Usually alkaline oxidative depolymerization reaction makes unreacted/residual lignin recalcitrant to further processing. Therefore, residual lignin is considered as waste in E factor calculation.

Waste (g) = 80 (NaOH) + (60-6.48) (residual lignin)

= 133.52

Product, Vanillin (g) = 6.48

E factor = 133.52/6.48 = 20.60

Kraft lignin (WestVaco Co.) using nitrobenzene as primary oxidant

30 mg LWest lignin, 7 cm$^3$ of 2M NaOH aq. solution is equivalent to 0.56 g NaOH.

0.45 cm$^3$ nitrobenzene is equivalent to 0.54 g or 4.38 mmol nitrobenzene.

Nitrobenzene is reduced to aniline during oxidation. Hence 4.38 mmol or 0.41 g aniline is considered as waste generated from primary oxidant.

Yield is 12.14% so 3.642 mg vanillin is isolated from 30 mg lignin.

Waste (g) = 0.56 (NaOH) + 0.41 (aniline) + (0.03- 0.003642) (residual lignin)

= 0.9964

Product, Vanillin (g) = 0.003642

E factor = 0.9964/0.003642 = 273.59

Indulin AT (this study) using sodium hypochlorite as primary oxidant

2 g lignin, 0.04 g sodium bromide, 10 mmol NaClO sodium hypochlorite is reduced to 10 mmol or 0.585 g NaCl during oxidation

Yield is 15% so 0.3 g vanillin is isolated from 2 g lignin.

Waste (g) = 0.04 (NaBr) + 0.585 (NaCl) + (2-0.3) (residual lignin)

= 2.325

Product, Vanillin (g) = 0.3

E factor = 2.325/0.3 = 7.75

**Table S2: Effect of pH on vanillin selectivity and phenolic monomer yield during oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst**

| pH | Oxidant loading ($mmol.g^{-1}_{lignin}$) | Phenolic monomer yield (%) | Vanillin selectivity (%) |
|---|---|---|---|
| 10 | 0 | 9.5 | 47 |
| 7 | 2.5 | 11 | 48 |
| 10 | 5 | 20 | 63.5 |
| 7 | 5 | 22.5 | 67 |

pH 10 maintained using 0.5 M sodium hydroxide, 0.175 mg. $cm^{-3}$ Fe@MagTEMPO used as catalyst, 0.1 mmol NaBr, 5 mmol. $g^{-1}_{lignin}$ NaClO as oxidant, 200 $cm^3$ water as solvent, 1% (w/w) Indulin AT

**Table S3: ICP analysis of reaction mixtures, post oxidation reaction**

| | Si | | Fe | |
|---|---|---|---|---|
| Reaction mixture type | Conc. [ ppb ] | Conc. RSD | Conc. [ ppb ] | Conc. RSD |
| Procedural blank reaction mixture (no catylst) | 2529.007 | 5.785 | 161.793 | 1.230 |
| Homogeneous TEMPO reaction mixture | 1550.483 | 7.474 | 219.104 | 0.507 |
| Fe@MagTEMPO reaction mixture | 3200.942 | 3.529 | 319.305 | 0.308 |

all reactions were conducted under the following conditions: (4h, 25° C, 5mmol.$g^{-1}$ NaClO, NaBr)

**Table S4: Semi quantitative analysis of ASKL and Oxidized ASKL after oxidative depolymerization using Fe@MagTEMPO catalyst (per 100 Ar)**

| Linkage | ASKL | Oxidized ASKL |
|---|---|---|
| β-O-4 | 6.61 | 9.08 |
| β-5 | 1.78 | 1.77 |
| β-β | 3.52 | 3.02 |
| Stilbene | 8.03 | 9.14 |

**Table S5: Molecular weight analysis of ASKL and oxidized ASKL**

| Lignin | Mn (kDa) | Mw (kDa) | Polydispersity (Mw/Mn) |
|---|---|---|---|
| ASKL | 0.73 | 1.56 | 2.14 |
| Oxidized ASKL | 0.54 | 1.45 | 2.69 |

Energy dispersive X ray spectroscopy was conducted to ensure fidelity of catalyst after reuse and to ensure that catalyst is not stuck in lignin sample. Sodium (Na) and chlorine (Cl) were detected in oxidized polymeric lignin samples as NaCl is generated as residue during oxidation.

**Table S6: EDX analysis of Fe@MagTEMPO, Indulin AT, Oxidized Indulin AT and oxidized ASKL**

| Sample | Elemental composition (wt %) | | | | | |
|---|---|---|---|---|---|---|
| | Fe | Si | C | O | Na | Cl |
| **Fe@MagTEMPO** | 18.97 | 17.50 | 14.86 | 48.67 | ND | ND |
| **Indulin AT** | ND | ND | 70.99 | 29.01 | ND | ND |
| **Oxidized Indulin AT** | ND | ND | 70.14 | 25.31 | 1.28 | 3.28 |
| **Oxidized ASKL** | ND | ND | 70.04 | 28.50 | 0.28 | 1.17 |

ND: Not Detected, Oxygen composition represents the relative number of oxygen atoms in the metal specimen assuming that oxygen is present as metal oxide.

**Figure S1: Schematic representation of Fe@MagTEMPO catalyst**

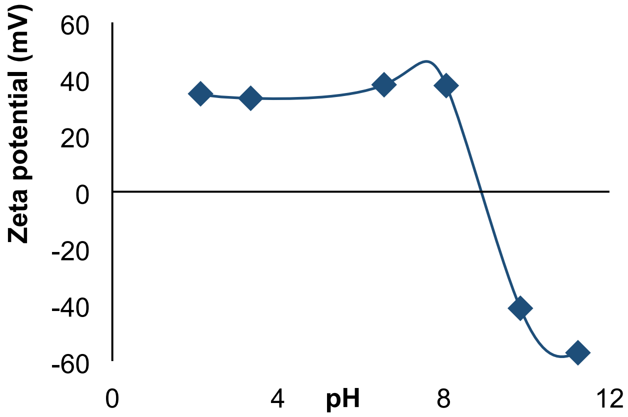
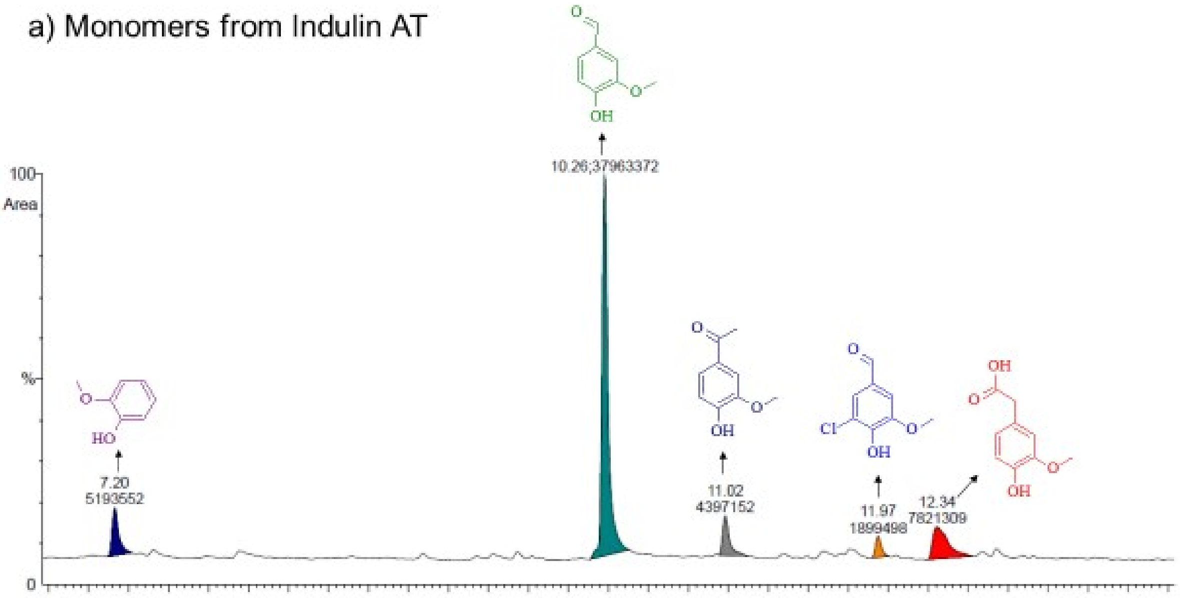
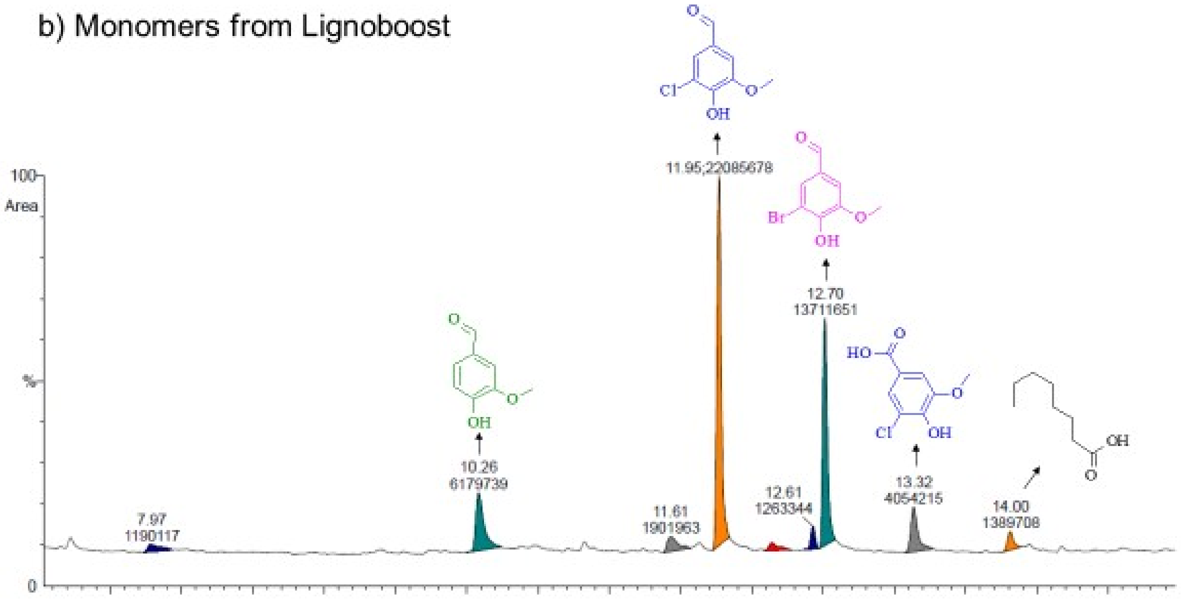


**Figure S2: Variation in zeta potential with respect to pH in Fe@MagTEMPO catalyst**

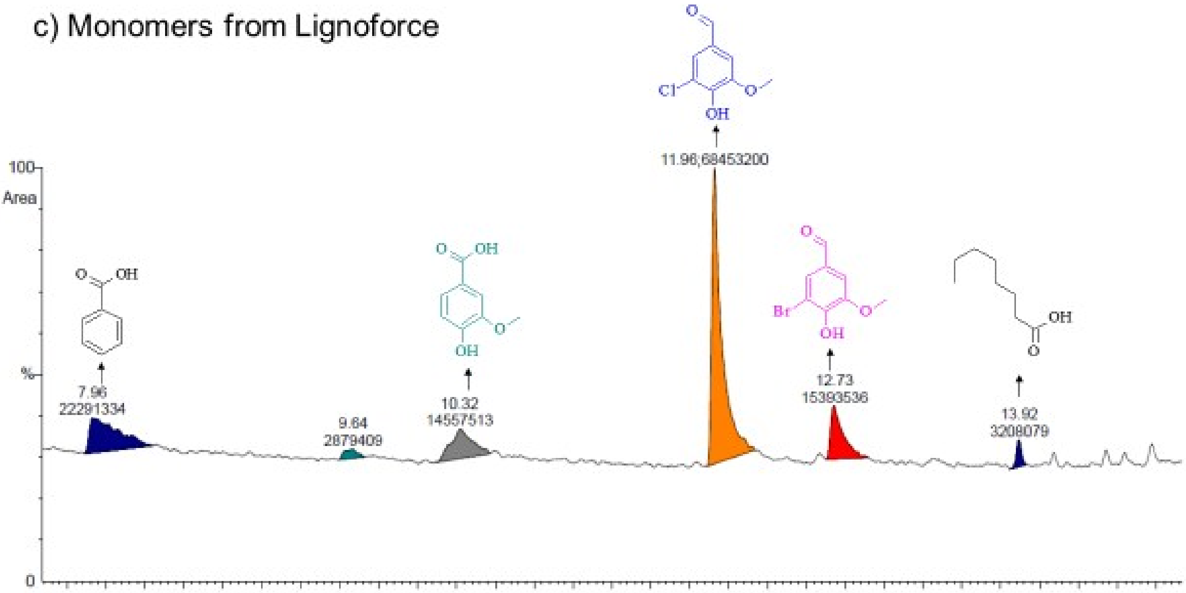


a) Monomers from Indulin AT

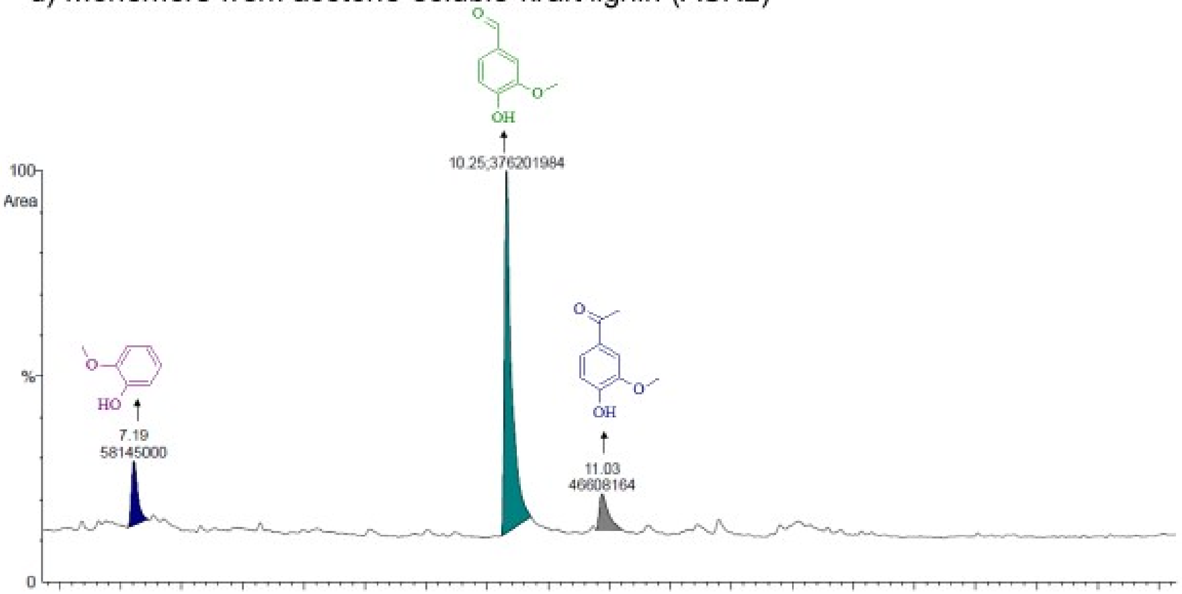


b) Monomers from Lignoboost

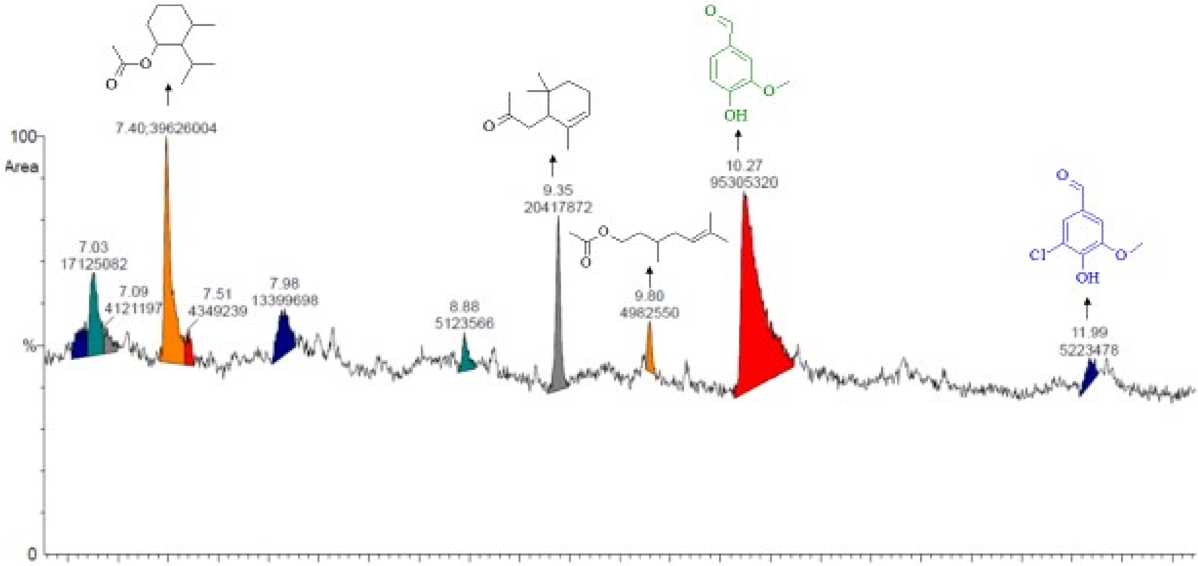
c) Monomers from Lignoforce



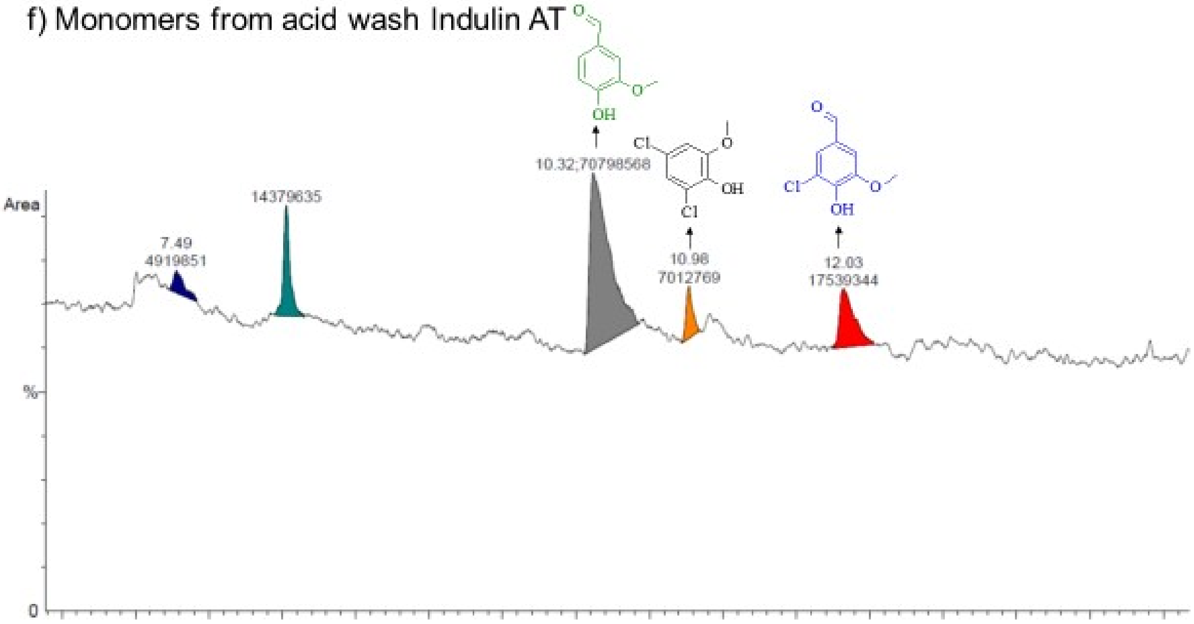
d) Monomers from acetone soluble kraft lignin (ASKL)



e) Monomers from acetone insoluble kraft lignin (AIKL)



f) Monomers from acid wash Indulin AT



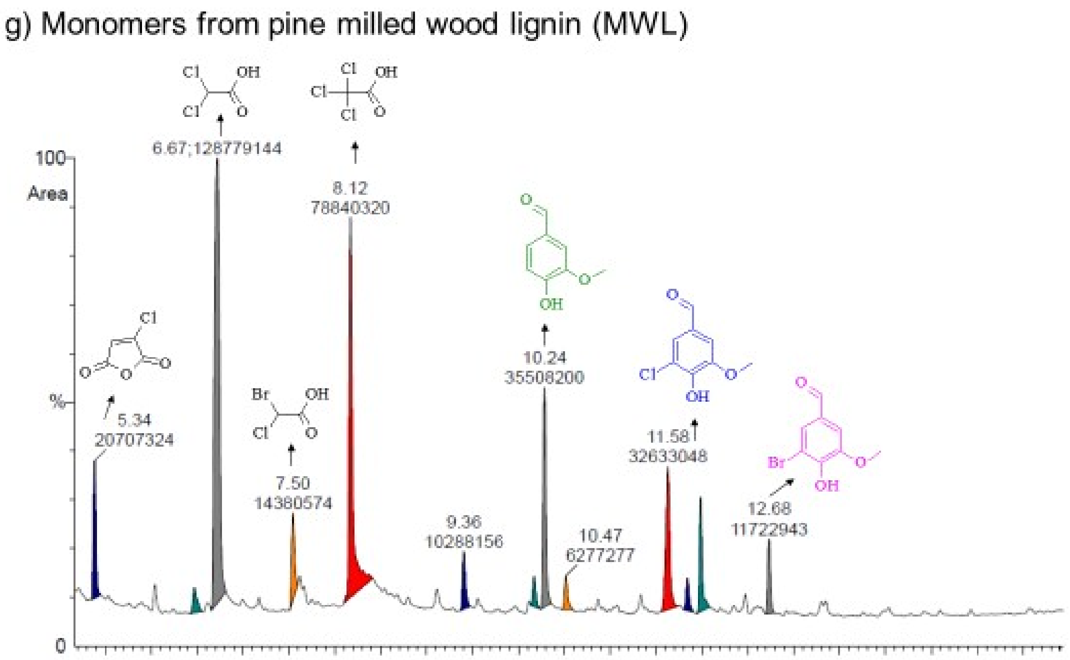


**Figure S3: GCMS spectra of monomers obtained from lignin during oxidative depolymerization using Fe@MagTEMPO catalyst**

a) Indulin AT from West Rock, b) BioChoice lignin from Lignoboost process of Domtar, c) Lignoforce from West Fraser, d) Acetone soluble Indulin AT (ASKL), e) Acetone insoluble Indulin AT (AIKL), f) Acid wash Indulin AT, g) Pine milled wood lignin (MWL)

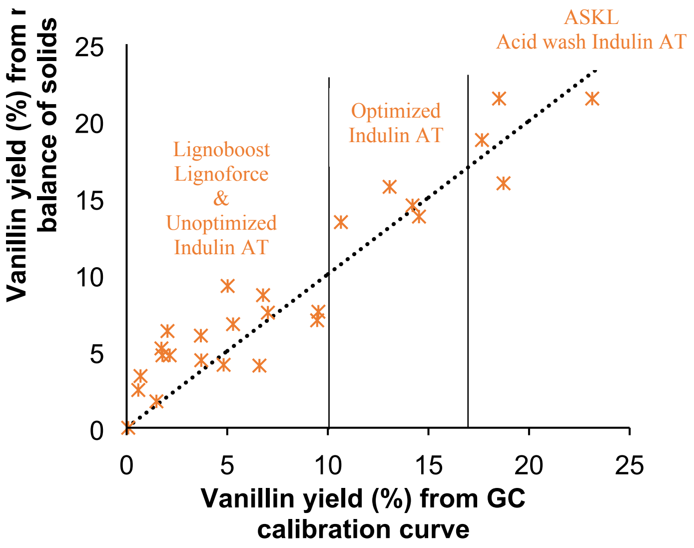


**Figure S4: Parity plot for vanillin yield calculated by mass balance of solids and by extrapolating calibration curve for vanillin concentration using flame ionization detector**

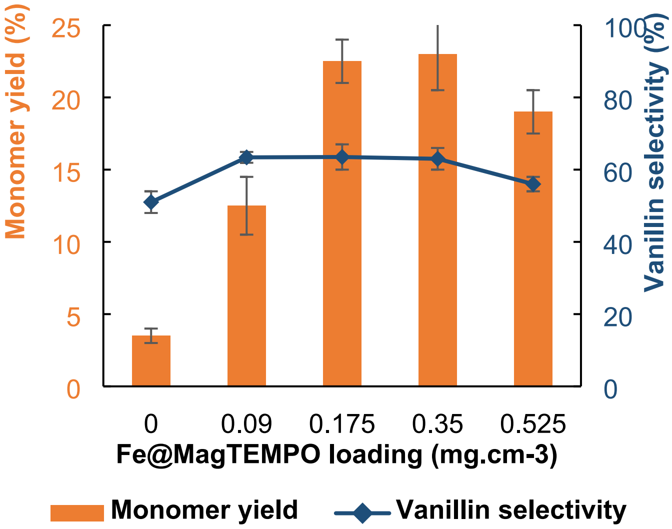


**Figure S5: Effect of catalyst loading on oxidative depolymerization of kraft lignin using Fe@MagTEMPO catalyst**

1% (w/w) Indulin AT, 0.1 mmol NaBr, 5 mmol. $g^{-1}{}_{lignin}$ NaClO as oxidant, 200 $cm^3$ water as solvent, 25° C

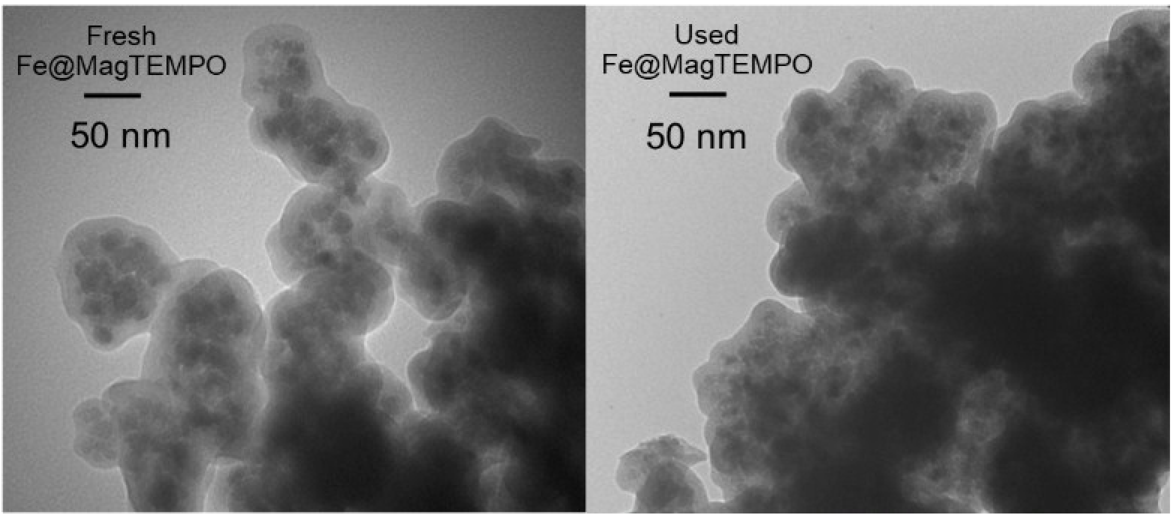


**Figure S6: TEM image of fresh and used Fe@MagTEMPO catalyst used for oxidative depolymerization of kraft lignin**

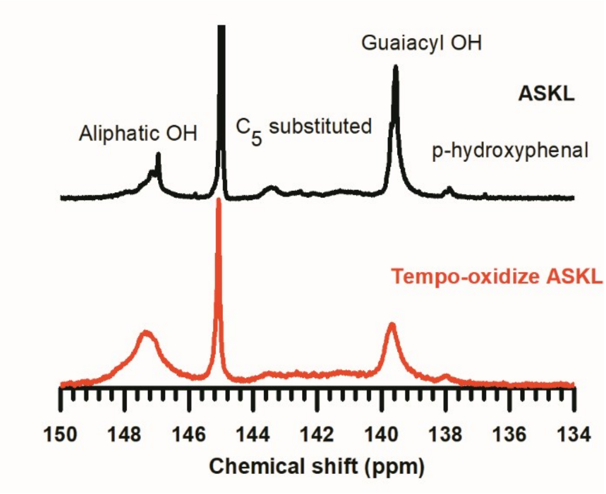


**Figure S7:** $^{31}$P NMR spectrum of ASKL and oxidized ASKL after oxidative depolymerization using Fe@MagTEMPO catalyst

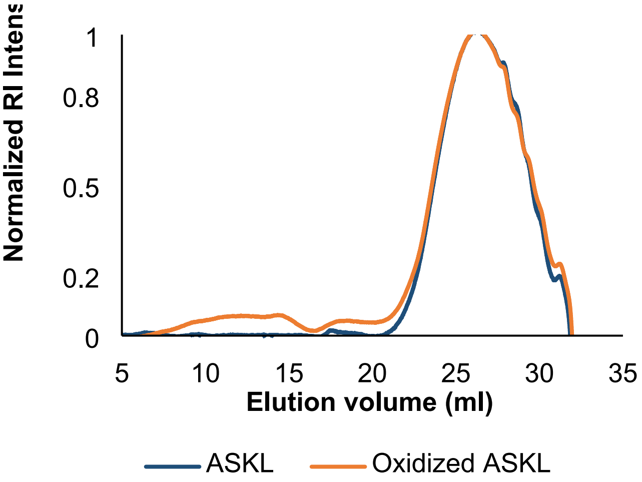
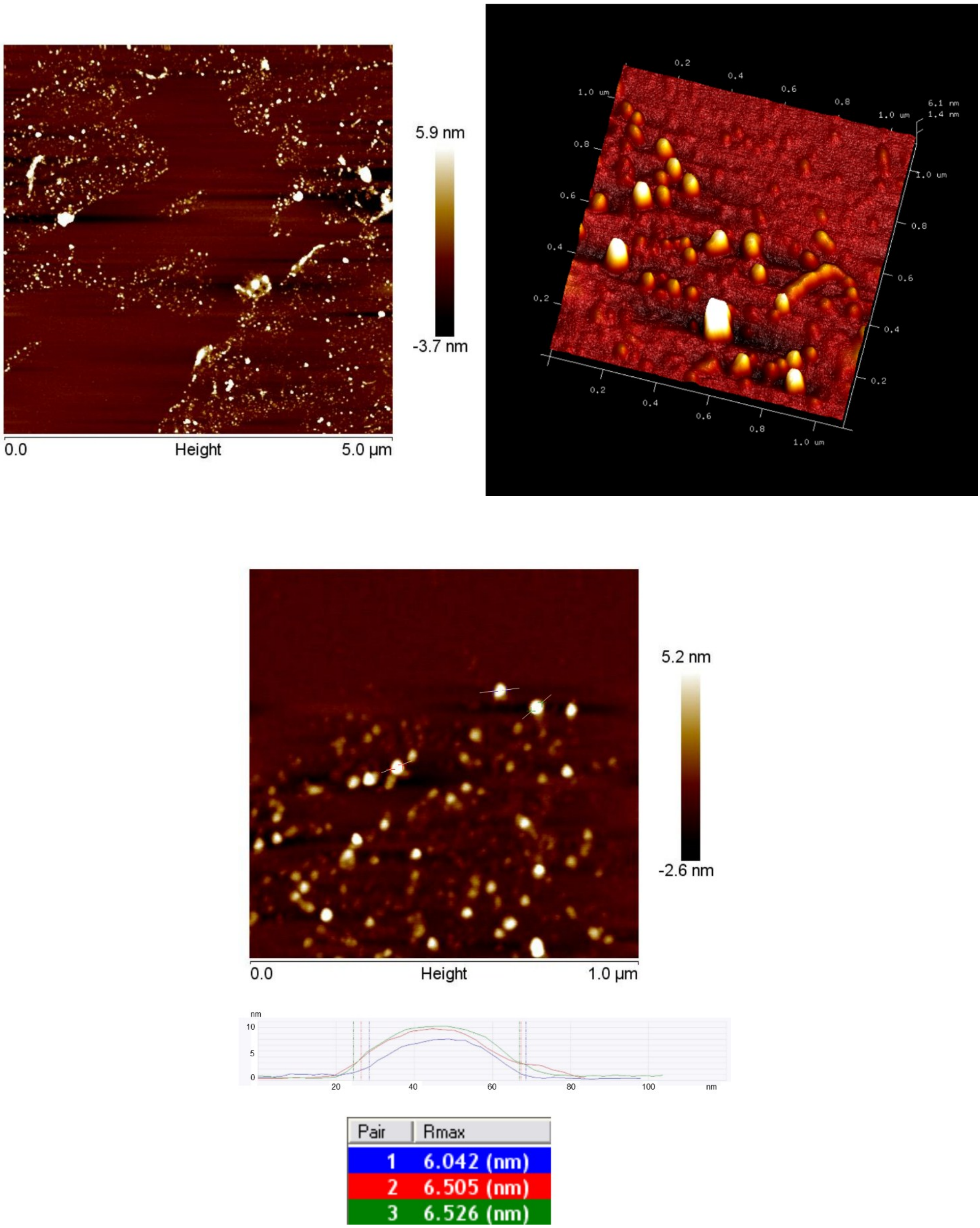


**Figure S8:** GPC chromatogram for ASKL and oxidized ASKL (4 h sample) using Fe@MagTEMPO catalyst

AFM analysis was conducted to ensure that Fe@MagTEMPO catalyst has individualized nanoparticles. The images indicate discrete nanoparticles of ~10 nm.



| Pair | Rmax |
|---|---|
| 1 | 6.042 (nm) |
| 2 | 6.505 (nm) |
| 3 | 6.526 (nm) |

**Figure S9: Atomic force microscopy images of Fe@MagTEMPO catalyst**

## Nomenclature

GCMS: Gas chromatography with mass spectroscopy
FID: Flame ionization detector
NMR: Nuclear magnetic resonance
GPC: Gel permeation chromatography
EDX: Energy dispersive X-ray spectroscopy
ASKL: Acetone soluble Indulin AT
AIKL: Acetone insoluble Indulin AT
TEMPO: 2,2,6,6-Tetramethylpipredinyl-1-oxyl
Fe@MagTEMPO: Heterogeneous catalyst with TEMPO anchored on magnetic nanoparticles
Fe@MagBasic: Heteogeneous catalyst with amine groups anchored on magnetic nanoparticles
TurboBeads: Commercial catalyst with TEMPO anchored on cobalt nanoparticles
ICP-MS: Inductively coupled plasma mass spectroscopy

## References

1. J. D. P. Araújo, Production of Vanillin from Lignin Present in the Kraft Black Liquor of the Pulp and Paper Industry, University of Porto, 2008.
2. M. I. F. Mota, P. C. R. Pinto, J. M. Loureiro, A. E. Rodrigues, *Sep. Purif. Rev.,* 2016, **45**, 227–259.
3. S. Constant, H. L. J. Wienk, A. E. Frissen, P. De Peinder, R. Boelens, D. S. Van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink, et al., *Green Chem.,* 2016, **18**, 2651–2665.
4. W. Zhang, N. Sathitsuksanoh, B. A. Simmons, C. E. Frazier, J. R. Barone, S. Renneckar, *RSC Adv.,* 2016, **6**, 30234–30246.
5. C. Fargues, A. Mathias, A. Rodrigues, *Ind. Eng. Chem. Res.,* 1996, **35**, 28-36.
6. H. Bjorsvik, *Org. Process Res. Dev.,* 1999, **3**, 330-340.
7. P. C. Rodrigues Pinto, E. A. Borges da Silva, A. E. Rodrigues, *Ind. Eng. Chem. Res.,* 2011, **50**, 741-748.
8. A. W. Pacek, P. Ding, M. Garrett, G. Sheldrake, A. W. Nienow, *Ind. Eng. Chem. Res.,* 2013, **52**, 8361-8372.
9. W. Schutyser, G. T. Beckham et.al, *Green Chem.,* 2018, **20**, 3828-3844.