Electronic Supplementary Information

Improved Pd/Ru metal supported Graphene oxide nano-catalysts for hydrodeoxygenation (HDO) of Vanillyl alcohol, Vanillin and Lignin

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General Methods

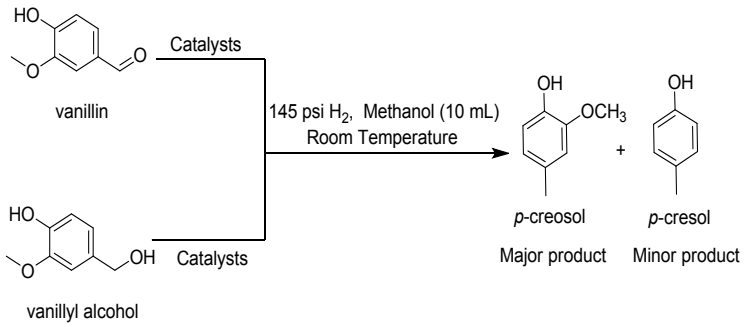
Vanillin, Vanillyl alcohol, Graphene oxide, Palladium (II) chloride, Ruthenium (II) chloride and Lignin were purchased from Sigma Aldrich and TCI. Tetrahydrofuran and concentrated hydrochloric acid were procured from Alfa Aesar. All the reagents were used without any further purification. Perkin Elmer RXI-FTIR and Panalytical's X'Pert Pro- XRD were used to record the FTIR and XRD data of the catalysts. JSM 6100 (JEOL) analytical instrument for EDS analysis, Nexsa base, XPS instrument for recording the X-Ray photoelectron spectroscopy, ARCOS, simultaneous ICP-AES-MS (induced coupled plasma) spectrometer for measuring the metal content. Waters 515 HPLC pumps, Waters 2998 PDA detector, manual single injection system and Empower 2 software were used for developing the calibration curves and for monitoring the reaction.

Method for preparation of Catalysts

A 20 ml solution containing 2.5 wt% each of the palladium chloride/ ruthenium chloride was prepared by adding 0.5 mL HCl and remaining deionized water. The resulting 0.01M solution (0.5 mL) was mixed with GO (0.3 g) and ultra-sonicated to completely disperse and exfoliate GO. Subsequently, the mixture was transferred to a borosil dish and placed in the center of the tube furnace. The temperature of the furnace was raised to 200^{o}C at a rate of 10^{o}C/min under an argon atmosphere. After attaining a temperature of 200^{o}C, hydrogen gas was purged into the furnace and the atmosphere was maintained for 2 h. The furnace was cooled to room temperature and the treated sample was labeled as Pd/Ru@GO. Further, Pd@GO and Ru@GO were also prepared by the same protocol using 5 wt% of Pd and Ru metal solutions respectively.

Hydrodeoxygenation (HDO) of Vanillyl alcohol and Vanillin

The conversion of vanillyl alcohol (4-hydroxy-3-methoxy benzylalcohol)/ vanillin (4-hydroxy-3-methoxy benzaldehyde) was performed in a high pressure stainless steel reactor of 100 mL capacity as shown in Scheme 1. Vanillyl alcohol (0.1 g, 0.649 mmol), catalyst (0.01 g, 0.083 mmol) and 10 mL of methanol were stirred at ambient temperature in the reactor for 12 h at 145 psi H_2 pressure. Similarly, for HDO of vanillin (0.1 g, 0.657 mmol), it was loaded with catalyst (0.02 g, 0.166 mmol) and 10 mL of methanol and stirred at ambient temperature in the reactor for 24 h at 145 psi H_2 pressure. H_2 gas was released and the catalyst was allowed to settle, filtered and the solution was analyzed by HPLC.



Scheme. 1 Schematic representation of HDO of Vanillyl alcohol and Vanillin

Photo-catalytic experiment of Lignin

Photo-catalytic fragmentation of commercial lignin was carried out at room temperature in an immersion photo-chemical reactor made of Pyrex glass equipped with a circulating cooling water jacket using 0.3 g Degussa P-25 TiO_2 added to 200 mL of lignin solution (0.2 g in 200 mL H_2O) and the solution was kept in the dark for adsorption for 30 min.[38] The suspension was then subjected to irradiation under UV light (125 W) with magnetic stirring for 5 h. After the UV treatment the sample was centrifuged to recover the catalyst. The clear aqueous fraction was extracted using dichloromethane and the solvent was evaporated under reduced pressure to give mixture of products mainly comprising of phenolic compounds. The phenolic compounds obtained were analyzed using HPLC-MS.

Comparative Study

Table S1. Comparative study of hydrodeoxygenation (HDO) of Vanillin

Entry	Catalyst/ Catalyst Loading	Reaction Conditions	Conversion /selectivity (%)	Product	Reference
1	Pd/C (50 mg)	100°C, 10 bar, 3 h octane-water	99/99	*p*-creosol	23
2	Ru/C (0.5 kg/m^3)	55°C, 13.8 bar, 1 h, water	100/91	Vanillyl alcohol	24
3	Pt/AC, Rh/AC, Pd/AC, Au/AC and Ru/C (50 mg)	100°C, 30 bar, 3 h water	99/95	*p*-creosol	25
4	Cu-Ni/SiO_2(10 mg)	150°C, 25 bar, 12 h, water,	96/76	*p*-creosol	26
5	Pd/KIT-6 (5 wt%)	300°C, 6 h, Methanol, atm pressure	98/94	*p*-creosol	27
6	Pd/Carbon nitride (10 mg)	70°C, 10 bar, 1 h, water	99/98	*p*-creosol	28
7	Ru/CNT (0.2 mol %)	150°C, 10 bar, 3 h, decalin-water	100/96	*p*-creosol	29
8	Au/CNT (0.68 mol %)	150°C, 10 bar, 6 h, decalin	94/100	*p*-creosol	30
9	MO_2C (50 mg)	180°C, 10 bar, 3 h, water	100/94	*p*-creosol	31
10	Ni/SiO_2-ZnO_2	300°C, 50 bar, 16 h octane	100/54	hydrocarbons	32

LCMS Analysis: The LCMS of crude sample obtained by photo-degradation of commercial lignin and after HDO showed peak at m/z value corresponding to M/M+1/M+2 for various phenolic molecules.

Table S2. Possible products obtained from photo-catalytic fragmentation of commercial Lignin

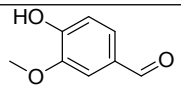
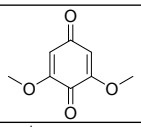
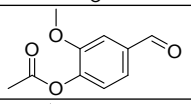
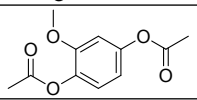
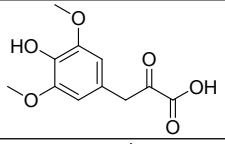
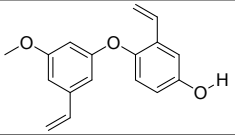
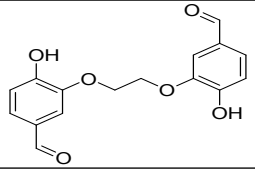
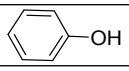
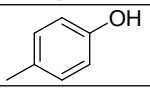
Entry	Compound identified in DCM extract	Chemical Structure	Retention Time (min)	LCMS m/z [M+1]
1.	Tetrahydro-*2H*pyran		3.43/ 12418.24	88.15
2.	4-hydroxy-2methoxy benzaldehyde		3.43/ 12418.24	153.10
3.	2,6-dimethoxybenzoquinone		3.43/ 12418.24	169.12
4.	4-formyl-2-methoxyphenyl acetate		3.43/ 12418.24	195.76
5.	2-methoxy-1,4-phenylene diacetate		3.43/ 12418.24	223.16
6.	Syringylglyoxalic Acid		5.90/ 53249.86	242.00
7.	4-(3-methoxy-5-vinylphenoxy)-3-vinylphenol		3.43/ 12418.24	267.16
8.	3,3-(ethane-1,2-diylbis(oxy))bis (4-hydroxybenzaldehyde) enol		7.01/ 296859.09	307

Table S3. Possible phenolic products obtained using Pd/Ru@GO after HDO of phenolic compounds obtained by photo-catalytic fragmentation of commercial Lignin

Entry	Compound identified in DCM extract	Chemical Structure	Retention Time (min)	LCMS m/z [M+1]
1.	Phenol		7.18/ 77342.57	94.00
2.	4-methyl phenol		7.18/ 77342.57	109.02

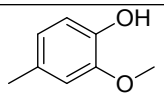
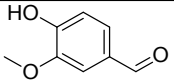
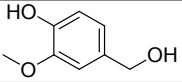
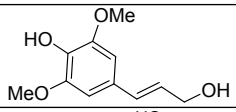
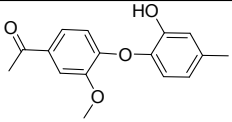
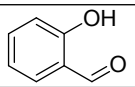
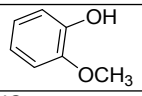
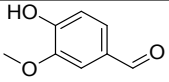
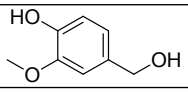
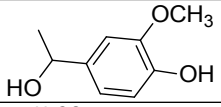
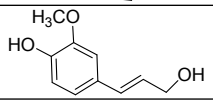
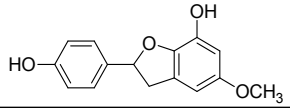
3.	2-methoxy-4-methyl phenol		3.52/ 38917.05	139.02
4.	4-hydroxy-3-methoxy benzaldehyde		4.75/ 5114.70	153.10
5.	4-hydroxy-3-methoxy benzylalcohol		7.18/ 77342.57	154.00
6.	4-(3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol		7.26/ 77342.57	211.00
7.	2-hydroxy-4-methylphenoxy-4methoxyphenyl ethanone		7.076/ 77342.57	275.02

Table S3. Possible phenolic products obtained using Ru@GO after HDO of phenolic compounds obtained by photo-catalytic fragmentation of commercial Lignin

Entry	**Compound identified in DCM extract**	**Chemical Structure**	**Retention time (min)**	**LCMS m/z [M+1]**
1.	4-hydroxybenzaldehyde		4.77	123.04
2.	2-methoxyphenol		12.66	137.46
3.	4-hydroxy-3-methoxy benzaldehyde		4.77	152.04
4.	4-hydroxy-3-methoxy benzylalcohol		7.06	154.00
5.	4-(1-hydroethyl)-2-methoxyphenol		4.77	167.07
6.	4-(3-hydroprop-1-en-1-yl)-2-methoxyphenol		12.66	181.48
7.	2-(4-hydroxyphenyl)-5—methoxy-2,3-dihydrobenzofuran-7-ol		12.66	261.51

Supplementary Figures

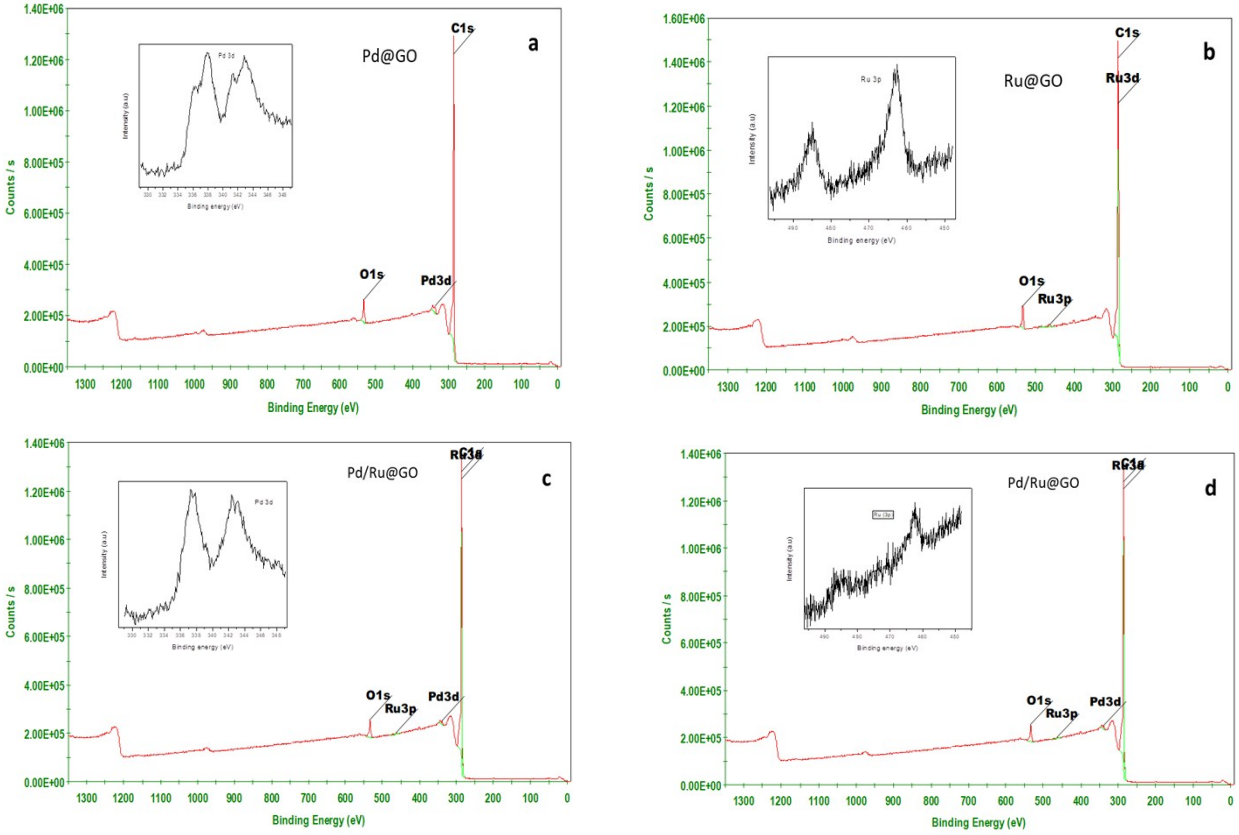


Fig. S1 (a) XPS graph of Pd 3d in Pd@GO, (b) XPS graph of Ru 3p in Ru@GO, **(c)** XPS graph of Pd 3d in Pd/Ru@GO, (d) XPS graph of Ru 3d in Pd/Ru@GO.

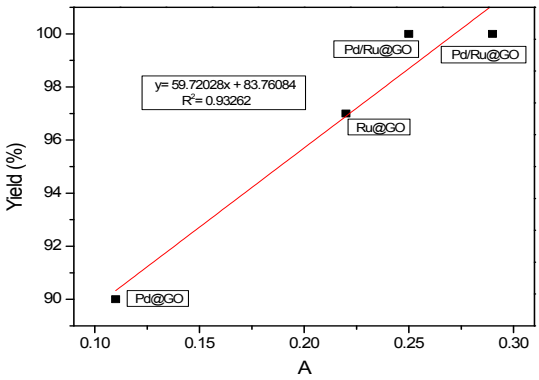


Fig. S2 Relationship between possible hydrogenation components (Pd and Ru), the O=C-O content and the yield of the product.

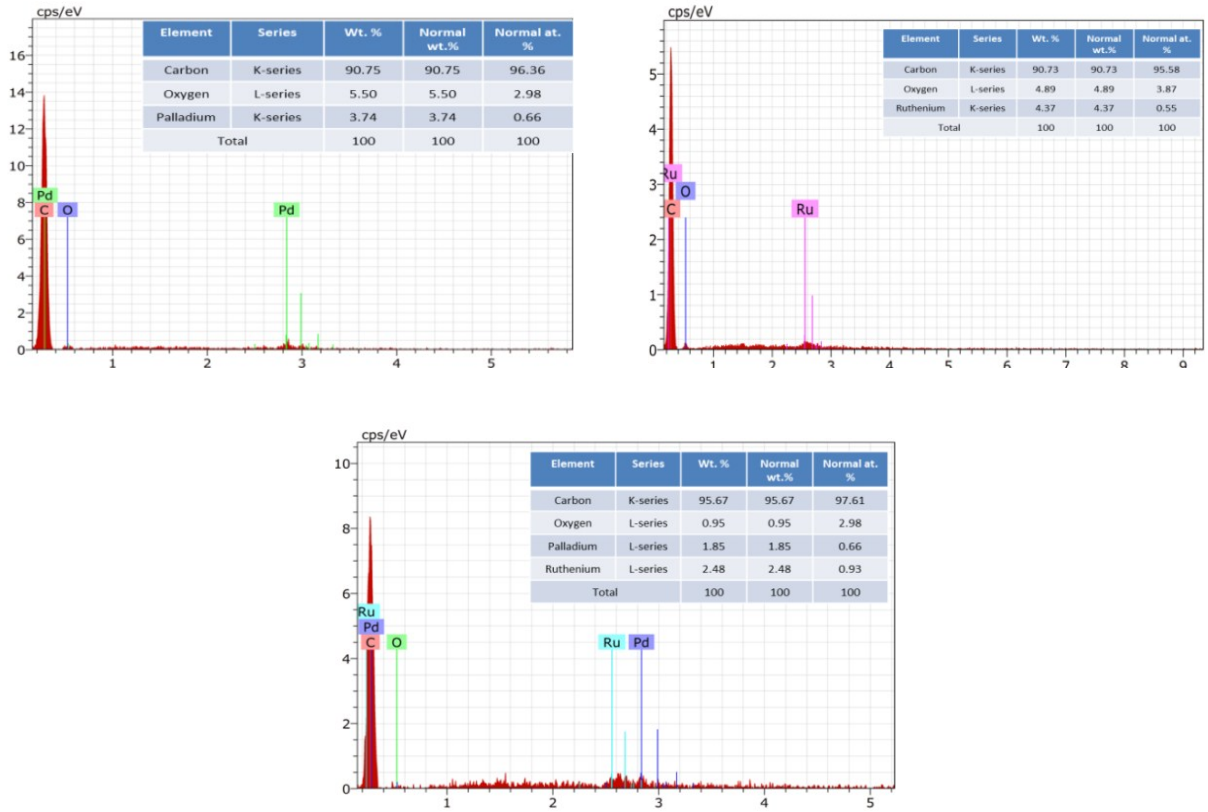


Fig. S3 EDS spectrum of Pd@GO, Ru@GO and Pd/Ru@GO.

HPLC analysis: The product was quantified by HPLC using PDA detector with a Waters Spherisorb 5µm ODS2 (4.6 X 250mm mm) C-18 reverse phase column. The HPLC conditions for analysis of product were; column temperature; 30^{o}C, methanol: water (1:1) as an eluent with flow rate of mobile phase 1.0 mL/min, injection volume 10µL with 20 minutes injection run time.

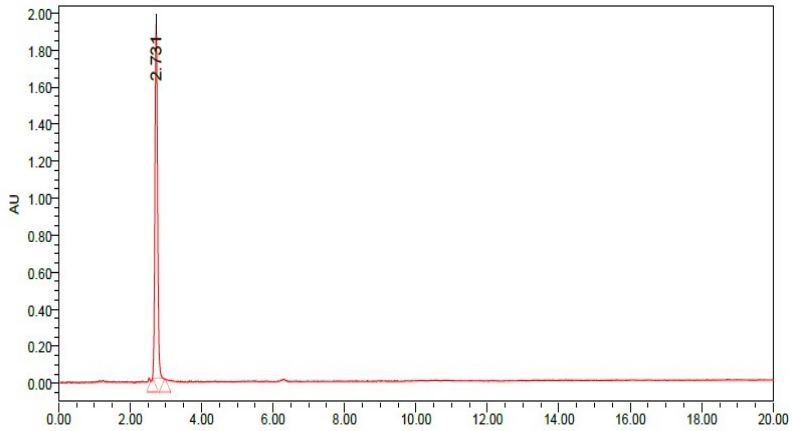


Fig. S4 HPLC Chromatogram showing complete conversion of vanillin by HDO to vanillyl alcohol using Pd/Ru@GO.

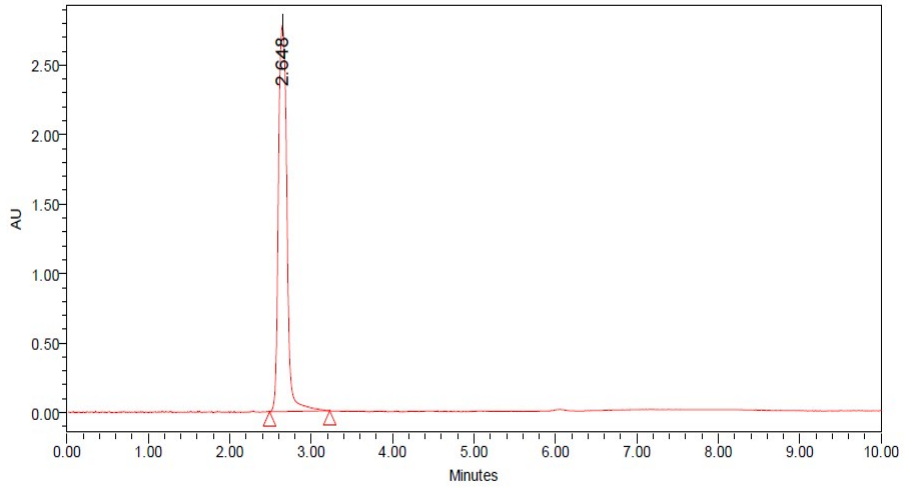


Fig. S5 HPLC Chromatogram showing complete conversion of vanillin by HDO to vanillyl alcohol using Ru@GO.

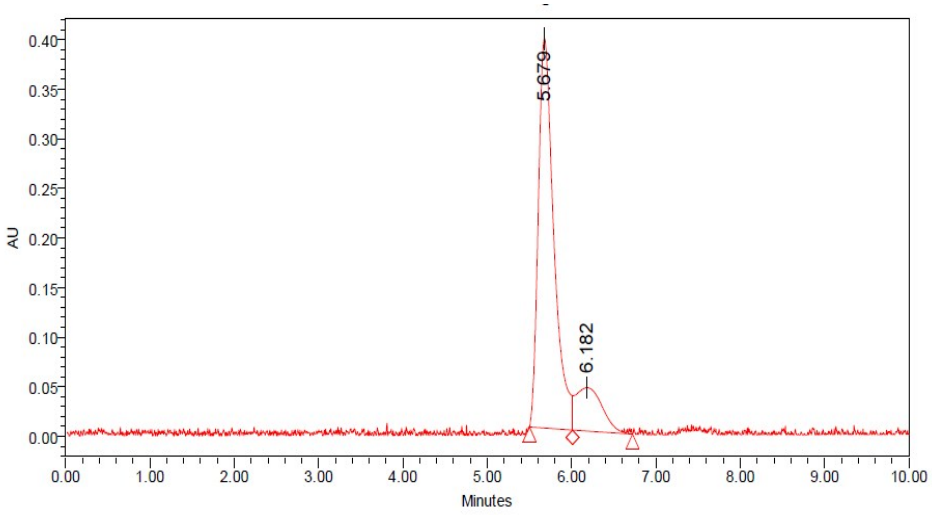


Fig. S6 HPLC Chromatogram shows complete conversion of vanillin by HDO to p-Creosol and p-Cresol using Pd/Ru@GO.

Fig. S7 HPLC Chromatogram shows complete conversion of vanillin by HDO to p-Creosol and p-Cresol using Ru@GO.

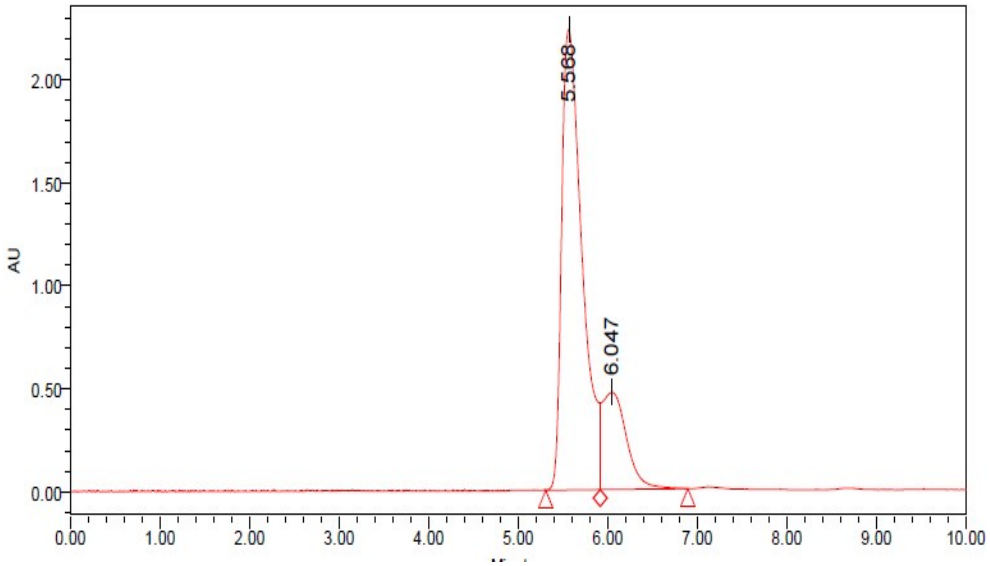


Fig. S8 HPLC Chromatogram shows complete conversion of vanillyl alcohol by HDO to p-Cresol and p-Cresol using Pd/Ru@GO.

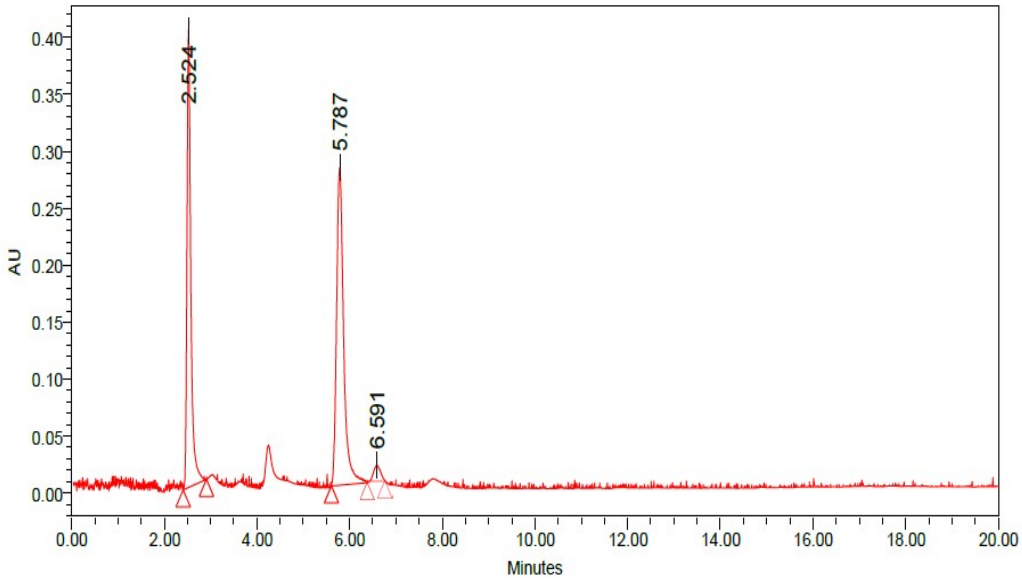


Fig. S9 HPLC Chromatogram of Vanillin HDO using Pd/Ru@GO with benzophenone.

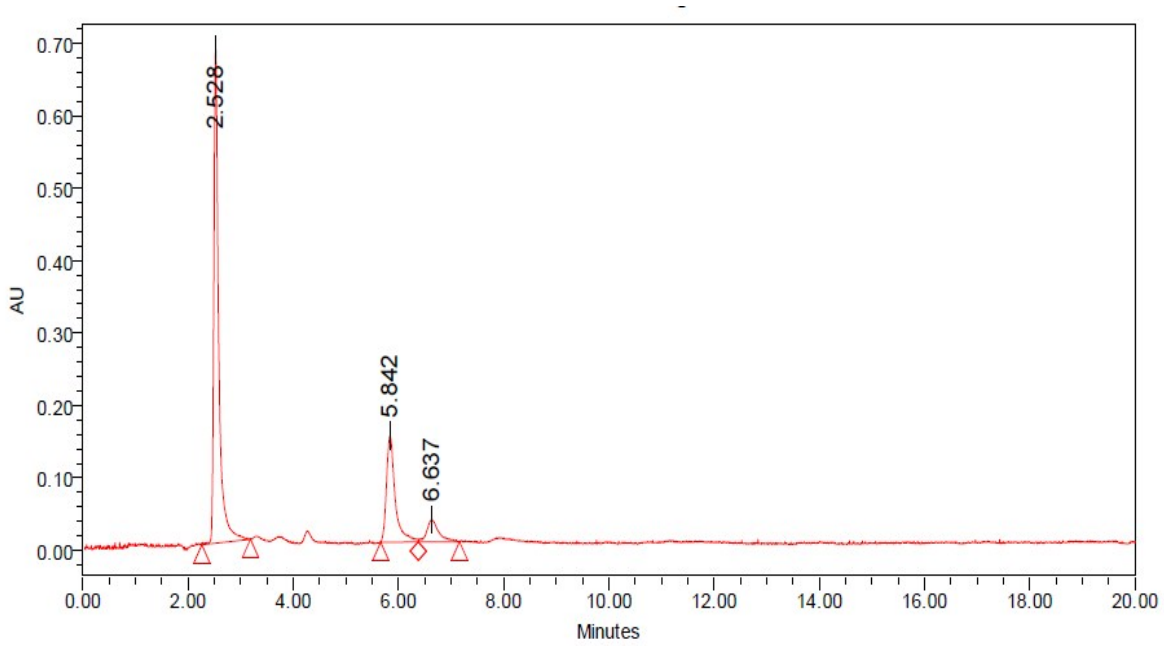


Fig. S10 HPLC Chromatogram of Vanillyl alcohol HDO using Pd/Ru@GO with benzophenone.

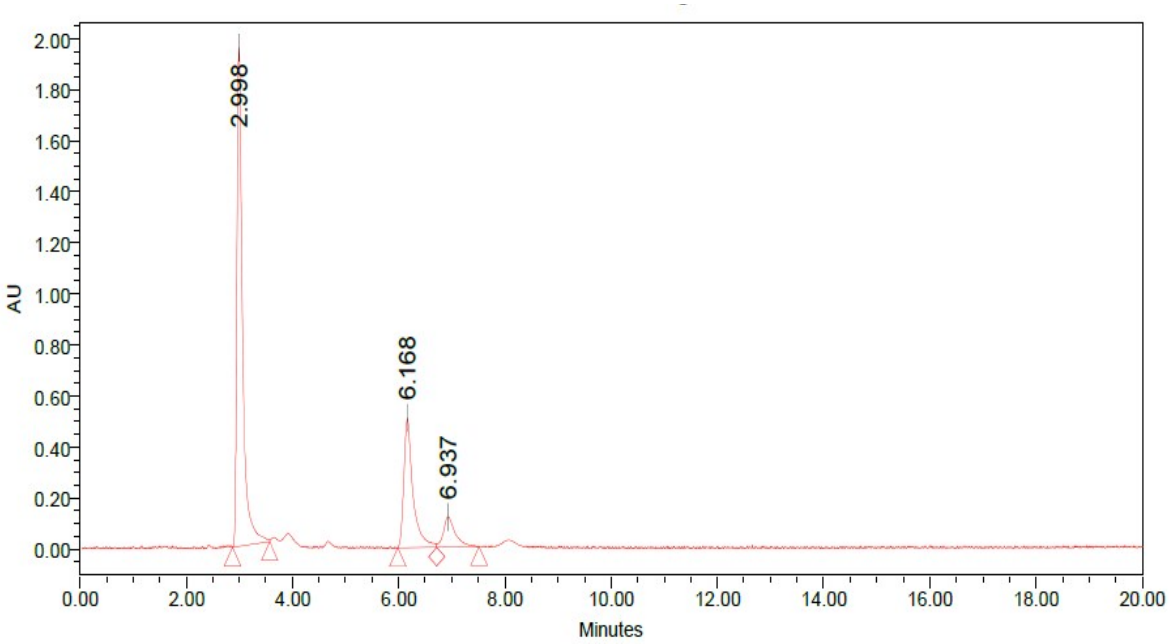


Fig. S11 HPLC Chromatogram of Vanillin HDO using Pd/Ru@Al_2O_3.

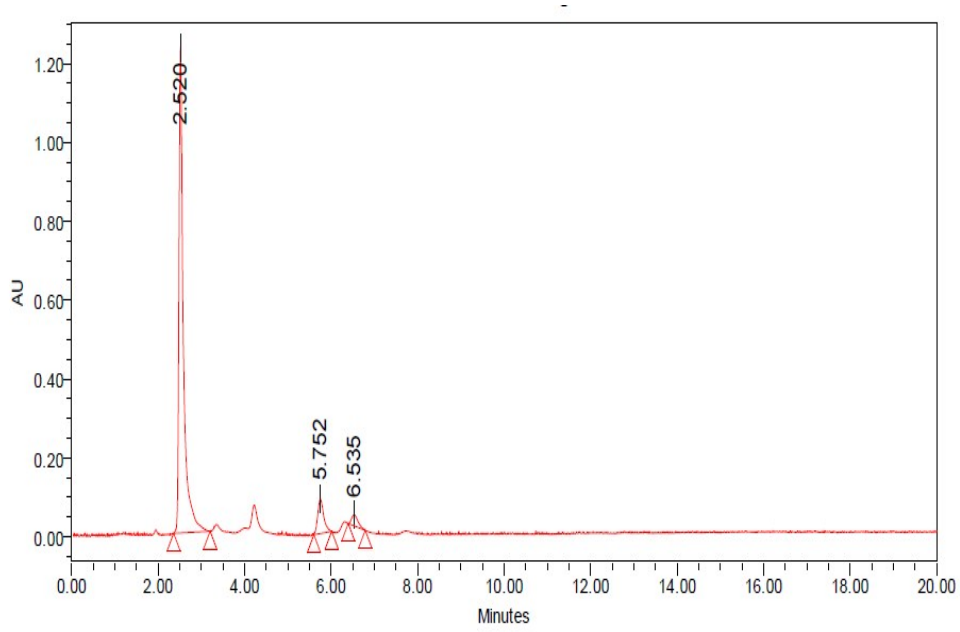


Fig. S12 HPLC Chromatogram of Vanillyl alcohol HDO using Pd/Ru@Al_2O_3.

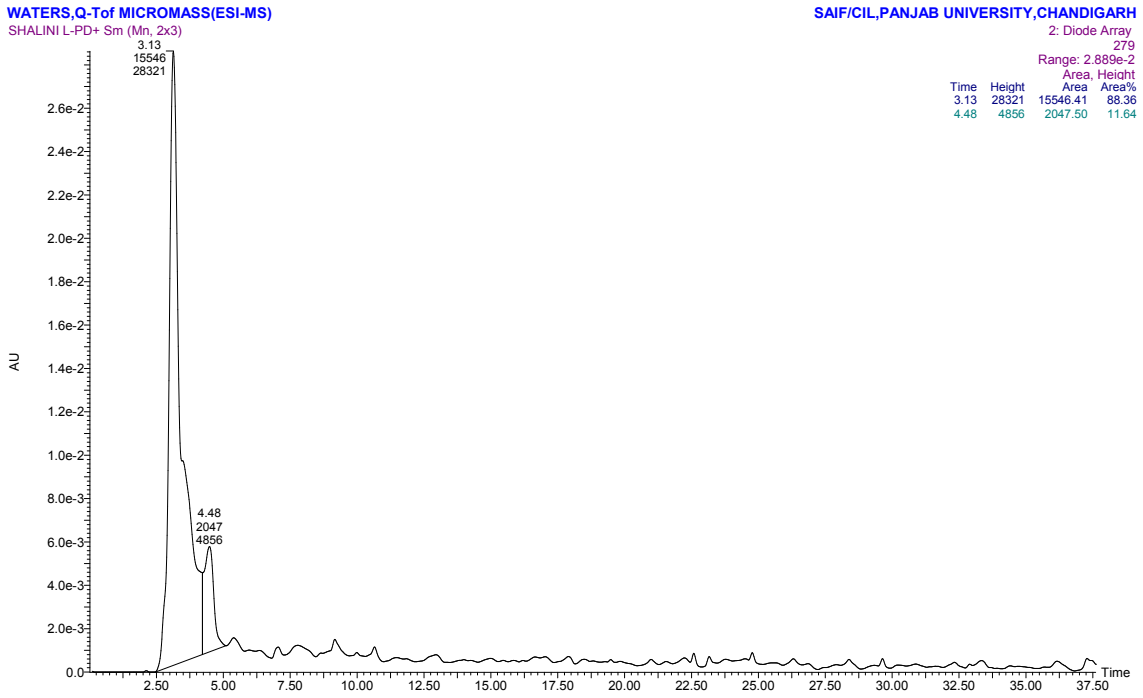


Fig. S13 HPLC-MS graph showing m/z peaks values for different possible phenolic compounds of photo-degradation of commercial lignin.

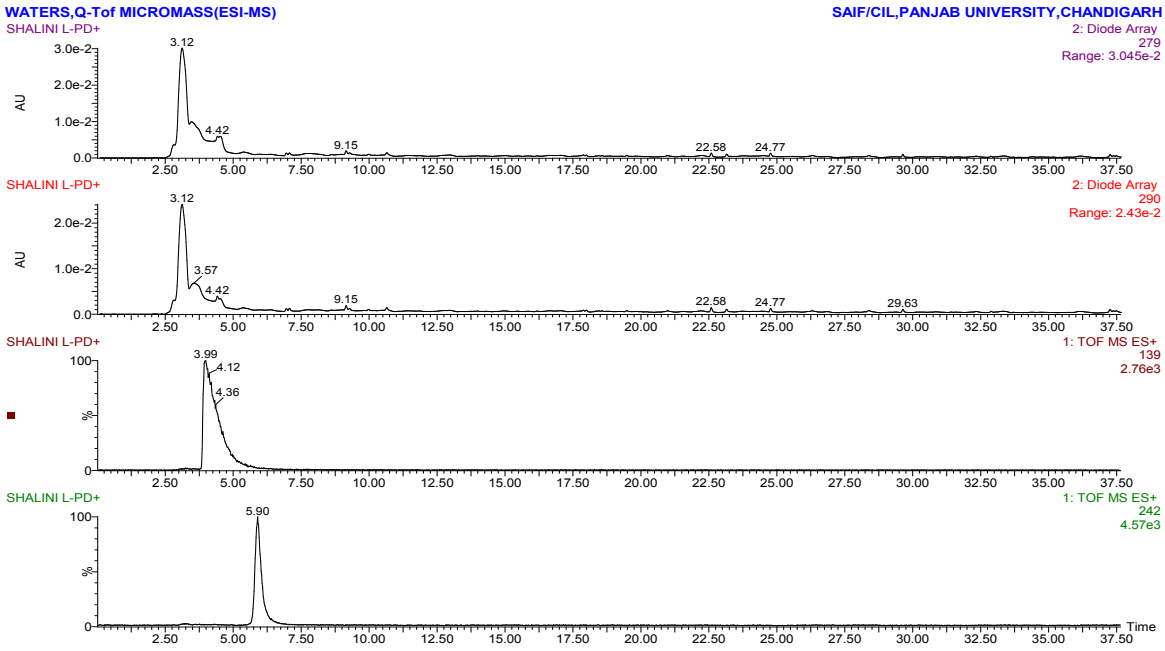


Fig. S14 HPLC-MS graph showing m/z peaks values for different possible phenolic compounds of photo-degradation of commercial lignin.

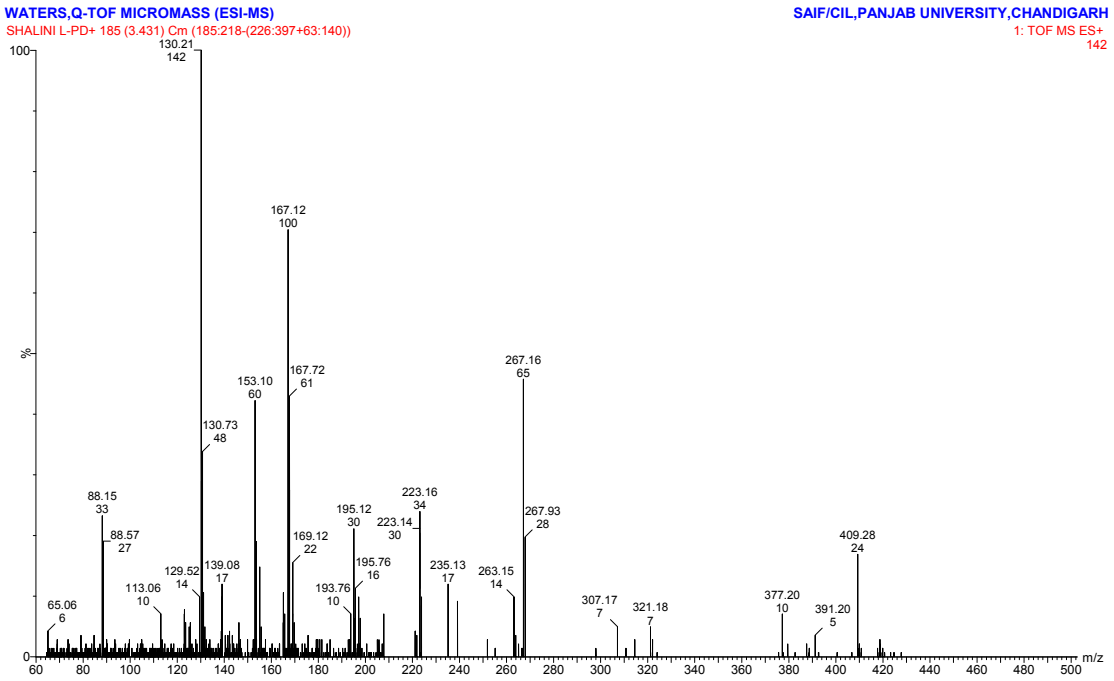


Fig. S15 HPLC-MS graph showing m/z peaks values for different possible phenolic compounds of photo-degradation of commercial lignin.

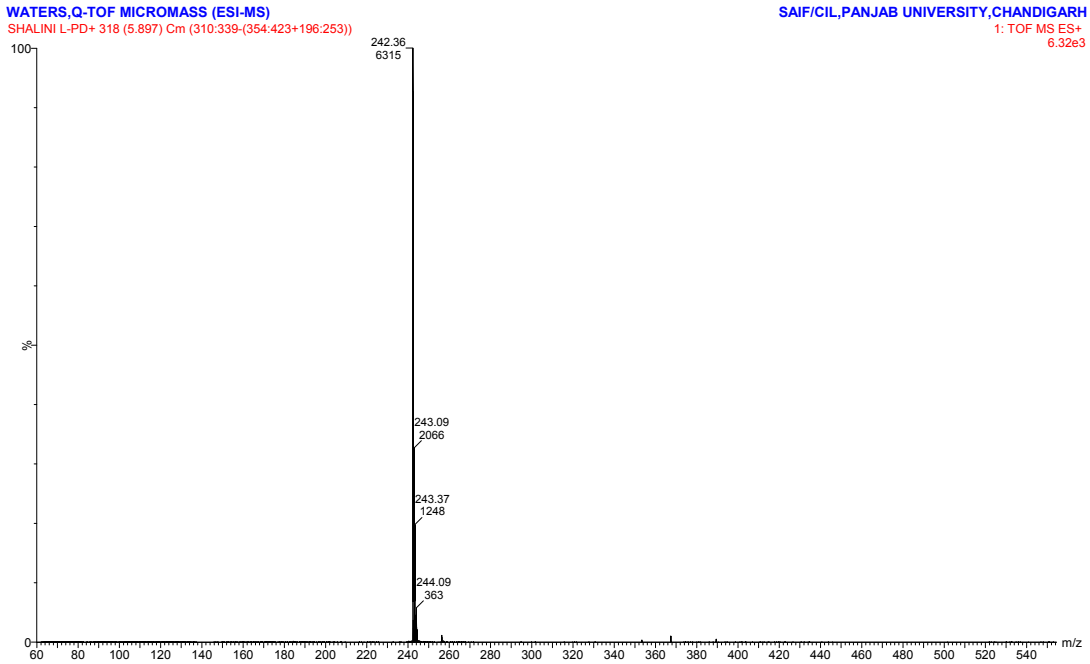


Fig. S16 HPLC-MS graph showing m/z peaks values for different possible phenolic compounds of photo-degradation of commercial lignin.

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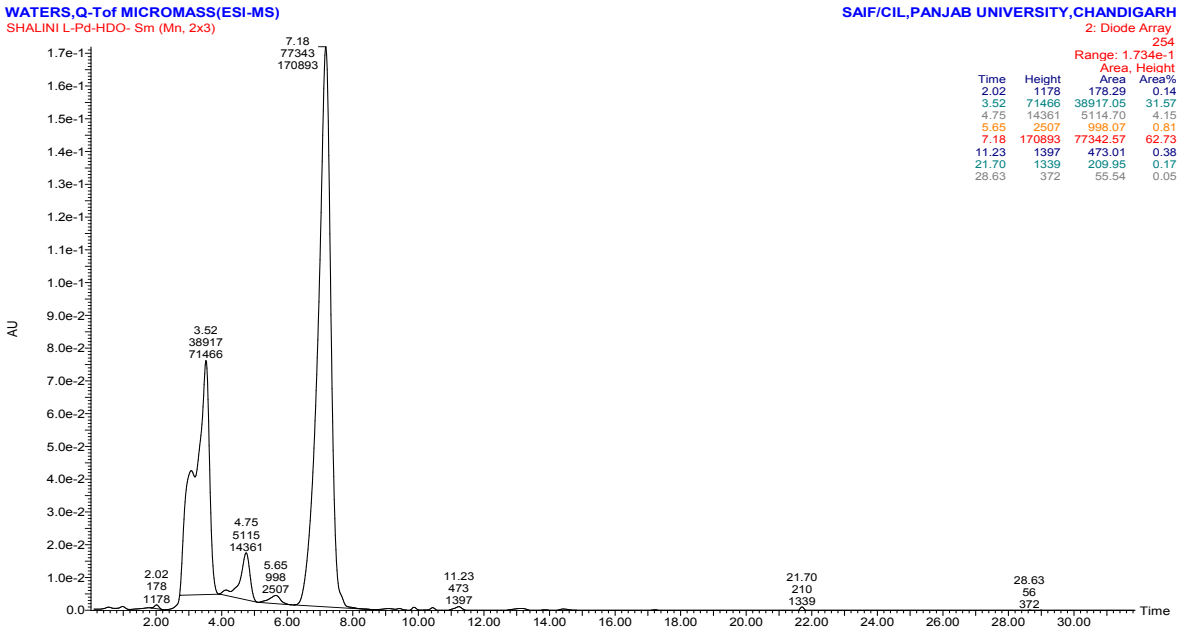

Fig. S17 HPLC-MS graph showing different peaks of possible products of HDO of phenolic compounds of commercial lignin using Pd/Ru@GO.

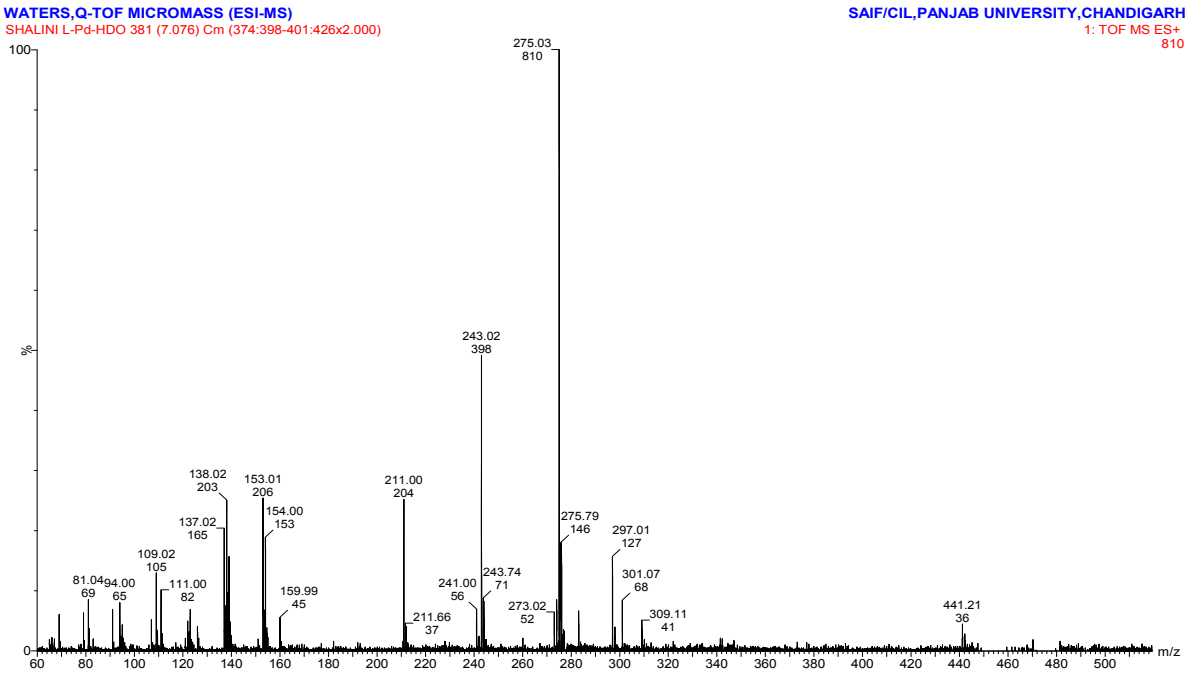

Fig. S18 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Pd/Ru@GO.

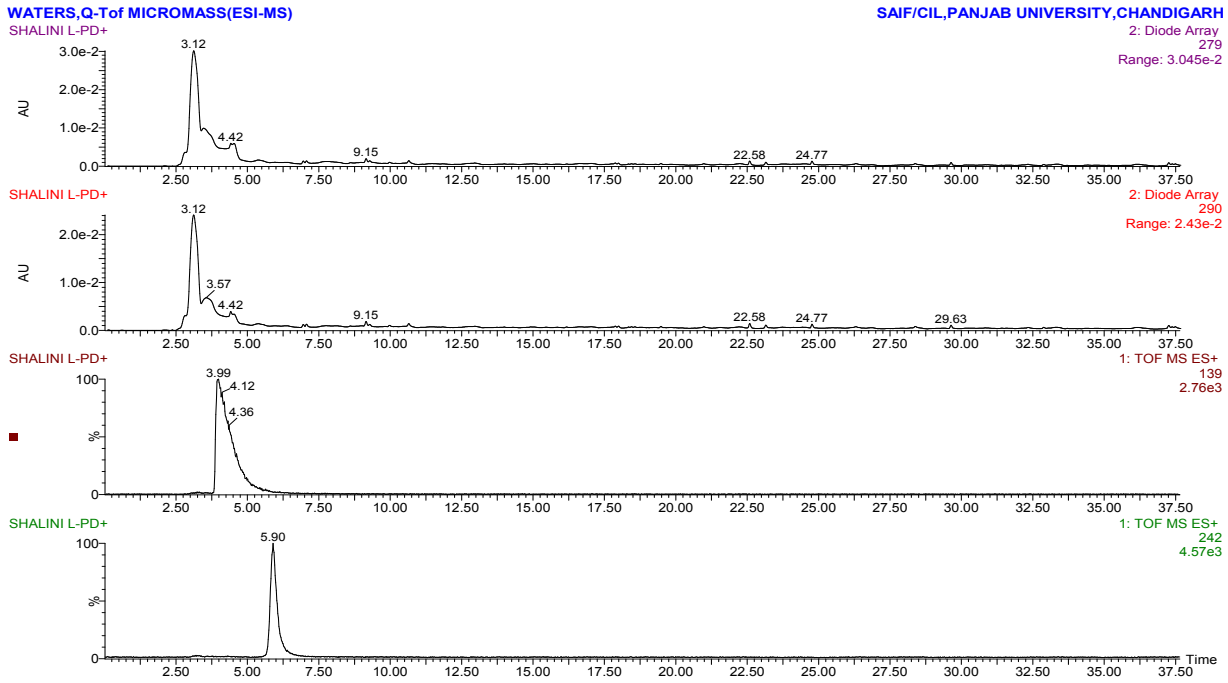

Fig. S19 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Ru@GO.

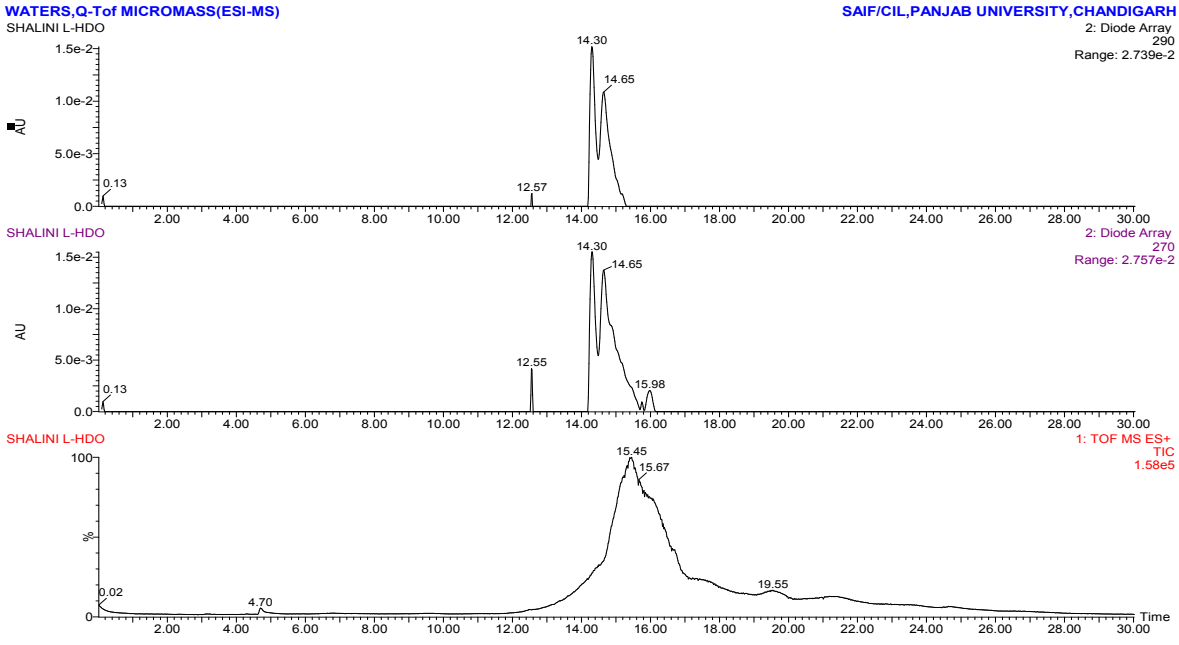

Fig. S20 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Ru@GO.

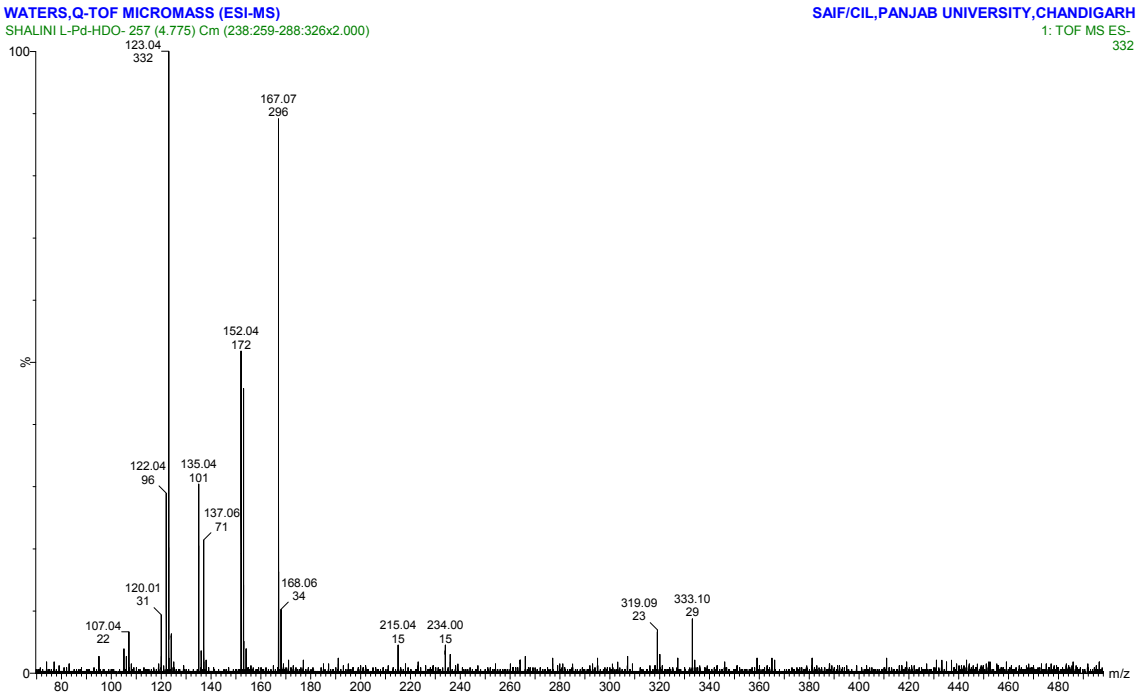

Fig. S21 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Ru@GO.

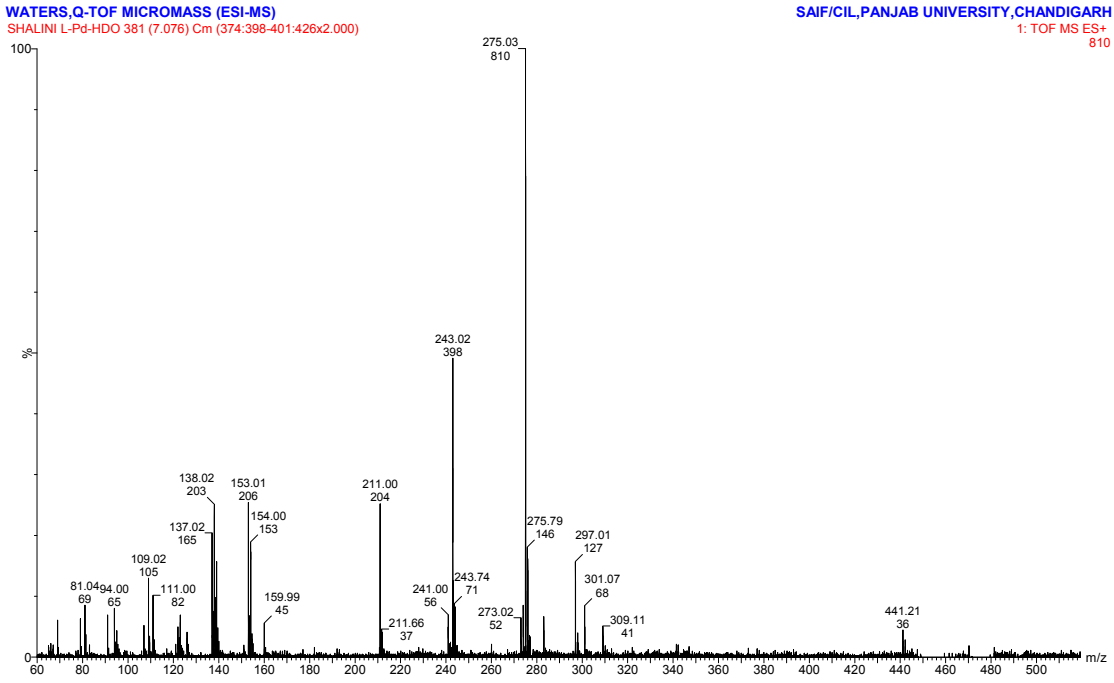

Fig. S22 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Ru@GO.

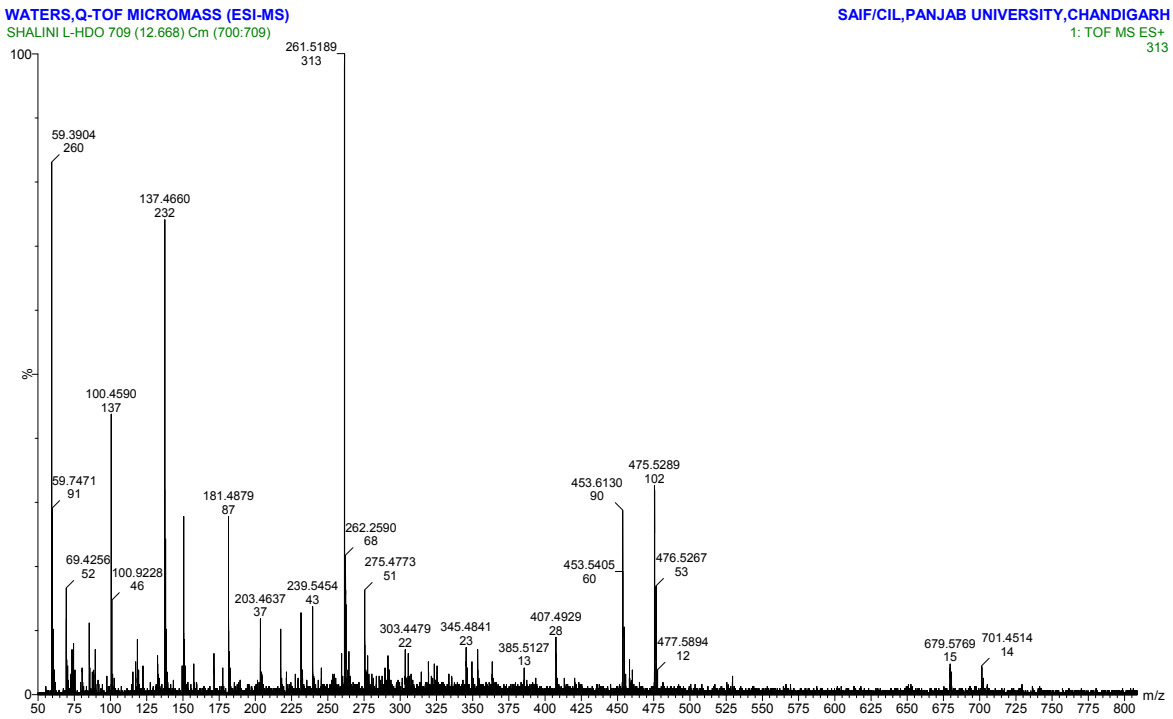

Fig. S23 HPLC-MS graph showing m/z peaks values of possible products of HDO of phenolic compounds of commercial lignin using Ru@GO.

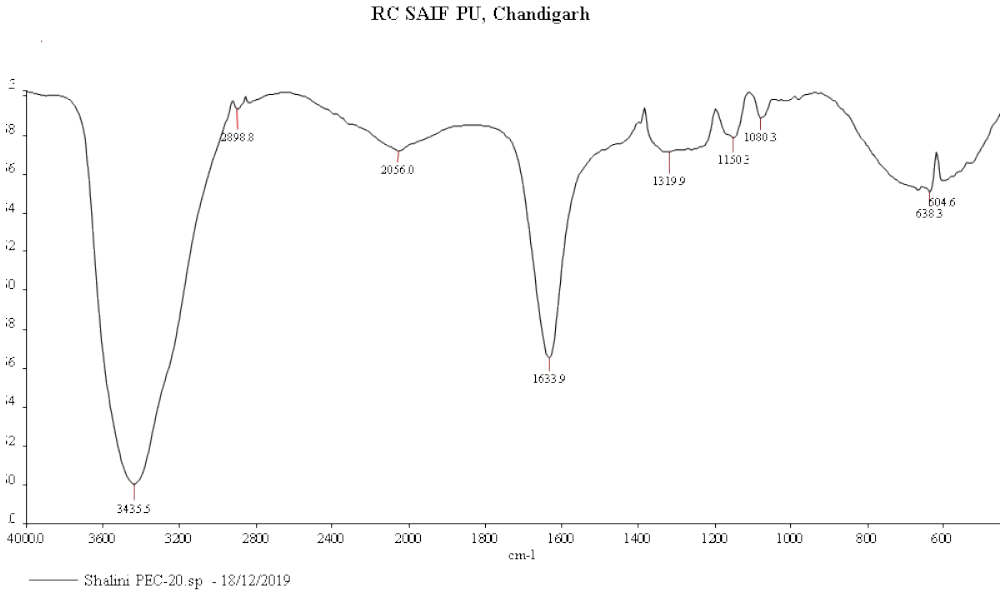

Fig. S24 FT-IR of bimetallic Ru@GO after seventh recycles.

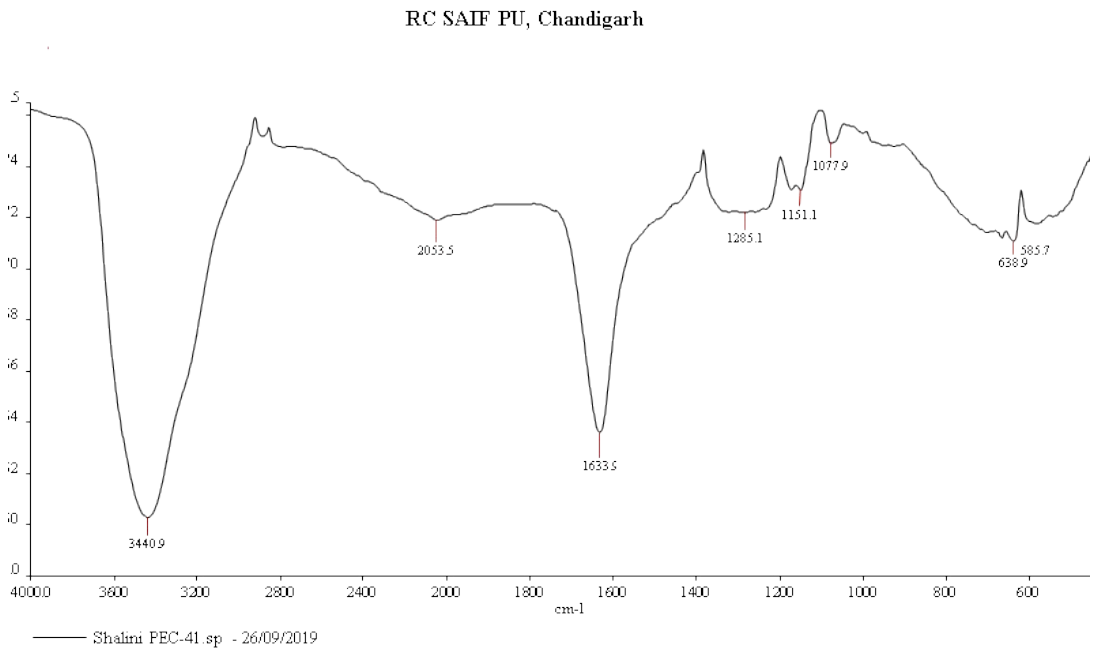

Fig. S25 FT-IR of bimetallic Pd/Ru@GO after seventh recycles.