Electronic Supporting information

Phytocat- A bio-derived Ni catalyst for rapid de-polymerization of polystyrene using a synergistic approach

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Experimental

Materials and methods

Two types of biomass were used in our experiments, the Ni hyper-accumulator (*Stackhousia tryonii*, collected from field on nickel-rich soils in Queensland, Australia) and hydroponically-grown willow plant species for the preparation of phyto-catalyst (1.5 wt% and 0.1 wt% Ni respectively) and Ni free controls (<0.01 wt% Ni). All Ni hyper-accumulators need trace quantities of Ni for growth; therefore, non-hyper-accumulator species were used as controls. Willow rods (*Salix viminalis*) were grown hydroponically for six weeks using the Aeroflo system (General Hydroponics) then dosed with 100 mg kg^{-1} of $Ni(NO_3)_2.6H_2O$ (Sigma Aldrich) solution for two weeks. Metal accumulation was determined in leaves and stems using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 700 series). Polystyrene (Sigma-Aldrich, $M_w \approx$ 192,000 g mol^{-1}, and density of 1.04 g cm^{-3}) and activated carbon (Sigma-Aldrich) were used for the co-pyrolysis experiments.

Reaction system set-up

Firstly, microwave assisted pyrolysis on air-dried, ground leaf tissues from the plant species was performed on a CEM Discover, equipped with 10 ml quartz vial at 250 ℃ and 200 W to produce bio-char with different Ni-loadings (termed as phytocat). The phytocat produced using microwave pyrolysis was then mixed with polystyrene to produce mixtures (1:1, 1:2, 1:5, 1:10 and 1:20) by weight. Microwave pyrolysis of these mixtures (1g each) was performed on CEM Discover, equipped with 10 mL quartz vial under N_2 atmosphere at 250 ℃ and 200 W. The feedstock was converted into vapors, which were passed through a condenser and collected as liquid oil. The mass yield of char and pyrolysis oil produced were measured and the gas yield calculated as the mass balance of the original sample. The total conversion was evaluated based on the sum total of liquid and gas yields. Further, the de-polymerization efficiency of the phytocat materials was calculated based on the percentage conversion of polystyrene into de-polymerized products. The evolved gas was trapped using gasbags (1L volume, Supel™-Inert Multi-Layer Foil) for qualitative analysis. The control experiments were carried out using willow bio-char without Ni (termed as control phytocat) and activated carbon. All the experiments were performed in triplicates.

Product yields are given as recovered yields expressed as per cent by weight of dry feed. The liquid and solid fractions were measured by weighing. Gas fraction mass was estimated by the difference between initial sample mass and sum of solid residue and liquid product mass.

(1) Conversion (%) = $\frac{Wi - Wr}{Wi} \times 100$

(2) Yield of oil (%) = $\frac{Wo}{Wi} \times 100$

(3) Yield of residue (%) = $\frac{Wr}{Wi} \times 100$

(4) Yield of gas (%) = $100 -$ (yield of oil + yield of residue)

Here, W_i, W_o and W_r are defined as initial weight of PS, weight of oil produced by microwave assisted pyrolysis of PS and weight of solid residue of PS after reaction, respectively.

The conventional study to monitor co-pyrolysis was done using the thermo-gravimetric analysis with fourier transform infrared (TGA-IR) profiles in the temperature range of 30 °C to 1000 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere of 100 ml min^{-1} flow rate. The analysis was done using the plant biomass (with and without Ni) and polystyrene mixtures as well as individual materials. TG-IR was carried out using Netsch STA409 linked to a gas cell in a Bruker Equinox 55 infra-red spectrometer by a heated gas line. The volatiles released during pyrolysis were immediately transferred to the FTIR gas cell and analyzed using a FTIR equipped with an MCT detector within the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

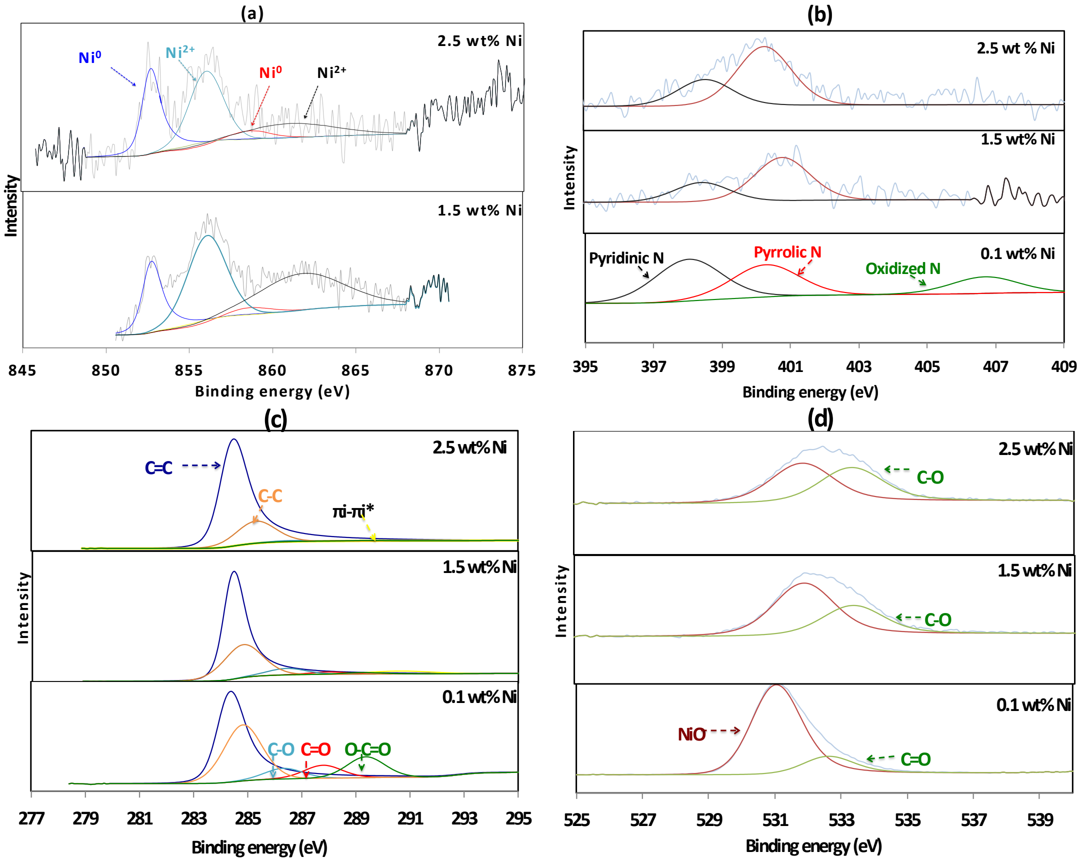
Material characterization

Transmission electron microscopy (TEM, JEOL 2010) was used under the accelerating voltage of 200 kV to investigate the microstructure of phytocat material. The TEM samples were prepared by suspending in methanol, followed by sonication for 10 minutes. A uniform thin layer of the sample was deposited on a carbon grid support followed by air-drying. Microstructural and chemical information of phytocat was obtained by using a field-emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray (EDX) spectrometer (JSM-7800F PRIME, JEOL Ltd.). Elemental composition and valence near the surface were measured using XPS (AXIS Ultra DLD, Kratos. Inc.), and the data were analyzed using CASA XPS software (Supplementary Fig. 1). XRD was performed at operating voltage of 40 kV, current, 40 mA, scan speed of 0.1 sec/step and the scan scope from 10 Θ to 90 Θ using a Bruker AXS D8 Advance (Supplementary Fig. 2).

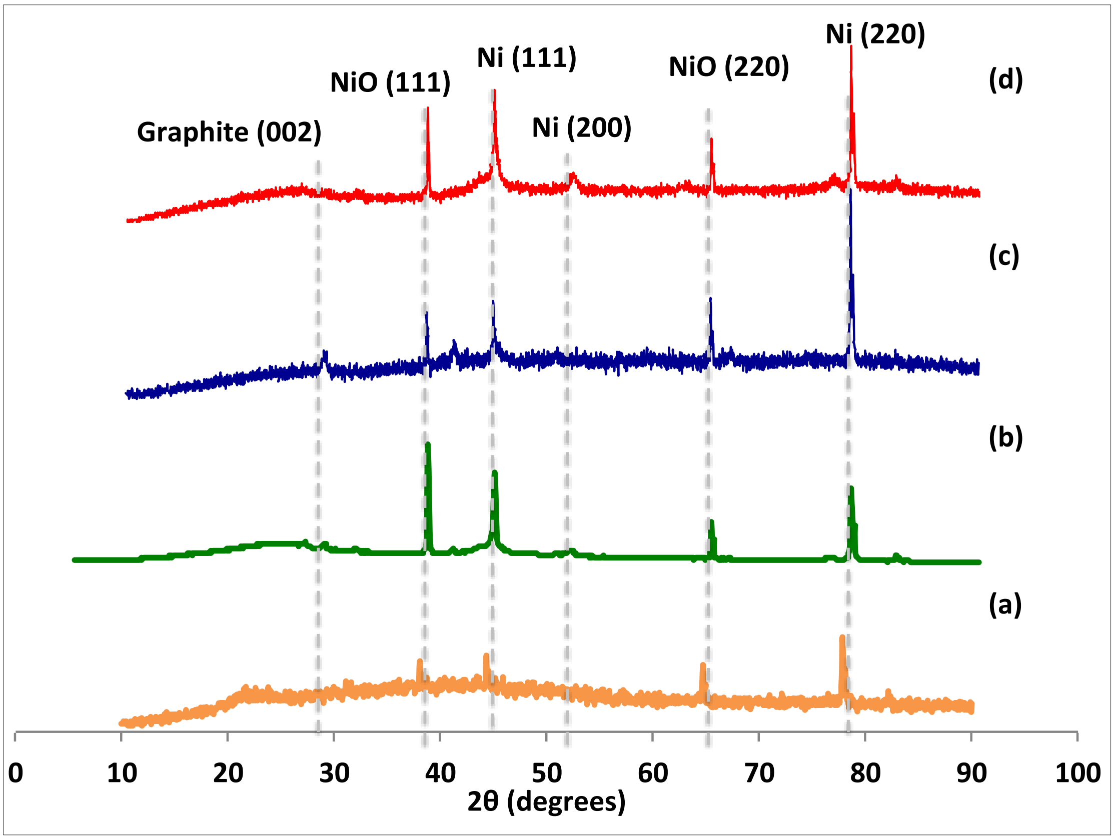
Qualitative analysis of de-polymerization products

Gas chromatography coupled with mass spectrometry, GC–MS (JEOL AccuTOF-GCx plus, Agilent 7890B GC) was used for analysis of liquid products. The column used was Phenomenex ZB-5MSplus (30m x 0.25 mm id x 0.25um film thickness) with film composition of 5% Phenyl-Arylene, 95% Dimethylpolysiloxane. The column oven was initially held at 45 °C for 1 min followed by a ramp at the rate of 5 °C min^{-1} to 300 °C, and finally held at this temperature for 10 min to allow elution of all the compounds. The constituents of samples were identified by comparing the mass spectra with national institute of standards and technology (NIST) research library. Relative content of each compound was measured by semi-quantitative method by calculating the chromatographic peak area (Supplementary Tables 2-10).

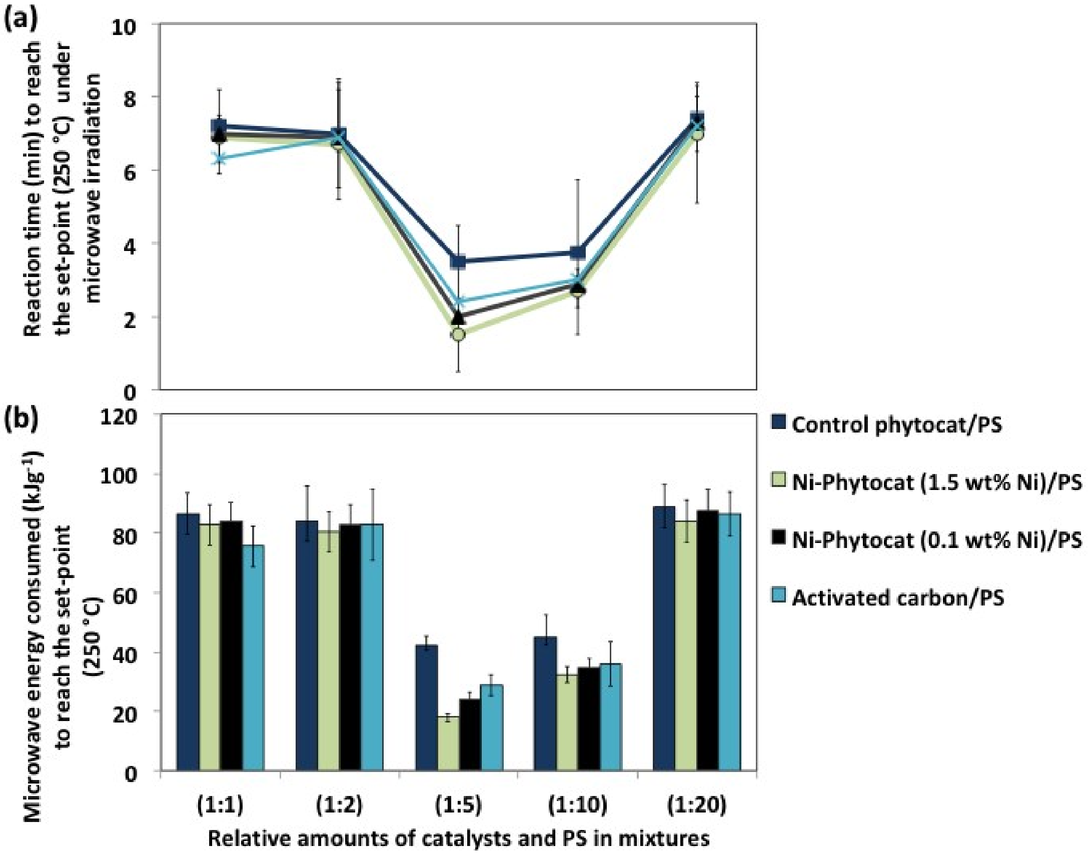
The qualitative analysis of gas was performed using attenuated total reflection Fourier transform infrared spectroscopy, ATR-FTIR (Bruker VERTEX 70). The spectra were recorded within the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. An initial background scan was collected before sampling in order to subtract the contribution from the ambient environment.



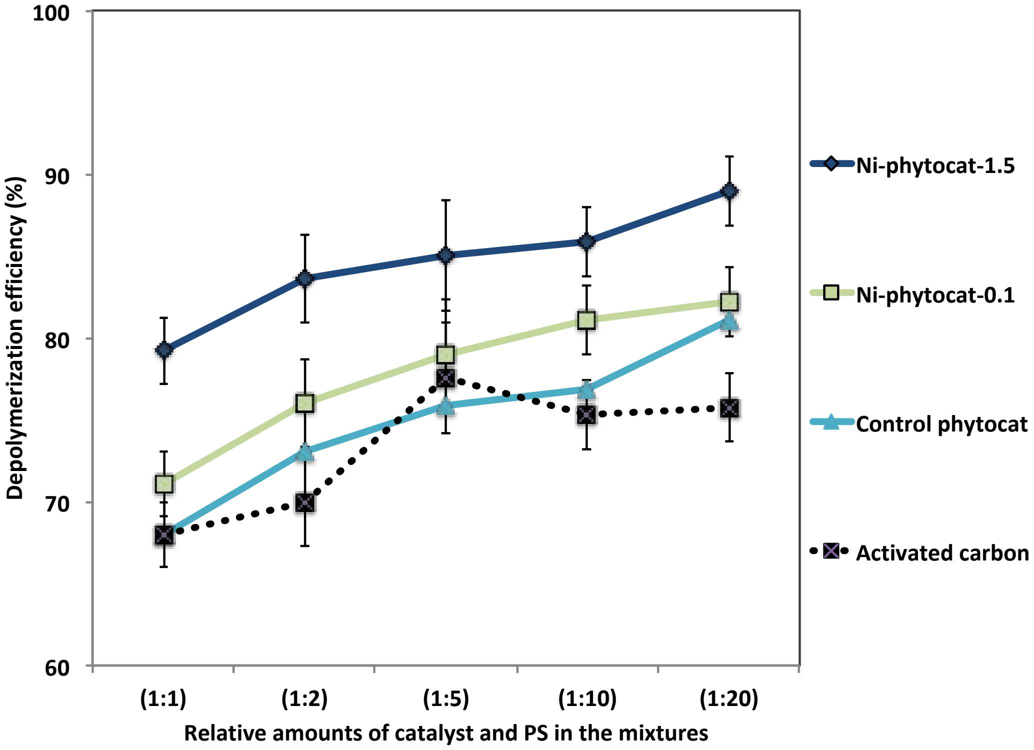
Supplementary Figure 1: XPS spectra of phytocat material with varying amount of naturally bound Ni in the matrix; (a) Ni2p3/2, (b) N1s, (c) C1s and (d) O1s



Supplementary Figure 2: XRD patterns for (a) Ni-phytocat (0.1wt% Ni), (b) Ni-phytocat (1.5 wt% Ni), (c) spent Ni-phytocat-0.1 (d) spent Ni-phytocat-1.5



Supplementary Figure 3: Time (a) and energy consumption (b) under microwave irradiation to reach the set-point of 250 ℃ for de-polymerization of polystyrene using various mixing ratios with phytocat and activated carbon (all the values were found to be statistically significant at significance level of 0.05).



Supplementary Figure 4: Comparison of efficiency of various catalysts for rapid de-polymerization of polystyrene (PS) (all the values were found to be statistically significant at significance level of 0.05).

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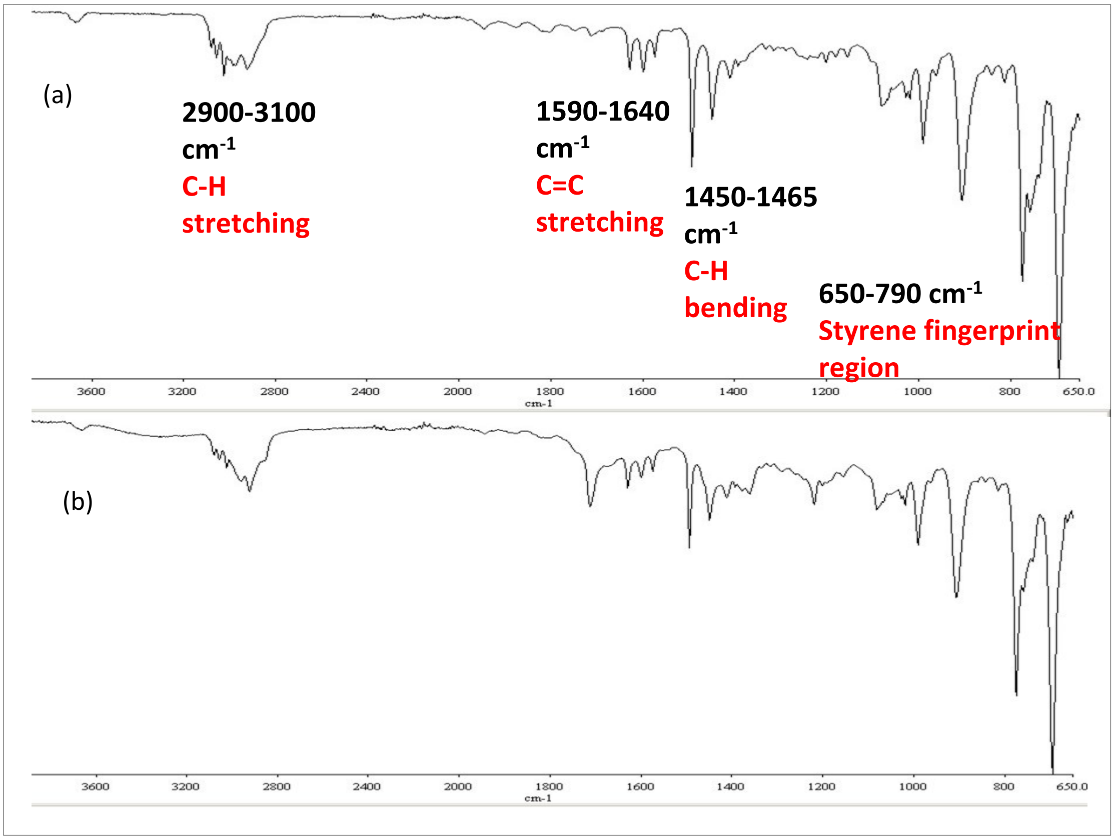
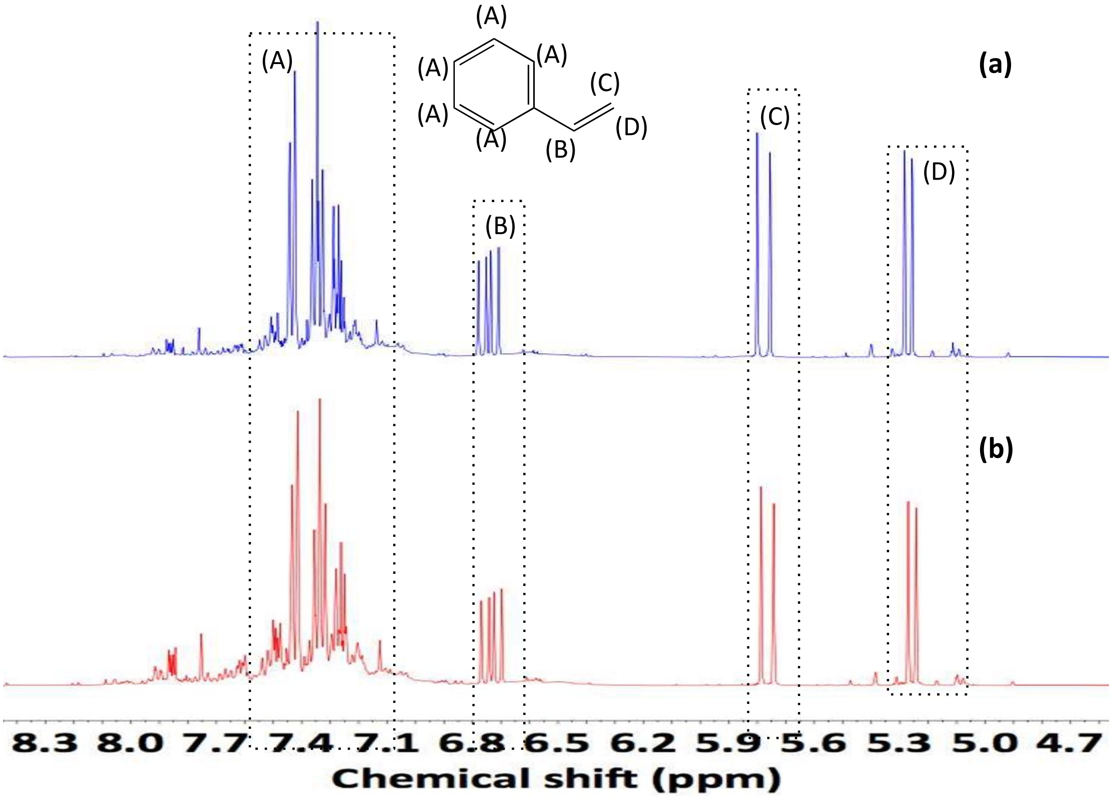
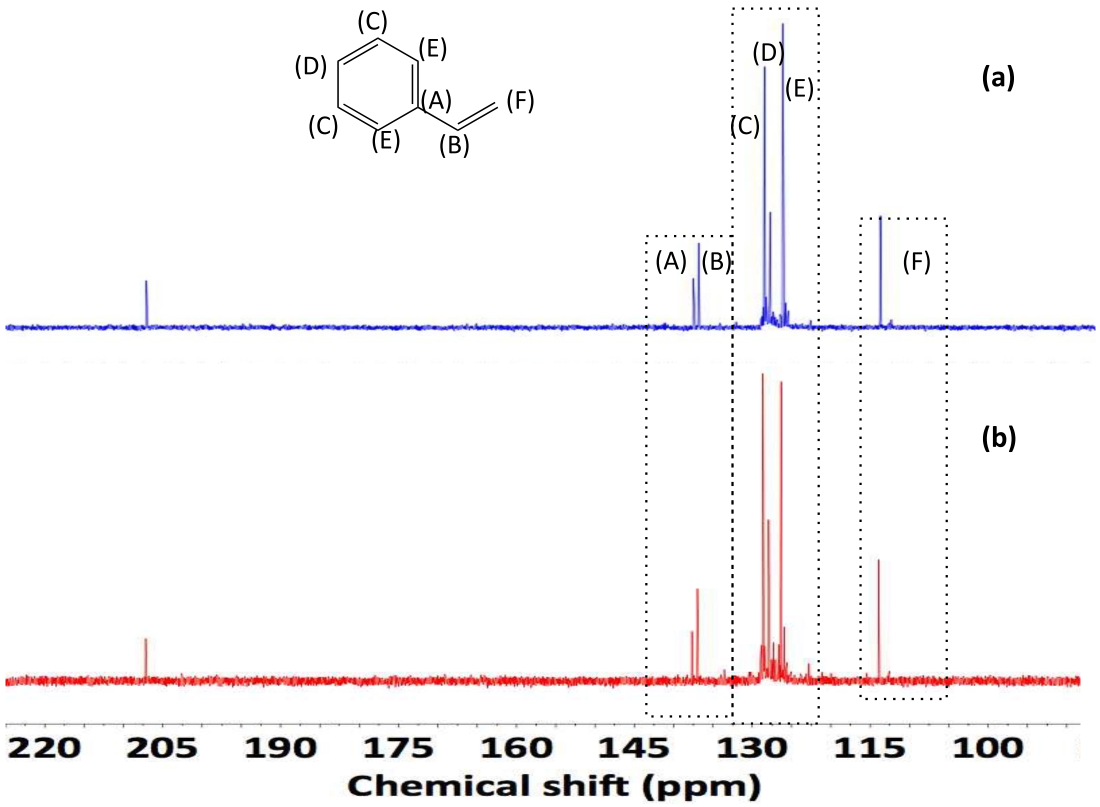


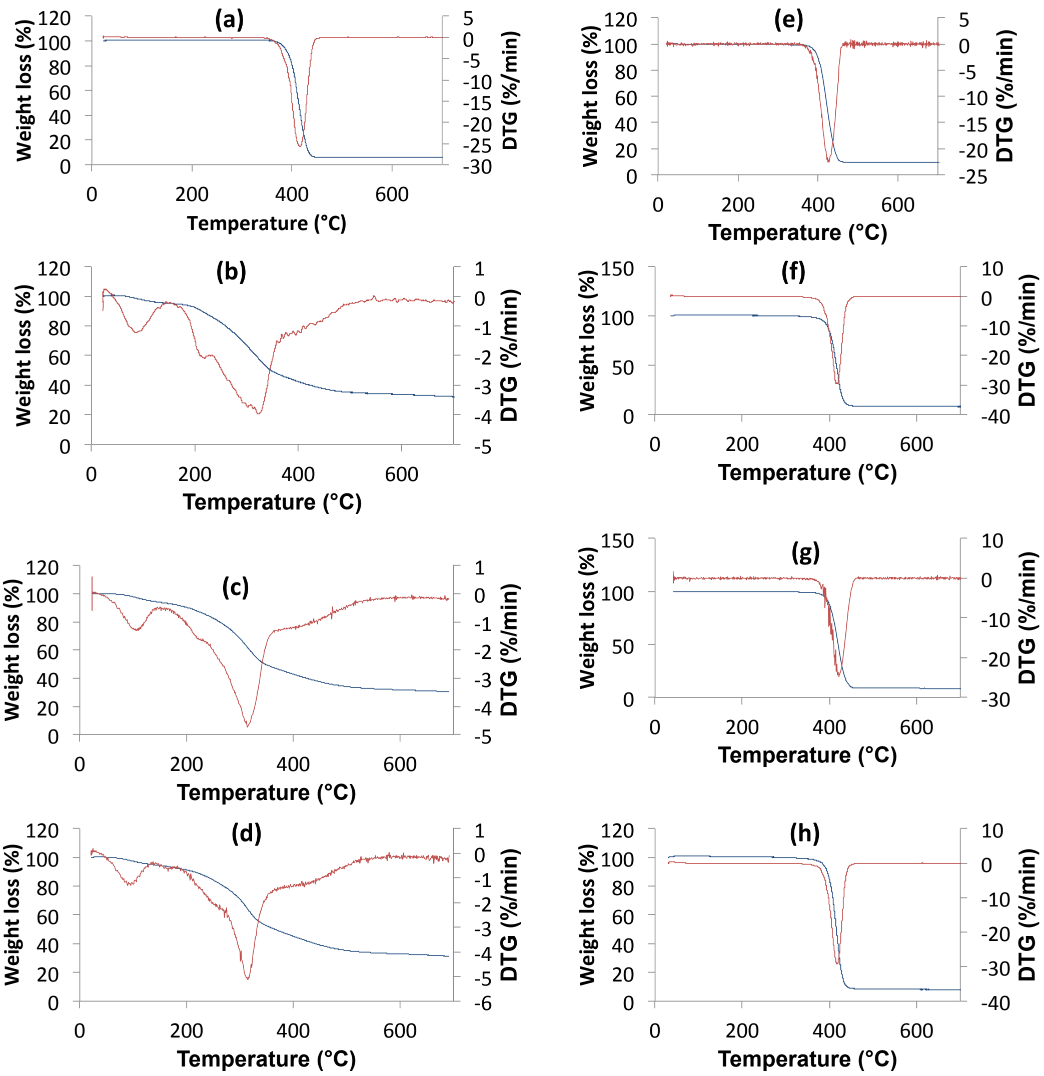
Supplementary Figure 5: FTIR analysis of pyrolysis oil produced by microwave assisted de-polymerization of Polystyrene using (a) phytocat and (b) control phytocat.



Supplementary Figure 6: ^{1}HNMR spectrum of pyrolysis oil produced by microwave assisted de-polymerization of Polystyrene using (a) phytocat and (b) control phytocat.



Supplementary Figure 7: ^{13}CNMR spectrum of pyrolysis oil produced by microwave assisted de-polymerization of Polystyrene using (a) phytocat and (b) control phytocat.



Supplementary Figure 8: Conventional TGA of (a) polystyrene (PS), (b) *S. tryonii* (Ni-phytocat-1.5), (c) *S. viminalis* (Ni-phytocat-0.1), (d) *S. viminalis* (<0.01 wt% Ni; control phytocat), (e) activated carbon: PS (1:10), (f) Ni-phytocat-1.5: PS (1:10), (g) Ni-phytocat-01: PS (1:10) and (h) control phytocat: PS (1:10) with a heating rate of 10°C min^{-1} under nitrogen atmosphere of 100 ml min^{-1} flow rate.

Supplementary Table 1: Comparison of our work with literature reports on pyrolysis of plastics

Raw material	**Reaction conditions**	**Catalyst: plastic (dry weight)**	**Oil yield (wt%)**	**Reference**
PS	250 °C	Plant bio-char containing naturally bound Ni in the matrix (Ni Phytocat), Ni free bio-char (control phytocat) and activated carbon; 1:1, 1:2, 1:5, 1:10, 1:20	47-72.5% (Ni-phytocat-1.5), 41-67 % (Ni-phytocat-0.1) 39.6-64.5% (control phytocat), 38.1-62% (activated carbon)	This research
PS, PP, PE, PET and mixtures there of	450 °*C*	Natural zeolite Synthetic zeolite 0.1	14–60%	1
HDPE	400–600 °C	Activated carbon, ratio not given	27.3–54.9%	2
PS	450-500 °C	Coconut sheath carbon 1:10	86.1%	3
PS, PP, LDPE, HDPE	500 °C	H–Y zeolite 0.5	42–71% for using catalyst, wax for no catalyst	4
LDPE	350–550 °C	MgO: plastic = 1:15–1:3	24.2–38.5 wt%	5
PS, PP, LDPE, HDPE	500 °C	Bentonite clay 0.05–0.2	85.6-89.5% for no catalyst 86.6-90.5% with catalyst	6
LDPE	450–600 °C	NiO: HY: plastic = (1–5): 15:150	48.08–51.23 wt%	7

Supplementary Table 2: Elemental distribution of metals in biomass and bio-chars using ICP-MS analysis

Sample Name	Sample type	Ni (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Ba (mg kg^{-1})
S. tryonii	Bio-mass	5691.7 ± 39	4.9 ± 2.1	26.4 ± 2.4	14.6 ± 4.2
S. viminalis	Bio-mass	84.7 ± 5.5	9.7 ± 1.4	37.1 ± 4.1	39.2 ± 3.7
S. viminalis	Bio-mass	0.997 ± 0.5	8.9 ± 1.5	39.2 ± 5.2	36.7 ± 2.2
S. tryonii (Ni-phytocat-1.5)	Bio-char	15377.9 ± 97	11.2 ± 2.6	67.9 ± 12	33.5 ± 2.1
S. viminalis (Ni-phytocat-0.1)	Bio-char	199.45 ± 25	16.9 ± 4.5	79.1 ± 14	64.1 ± 5.4
S. viminalis (control phytocat)	Bio-char	2.37 ± 1.5	15.6 ± 3.2	82.4 ± 22	62.9 ± 5.2

Supplementary Table 3: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Phytocat/PS (1:1)

Compound	**Peak area (%)**	**RT (min)**
Toluene	2.76	3.58
Ethyl benzene	0.93	5.88
Styrene	41.14	6.79
α-methyl styrene	2.27	9.61
Naphthalene	2.72	15.83
Biphenyl	1.58	21.25
Bibenzyl	0.71	24.75
Fluorene	1.09	26.22
Stilbene	4.81	29.13
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	1.72	29.29
Anthracene	5.64	30.57
1-Phenylnaphthalene	2.00	32.16
1H-Indene-2-phenyl	1.59	32.34
3,3-Diphenyl 5-methyl 3H-pyrazole	0.65	34.09
2-Phenylnaphthalene	4.46	34.44

Supplementary Table 4: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Phytocat/PS (1:2)

Compound	**Peak area (%)**	**RT (min)**
Toluene	0.85	3.01
Styrene	56.34	5.19
α-methyl styrene	2.87	7.35
Indene	1.63	9.03
Naphthalene	1.78	13.01
Biphenyl	0.87	18.29
Bibenzyl	1.72	21.76
Benzene, 1,1'-(1-methyl-1,2-ethanediyl)-bis-	0.61	22.47
Anthracene, 9,10-dihydro	0.63	25.67
Stilbene	2.80	26.13
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	6.30	26.31
Anthracene	2.20	27.57
1-Phenylnaphthalene	0.97	29.16
1H-Indene-1-phenyl	0.97	29.34
2,5-Diphenyl-1,5-hexadiene	1.21	29.87
2-Phenylnaphthalene	2.02	31.44
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	6.89	39.56

Supplementary Table 5: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Phytocat/PS (1:5)

Compound	**Peak area (%)**	**RT (min)**
Toluene	6.35	2.94
Ethyl benzene	2.26	4.46
Styrene	73.98	5.2
α-methyl styrene	3.56	7.33
Indene	0.74	9.00
Naphthalene	2.56	13.0
Biphenyl	1.54	18.28
Stilbene	3.45	26.14
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	0.96	26.29
Anthracene	2.59	27.58
2-Phenylnaphthalene	2.27	31.44
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	0.75	39.53

Supplementary Table 6: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Phytocat/PS (1:10)

Compound	Peak area (%)	RT (min)
Toluene	4.66	2.94
Ethyl benzene	1.58	4.46
Phenylacetylene	0.41	4.79
Styrene	68.1	5.2
α-methyl styrene	3.95	7.33
Indene	1.35	9.00
Naphthalene	2.07	12.99
Biphenyl	1.06	18.28
Bibenzyl	0.35	21.76
Benzene 1,1’-(1,3-Propanediyl)bis-	0.86	24.84
Stilbene	2.42	26.14
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	3.49	26.3
Anthracene	2.40	27.58
1-Phenylnaphthalene	0.76	29.16
2-Phenylnaphthalene	1.65	31.44
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	4.50	39.56

Supplementary Table 7: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Phytocat/PS (1:20)

Compound	**Peak area (%)**	**RT (min)**
Toluene	11.07	2.93
Ethyl benzene	10.05	4.47
Styrene	45.96	5.18
α-methyl styrene	5.85	7.33
Indene	1.35	9.00
Naphthalene	4.21	13.01
Biphenyl	2.5	18.29
Benzene 1,1’-(1,3-Propanediyl)bis-	2.15	24.86
Stilbene	4.48	26.16
Anthracene	5.63	27.61
1-Phenylnaphthalene	2.63	29.17
2-Phenylnaphthalene	5.93	31.47

Supplementary Table 8: List of compounds identified using GC-MS chromatograms of pyrolysis oil Control phytocat/PS (1:2)

Compound	**Peak area (%)**	**RT (min)**
Toluene	10.02	2.94
Ethylbenzene	3.63	4.46
Styrene	44.7	5.20
α-methyl styrene	3.66	7.33
Indene	1.30	9.01
Naphthalene	4.56	13.01
Biphenyl	1.94	18.30
Fluorene	0.73	23.22
Benzene, 1,1'-(1,3-propanediyl)-bis-	0.69	24.84
Stilbene	3.87	26.15
Anthracene	5.93	27.61
1-Phenylnaphthalene	2.13	29.17
1H-Indene-1-phenyl	0.77	29.35
2-Phenylnaphthalene	5.07	31.46
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	0.65	39.56

Supplementary Table 9: List of compounds identified using GC-MS chromatograms of pyrolysis oil of Control/PS (1:5)

Compound	**Peak area (%)**	**RT (min)**
Toluene	8.34	2.93
Ethyl benzene	5.01	4.45
Styrene	49.26	5.16
α-methyl styre ne	3.37	7.32
Indene	0.96	9.00
Naphthalene	3.49	13.0
Biphenyl	1.95	18.28
Fluorene	0.71	23.22
Stilbene	2.59	26.14
Anthracene	4.27	27.58
1-Phenylnaphthalene	1.70	29.16
1H Indene 2-phenyl	0.69	29.34
2-Phenylnaphthalene	3.69	31.45

Supplementary Table 10: List of compounds identified using GC-MS chromatograms of pyrolysis oil of control/PS (1:10)

Compound	**Peak area (%)**	**RT (min)**
Toluene	4.81	2.94
Ethylbenzene	1.76	4.46
Styrene	52.6	5.20
α-methyl styrene	3.39	7.33
Indene	1.76	9.01
Naphthalene	4.96	13.02
Biphenyl	3.36	18.30
Bibenzyl	0.68	21.76
Fluorene	0.69	23.23
Benzene, 1,1'-(1,3-propanediyl)-bis-	0.69	24.84
Stilbene	3.62	26.15
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	3.19	26.31
Anthracene	5.41	27.61
1-Phenylnaphthalene	1.52	29.17
1H-Indene-1-phenyl	1.03	29.35
2-Phenylnaphthalene	3.57	31.46
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	3.89	39.56

Supplementary Table 11: List of compounds identified using GC-MS chromatograms of pyrolysis oil of control/PS (1:20)

Compound	**Peak area (%)**	**RT (min)**
Toluene	6.28	2.93
Ethyl benzene	2.47	4.46
Styrene	45.4	5.19
α-methyl styrene	3.50	7.32
Indene	1.26	9.00
Naphthalene	1.90	13.0
Stilbene	1.37	26.13
Naphthalene 1,2,3,4-tetrahydro-2-phenyl	2.61	26.3
Anthracene	2.05	27.50
2-Phenylnaphthalene	1.23	31.44
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	1.84	39.50

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