Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information for

Application of highly stable biochar catalysts for efficient pyrolysis of plastics: a readily accessible potential solution to a global waste crisis

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fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Fig. S6 Liquid product compositions of model LDPE pyrolysis over Douglas fir derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Fig. S7 Gas product compositions of model LDPE pyrolysis over Douglas fir derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Fig. S8 Response surface and contour line for product yield (a: liquid, b: gas) with respect to temperatures and corn stover derived biochar to model LDPE ratios.

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Table S6 Complete minerals analysis of used biochar.

Biochar catalyst characterizations

Elemental analysis of biochar catalysts was conducted in a 2400 Series II CHN/O Elemental Analyzer (PerkinElmer, USA).

N_2 adsorption/desorption isotherms were obtained by employing a physisorption analyzer (Micromeritics R TristarII 3020) to analyze the porous characters of biochar catalysts.

NH_3 temperature-programmed desorption (NH_3-TPD) was performed using a Micromeritics Autochem 2920 instrument. The analysis conditions of that were as follows. Initially, an approximate 0.1 g sample was purged at a flow of Ar/He gas (5%/95%, 50 mL/min) at 300 °C for 1 h. After cooling down to the room temperature, the sample was saturated with 10% NH_3/He for 1 h at 100 °C. After saturation, the sample was purged with Ar/He gas (5%/95%, 50 mL/min) until no NH_3 was detected in the outlet gas. The desorption was performed by ramping the temperature up to 400 °C at a heating rate of 10 °C/min.

The complete mineral profile analysis (including Ca, P, K, Fe, Mg, Mn, S, Cu, Zn, Na, Al) was implemented by CEPS central analytical laboratory at the University of Arkansas, Fayetteville, AR, USA.

Scanning electron microscope (SEM, TESCAN VEGA3) and Scanning electron microscope-energy dispersive X-ray (SEM-EDX, TESCAN VEGA3) was used to identify the surface morphology of biochar catalysts.

Fourier-transform infrared spectroscopy (FT-IR) of biochar was obtained with an IR Prestige 21 spectrometer in attenuated total reflection (ATR) mode (Shimadzu, Japan). The spectra were recorded at a range of 500-4500 cm^{-1} at a resolution of 8 cm^{-1} using a combined 64 scans.

Thermo-gravimetric analysis (TGA) was carried out in a Mettler Toledo unit. The biochar samples were placed in a crucible to ascertain uniform heating and kinetic control during the degradation process. N_2 was employed to create the inert conditions at a flow rate of 50 ml/min. Then the samples was heated from room temperature to 600 °C at the ramping rate of 60 °C/min.

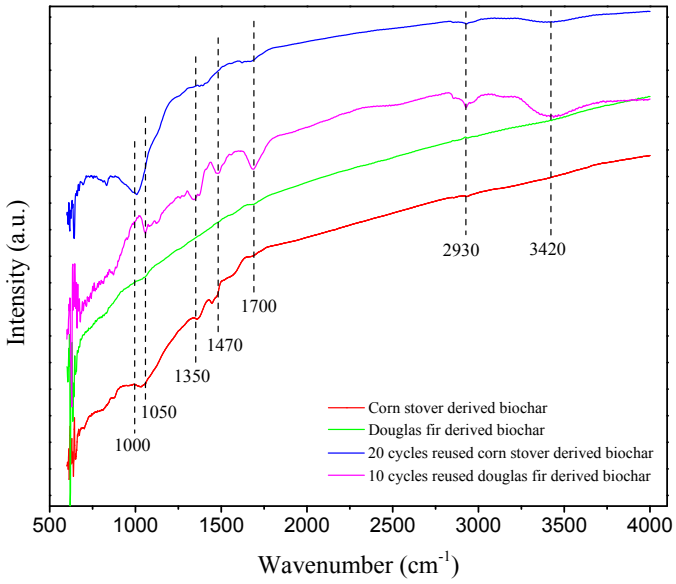

Fig. S1 FT-IR spectra of fresh and reused corn stover and Douglas fir derived biochars.

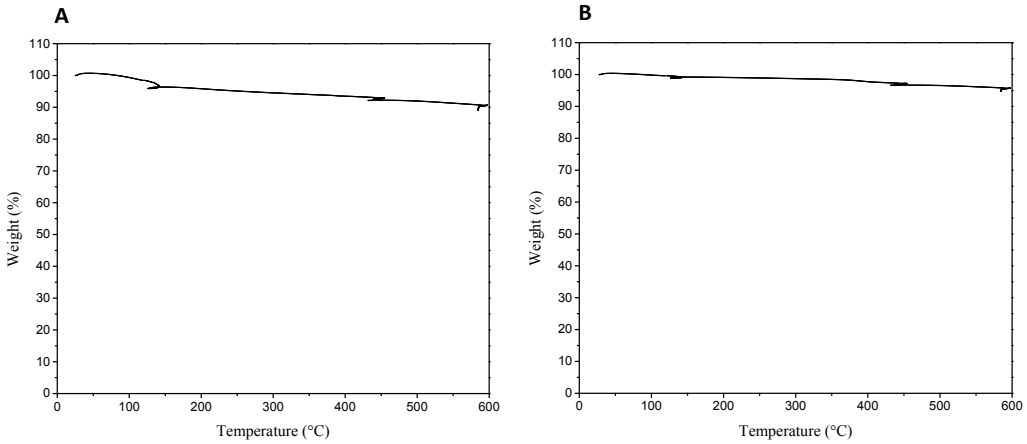

Fig. S2 TGA profiles of biochar catalysts: (A) corn stover derived biochar; and (B) Douglas fir derived biochar.

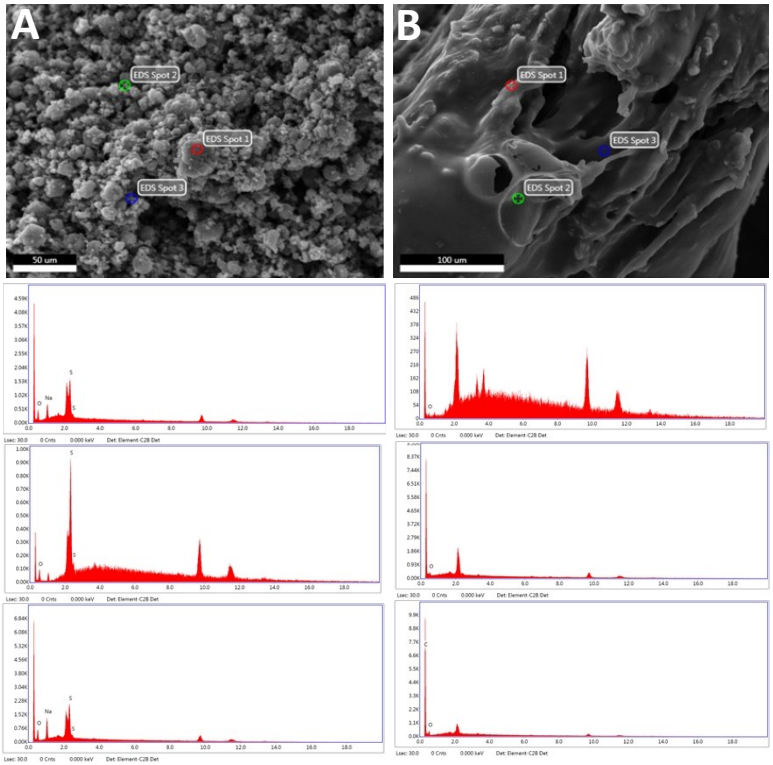

Fig. S3 EDS surface element analysis: (A) corn stover derived biochar; and (B) Douglas fir derived biochar.

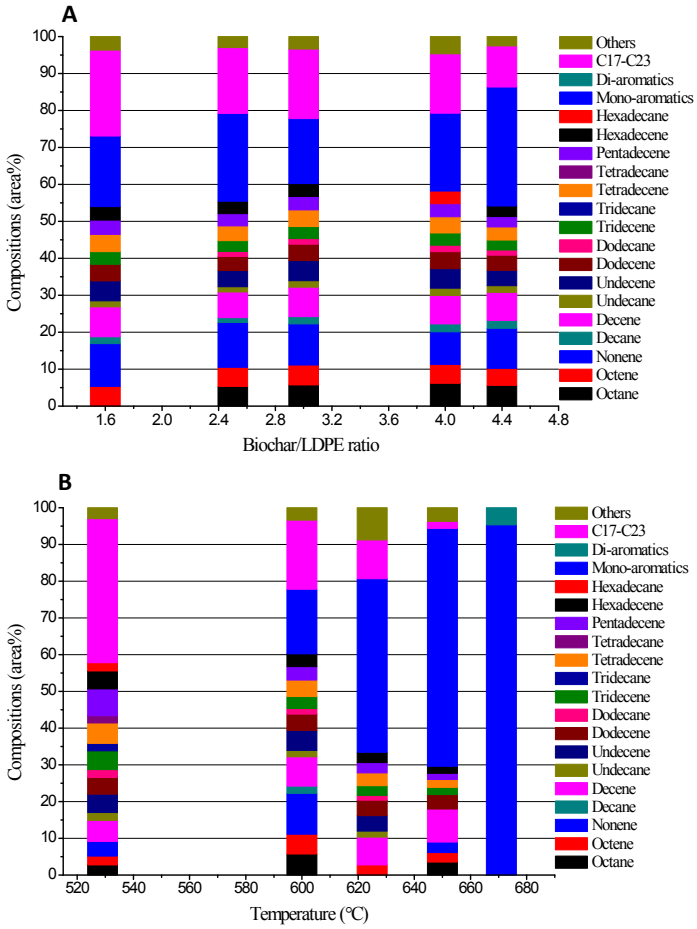

Fig. S4 Liquid product compositions of model LDPE pyrolysis over corn stover derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Note: (A) shows the effects of biochar to LDPE ratios on liquid compositions, it can be seen that the content of C8-C16 aliphatics went up with the increasing biochar to LDPE ratios, and then declined after the ratio exceeding 3. This was attributed to the increasing content of mono-aromatic hydrocarbons at higher biochar to LDPE ratios. At the temperature of 650 ºC, the content of monocyclic aromatic hydrocarbons in Run 1, Run 8 and Run 17 were respectively about 70%, 58% and 65%, suggesting that the higher biochar to LDPE ratio gives more monocyclic aromatics formation. The content of C17-C23 aliphatic hydrocarbons was declined from about 23% (Run 12) to 11% (Run 7) with the increasing biochar to LDPE ratios from 1.6 to 4.4. With the temperature increasing, as shown in **(B)**, the content of both C8-C16 and C17-C23 aliphatic hydrocarbons decreased because of the sharp increasing content of monocyclic aromatics, indicating that high temperature favors enhancing the production of aromatics. And when the temperature increased to 671 ºC in Run 6, about 4.6% of dicyclic and more than 95% of monocyclic aromatic hydrocarbons have been produced in the liquid product.

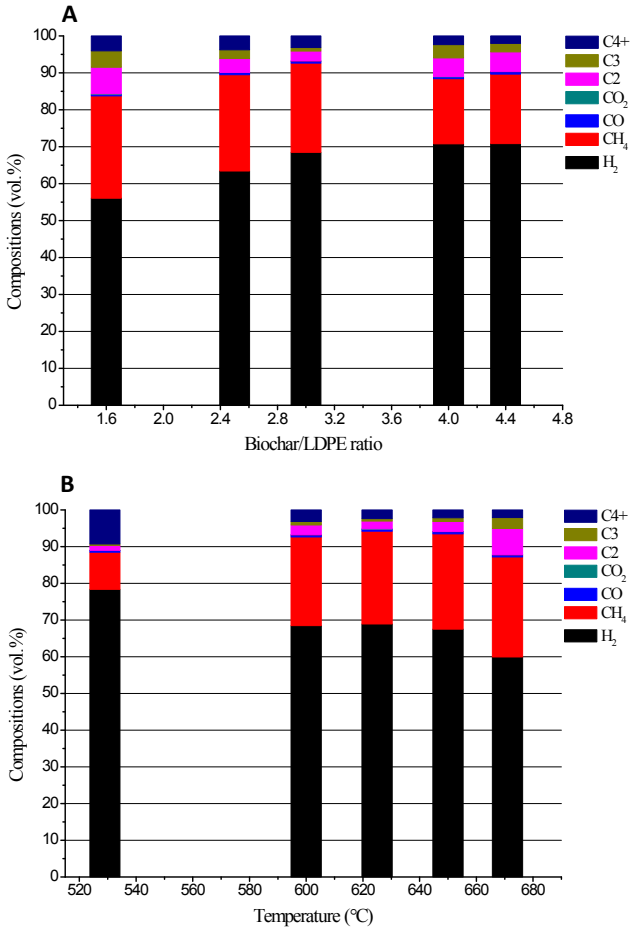

Fig. S5 Gas product compositions of model LDPE pyrolysis over corn stover derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Note: In **(A)**, it was found that the generation of H_2 was enhanced by rising biochar to LDPE ratios from 1.6 to 4 at the expense of the H atom, leading to the reducing concentration of CH_4. With the temperature increasing, as **(B)** introduces, a gradual decrease of H_2 concentration appeared, which can be explained that random bond scission has been strengthened with more formation of $\cdot CH_2$ or $\cdot CH_3$ radicals at high catalytic temperatures, meanwhile resulting in a higher content of CH_4, C_2 and C_3 gas.

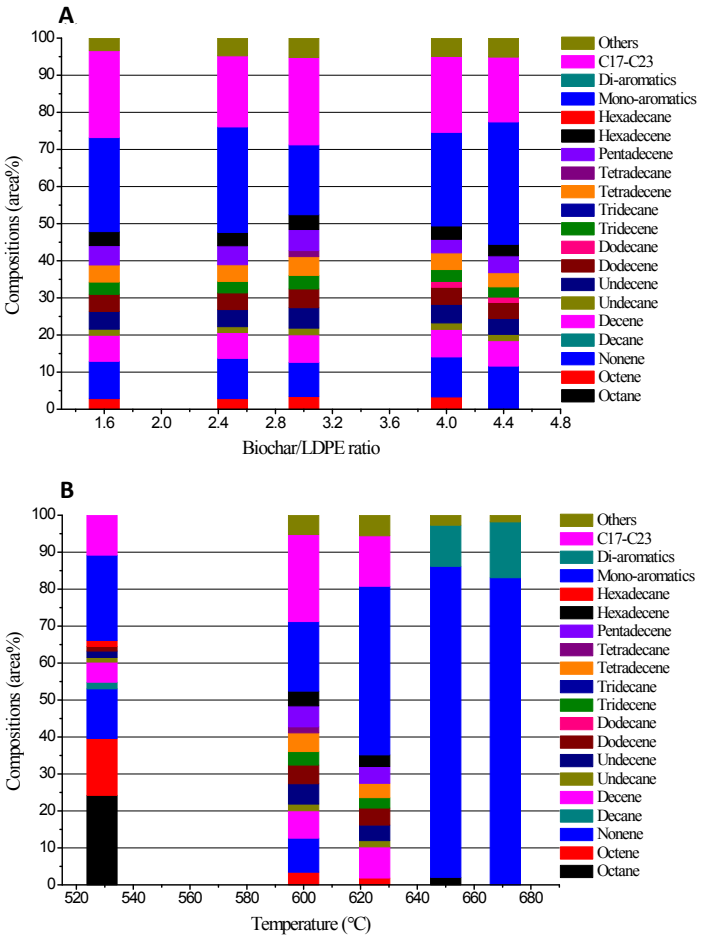

Fig. S6 Liquid product compositions of model LDPE pyrolysis over Douglas fir derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Note: As shown in **(A)**, when the biochar to LDPE ratio increased from 1.6 to 4.4, , the C8-C16 content kept at about 50% and the only small difference was observed, and the content of monocyclic aromatics was increased from 25% (Run 12) to 33% (Run 7). A higher ratio of biochar to LDPE resulted in the decline of C17-C23 content from 23.5% to 17.5%. **(B)** presents the effects of temperature, and the content of C8-C16 aliphatic and monocyclic aromatic hydrocarbons were respectively changed from about 50%, 20% to about zero, 83%. The content of C17-C23 aliphatic hydrocarbons was also reduced dramatically as the temperature went up.

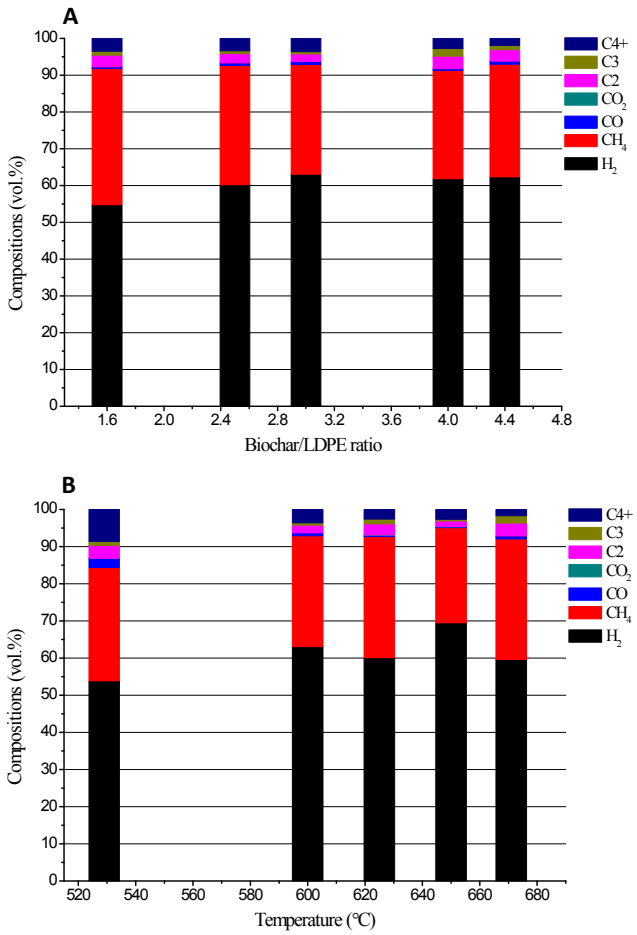

Fig. S7 Gas product compositions of model LDPE pyrolysis over Douglas fir derived biochar: (**A**) Compositions change along with different biochar/LDPE ratios (1.6, 2.5, 3, 4, and 4.4) at a fixed temperature of 600 °C. (**B**) Compositions change along with different temperatures (529, 600, 625, 650 and 671 °C) at a fixed biochar/LDPE ratio of 3.

Note: (A) and **(B)** express the effects of catalytic temperature and biochar to LDPE ratio on gas compositions. Similar to the pyrolysis process over corn stover derived biochar, H_2 content got a moderate increase with the decline of CH_4 generation, and then experienced almost a stable level of concentration after biochar to LDPE ratio being above 4. In terms of temperature factor, there were no regular variations observed for both H_2 and CH_4. On the whole, however, H_2 content displayed a downward trend as the temperature moved up, which was contrary to the CH_4 and other gas compounds.

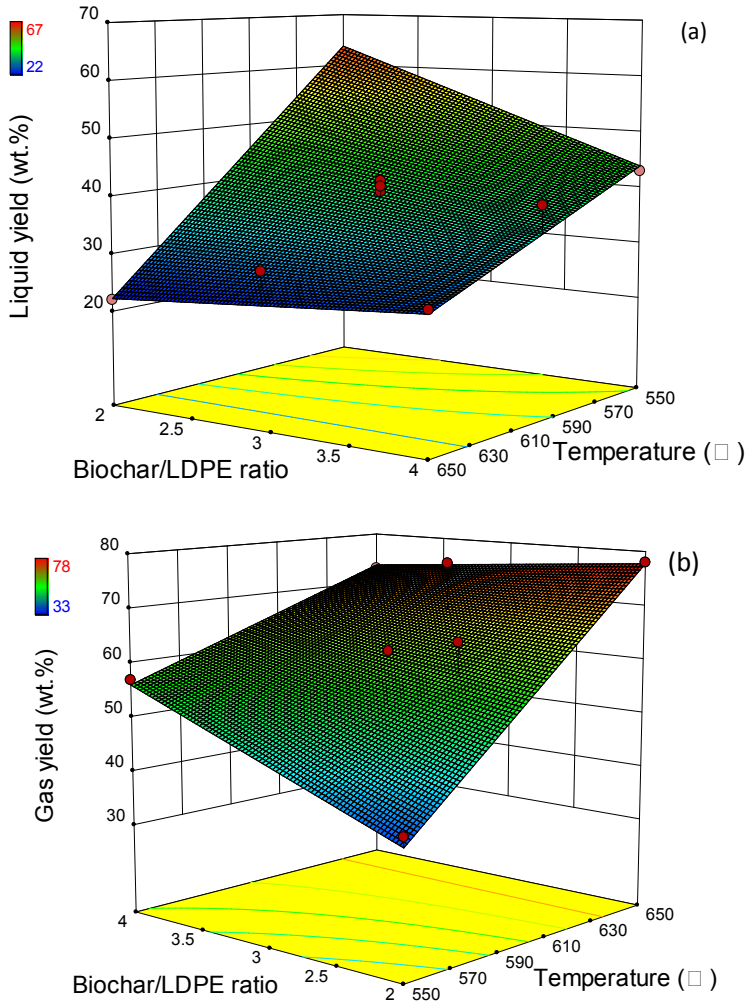

Fig. S8 Response surface and contour line for product yield (a: liquid, b: gas) with respect to temperatures and corn stover derived biochar to model LDPE ratios.

Note: The liquid product yield increased with the decrease of temperatures or biochar to LDPE ratios. However, temperatures lower than 550 ºC resulted in the severe formation of solid wax (Run 9 and Run 11), which indicates that the temperature was of great importance in the LDPE pyrolysis because higher temperature intensified the bond dissociation of pyrolytic volatiles towards light fractions. It should be noted that high temperatures could reduce the yield of the liquid product with a rapid increase in gas yield. As (b) shows, more than 70 wt.% yield of gas product was observed with full ranges of biochar to LDPE ratios when the temperature was at 650 ºC or higher.

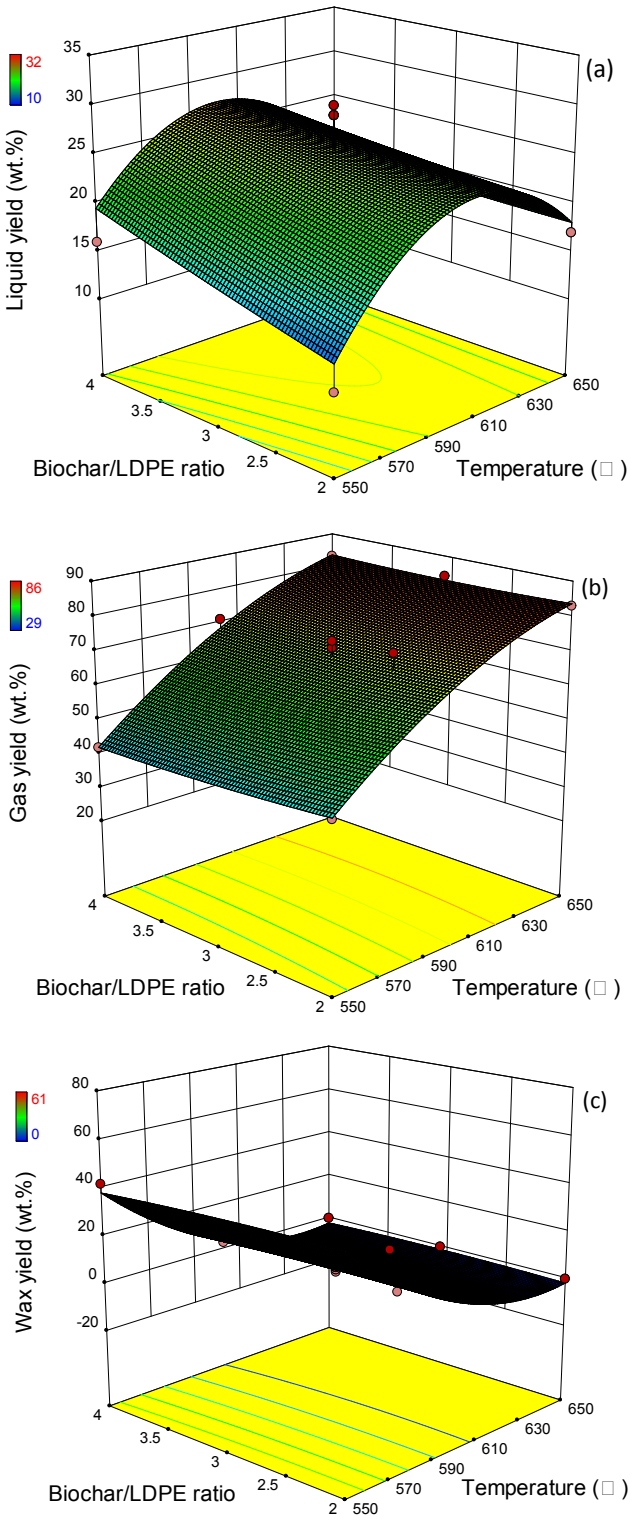

Fig. S9 Response surface and contour line for product yield (a: liquid, b: gas, c: wax) with respect to temperatures and Douglas fir derived biochar to model LDPE ratios.

Note: The maximum liquid yield lied in the temperature of around 600 ºC, and the liquid yield would decrease as the temperature increased, which was attributed to the enhanced bond scission at the temperature of more than 610 ºC. This can also be illustrated that the yield of gas has

increased to more than 80 wt.% at the catalytic temperature of 650 ºC. The temperature had a significant influence on the yield. And at the fixed temperature, the biochar/ratio impacted slightly on wax yields.

Table S1 Liquid product compositions of model LDPE pyrolysis over corn stover derived biochar.

Run	Liquid compositions/area%																			
	Octane	Octene	Nonene	Decane	Decene	Undecane	Undecene	Dodecene	Dodecane	Tridecene	Tridecane	Tetradecene	Tetradecane	Pentadecene	Hexadecene	Hexadecane	Mono-aromatics	Di-aromatics	C_{17}-C_{23}	Others
1	4.33	3.19	0.00	0.00	6.36	0.00	3.12	4.41	0.00	2.38	0.00	2.47	0.00	0.00	2.23	0.00	69.45	0.00	2.06	0.00
2	5.61	5.35	8.74	2.57	7.81	2.04	5.33	4.69	1.81	3.39	0.00	4.64	1.51	3.82	3.73	0.00	17.88	0.00	19.16	1.92
3	6.00	5.33	11.13	2.73	8.01	2.00	4.56	4.16	1.61	2.88	0.00	3.87	0.00	3.15	3.11	0.00	26.06	0.00	12.72	2.70
4	2.54	2.42	4.64	1.80	6.58	2.21	5.64	5.10	2.14	5.67	2.09	6.05	2.02	7.55	0.00	2.15	0.00	0.00	34.13	7.26
5	5.47	5.84	11.67	1.92	7.81	1.67	5.17	4.26	1.40	3.17	0.00	4.30	0.00	3.60	3.47	0.00	18.39	0.00	18.57	3.27
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	95.36	4.64	0.00	0.00
7	5.64	4.56	10.88	2.15	7.54	1.79	4.20	4.06	1.46	2.67	0.00	3.53	0.00	2.84	2.85	0.00	32.18	0.00	11.12	2.53
8	0.00	1.57	0.00	0.00	7.22	1.50	3.59	3.94	0.00	2.46	0.00	2.92	0.00	2.36	2.44	0.00	57.89	0.00	8.91	5.20
9	2.73	2.44	4.00	0.00	5.73	2.14	4.95	4.59	2.10	5.10	2.03	5.57	1.97	7.30	4.90	2.22	0.00	0.00	39.23	2.98
10	0.00	5.65	8.52	2.21	7.51	2.03	5.08	4.36	1.70	3.17	0.00	4.35	1.43	3.61	3.54	0.00	13.84	0.00	20.58	12.42
11	3.27	3.23	4.58	0.00	6.15	2.09	5.15	4.64	0.00	4.18	0.00	5.62	0.00	4.89	4.90	2.05	2.23	0.00	43.96	3.04
12	0.00	5.35	11.56	1.84	8.11	1.62	5.41	4.46	0.00	3.44	0.00	4.67	0.00	3.90	3.64	0.00	19.09	0.00	23.29	3.63
13	5.76	5.36	11.11	1.97	7.98	1.78	5.41	4.47	1.48	3.30	0.00	4.44	0.00	3.68	3.49	0.00	17.59	0.00	18.82	3.36
14	5.31	5.20	12.14	1.29	6.94	1.46	4.36	3.85	1.31	2.95	0.00	3.95	0.00	3.36	3.35	0.00	23.79	0.00	17.77	2.99
15	6.19	5.11	8.81	2.12	7.71	1.96	5.25	4.64	1.72	3.36	0.00	4.34	0.00	3.56	0.00	3.44	21.02	0.00	16.08	4.67
16	0.00	2.75	0.00	0.00	7.58	1.66	4.19	4.19	1.32	2.62	0.00	3.51	0.00	2.80	2.79	0.00	47.25	0.00	10.54	8.79
17	3.54	2.58	2.88	0.00	8.96	0.00	0.00	3.96	0.00	1.95	0.00	2.17	0.00	1.66	1.92	0.00	64.76	0.00	1.93	3.70
18	0.00	7.01	12.56	2.40	7.72	1.75	4.98	4.11	1.55	3.36	1.48	4.02	1.47	3.35	3.10	0.00	22.04	0.00	17.31	1.77
19	0.00	8.29	14.35	0.00	7.73	1.72	5.07	3.94	1.52	3.25	1.39	3.92	0.00	3.23	3.08	0.00	20.77	0.00	17.49	4.23
20	0.00	4.47	10.91	1.73	7.55	1.52	5.07	4.39	1.42	3.46	0.00	4.77	0.00	4.10	3.96	0.00	20.42	0.00	24.58	1.64
21	0.00	6.95	11.30	1.70	7.23	1.48	4.65	3.86	1.32	3.09	0.00	4.01	0.00	3.39	3.26	0.00	25.84	0.00	20.39	1.54
22	0.00	3.93	11.97	1.79	7.50	1.50	4.89	4.26	1.34	3.33	0.00	4.38	0.00	3.74	3.63	0.00	26.14	0.00	18.68	2.94
23	0.00	4.06	10.64	2.14	7.76	1.69	5.10	4.35	0.00	3.31	0.00	4.51	0.00	3.80	3.63	0.00	25.15	0.00	20.70	3.16
24	0.00	4.66	10.96	1.69	7.68	1.52	5.25	4.38	0.00	3.42	0.00	4.66	0.00	3.95	3.79	0.00	22.04	0.00	20.17	5.83
25	0.00	4.53	10.35	1.99	7.43	1.47	4.92	4.02	0.00	3.18	0.00	4.38	0.00	3.80	3.66	0.00	23.26	0.00	23.72	3.30
26	0.00	3.91	10.98	2.07	7.51	1.61	4.73	4.19	0.00	3.13	0.00	4.18	0.00	3.59	3.53	0.00	26.74	0.00	19.27	4.58
27	0.00	4.26	11.33	0.00	6.67	1.38	4.72	4.05	0.00	3.18	0.00	4.44	0.00	3.83	3.80	0.00	23.22	0.00	24.88	4.22

28	0.00	5.06	11.79	1.69	7.66	1.41	4.89	4.10	0.00	3.22	0.00	4.38	0.00	3.77	3.61	0.00	22.59	0.00	21.19	4.65
29	0.00	3.97	9.59	0.00	7.13	1.40	4.77	4.12	0.00	4.77	0.00	4.39	0.00	5.33	3.90	0.00	19.95	0.00	23.97	6.72
30	0.00	4.54	9.74	0.00	6.89	1.41	4.86	4.18	0.00	3.33	0.00	4.73	0.00	5.33	3.98	0.00	20.21	0.00	25.98	4.82
31	0.00	4.92	10.58	0.00	7.10	1.42	4.72	4.08	0.00	4.58	0.00	4.21	0.00	5.03	3.64	0.00	23.05	0.00	21.83	4.84
32	0.00	4.42	11.14	0.00	7.25	1.45	4.83	4.27	0.00	3.28	0.00	4.60	0.00	5.11	3.77	0.00	21.92	0.00	23.21	4.76
33	0.00	3.93	11.53	0.00	6.92	1.44	4.56	4.17	0.00	4.57	0.00	4.25	0.00	4.79	3.51	0.00	26.16	0.00	19.52	4.65
34	0.00	4.31	12.27	1.96	7.38	1.40	4.69	4.17	0.00	3.12	0.00	4.26	0.00	5.11	4.69	0.00	21.58	0.00	20.29	4.77
35	0.00	4.50	13.53	0.00	7.63	1.45	4.81	4.13	0.00	4.47	0.00	4.17	0.00	4.53	3.28	0.00	24.07	0.00	18.60	4.83
36	0.00	3.31	10.00	0.00	7.29	0.00	5.08	4.52	0.00	3.55	1.55	4.57	0.00	3.81	3.73	0.00	23.96	0.00	23.26	5.37
37	0.00	2.76	10.75	0.00	6.98	0.00	4.25	4.47	0.00	3.08	0.00	5.75	0.00	4.90	3.68	0.00	26.94	0.00	21.49	4.95

Table S2 Gas compositions of model LDPE pyrolysis over corn stover derived biochar.

	Gas compositions/vol.%						
Run	H_2	CH_4	CO	CO_2	C_2	C_3	C_4+
1	79.45	15.21	0.42	0.00	2.05	0.68	2.18
2	78.51	14.55	0.33	0.00	2.29	0.71	3.62
3	78.65	13.92	0.36	0.01	2.10	0.68	4.28
4	75.29	12.07	0.53	0.01	5.52	2.52	4.05
5	66.22	16.52	0.58	0.03	8.98	5.74	1.93
6	59.92	27.27	0.54	0.00	7.22	2.98	2.07
7	70.87	18.80	0.65	0.00	5.35	2.30	2.02
8	62.10	22.53	0.73	0.03	5.70	2.38	6.54
9	78.35	10.13	0.50	0.01	1.33	0.40	9.27
10	73.01	19.72	0.47	0.00	1.79	0.54	4.47
11	73.53	16.31	0.38	0.02	2.27	0.76	6.74
12	56.06	27.72	0.35	0.19	7.17	4.45	4.04
13	68.48	24.17	0.54	0.04	2.65	1.00	3.12
14	63.41	26.10	0.58	0.00	3.79	2.36	3.76
15	70.79	17.64	0.49	0.05	5.05	3.61	2.37
16	68.93	25.29	0.57	0.01	2.13	0.71	2.35
17	67.53	25.95	0.61	0.02	2.74	1.01	2.15
18	60.31	29.09	0.50	0.04	4.63	1.62	3.82
19	51.48	32.95	0.33	0.04	6.96	4.45	3.79
20	56.81	33.97	0.44	0.03	3.06	0.98	4.71
21	54.06	36.98	0.49	0.02	3.44	1.09	3.93
22	56.31	35.69	0.36	0.04	2.90	0.87	3.82
23	54.92	35.76	0.36	0.03	4.17	1.34	3.43
24	55.26	34.87	0.29	0.03	3.16	0.93	5.46
25	50.09	39.95	0.39	0.02	3.60	1.17	4.78
26	50.67	39.37	0.37	0.03	4.06	1.31	4.19
27	52.12	38.36	0.31	0.02	2.98	0.85	5.35
28	53.15	38.04	0.40	0.01	3.13	1.01	4.26
29	55.55	35.09	0.25	0.02	2.61	0.75	5.74
30	51.45	39.19	0.24	0.05	3.65	1.16	4.26
31	51.51	39.34	0.28	0.03	3.56	1.11	4.18
32	48.29	41.28	0.29	0.03	3.98	1.22	4.91
33	54.05	38.56	0.30	0.03	2.81	0.82	3.42
34	51.12	40.58	0.35	0.05	3.68	1.04	3.18
35	46.78	43.97	0.28	0.03	4.40	1.28	3.26
36	45.16	40.08	0.28	0.02	8.38	3.01	3.07
37	53.10	39.07	0.22	0.00	3.20	0.91	3.49
38	39.56	44.51	0.09	0.13	7.06	3.72	4.93
39	47.80	44.22	0.00	0.00	4.20	1.35	2.43

Note: Trace amounts of CO_x appeared owing to the release of inherent oxygen-containing groups or adsorbates existing on biochar. The biochar weight reduced slightly before and after the

reaction, which may be attributed to the release of some volatile molecules such as water adsorbed on the surface and inside of biochar or caused by the reaction of VOCs with biochar at elevated temperatures.

Table S3 Liquid product compositions of model LDPE pyrolysis over Douglas fir derived biochar.

Run	Liquid compositions/area%																			
	Octane	Octene	Nonene	Decane	Decene	Undecane	Undecene	Dodecene	Dodecane	Tridecene	Tridecane	Tetradecene	Tetradecane	Pentadecene	Hexadecene	Hexadecane	Mono-aromatics	Di-aromatics	C_{17}-C_{23}	Others
1	2.33	0.00	0.00	0.00	0.00	1.35	1.92	0.00	0.00	1.69	0.00	1.80	0.00	0.00	1.65	0.00	79.14	8.61	1.51	0.00
2	0.00	3.59	9.06	0.00	7.14	1.84	5.19	4.84	1.63	3.56	0.00	6.75	0.00	5.75	3.97	0.00	17.23	0.00	24.27	5.17
3	0.00	3.05	9.50	0.00	7.14	1.58	5.04	4.66	0.00	3.36	0.00	6.26	0.00	5.28	3.82	0.00	19.95	0.00	23.40	6.95
4	0.00	8.04	6.47	1.84	6.02	1.97	4.44	3.79	1.75	3.19	0.00	3.85	0.00	3.14	3.22	0.00	11.62	0.00	24.71	15.95
5	0.00	2.76	12.36	0.00	7.20	1.70	4.64	4.50	1.47	3.13	0.00	4.29	0.00	4.91	3.36	0.00	27.79	0.00	18.36	3.54
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.11	15.09	0.00	1.80
7	0.00	0.00	11.64	0.00	6.85	1.66	4.29	4.31	1.47	2.77	0.00	3.80	0.00	4.58	3.08	0.00	32.96	0.00	17.53	5.09
8	2.80	0.00	0.00	0.00	7.67	0.00	2.30	0.00	0.00	2.06	0.00	2.13	0.00	0.00	2.03	0.00	68.65	7.61	2.04	2.71
9	24.20	15.39	13.43	1.82	5.42	1.25	1.73	1.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.61	23.13	0.00	10.76	0.00
10	2.93	0.00	11.12	0.00	7.12	1.67	4.64	4.52	0.00	3.12	0.00	4.37	0.00	5.04	3.53	0.00	25.71	0.00	19.79	6.45
11	0.00	7.35	7.94	1.82	6.84	1.98	4.51	3.84	0.00	3.15	0.00	4.00	0.00	3.46	3.51	0.00	11.63	0.00	35.24	4.73
12	0.00	2.85	10.07	0.00	7.00	1.62	4.82	4.60	0.00	3.28	0.00	4.65	0.00	5.23	3.73	0.00	25.37	0.00	23.40	3.39
13	0.00	3.44	9.21	0.00	7.40	1.78	5.56	5.04	0.00	3.62	0.00	5.11	1.59	5.68	4.01	0.00	18.81	0.00	23.53	5.24
14	0.00	2.87	10.83	0.00	6.98	1.59	4.58	4.49	0.00	3.11	0.00	4.48	0.00	5.12	3.61	0.00	28.40	0.00	19.14	4.80
15	0.00	3.32	10.79	0.00	7.42	1.76	4.97	4.64	1.54	3.19	0.00	4.49	0.00	3.68	3.62	0.00	25.21	0.00	20.43	4.96
16	0.00	1.86	0.00	0.00	8.44	1.65	4.23	4.58	0.00	2.81	0.00	3.92	0.00	4.56	3.14	0.00	45.61	0.00	13.68	5.54
17	2.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	84.17	11.12	0.00	2.70
18	0.00	4.06	11.09	0.00	7.19	1.48	3.93	4.20	0.00	3.00	0.00	4.29	1.34	3.55	3.46	0.00	29.82	0.00	19.42	3.17
19	0.00	4.55	10.48	1.73	7.09	1.59	4.89	4.47	1.41	3.28	0.00	4.46	0.00	5.08	3.47	0.00	25.63	0.00	20.42	1.46
20	0.00	3.18	9.87	1.60	6.68	1.47	4.42	4.41	0.00	3.12	0.00	5.83	0.00	4.97	3.53	0.00	28.68	0.00	20.68	1.57
21	0.00	4.65	11.27	2.08	8.38	1.75	5.52	4.91	0.00	3.53	0.00	4.95	0.00	5.61	5.11	0.00	13.97	0.00	23.08	5.19
22	0.00	13.27	18.67	0.00	6.78	0.00	2.90	2.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	53.54	0.00	0.00	2.65
23	0.00	4.18	9.23	1.73	7.19	1.58	5.08	4.60	0.00	3.33	0.00	4.63	0.00	5.03	3.62	0.00	20.49	0.00	25.53	3.78
24	0.00	2.65	10.87	0.00	7.28	1.51	4.72	4.62	0.00	3.09	0.00	4.30	0.00	3.59	3.40	0.00	29.07	0.00	18.51	6.39
25	0.00	3.26	9.45	1.72	7.03	1.52	4.94	4.73	0.00	3.33	0.00	4.74	0.00	5.27	3.80	0.00	25.73	0.00	21.15	3.32
26	0.00	5.04	10.49	1.66	6.93	1.41	4.66	4.30	0.00	3.22	0.00	4.42	0.00	4.86	3.47	0.00	27.19	0.00	20.92	1.45
27	0.00	3.69	10.00	1.70	7.01	0.00	4.84	4.49	0.00	3.29	0.00	4.70	0.00	5.15	3.72	0.00	22.97	0.00	24.98	3.46

Table S4 Gas compositions of model LDPE pyrolysis over Douglas fir derived biochar.

	Gas compositions/vol.%						
Run	H_2	CH_4	CO	CO_2	C_2	C_3	C_4+
1	69.15	24.97	0.34	0.03	1.65	0.44	3.41
2	60.29	28.35	0.54	0.09	4.00	2.24	4.49
3	51.21	38.60	1.18	0.00	4.33	1.51	3.17
4	53.57	31.51	1.85	0.05	5.39	3.26	4.38
5	52.73	38.26	0.82	0.00	4.22	1.55	2.42
6	59.61	32.46	0.77	0.00	3.48	1.96	1.71
7	62.37	30.62	0.82	0.01	3.09	1.17	1.92
8	56.09	35.56	0.31	0.10	3.74	2.04	2.15
9	53.88	30.53	2.43	0.02	3.48	1.07	8.59
10	53.98	34.90	1.31	0.00	4.84	2.09	2.87
11	53.41	35.43	1.09	0.02	3.78	1.22	5.06
12	54.76	37.05	0.43	0.01	3.22	1.04	3.50
13	63.11	29.81	0.77	0.00	2.09	0.63	3.59
14	60.25	32.39	0.66	0.01	2.59	0.76	3.35
15	61.86	29.44	0.43	0.00	3.42	2.08	2.77
16	60.12	32.55	0.43	0.03	2.98	1.31	2.57
17	69.47	25.67	0.22	0.01	1.55	0.43	2.64
18	47.86	42.99	0.42	0.02	3.96	1.16	3.59
19	46.63	43.85	0.20	0.05	4.16	1.28	3.83
20	46.81	44.17	0.18	0.01	4.03	1.27	3.52
21	42.87	44.54	0.12	0.11	5.76	2.94	3.67
22	39.67	43.46	0.11	0.02	8.36	5.18	3.20
23	42.84	46.67	0.16	0.00	5.29	1.77	3.27
24	43.87	45.68	0.15	0.01	5.40	1.84	3.04
25	38.79	43.24	0.07	0.04	9.59	5.46	2.82
26	42.67	45.66	0.10	0.08	5.22	2.36	3.90
27	43.13	46.36	0.10	0.04	4.91	1.53	3.92

Table S5 Products distribution and composition of real waste plastics pyrolysis over corn stover and Douglas fir derived biochar*.

Composition of real waste plastics	Catalyst	Products Yield/wt.%			Liquid distribution/area%					Gas composition/vol.%							Weight change of catalyst, Δ/g
		Liquid	Wax	Gas	C_8-C_{16} aliphatics	Mono-aromatics	C_{17}-C_{23} aliphatics	Biphenyls	Others	H_2	CH_4	CO	CO_2	C_2	C_3	C_4+	
LDPE	Corn stover derived biochar	30.0	0	70.0	51.00	23.72	17.22	0	8.05	75.4	20.3	0.4	0.0	1.3	0.4	2.2	-0.11
HDPE		39.0	0	61.0	64.06	14.96	17.31	0	3.67	75.9	17.4	0.4	0.0	2.6	1.6	2.0	-0.14
PP		36.0	0	64.0	49.27	42.01	8.72	0	0	72.5	20.5	0.4	0.0	2.2	1.8	2.6	-0.15
PS		93.0	-	7.0	0	91.61	0	0	8.39	86.6	4.1	1.6	0.1	0.6	0.0	7.0	0.04
PET		20.0	-	80.0	0	27.82	0	52.15	20.03	70.2	9.7	14.6	1.6	1.0	1.1	1.7	0.29
LDPE	Douglas fir derived biochar	25.0	3.0	72.0	53.52	27.65	17.20	0	1.62	51.5	35.3	1.0	0.2	5.9	3.3	2.8	-0.09
HDPE		18.0	9.0	73.0	42.62	20.98	30.18	0	6.22	54.6	36.4	1.1	0.0	3.3	1.0	3.6	-0.1
PP		23.0	2.0	75.0	28.99	58.75	10.41	0	1.85	51.8	38.8	1.0	0.0	3.0	1.9	3.4	-0.1
PS		96.0	-	4.0	0	96.50	0	0	3.50	69.3	11.0	2.6	0.0	4.5	7.1	5.5	-0.12
PET		23.0	-	77.0	0	24.32	0	34.56	41.12	36.8	25.5	29.4	4.3	0.2	0.0	3.8	-0.1

*Reaction conditions: 600 °C, catalyst/feeding ratio = 3.

Note: For corn stover derived biochar, the liquid yield observed for real LDPE pyrolysis (30 wt.%) was lower than model LDPE (40 wt.%), while the distributions of C8-C16 aliphatics, mono-aromatics, and C17-C23 aliphatics were similar to that from model LDPE. It was obvious that the concentration of other compounds left in the liquid were higher than that from model LDPE pyrolysis, which could be ascribed to the additives that are required for the manufacture of plastics. The gas compositions were almost the same as the process of model LDPE pyrolysis, especially the generation of H_2 was still dominant with more than 70 vol.% content. Compared to real LDPE, real HDPE pyrolysis showed the higher liquid yield and C8-C16 aliphatics content, and the C17-C23 aliphatics and gas compositions were exactly similar to real LDPE pyrolysis. The concentration of mono-aromatics observed for real HDPE was lower than that from real HDPE, which could be owing to more quantity of short- and long-chain branches existing in LDPE compared to HDPE. The pyrolysis of real PP led to an obviously higher yield of monocyclic aromatic hydrocarbons than that from both LDPE and HDPE pyrolysis. This can be explained that large quantities of monomer propylene, as an elementary unit constituting PP, could be more easily formed and subsequently converted into aromatics. Similarly, up to 92% content of mono-aromatics were detected in the liquid from PS pyrolysis because a small styrene unit is of great abundance in the framework of PS. About 87 vol.% content of H_2 was found during PS pyrolysis in only 7 wt.% yield of the gas product. 14.6 vol.% concentration of CO was observed for the pyrolysis of PET, which indicates that decarbonylation occurred in this process. Similar to PS, benzenes monomer are also with large amounts in PET skeleton, however, despite that, only 28% of mono-aromatics were observed, which was caused by the easy condensation of active oxygen-bearing intermediates formed in PET pyrolysis, while resulted in about 52% concentration of Biphenyls. Compared with corn stover derived biochar tending to enhance H_2 generation, Douglas fir derived biochar was still inclined to provoke more formation of CH_4. For the pyrolysis of real LDPE, HDPE and PP, there was small amount of wax produced over Douglas fir derived biochar, and the yield of liquid and H_2 selectivity in gas product was lower than that over corn stover derived biochar, whereas the monocyclic aromatics were still with a higher content, which were in

accordance with the results of model LDPE pyrolysis. The yields and compositions of liquid products from real PS and PET pyrolysis over biochar derived from Douglas fir were similar to that over corn stover derived biochar, except that the biphenyls were with an obviously lower content (about 52% *vs* 35%).

Table S6 Complete minerals analysis of used biochar.

Biochar derivation	Complete mineral profile (ppm)										
	Ca	P	K	Fe	Mg	Mn	S	Cu	Zn	Na	Al
Corn stover	8039	8170	29488	125	4127	163	1029	15.1	45.8	395	79.2
Douglas fir	1845	195	746	124	114	53.7	10.3	7.52	4.89	163	68.2