

Supporting Information

Efficient conversion of wheat straw into furan compounds, bio-oils, and phosphate fertilizers by a combination of hydrolysis and catalytic pyrolysis

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1. *The conversion of wheat straw with the FePO₄ catalyst*

Table S1 shows the results for the conversion of untreated wheat straw to HMF and furfural using the FePO₄ catalyst in the H₂O/THF biphasic reaction system. When the reaction temperature was 160 °C, the HMF yield increased from 5% for 60 min to 18% for 150 min, while the furfural yield reached a maximum to 25% for 120 min. This suggests that the reaction conditions are different for the production of HMF and furfural. As the reaction temperature was further elevated to 180 or 190 °C, no remarkable increases in the HMF and furfural yield were observed. Moreover, it was found that the maximum solid residue was obtained together with the low HMF yield of 13% and furfural yield of 19% when the reaction was conducted at 190 °C for 60 min, meaning that the solid residue was humans due to higher reaction temperature. In addition, higher reaction temperatures and longer reaction time could promote the degradation of HMF and furfural into humins as well as the rehydration reaction of HMF to levulinic and formic acid¹⁻⁵. It has been reported that the optimal reaction temperature for furfural formation is 160 °C (Weingarten et al.), which is in good agreement with our results. These results clearly demonstrate that a single FePO₄ catalyst can simultaneously catalyze the conversion of hemi-cellulose and cellulose to furfural and HMF without the addition of homogeneous acid such as HCl or H₂SO₄. This is because the FePO₄ catalyst is able to hydrolyze to produce H⁺ ions and Lewis acid sites such as soluble hydroxylated iron speices^{3,6}, both of which can catalyze the isomerization of glucose or xylose to fructose and xylouse and then the dehydration reaction into HMF and furfural, respectively.

Table S1 Results for the conversion of wheat straw into HMF and furfural using FePO₄ as the catalyst

Entry	Temperature /°C	Time /min	HMF yield/%	Furfural yield/%	Solid residues /g
1	160	60	5	35	0.454
2	160	90	13	33	0.472
3	160	120	17	47	0.510
4	160	150	18	41	0.453
5	170	60	18	39	0.426
6	170	90	14	33	0.362
7	180	60	16	37	0.471
8	180	90	13	36	0.456
9	190	60	13	36	0.640

^aReaction conditions: 1.0 g wheat straw, 0.1 g FePO₄ catalyst, 10.0 mL deionized water, 30.0 mL THF, 3.5 g NaCl

To further improve the HMF and furfural yields, the catalyst loading was examined. Fig. S1 illustrates that effect of FePO₄ catalyst loading on the conversion of wheat straw to HMF and furfural yields. It can be seen that the use of 0.2 g catalyst gave the highest HMF yield of 21%, while the use of 0.5 g catalyst produce the

maximum furfural yield of 37%. This shows that the production condition of furfural from xylan is different from that of HMF from cellulose under identical conditions. The possible explanation is that the energy barriers of depolymerization of hemicellulose, the isomerization of xylose to xylouse, and the dehydration of xylouse are completely different from the conversion of cellulose into HMF. It is thus reasonable that different concentrations of Lewis and Brønsted acid sites are required to obtain high furfural yield.

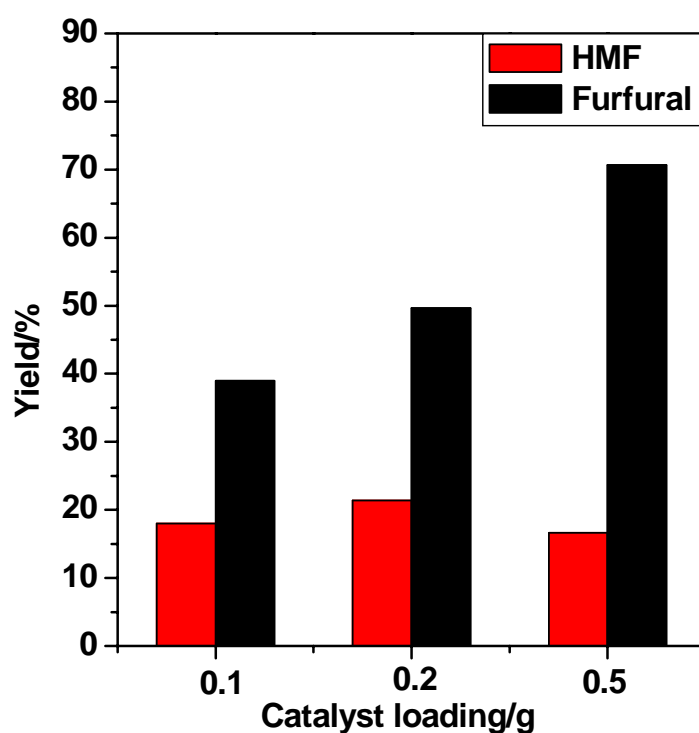


Figure S1 Effect of FePO₄ catalyst loading on the conversion of wheat straw and HMF and furfural yields. Reaction conditions: 1.0 g wheat straw, FePO₄ catalyst, 10.0 mL deionized water, 30.0 mL THF, 3.5 g NaCl, 170 °C, 60 min. Solid residues is 0.43, 0.51, 0.80 g, respectively.

2. *The pyrolysis of the solid residues*

Table S2 The yields of solid, liquid, and gas produced from the pyrolysis of the solid residues ^a

Entry	The yield (%)		
	Bio-oil	Gas	Bio-char
1	18.4	24.2	57.4
2	40.4	4.0	55.6
3	24.2	19.6	56.2

^aEntries 1, 2, 3 are defined as the solid residues obtained from the conversion of untreated wheat straw at 160 °C for 30, 60, and 90 min, respectively;

Table S2 illustrates the yields of solid, liquid, and gas produced from the pyrolysis of the solid residues. As can be seen, a high bio-oil yield up to 40.4% was achieved as the use of the solid residue produced from the conversion of untreated wheat straw at 160 °C for 60 min. The different yields of solid, liquid and gas can be explained by the fact that the hydrolyzed solid residues have different cellulose and lignin contents, as well as could contain various amounts of humins, which may affect the yield of the pyrolyzed products.

3. *The IR spectra of the solid residues*

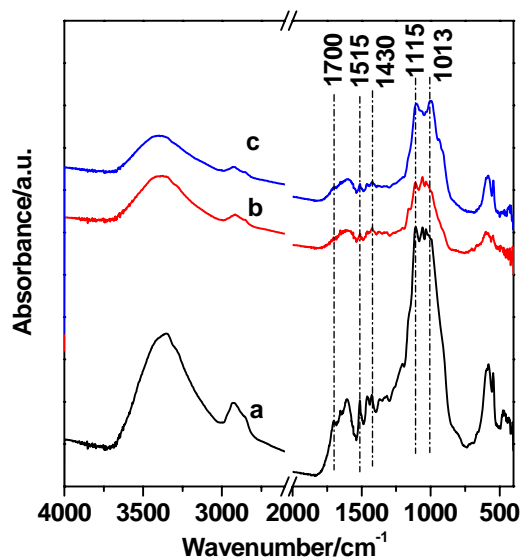


Figure S2 IR spectra of the solid residue obtained by the conversion of wheat straw at different temperature: (a) 150 °C, (b) 160 °C, and (c) 170 °C. Reaction conditions: 1.0 g wheat straw, 0.2 g FePO₄ catalyst, 60 min, 10.0 mL deionized water, 30.0 mL THF, 3.5 g NaCl.

4. *The XRD and XPS results of the solid produced from catalytic pyrolysis*

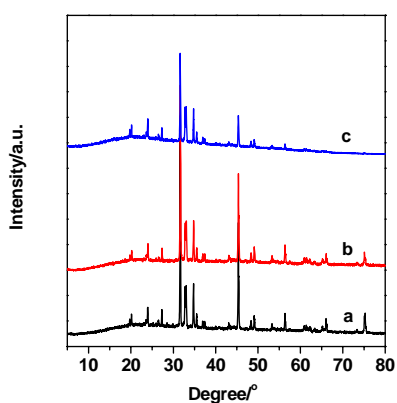


Figure S3 XRD patterns of bio-char produced from slow pyrolysis of the solid residues which were formed after the conversion of untreated wheat straw at 160 °C for (a) 30 min, (b) 60 min, and (c) 90 min.

XPS analyses were performed using KRATOS AXIS Ultra DLD. An Al K α x-ray source was used for all samples, along with pressure in the analysis chamber of 7×10^{-8} Pa. The step size of 1 eV and dwell time of 0.1 s was employed and each peak scanned once for the survey scans.

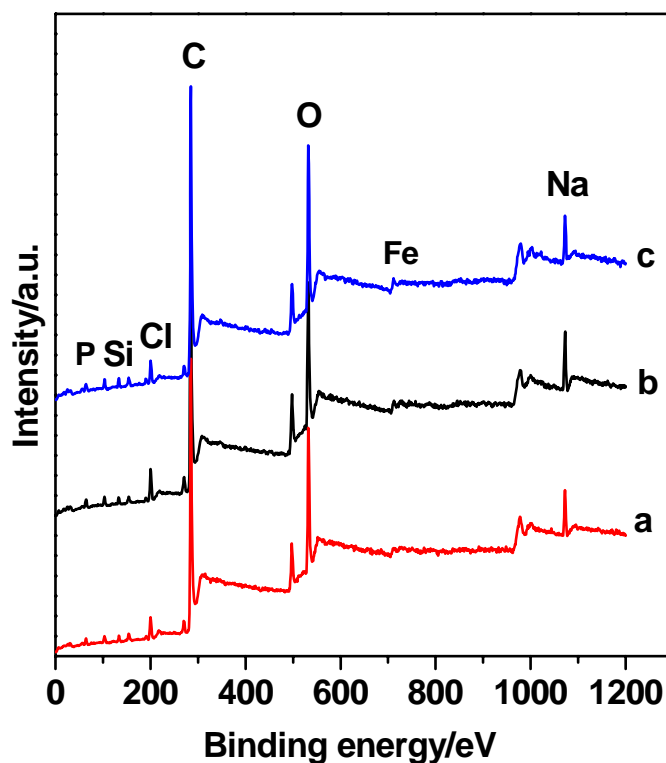


Figure S4 XPS of bio-char obtained from slow pyrolysis of solid residue after the conversion of untreated wheat straw at 160 °C for (a) 30 min, (b) 60 min, and (c) 90 min.

Fig. S3 shows the C1s XPS of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for different times. The spectra were deconvoluted into five components according to the literature results. The components are assigned to graphitic carbon, carbon

species in ether and alcohol groups, carbon in carbonyl, carboxyl and/or ester groups, and a shake-up satellite due to π - π^* transitions in aromatic rings ⁶. The binding energies and area percentages of these components are listed in Table S3. As shown in Table S3, the O content derived from the carbonyl and carboxyl groups decreased with increasing the hydrolysis time of untreated wheat straw.

Table S3 Deconvolution results of the XPS spectra of untreated CNTs, treated CNTs, and 1Pt/CNTs.

Region	Assignment	1#		2#		3#	
		Position(eV)	area(%)	Position(eV)	area(%)	Position(eV)	area(%)
C1s	Graphite	284.6	24.6	284.6	20.0	284.6	26.7
	R-OH+C-O-C	285.0	16.2	285.0	24.9	285.0	11.2
	C=O + >C=O	285.7	38.7	285.7	35.6	285.7	41.7
	COOH+	287.0	14.3	287.0	14.0	287.0	11.1
	C-O-C						
	π - π^*	289.5	6.2	289.5	5.5	289.5	6.0
O1s	=O in	532.3	73.4	532.5	65.0	532.3	59.5
	carbonyl, and						
	carboxyl						
	-O-	533.7	26.6	533.9	35.0	533.7	40.5

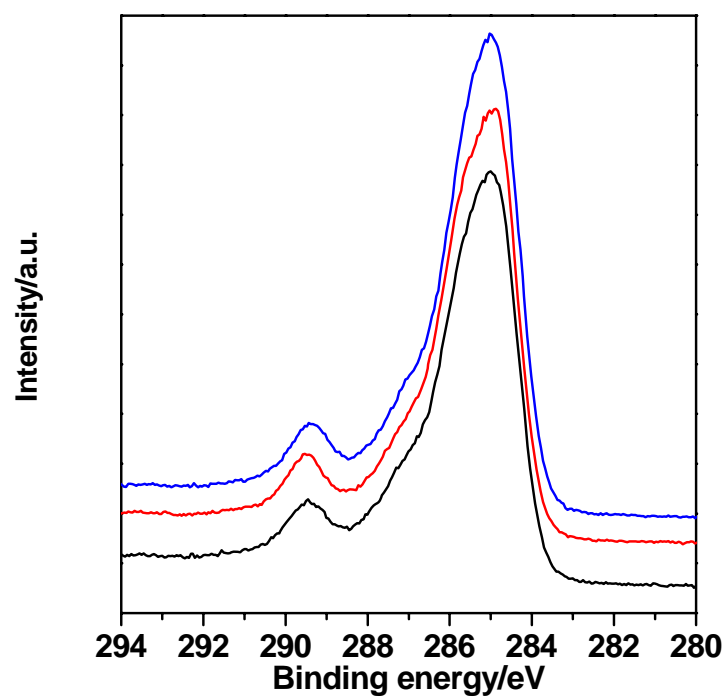


Figure S5 X-ray photoelectron spectrum of the C1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for (a) 30 min, (b) 60 min, and (c) 90 min.

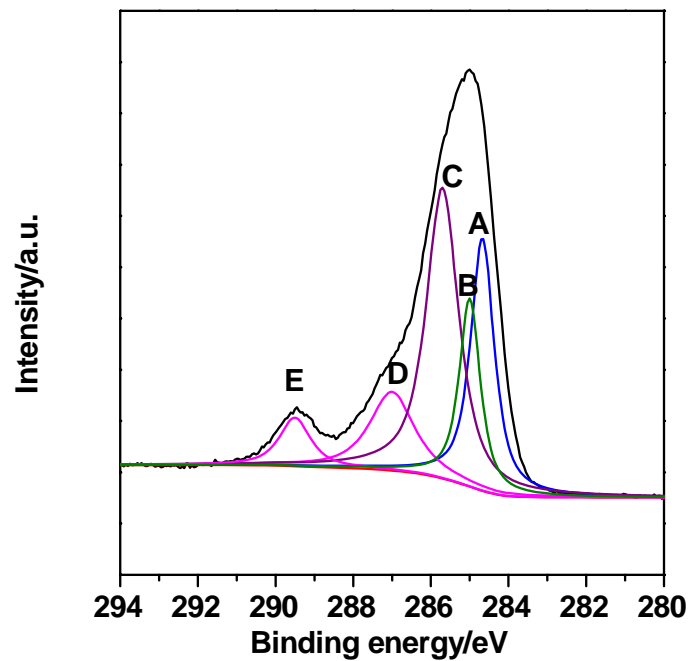


Figure S6 Deconvolution XPS of the C1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 30 min. For details see Table S3. The peaks are assigned as follows: A-graphite; B-R-OH + C-O-C; C-C=O + >C=O; D- COOH + -C(O)-O-C; E- π - π^* .

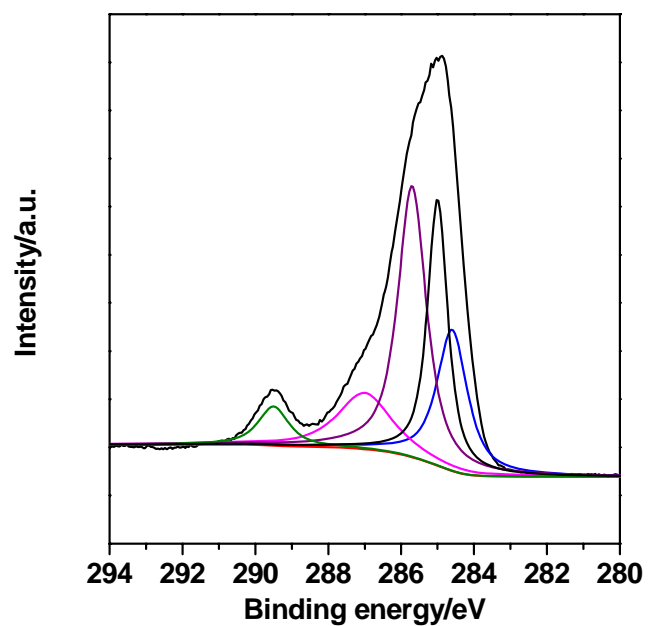


Figure S7 Deconvolution XPS of the C1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 60 min.

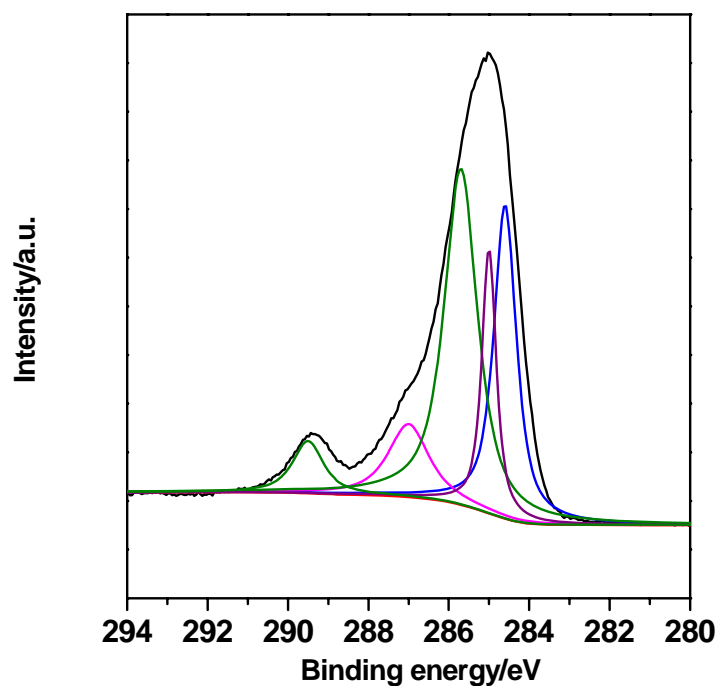


Figure S8 Deconvolution XPS of the C1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 90 min.

To further investigate the change in the oxygen content, the XPS spectra of O1s was also recorded. Fig. S9 shows the XPS spectra of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for different times. The spectra were deconvoluted into two components according to the literature results⁶. The components were

attributed to oxygen in carbonyl and carboxyl groups and chemisorbed oxygen species and H₂O⁶. The binding energies and area percentages of these components are summarized in Table S3. The carbonyl group content decreased with increased the hydrolysis time, which is consistent with the results obtained in the C1s XPS results. These results demonstrate that a portion of longer hydrolysis time would increase the conversion of untreated wheat straw, thereby resulting in a decrease in the oxygen content of the hydrolyzed solid residues.

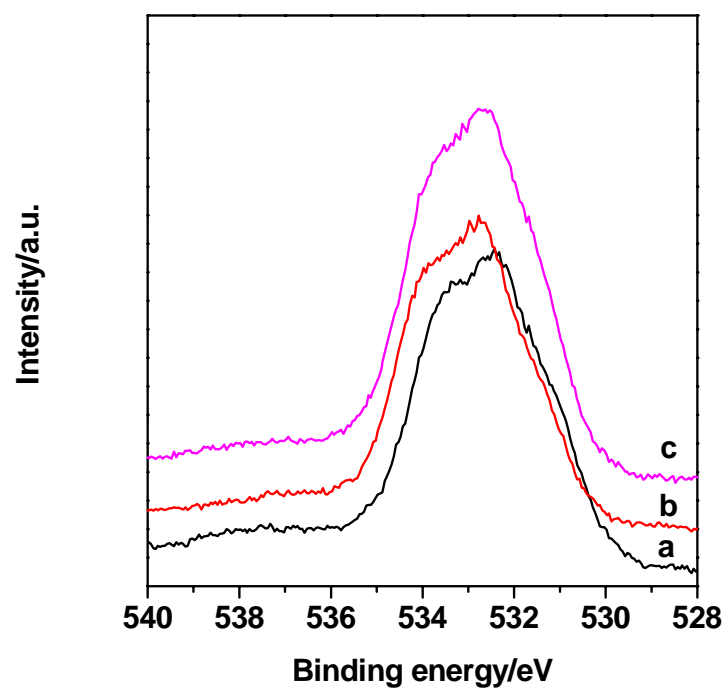


Figure S9 XPS of O1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for (a) 30 min, (b) 60 min, and (c) 90 min.

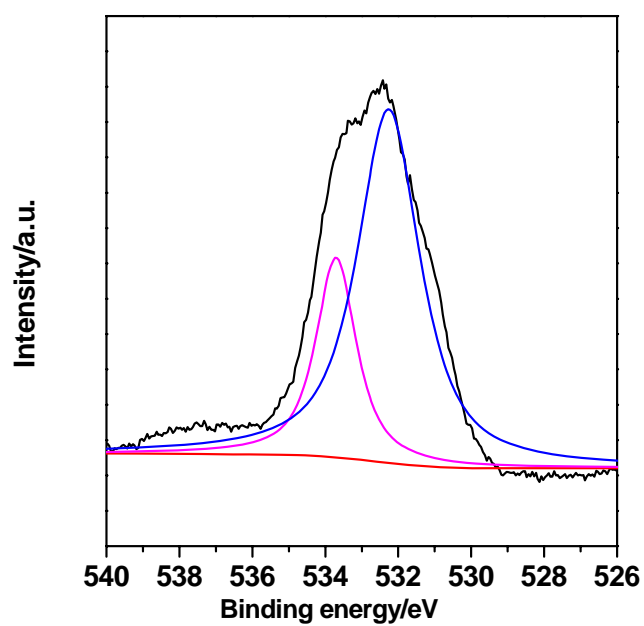


Figure S10 Deconvolution XPS of the O1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 30 min.

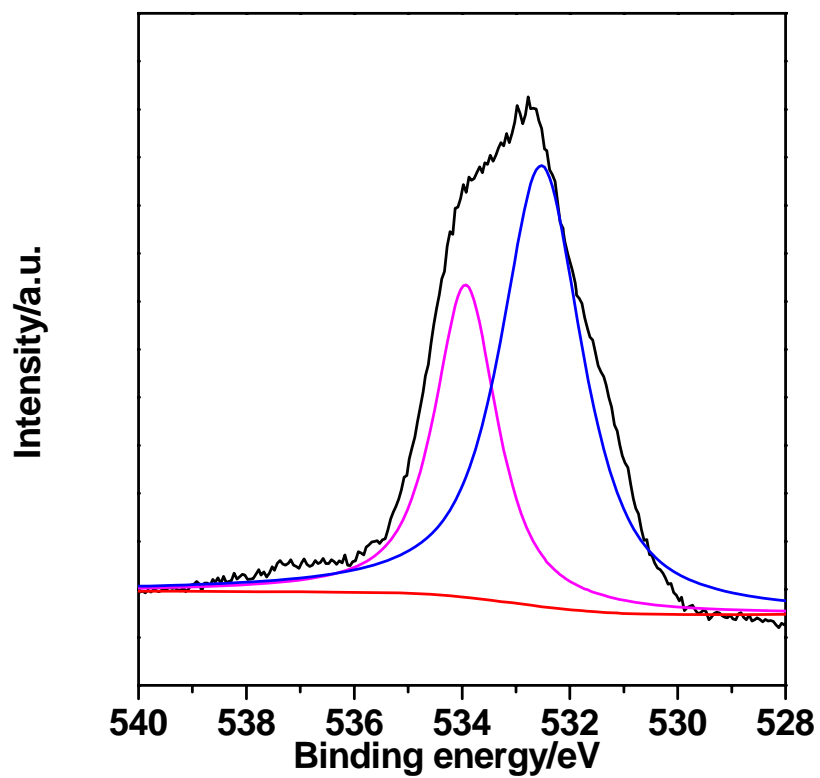


Figure S11 Deconvolution XPS of the O1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 60 min.

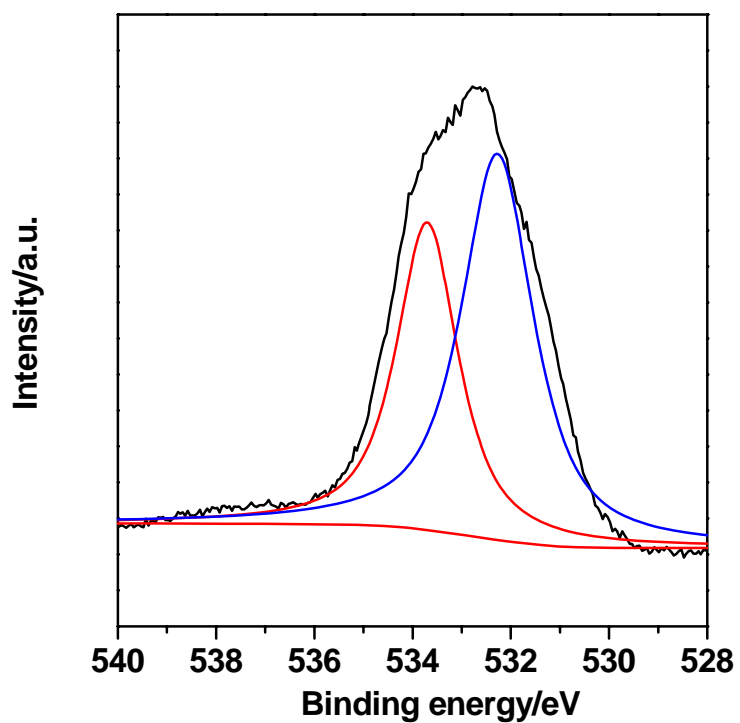


Figure S12 Deconvolution XPS of the O1s peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for 90 min.

Fig. S13 illustrates the XPS of P2p peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for different time. It can be seen that the P content of bio-chars increased with extending the hydrolysis time of untreated wheat straw.

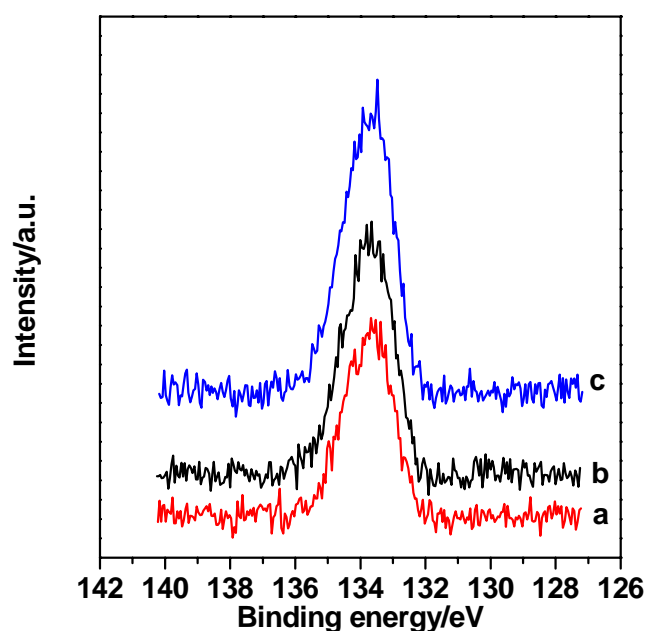


Figure S13 XPS of P2p peak of bio-char obtained from the catalytic pyrolysis of the hydrolyzed solid residue derived from conversion of untreated wheat straw at 160 °C for (a) 30 min, (b) 60 min, and (c) 90 min.

References

1. H. Xia, S. Xu, X. Yan and S. Zuo, *Fuel Process. Tech.*, 2016, **152**, 140-146.
2. S. Xu, X. Yan, Q. Bu and H. Xia, *RSC Adv.*, 2016, **6**, 8048-8052.
3. L. Yang, X. Yan, S. Xu, H. Chen, H. Xia and S. Zuo, *RSC Adv.*, 2015, **5**, 19900-19906.

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4. R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem Rev*, 2013, **113**, 1499-1597.
 5. M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chem Rev*, 2010, **111**, 397-417.
 6. L. Yang, X. Yan, Q. Wang, Q. Wang and H. Xia, *Carbohydr Res*, 2015, **404**, 87-92