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# Jet fuel range hydrocarbons production by co-pyrolysis of low density polyethylene and wheat straw over activated carbon catalyst

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**Abstract:** High-efficiency and low-cost catalyst matters a great deal to convert solid wastes into high valued chemicals and biofuels. In this study, catalytic co-pyrolysis of wheat straw and low density polyethylene is studied to expound the effect of biomass-derived activated carbon catalyst on the distribution and proportion of jet fuel range hydrocarbons. The effects of pyrolysis temperature, catalyst to feedstock ratio and LDPE to wheat straw ratio on the pyrolysis products yields and distributions are investigated. The result indicates that the LDPE as the hydrogen additive with wheat straw showed a remarkable synergistic effect on increasing the proportion of aromatic products. Activated carbon catalyst with the P-containing function groups has an excellent performance in the co-pyrolysis of wheat straw and LDPE to generate aromatics through the aromatization of alkanes and olefines, the dehydroxylation and oligomerization of alkylated

24 phenols, and the deoxygenation and aromatization of carbonyls. 95.4 area.% jet fuel range  
25 hydrocarbons is acquired at the temperature of 550 °C, catalyst to feedstock ratio of 2:1 and LDPE  
26 to wheat straw ratio of 1:1. The present study provided an economical, simple and effective way to  
27 obtain high purity jet fuel range hydrocarbons from agricultural wastes and plastics.

28 **Keywords:** Activated carbon catalyst ; LDPE; Wheat straw; Co-pyrolysis; Jet fuel

## 29 **1. Introduction**

30 The liquid fuel obtained from the conversion of biomass, an important alternative to fossil  
31 fuels and one of the most promising way to utilize biomass, has attracted increasing attention  
32 because of the carbon-neutral, renewable and abundant properties of biomass [1-3]. In the past 30  
33 years, 56% of global renewable energy research has studied the conversion of biomass into high  
34 purity fuels in response to energy crises and environmental issues[4, 5]. Compared to the raw  
35 biomass, the liquid fuel derived from biomass has the properties of convenient transportation and  
36 handling, and high energy density[6]. For this type of liquid fuel, it has the problems of  
37 immiscibility, instability, low heating value, acidity, corrosion and viscosity because of the  
38 biomass contains a high oxygen content[7-9]. Therefore, the undesirable characteristics of liquid  
39 fuel produced by the conversion of biomass make it impossible to be directly used in boilers and  
40 engines[2].

41 Wheat is widely cultivated as a promising source of renewable raw materials for the  
42 production of chemicals and biofuels[10]. From an environmental point of view, the use of  
43 biomass or waste biomass, such as wheat straw, to produce energy will have several advantages.  
44 However, wheat straw is the same as other types of biomass, and the bio-oil produced by its  
45 pyrolysis also has the disadvantage of high oxygen content[11-13]. Therefore, further research is

46 needed to improve the quality of the bio-oil obtained from the pyrolysis of wheat straw.

47       Plastics, one of hydrogen-rich materials and municipal solid wastes, is considered to be an  
48 remarkable additive for the pyrolysis of biomass due to its high hydrogen to carbon ratio [14, 15].  
49 On the other hand, The solid pollution caused by the rapid increase in the use of plastics has  
50 seriously deteriorated the environment[16]. Thus, the co-pyrolysis of waste plastics and biomass  
51 could provide an effective way to solve the environmental pollution and energy crisis. The  
52 previous studies indicated that the co-pyrolysis of plastics and biomass could improve the yield  
53 and quality of liquid products. Ghorbannezhad et al. [17] showed that the pyrolysis of lignin can  
54 be influenced by plastics in the co-pyrolysis process, and the hydrogen transfer reactions from  
55 plastics to biomass promoted the production of aromatic hydrocarbons. Lee et al. [18] investigated  
56 the co-pyrolysis of polypropylene and torrefied cellulose with HBeta and HZSM-5 catalysts, the  
57 results indicated that high yield of aromatic hydrocarbons could be acquired in the presence of  
58 plastic. Fan et al.[19] investigated the co-pyrolysis of low-density polyethylene (LDPE) and lignin  
59 over HZSM-5 and MgO, the results indicated that the yield of aromatic hydrocarbons rose with  
60 increasing the content of LDPE, and the methoxyl-phenols was completely converted at the lignin  
61 to LDPE ratio of 1:2. Nguyen et al.[20] found that the content of water and the concentration of  
62 acetic acid in bio-oil obtained from co-pyrolysis of waste polystyrene foam and pine sawdust were  
63 decreased with the increasing waste polystyrene foam ratio. Bu et al.[21] studied the co-pyrolysis  
64 of LDPE and microwave-torrefied lignin using microwave heating, the results showed that the  
65 content of aromatics rose from 1.94% to 22.83% in the presence of LDPE, and the LDPE mixed  
66 with microwave-torrefied lignin can promoted the thermal degradation of microwave-torrefied  
67 lignin and improved the reaction rate. There is, however, a further and even more serious

68 objection from the previous study, the bio-oils acquired from the co-pyrolysis of plastics and  
69 biomass are a complex mixture of aliphatic hydrocarbons and oxygenated compounds[22]. The  
70 complex compositions of liquid fuel bring certain difficulties to its purification and use. Therefore,  
71 it is necessary to seek a low-cost, convenient, efficient and simple way for the conversion of waste  
72 plastics and wheat straw into high value-added fuel products.

73 Catalytic pyrolysis is an efficient method for the conversion of waste plastics and biomass  
74 into high purity fuel products [23-28]. A suitable catalyst can be used to catalytic upgrade the  
75 pyrolysis volatiles because it is beneficial to produce the desired target products. That is, the target  
76 hydrocarbon products can generated selectively over a suitable catalyst. The energy requirement  
77 of the conversion process can be reduced because of the reaction temperature is reduced by  
78 catalytic pyrolysis [29, 30]. Recently years, many kinds of catalysts are used to catalytic convert  
79 waste plastics (especially low density polyethylene (LDPE), which is recognized as the second  
80 largest plastic wastes with higher H/C ratio and high calorific value) and biomass into  
81 hydrocarbons. Among them, solid acids, such as zeolites and activated carbons, are the most  
82 promising catalyst types. Zeolites are widely used in the co-pyrolysis study of waste plastics and  
83 biomass because of their high selectivity of aromatic products and high acidity [31-33]. However,  
84 there are some problems, such as high yield of poly-aromatics, low yield of organic products and  
85 poor thermal stability, in the process of catalytic pyrolysis over zeolite catalysts[34]. Activated  
86 carbon catalyst used in the co-pyrolysis of plastics and biomass revealed an excellent catalytic  
87 effect on the production of jet fuel range hydrocarbons. Lin et al. [2] investigated the co-pyrolysis  
88 of Douglas fir and LDPE with activated carbon based catalysts, the results indicated that the jet  
89 fuel range mono-aromatics in the bio-oil products could be up to 44 area.%. Mateo et al.[35]

90 found that 97.5 area.% selectivity of aromatics and C9-16 alkanes could be obtained from LDPE  
91 and Douglas fir over sulfonated activated carbon catalyst. These studies indicated that activated  
92 carbon catalyst has excellent future for the co-pyrolysis of waste plastics and biomass to produce  
93 high purity jet fuel range hydrocarbons. Therefore, the fast catalytic co-pyrolysis of biomass and  
94 LDPE over activated carbon catalyst is an effective way to improve the quality of bio-oil. To the  
95 best of our knowledge, there is no report on the pyrolysis of wheat straw to generate jet fuel range  
96 hydrocarbon fuels, and there is no research on the catalytic co-pyrolysis of wheat and LDPE over  
97 activated carbon catalysts. As an effective method for upgrading bio-oil, it is necessary to  
98 investigate the effect of the co-pyrolysis of LDPE and wheat straw over activated carbon catalyst  
99 on the upgrading of the bio-oil produced and formation of jet fuel range hydrocarbon fuels in the  
100 bio-oils, which is of special significance for the efficient utilization of wheat straw and LDPE.

101 Therefore, the prime objective of the present work is to investigate the production of jet fuel  
102 range hydrocarbons from wheat straw and LDPE via activated carbon catalyst. The effects of  
103 catalyst to feedstock ratio, LDPE to wheat straw ratio, and experimental temperature on the  
104 distribution of products are discussed and concluded in details.

## 105 **2. Material and methods**

### 106 **2.1. Materials**

107 The raw wheat straw (moisture: 7.25%, volatile matter: 70.34%, fixed carbon: 17.66 and ash:  
108 4.75%; C: 43.71%, H: 5.38%, N: 1.15 and O (bal): 49.76%) and corncob (moisture: 6.33%,  
109 volatile matter: 71.91%, fixed carbon: 18.95 and ash: 2.81%; C: 45.32%, H: 5.57%, N: 0.81 and O  
110 (bal): 48.30%) are collected from fields of Kaifeng, Henan Province, China. Phosphoric acid  
111 ( $\text{H}_3\text{PO}_4$ , 85 wt.%) and LDPE are purchased from commercial suppliers. In addition, the

112 thermogravimetric analysis of wheat straw is represented in Fig.S1, it can be seen that the wheat  
113 straw weight loss at 400 °C is 62.47% and the residue weight is about 20.5% at 600 °C . The  
114 thermogravimetric analysis of LDPE is relatively common in the literatures[36, 37], the weight  
115 loss at 600°C is less than 10% with the heating rate of 10°C/min.

## 116 **2.2. Activated carbon catalyst preparation**

117 In this work, the activated carbon catalyst is synthesized from corncob[38, 39], which is  
118 prepared by the phosphoric acid activation and microwave carbonization. The four steps can be  
119 summarized in the process of preparing activated carbon catalyst. In the first step, the impurities  
120 on the corncob surface are washed using deionized water. Subsequently, the corncob is dried on  
121 an oven at 90°C until the mass keep in the same. The second step is the phosphoric acid activation  
122 process. Deionized water and phosphoric acid are mixed at a volume ratio of 7:1 to prepare the  
123 phosphoric acid solution. In the next moment, the prepared phosphoric acid solution is used to  
124 soak the dried corncob. And then the mixture is put in the oven until the mass no longer changes.  
125 In the third step, the obtained corncob sample is microwave-induced carbonized to produce  
126 activated carbon catalyst, the power input of 700 W and 60 min are set to obtain catalyst sample  
127 [38-41]. In the last stage, the activated carbon catalyst is washed with deionized water at room  
128 temperature, and then the catalyst is dried using the oven (90°C). The characterization of prepared  
129 activated carbon catalyst can be seen in the previous study [38]. In addition, in order to investigate  
130 the role of mineral elements in the catalyst in co-pyrolysis process, the dried but not yet pyrolyzed  
131 phosphoric acid-impregnated corncob (the weight before dipping in the phosphoric acid solution is  
132 100 g) is immersed in a 100 ml CaCl<sub>2</sub>, KCl, and MgCl<sub>2</sub> solution with a concentration of 2 wt.%.  
133 The obtained dried samples are pyrolyzed to obtain Ca-loaded, K-loaded and Mg-loaded activated

134 carbon catalysts using the preparation method described above.

### 135 **2.3. Characterization of activated carbon catalyst**

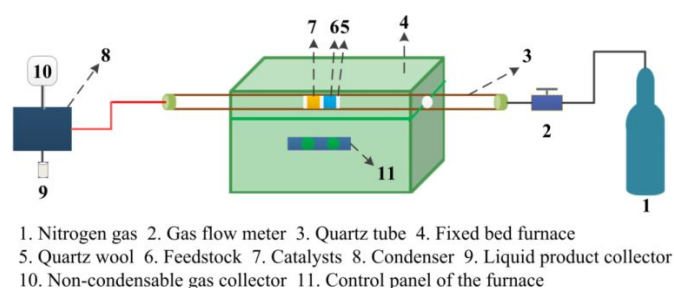
136 In this work, the surface area and pore structure of prepared activated carbon catalyst are  
137 measured by a physisorption analyzer (Micromeritics R TristarII 3020). Before the analysis, the  
138 activated carbon catalyst is degassed with a temperature of 250 °C . Fourier Transform Infrared  
139 Spectroscopy (FTIR) of activated carbon is used to detect functional groups on the surface of the  
140 selected catalyst samples by the IR Prestige 21 spectrometer with the spectra range of 500-4500  
141  $\text{cm}^{-1}$  and the resolution of 8  $\text{cm}^{-1}$ . The surface morphology of the catalyst samples is identified  
142 using scanning electron microscope (SEM, FEI Quanta 200 F). In addition, the proximate analysis  
143 of activated carbon catalyst is performed and the elemental composition and mineral profile are  
144 also determined. Thermoanalytical measurement of activated carbon catalyst is made by TGA  
145 (Mettler Toledo). Nitrogen flow rate of 50 ml/min to provide the inert conditions, the catalyst then  
146 heated from ambient temperature to 600 °C at a ramp of 60 °C/min.

### 147 **2.4. Catalytic co-pyrolysis process of wheat straw and LDPE**

148 The co-pyrolysis of wheat straw and LDPE, activated carbon as catalyst, is performed in a  
149 fixed tube reactor, the catalytic co-pyrolysis system as shown in Fig.1. Placed 5 g feedstock (6 in  
150 Fig.1, the mixture of wheat straw and LDPE) and activated carbon catalyst (7 in Fig.1, the mass of  
151 catalyst is calculated based on the ratio of catalyst to feedstock) sequentially in the quartz tube,  
152 and the middle and both ends were filled with quartz wool. Nitrogen purge with a flow rate of  
153 160ml/min for 20 minutes provides an oxygen-free environment for this apparatus. The tube  
154 furnace is heated to the set temperatures, and then the quartz tube with activated carbon and  
155 feedstock is moved in the furnace. All experiments are employed at the set temperatures with 20



156 minutes. The flow rate of nitrogen is changed to 70 mL/min during the catalytic co-pyrolysis  
 157 process (pyrolysis time is 20 min). The pyrolysis temperatures are set to 400, 450, 500, 550 and  
 158 600 °C, the catalyst to feedstock ratios (This ratio is the mass ratio in wt.%, which is directly  
 159 expressed by numbers in the following text. For example, 1:1 refers to 50 wt.%: 50 wt.%. The  
 160 same is true for the LDPE to Wheat Straw ratios in the latter.) are only feedstock, 1:2, 1:1 and 2:1,  
 161 the LDPE to wheat straw ratios are only wheat straw, 1:2, 1:1, 2:1 and only LDPE. The  
 162 experiments are repeated three times at each condition.



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Fig. 1. The catalytic pyrolysis system

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After each experiment, the end of the quartz tube is moved into the tube furnace to evaporate  
 the remaining liquid product in the quartz tube to ensure that most of the liquid product obtained  
 by the co-pyrolysis of wheat straw and LDPE flows into the collector. The pyrolytic vapor is  
 condensed into a liquid state in the collector. Only a very small amount of liquid product sticks to  
 the collection tube and rubber O-ring. The weight of the liquid product can be calculated based on  
 the weight change of the collector, collection tube and O-shaped rubber ring before and after each  
 experiment. The weight of char is measured when the temperature of quartz tube dropped to room  
 temperature. The weight of coke is the change in the weight of the activated carbon catalyst before  
 and after the experiment. The weight of gas products could be computed that the weight of Wheat  
 straw and LDPE minus the weights of bio-oil, char and coke:

Weight of gaseous products = (Starting weight of wheat straw and LPDE, various

176 compositions)-(collected bio-oil) – (Coke formed on catalyst) –(remaining solid char)

177 A Micro-GC system (INFICON 3000) and Agilent 7890A GC-MS are used to analyze the  
178 components of gas and liquid products, respectively. Prior to the quantitative analysis, ethyl  
179 acetate is used to extract the organic components of liquid products. The temperature of GC is first  
180 set to 40 °C for 5 min. Subsequently, the temperature is increased to 280 °C with the heating rate  
181 of 10 °C/min, and then this temperature is kept for 5 min. 1 μL sample is injected into GC-MS  
182 for each test with the carrier gas (high purity of helium) of 0.6 mL/min. The temperature of MS  
183 detector ion source is set to 230 °C.

### 184 **3. Results and discussion**

#### 185 **3.1. Catalyst characterizations**

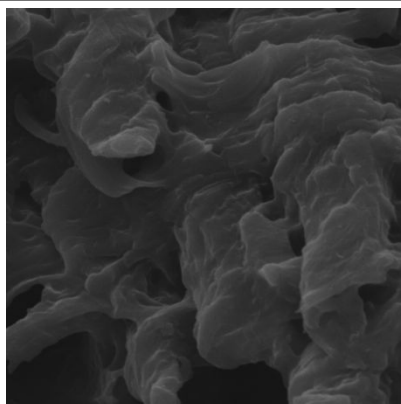
186 The residence time of pyrolytic volatiles can be enhanced by the porous structures of  
187 activated carbon catalyst, therefore, the developed pore structure is one of the foundations for  
188 activated carbon catalyst for the upgrading of the pyrolytic volatiles. The related structural  
189 properties of activated carbon catalyst are represented in Table 1. It can be seen that the BET  
190 surface area of activated carbon catalyst is 1156.65 m<sup>2</sup>·g<sup>-1</sup>, it shows that a highly developed  
191 mesoporous structure can be found on the surface of the corncob derived activated carbon  
192 catalyst. The large surface area of the catalyst provides more large reaction surface to catalytic  
193 convert the wheat straw and LDPE into ideal products. As displayed in Fig.2, the surface  
194 morphologies of activated carbon catalyst are observed by using SEM. The surface of activated  
195 carbon catalyst is activated by phosphoric acid to increase the surface area. The catalytic  
196 properties of the catalyst are determined by the surface functional groups, the catalytic pyrolysis  
197 mechanism can be better understand through the measurement of surface functional groups. Fig. 3

198 shows the –OH group with a  $3400\text{ cm}^{-1}$  is found in the FTIR spectra of the activated carbon  
 199 catalyst, which may be adsorbed moisture or hydroxyl group. The absorption peaks of  $\text{-C=C}$   
 200 groups are found at around  $880$  and  $1550\text{ cm}^{-1}$ ,  $700$  and  $2880\text{ cm}^{-1}$  are belonged to  $\text{-C-H}$  groups.  
 201 The absorption peaks of  $\text{-C-O-P}$ ,  $\text{-P=O}$  and  $\text{-P-O}$  groups at  $1050$ ,  $1140$  and  $1150\text{ cm}^{-1}$  indicate that  
 202 the phosphate groups have been successfully integrated into the surface of the activated carbon  
 203 catalyst. Proximate and elemental analysis show that compared with the raw corncob, the activated  
 204 carbon catalyst (Table 2) has a significant increase in fixed carbon and carbon element by % wt  
 205 and decrease in volatile matter, hydrogen and oxygen elements at the same time. It can be seen that  
 206 the volatile matter is almost removed from the activated carbon catalyst, which has almost no  
 207 effect on the subsequent production of bio-oil. As shown in Table 3, the mineral profile of  
 208 activated carbon catalyst is similar to that of corn stover derived biochar[42], the result reveals  
 209 that the activated carbon catalyst is rich in minerals such as Ca, P, K, Mg, etc. The role of the  
 210 dominant mineral elements such as Ca, K and Mg on the co-pyrolysis of wheat straw and LDPE  
 211 are analyzed over Ca-loaded, K-loaded, and Mg-loaded on activated carbon catalysts. From  
 212 Fig.S2, we can see that the co-pyrolysis results of wheat straw and LDPE over the activated  
 213 carbon catalyst impregnated in the 2 wt.%  $\text{CaCl}_2$ ,  $\text{KCl}$  and  $\text{MgCl}_2$  solution are roughly the same,  
 214 with only some minor differences. It is possible that under the action of Ca and K, a slight increase  
 215 in the yield of aromatic hydrocarbons is accompanied by a slight decrease in the yield of alkanes,  
 216 but the opposite is true with the participation of Mg. It can be seen from Fig.4 that 6.2 wt.%  
 217 activated carbon catalyst is decomposed from 25 to  $600^\circ\text{C}$ .

218 Table 1. Porous structure parameters of activated carbon catalyst measured by  $\text{N}_2$  isotherms

Sample	$S_{\text{ext}}$	$S_{\text{micro}}$	$S_{\text{bet,total}}$	$V_{\text{ext}}$	$V_{\text{micro}}$	$V_{\text{bet,total}}$	$D_{\text{average}}$
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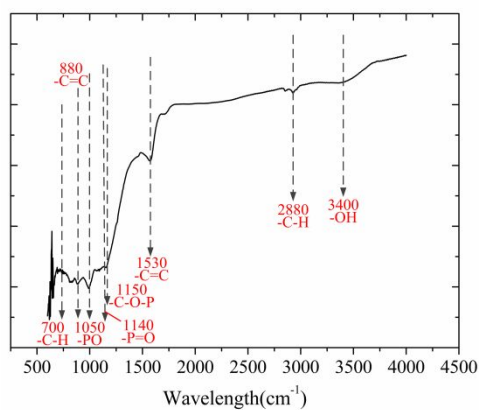
	$(\text{m}^2 \cdot \text{g}^{-1})$	$(\text{m}^2 \cdot \text{g}^{-1})$	$(\text{m}^2 \cdot \text{g}^{-1})$	$(\text{cm}^3 \cdot \text{g}^{-1})$	$(\text{cm}^3 \cdot \text{g}^{-1})$	$(\text{cm}^3 \cdot \text{g}^{-1})$	$(\text{\AA})$
Catalyst	1025.37	131.28	1156.65	0.5828	0.0704	0.6532	26.77



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Fig.2. SEM image of the activated carbon catalyst



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Fig.3. FTIR spectra of the activated carbon catalyst

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Table 2. Proximate and elemental compositions of activated carbon catalyst

	Proximate composition				Elemental composition			
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	O (bal)
Catalyst	5.84	3.11	85.32	5.73	89.47	1.69	0.47	8.37

225

226

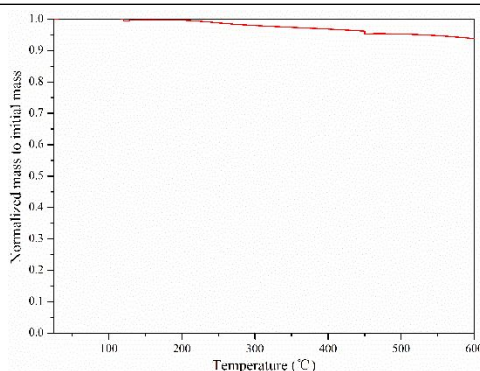
Table3. Mineral profile of activated carbon catalyst (ppm)

Ca	P	K	Fe	Mg	Mn	Cu	Zn	Na	Al
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8847	18563	32375	137	4352	179	12.7	44.3	526	95
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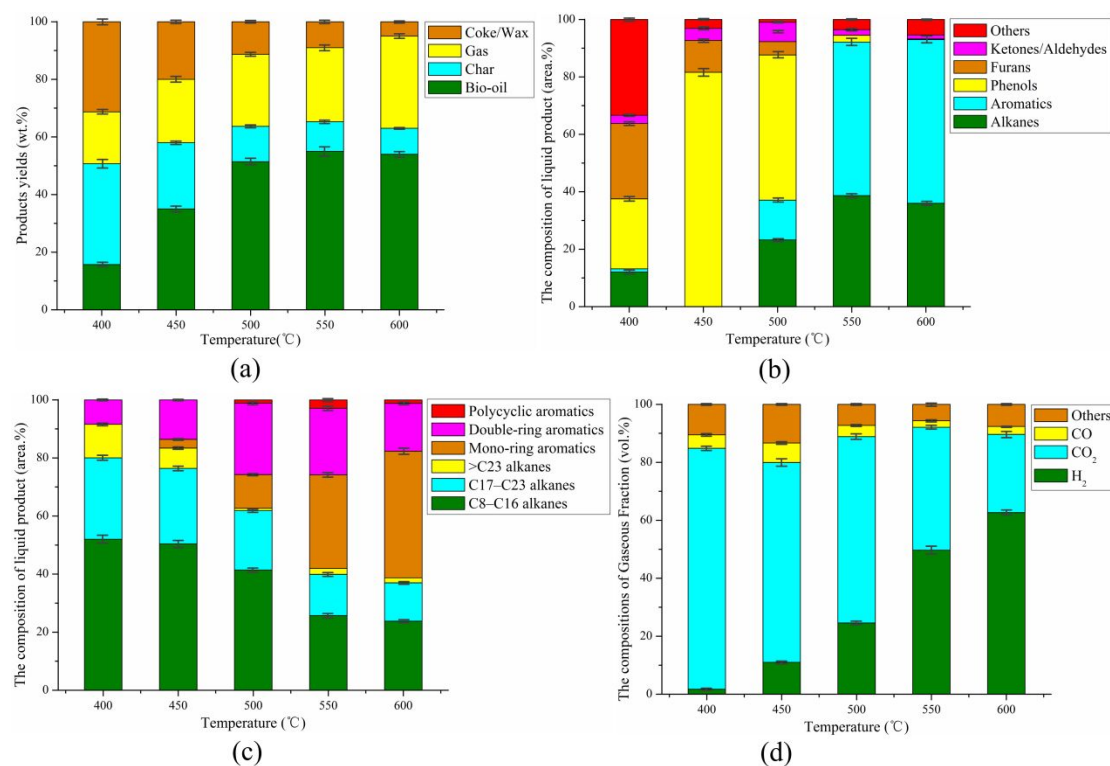
Fig.4. Thermogravimetric curve of activated carbon catalyst

### 229 3.2 Temperature effect

230 Pyrolysis temperature is a critical factor for the pyrolysis of waste plastics and biomass, a  
 231 better catalytic effect is inextricably linked to a suitable pyrolysis temperature. Pyrolysis  
 232 temperature also played an incalculable role on the co-pyrolysis of waste plastics and biomass,  
 233 and therefore the effect of pyrolysis temperature on the pyrolysis products yields should be  
 234 investigated. The pyrolysis products yields and compositions at different temperatures (400, 450,  
 235 500, 550 and 600 °C ) are showed in Fig. 5. In this section, the conditions are set as: catalyst to  
 236 feedstock ratio = 1:1, LDPE to wheat straw ratio = 1:1.

237 As shown in Fig. 5(a), waxes are formed in the catalytic co-pyrolysis of LDPE and Wheat  
 238 straw in the range of the experimental temperature of 400-500 °C . This is due to the lower  
 239 pyrolysis rate at lower temperatures, so a part of the large polymer chains generated by the  
 240 decomposition of LDPE have not been continued to decompose into liquid and gas products  
 241 during the experimental period but formed waxes. The proportion of char and waxes gradually  
 242 decreases with increasing the temperature, these products are converted into liquid and gaseous  
 243 products, resulting in a gradual increase in the yield of liquid and gas products. In addition, the  
 244 decomposition reactions of feedstock are endothermic processes, hence the higher pyrolysis

245 temperature could provide the more energy to promote the breakage of strong bonds and  
246 accelerates the decomposition of feedstock[43]. Therefore, the liquid products yields collected  
247 from the co-pyrolysis of wheat straw and LDPE is added from 15.7 wt.% (400 °C) to 55.0 wt.%  
248 (550 °C). Nevertheless, the yield of the liquid product showed a downward trend when the  
249 temperature is higher than 550 °C, and it dropped to 53.8 wt.% at 600 °C, this is because the  
250 secondary thermal cracking[44], which causes the liquid products decomposed to generate  
251 gaseous products. Higher pyrolysis temperature will increase the catalytic activity of activated  
252 carbon and facilitate the generation of gaseous products from liquid products decomposition.  
253 Thus, the gaseous products yields is increased from 18.1 wt.% to 32.0 wt.% from the temperature  
254 of 400 to 600 °C, respectively. In addition, according to the TGA analysis of the activated carbon  
255 catalyst, it can be seen that a small amount of catalyst may undergo pyrolysis during the high  
256 temperature catalytic pyrolysis process, which may cause the measured mass of Coke being  
257 slightly lower than the actual mass, and the mass of the liquid and gaseous products is slightly  
258 higher than the actual mass.



259

260 Fig.5. Products yields (a), compositions of liquid products (b), hydrocarbons (c) and gaseous

261 products (d) at different temperatures (Catalyst to feedstock ratio = 1:1, LDPE to wheat straw ratio

262 = 1:1)

263 For the co-pyrolysis of waste plastics and biomass, the dominant products are generally

264 phenols, aromatics, alkanes and other oxygenates. As represented in Fig. 5(b), the pyrolysis

265 temperature has a significant promoting effect on the formation of hydrocarbon products with the

266 selectivity of hydrocarbon products (alkanes and aromatics) is increased from 13.2 area.% (400 °C)

267 to 93.1 area.% (600 °C). However, the selectivity trends of alkanes and aromatics are not consistent

268 separately. The selectivity of alkanes is increased from 12.0 area.% (400 °C) to 38.7 area.%

269 (550 °C), and then dropped to 36.1 area.% (600 °C). For the selectivity of aromatics, with the

270 pyrolysis temperature increased, the selectivity of aromatics increased and reached a maximum

271 value of 57.0 area.% at a temperature of 600 °C. The synergistic effect between the catalytic

272 performance of activated carbon catalyst and high temperature that accelerated the decomposition

273 and aromatization of long-chain hydrocarbons, which leads to the reduction of alkanes selectivity  
274 and the increases of aromatics selectivity[38]. In addition, the proportion of oxygenates is higher  
275 than that of hydrocarbons at lower pyrolysis temperatures (400, 450 and 500 °C ). When the  
276 temperature is higher than 550 °C , the proportion of hydrocarbons starts to be higher than that of  
277 oxygenates. This result indicated that LDPE is more difficult to decompose than wheat straw, so  
278 the co-pyrolysis of LDPE and wheat straw needs to be carried out at a higher temperature. The  
279 selectivities of phenols, furans and other oxygenates have a common trend that decreases with  
280 increasing temperature at 450 to 600 °C . In particular, phenols, furans, ketones and aldehydes are  
281 almost not produced at 600 °C . This can be ascribed to that LDPE undergoes more decomposition  
282 reactions and aromatization reactions at high temperatures to supply more H atoms for the  
283 co-pyrolysis process. The generated hydrogen will promote the decarboxylic and dehydroxylation  
284 reactions of phenols, resulting in the conversion of phenols into aromatics [45-47]. The higher  
285 temperature more prone to promote the decarboxylic reactions of other oxygenates (such as  
286 furans, ketones, aldehydes and others) in micropores on the surface of the activated carbon  
287 catalyst to decrease the selectivities of these compounds. Therefore, the selectivity of  
288 hydrocarbons (alkanes and aromatics) is increased from 400 °C to 600 °C and reached the  
289 maximum value of 93.0 area.%. Actually, the selectivity of hydrocarbons at 550 °C is 92.1 area.%,  
290 which is only slightly lower than that of at 600 °C .

291 The proportions of different hydrocarbon products are represented in Fig. 5(c) for the better  
292 understanding of the distribution of hydrocarbon products in the co-pyrolysis process at different  
293 temperatures. The hydrocarbon products in this study are mainly include C8–C16 alkanes, C17–  
294 C23 alkanes, > C23 alkanes, mono-ring aromatics, double-ring aromatics and polycyclic

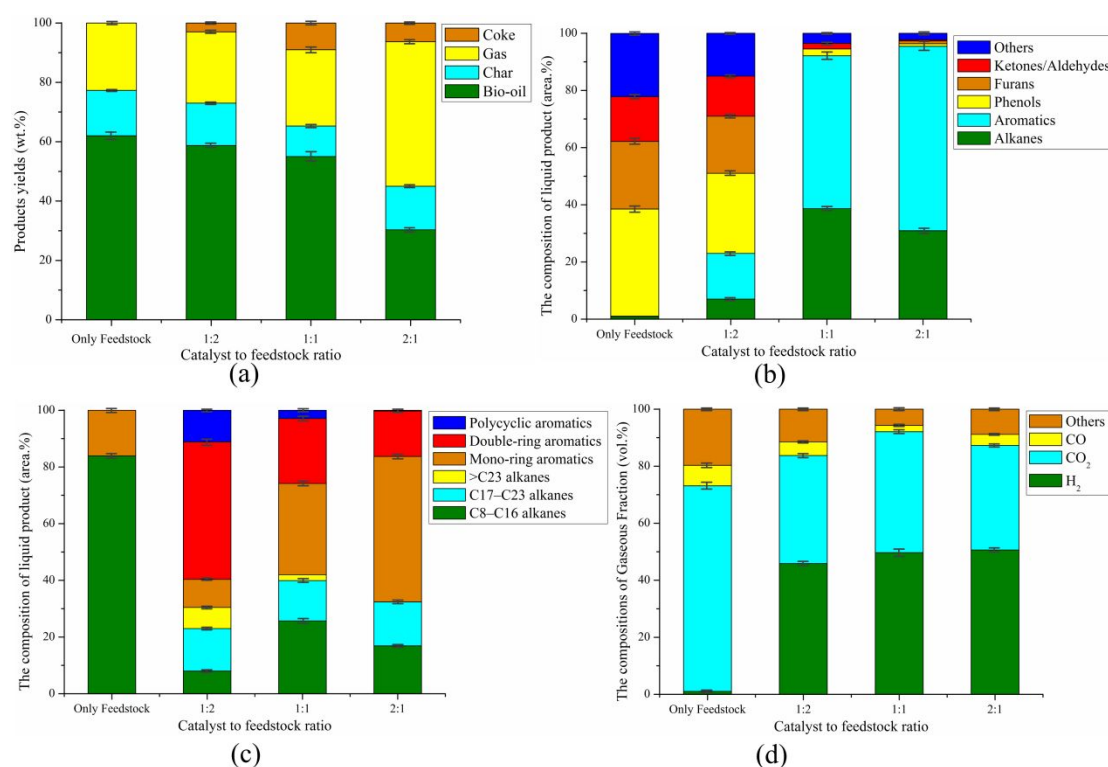


295 aromatics. It can be seen that the proportion of alkanes in hydrocarbons is decreased  
296 monotonously with the temperature increased, but the proportion of aromatics is opposite. The  
297 proportions of C8–C16 and C17–C23 alkanes has shown a downward trend, from 52.0 and 28.1  
298 area.% (400 °C) to 23.8 and 13.2 area.% (600 °C). On the contrary, The proportion of mono-ring  
299 aromatics increased from 0 area.% (400 °C) and 43.6 area.% (600 °C). The proportion of  
300 double-ring aromatics firstly added from 8.4 area.% (400 °C) to 22.9 area.% (550 °C), whereafter  
301 dropped to 16.5 area.% (600 °C). This result may be because the activated carbon catalyst has  
302 aromatization effect on the conversion of long-chain hydrocarbons into aromatics[38]. Higher  
303 pyrolysis temperature also could accelerate the double-ring aromatics decomposed into mono-ring  
304 aromatics.

305 Gaseous products occupied a large proportion of the co-pyrolysis products of waste plastics  
306 and biomass. The distribution of gaseous products is investigated could provides more information  
307 for further understanding of co-pyrolysis of wheat straw and LDPE. For the catalytic conversion  
308 of biomass with activated carbon catalyst, the main gaseous product is CO<sub>2</sub> due to the  
309 decarboxylic reactions of oxygenates [39]. H<sub>2</sub> is the dominant gaseous product in the thermal  
310 conversion process of LDPE with activated carbon catalyst, which is mainly due to the  
311 aromatization reactions of chain hydrocarbons[38]. Even for co-pyrolysis of biomass and LDPE,  
312 H<sub>2</sub> is also the dominant gaseous product under certain conditions over activated carbon catalyst  
313 [2]. The component of gaseous products for the co-pyrolysis of LDPE and wheat straw is showed  
314 in Fig. 5(d). It can be seen that the main gaseous products for the co-pyrolysis of wheat straw and  
315 LDPE are CO, CO<sub>2</sub> and H<sub>2</sub>. CO<sub>2</sub> occupied the dominant site in the gaseous products from 400 to  
316 500 °C, however, the main product is changed to H<sub>2</sub> when the pyrolysis temperature increased to

317 550 and 600 °C . The highest H<sub>2</sub> proportion of 62.7 vol.% is obtained at 600 °C . This result is  
 318 attributed to LDPE decomposed only a small amount at lower pyrolysis temperatures, and the  
 319 liquid product is mainly wax, which leads to less dehydrogenation reactions, so H<sub>2</sub> occupied a  
 320 minor proportion of the gaseous product at lower temperatures.

### 321 3.3. Catalyst to feedstock ratio effect



322

323 Fig.6. Products yields (a), compositions of liquid products (b), hydrocarbons (c) and gaseous  
 324 products (d) at different catalyst to feedstock ratios (Temperature = 550 °C, LDPE to wheat straw  
 325 ratio = 1:1)

326 The catalytic effect of the catalyst on the target products is directly connected with the  
 327 catalyst to feedstock ratio. Different catalyst to feedstock ratios (only feedstock, 1:2, 1:1 and 2:1)  
 328 are mentioned to investigate the effect of activated carbon to feedstock ratio on the distribution of  
 329 pyrolysis products, as represented in Fig. 6. In this section, the temperature and the LDPE to  
 330 wheat straw ratio are set as 550°C and 1:1.

331 A slight change of char yield versus the catalyst to feedstock ratio can be found in the Fig.  
332 6(a), which indicated that the generation of char is hardly affected by the ratio of catalyst to  
333 feedstock. It is observed that the proportion of coke added monotonously with the increase of  
334 catalyst to feedstock ratio. The proportion of gaseous products has a similar trend to that of coke,  
335 but the proportion of liquid products is opposite. The proportion of gaseous products is increased  
336 from 22.7 wt.% to 48.7 wt.% and the proportion of liquid products is decreased from 62.0 wt.% to  
337 30.3 wt.% with the ratio of catalyst to feedstock (only feedstock to 2:1). This is due to the  
338 residence time of the pyrolysis volatiles in the micropores of activated carbon is augmented with  
339 the ratio of catalyst to feedstock increased, resulting in a more complete catalytic effect of the  
340 pyrolysis volatiles, and increased the coke and gas yields, reduced the bio-oil yield. This result  
341 represented that the higher ratio of catalyst to feedstock is not conducive to promoting the  
342 production of bio-oil, resulting in the continued cracking of liquid products to generate gas, which  
343 is consistent with the previous literatures [47, 48].

344 The component of liquid products with the different ratios of catalyst to feedstock is showed  
345 in Fig. 6(b). The yield of aromatics is augmented from 0.2 area.% to 64.5 area.% with the increase  
346 of activated carbon to feedstock ratio (only feedstock to 2:1). However, for the alkanes obtained  
347 from the co-pyrolysis of LDPE and wheat straw, the selectivity firstly increased from 0.96 area.%  
348 (only feedstock) to 38.7 area.% (catalyst to feedstock = 1:1) then dropped to 30.9 area.% (catalyst  
349 to feedstock = 2:1). In general, the highest yield of hydrocarbons was 95.4 area.% at the catalyst to  
350 feedstock ratio of 2:1. It can be seen that the yields of oxygenates decreased monotonously with  
351 the increases of catalyst to feedstock ratio. The yields of phenols, furans and ketones/aldehydes  
352 were decreased from 37.5, 23.7 and 15.7 area.% to 0.9, 1.0 and 0.4 area.% at the catalyst to

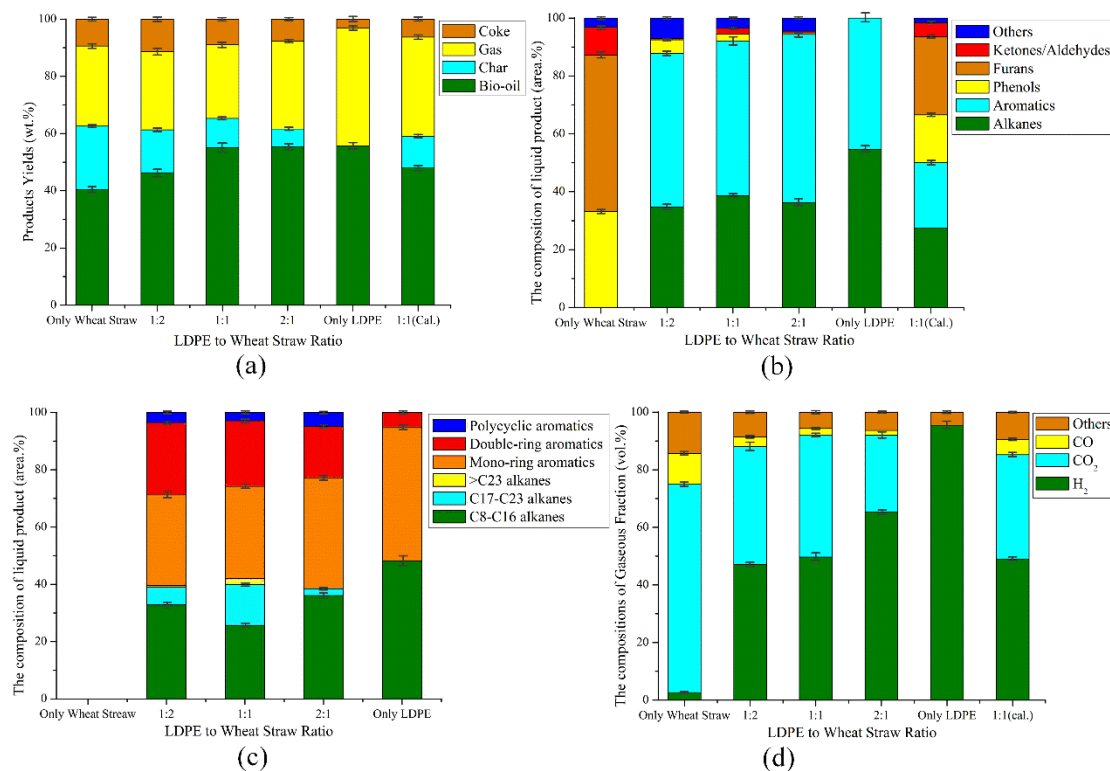
353 feedstock ratios of only feedstock to 2:1. In the previous studies, the P-containing function groups  
354 in the activated carbon catalyst shows the positive effect of promoting the aromatization reaction  
355 of alkanes to aromatic hydrocarbons[49], the decarboxylation and rearrangement of the other  
356 oxygenates to phenols[48] and the demethoxylation and dehydroxylation of phenols to aromatic  
357 hydrocarbons[2]. In addition, surface functional groups in mesopores and macropores show the  
358 properties of promoting aromatization reaction[49], so the activated carbon catalyst with a large  
359 average pore size of 26.77 Å obtained in this work is considered to have a high active catalyst  
360 potential in the aromatization reaction. Therefore, in this study, most of aromatic hydrocarbons in  
361 the co-pyrolysis of wheat straw and LDPE produced from the aromatization of alkanes, the  
362 demethoxylation and dehydroxylation of phenols in the pores of catalysts. The catalytic sites on  
363 the catalyst surface would be increased with the catalyst to feedstock ratio, and the residence time  
364 of the pyrolysis volatiles will be correspondingly extended when passing through the activated  
365 carbon catalyst, thus promoting the conversion of oxygenates and alkanes into aromatic  
366 hydrocarbons, resulting in the yield of hydrocarbons increased.

367 Fig.6(c) showed the proportions of different hydrocarbon products versus the ratio of catalyst  
368 to feedstock. For the co-pyrolysis in the absence of catalyst, the yield of hydrocarbon products  
369 only 1.16%, so the distribution of hydrocarbons under this condition is not discussed in this  
370 section. The yield of C8-C16 alkanes is firstly increased from 8.0 area.% (catalyst to feedstock =  
371 1:2) to 25.7 area.% (catalyst to feedstock = 1:1), and then decreased to 16.9 area.% (catalyst to  
372 feedstock = 2:1). The selectivity of > C23 alkanes is dropped from 7.4 area.% (catalyst to  
373 feedstock = 1:2) to 0.0 area.% (catalyst to feedstock = 2:1). The > C23 alkanes decomposed to  
374 generate C8-C16 alkanes and C17-C23 alkanes, the latter will dissociated to form C8-C16

375 alkanes, which causes the selectivity of > C<sub>23</sub> alkanes decreased monotonously and the selectivity  
376 of C<sub>17</sub>-C<sub>23</sub> alkanes exhibited mild change. The decreases of C<sub>8</sub>-C<sub>16</sub> alkanes selectivity can be  
377 ascribed to the fact that the aromatization of C<sub>8</sub>-C<sub>16</sub> alkanes to form aromatics. The proportion of  
378 mono-ring aromatics is increased from 9.9 area.% (catalyst to feedstock = 1:2) to 51.3 area.%  
379 (catalyst to feedstock = 2:1) with the proportions of double-ring aromatics and polycyclic  
380 aromatics are decreased from 48.5 and 11.2 area.% to 16.0 and 0.3 area.%, respectively. As the  
381 ratio of catalyst to feedstock increases, the minerals content and phosphoric acid functional groups  
382 of activated carbon catalyst also increase, and the minerals have a dehydrogenation effect in the  
383 catalytic reforming of hydrocarbons[42] and the phosphoric acid functional groups can promote  
384 the formation of aromatic hydrocarbons[50]. Therefore, the synergistic effect between the  
385 catalytic performance of activated carbon catalyst and high temperature that accelerated the  
386 decomposition and aromatization of alkanes, the decomposition of double-ring aromatics and  
387 polycyclic aromatics, the isomerization, decarboxylation, deoxygenation and aromatization of  
388 oxygenates, which resulting in the decrease of alkanes, double-ring and polycyclic aromatics  
389 proportions and the increases of mono-ring aromatics proportion

390 The effect of catalyst to feedstock ratio on the gaseous fraction is displayed in Fig. 6(d). CO<sub>2</sub>  
391 obtained from co-pyrolysis of LDPE and wheat straw in the absence of activated carbon catalyst  
392 was the dominant product, the proportion is much higher than that of in the presence of activated  
393 carbon catalyst. However, H<sub>2</sub> was the main gaseous product at the catalyst to feedstock ratios of  
394 1:2 to 2:1, the highest value of H<sub>2</sub> yield of 50.6 vol.% could be obtained at the catalyst to  
395 feedstock ratio of 2:1.

#### 396 **3.4. LDPE to wheat straw ratio effect**



397

398 Fig. 7. Products yields (a), compositions of liquid products (b), hydrocarbons (c) and gaseous  
 399 products (d) at different LDPE to wheat straw ratios (Temperature = 550°C, catalyst to feedstock  
 400 ratio = 1:1)

401 The effect of LDPE to wheat straw ratio on the distribution of products obtained from  
 402 co-pyrolysis of wheat straw and LDPE is investigated as shown in Fig. 7. The pyrolysis  
 403 temperature and the catalyst to feedstock ratio are set as 550°C and 1:1. In order to analyze the  
 404 synergistic effect of LDPE and wheat straw on the surface of the activated carbon catalyst, the  
 405 sum of the yields of the products obtained from the pyrolysis of only wheat straw and only LDPE  
 406 of the same quality is halved to obtain a calculated value. Then, the calculated value is compared  
 407 with the experimental value when the ratio of LDPE to wheat straw is 1:1.

408 LDPE plays the role of providing hydrogen for biomass pyrolysis volatiles. Therefore, it is  
 409 very important to study the ratio of LDPE to wheat straw for the distribution of pyrolysis products.  
 410 As shown in Fig. 7(a), the yield of coke obtained by co-pyrolysis generally decreases with the

411 ratio of LDPE to wheat straw increases, it indicated that the yield of coke is sensitive to changes in  
412 the ratio of LDPE to wheat straw, and an increase in the LDPE loading will reduce the production  
413 of coke. The yield of char decreases with the increases of LDPE to wheat straw ratio. This is due  
414 to the LDPE at this temperature is converted into pyrolysis volatiles in the catalyst for the catalytic  
415 conversion. In addition, the experimental yield of char is lower than the calculated values. The  
416 bio-oil yield is increased monotonously with the LDPE to wheat straw ratio, which increased from  
417 40.3 wt.% (only wheat straw) to 55.6 wt.% (only LDPE). This result can be ascribed to the fact  
418 that most of the LDPE is pyrolyzed into bio-oil under the catalysis of activated carbon [38]. The  
419 calculated bio-oil yield is lower than that of the calculated value, indicating that the synergistic  
420 effect of LDPE and wheat straw reduces char yield and promotes the production of bio-oil.

421 The compositions of liquid products at different ratios of LDPE to wheat straw are displayed  
422 in Fig. 7(b). The liquid products obtained from the catalytic conversion of wheat straw over  
423 activated carbon catalyst mainly consist of phenols and furans, but no hydrocarbons produced. It  
424 can be seen that the phenols, furans and other oxygenates obtained from co-pyrolysis of LDPE and  
425 wheat straw are significantly lower than that from the pyrolysis of only wheat straw. Meanwhile,  
426 the catalytic co-pyrolysis LDPE and wheat straw obviously increased the selectivity of  
427 hydrocarbons. The selectivity of hydrocarbons firstly increased then dropped with different ratios  
428 of LDPE to wheat straw from only wheat straw to 2:1 and obtained a highest selectivity of 94.3  
429 area.% at the LDPE to wheat straw ratio of 2:1. The result indicated that the quality of liquid  
430 products is sublimated by the co-pyrolysis of LDPE and wheat straw. The aromatics  
431 monotonically increased from the LDPE to wheat straw ratio of 1:2 to 2:1 and obtained the  
432 maximum selectivity of 58.1 area.%. This may be because the remarkable hydrogenation of LDPE

433 to promote the conversion of oxygenates into aromatics. The calculated yields of alkanes and  
434 aromatics are much lower than that of the experimental values. In contrast, the calculated yields of  
435 oxygenates are much higher than that of the experimental values. The experimental yield of  
436 phenols (2.4 area.%) is obviously lower than the calculated value (16.6 area.%), and no ketones  
437 and furans are obtained during in the experimental process. It indicated that the synergistic effect  
438 of LDPE and Wheat straw promotes the generation of hydrocarbons by converting oxygenates.

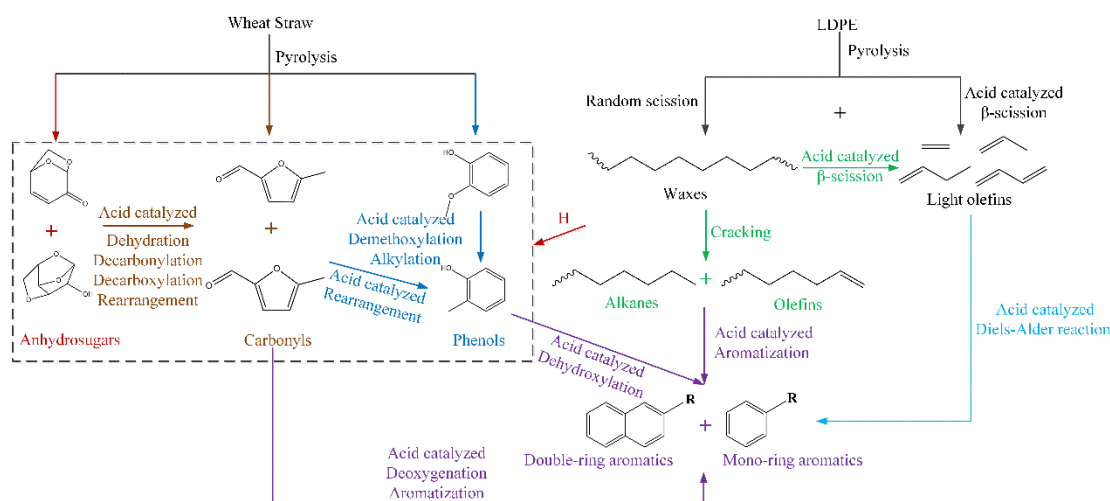
439 In order to have a more comprehensive understanding of the high-purity hydrocarbons  
440 generated by the co-pyrolysis of LDPE and wheat straw, the components of the hydrocarbons  
441 produced by different ratios of LDPE and wheat straw are described in detail, as displayed in Fig.  
442 7(c). No alkanes and aromatics in the liquid products obtained from the catalytic pyrolysis of  
443 wheat straw over activated carbon catalyst. Nevertheless, the proportions of alkanes and aromatics  
444 could be drastically increased by introducing LDPE into wheat straw. The selectivity of mono-ring  
445 aromatics increased gradually with the increasing ration of LDPE to wheat straw and acquired the  
446 highest value of 38.6 area.%, whereas the trend of double-ring aromatics selectivity is the  
447 opposite. The C8-C16 alkanes firstly reduced and then enhanced with the maximum value of 36.1  
448 area.% at the LDPE to wheat straw ratio of 2:1. This is because the LDPE provides hydrogen for  
449 the co-pyrolysis process and promotes the formation of hydrocarbons.

450 The distribution of the gaseous compositions versus different LDPE to wheat straw ratios is  
451 displayed in Fig. 7(d). The dominant component of gaseous products generated from the catalytic  
452 conversion of wheat straw is CO<sub>2</sub> with the concentration of 72.3 vol.%. This result showed that  
453 the decarboxylation reaction is the main pathway for the catalytic conversion of wheat straw. The  
454 proportion of H<sub>2</sub> increased with the ratio of LDPE to wheat straw, and the maximum value could



455 be reached to 95.5 vol.%. This can be ascribed to the fact that more hydrogen provided by the  
 456 presence of LDPE to form H<sub>2</sub>. In addition, the decrease in the ratio of wheat straw in feedstock  
 457 leads to a reduction in the proportions of CO, CO<sub>2</sub> and other oxygen-containing gaseous products.  
 458 Compared to the experimental values, the lower CO<sub>2</sub> yield and higher CO yield are obtained from  
 459 the calculation, this result shows that the synergistic effect of LDPE and wheat straw promotes the  
 460 decarboxylation reactions and suppresses the decarbonylation of oxygenates.

### 461 3.5. The reaction mechanism



462

463 Fig.8. Proposed reaction mechanism for the catalytic co-pyrolysis of LDPE and wheat straw  
 464 over activated carbon catalyst

465 According to the above discussion, the hydrocarbons are the dominant bio-oil product in the  
 466 co-pyrolysis of LDPE and wheat straw, the proposed mechanism of wheat straw and LDPE  
 467 catalytic converted into the hydrocarbon products is showed in Fig. 8.

468 Phenols, carbonyls and anhydrosugars are the primary products for the pyrolysis of wheat  
 469 straw with the generation of H<sub>2</sub>O, CO<sub>2</sub> and CO. The anhydrosugars are underwnt the  
 470 decarboxylation, decarbonylation and dehydration reactions of on the acid sites of activated  
 471 carbon catalyst to generate smaller carbonyls. Subsequently, the rearrangement reactions of

472 carbonyls in the pores of activated carbon catalyst are promoted by the acid sites, which converted  
473 the carbonyls into alkylated phenols. In addition, the methoxy phenols derived from the pyrolysis  
474 of lignin undergo the demethoxylation and alkylation reactions to generate the alkylated phenols.  
475 This chemical step is promoted by the acid sites on the pores of activated carbons. Finally,  
476 aromatic hydrocarbons are formed by the dehydroxylation reaction of alkylated phenol, as well as  
477 the deoxygenation and aromatization reactions of carbonyl groups. On the other hand, during the  
478 pyrolysis process, the LDPE is partly converted to waxes through random scission and partly  
479 undergo  $\beta$ -scission in the presence of activated carbon catalyst to form light olefins and hydrogen  
480 radicals, the latter reaction is mainly due to a large amount of chain ends of LDPE have access to  
481 the active sites inside the pores of activated carbon catalyst, in which  $\beta$ -scission is the dominant  
482 reaction to generate light olefins. The catalytic cracking of the waxes into small molecules over  
483 activated carbon catalyst is generally related to hydrogen transfer,  $\beta$ -scission, and termination. The  
484 acidic sites of catalyst abstracted hydrogen atoms from chain hydrocarbons to produce carbanions,  
485 which are unstable and easily underwent  $\beta$ -scission to form light olefins, and then to form  
486 aromatics through the Diels–Alder reaction. In fact, there is no hydrocarbon product larger than  
487 C<sub>23</sub> after LDPE has been fully catalyzed over activated carbon, which is determined by the size of  
488 the product molecules, because the pore inner diameter of activated carbon is 26.77 Å. The  
489 alkanes and olefins generated by the cracking of waxes undergo aromatization reactions under  
490 acid catalysis to generate aromatic hydrocarbons and release a large amount of hydrogen. The  
491 most important thing is that LDPE as the hydrogen source promotes the conversion of oxygenates  
492 generated by the pyrolysis of wheat straw to produce the aromatics.

#### 493 **4. Conclusion**

494 The catalytic co-pyrolysis of LDPE and wheat straw over biomass-derived activated carbon  
495 catalyst is studied to generate high purity hydrocarbon fuel in this work. The result indicated that  
496 the activated carbon catalyst exhibited a remarkable catalytic effect on the production of  
497 hydrocarbons. The higher pyrolysis temperature is inclined to accelerate the decarboxylic  
498 reactions, deoxidization reactions and dehydroxylation reactions of oxygenates to generate the  
499 aromatics. The activated carbon catalyst and pyrolysis temperature has a synergistic effect on the  
500 the decomposition and aromatization of long-chain hydrocarbons, and accelerated the production  
501 of aromatics. In addition, the presence of mineral elements Ca and K in the catalyst have a  
502 positive effect on the formation of aromatic hydrocarbons, while Mg has the opposite effect. The  
503 highest proportion of hydrocarbon fuel in the liquid products obtained from the co-pyrolysis of  
504 wheat straw and LDPE is 95.4 area.% at the conditions of temperature is 550 °C, the ratio of  
505 catalyst to feedstock is 2:1 and LDPE to wheat straw ratio is 1:1. The present work confirmed the  
506 co-pyrolysis of LDPE and wheat straw could generated high-purity hydrocarbon fuel over  
507 activated carbon catalyst, and provided an economical, simple and effective path to produce the  
508 hydrocarbon fuel from LDPE and wheat straw.

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