

1 Preparation of aromatic hydrocarbons from digestate catalytic 2 pyrolysis

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17 **Abstract**

18 The catalytic pyrolysis of digestate to produce aromatic hydrocarbons can be combined with
19 anaerobic fermentation to effectively transform and utilize the whole biomass components. This
20 study explored the feasibility of catalytic pyrolysis of digestate to prepare aromatic hydrocarbons
21 with analyzing the thermogravimetric characteristics, pyrolysis characteristics and catalytic
22 pyrolysis characteristics of digestate. Meanwhile, pyrolysis mechanism and catalytic pyrolysis
23 mechanism of digestate were explored in detail. For individual pyrolysis of digestate, it was found
24 that with temperature increasing, the content of CO and CH₄ increased, while the content of phenols,
25 acids, aldehydes and other oxygenates decreased, while the content of monocyclic aromatic
26 hydrocarbons (Benzene, Toluene and Xylene, BTX) increased. Respected to the catalytic pyrolysis
27 process, the acids, phenols and furans in the liquid were effectively inhibited, and the aromatic
28 hydrocarbons content and the BTX selectivity increased significantly with ZSM-5 addition. ZSM-5
29 also inhibited the production of nitrogenous compounds.

30 **Key words:** digestate, catalytic pyrolysis, aromatic hydrocarbons, BTX, molecular sieve catalyst,
31 ZSM-5

32

33 1. Introduction

34 Bioenergy plays a very important role in the future energy supply, but the energy crops needed
35 for the production of bioenergy compete with the production of food and feed, so the use of
36 agricultural waste to produce bioenergy has become an inevitable development trend^{1,2}. Anaerobic
37 fermentation is a popular biomass conversion technology, which can degrade biomass resources and
38 produce methane gas through microorganisms^{3,4}. However, anaerobic fermentation processes do not
39 degrade all the raw materials and produce a residue that is difficult to degrade, known as digestate⁵.
40 ⁶. Digestate contains a large amount of lignocellulose, which is difficult to be used through the
41 biodegradation process, and accompanied by heavy metals, organic pollutants, microorganisms,
42 antibiotic and other substances^{7,8}. The global digestate resource is about 550 million tons per year⁹.
43 ¹⁰. In the face of such a huge amount of resources, researchers have developed a lot of digestate
44 treatment methods, such as using digestate as a land nutrient supplement and soil conditioner;
45 transforming digestate into valuable products for utilization through hydrothermal carbonization,
46 pyrolysis and gasification^{11,12}.

47 The pyrolysis of digestate has attracted much attention. Wei¹³ et al. investigated the pyrolysis
48 behavior of the digestate from sargassum fermentation. It was found that the highest yield of bio-oil
49 was 31.05wt% at 450°C, and 43.16wt% of char and 23.02wt% of gas can be obtained at the same
50 time. Opatokun¹⁴ et al. analyzed kitchen waste and the fermented digestate pyrolysis. It was found
51 that the yield of bio-oil from digestate pyrolysis at 500°C was 52.2wt%. The components of bio-oil
52 included phenols, esters, saturated and unsaturated hydrocarbons and their derivatives. Compared
53 with the pyrolysis oil composition of food waste, it was found that the pyrolysis oil of digestate

54 contained more phenols and esters, higher molecular weight, and higher calorific value reached
55 13.5MJ/kg¹⁴. Karaeva¹⁵ et al. pyrolyzed digestate from cow manure as fermentation material, they
56 found that the yield of bio-oil was 31% at 550°C, and the pyrolysis oil contained a large amount of
57 acetic acid, accounting for 71.44% of bio-oil. However, the above research results showed that
58 liquid oil from digestate pyrolysis is rich of ester and acetic acid, it cannot be used directly.
59 Therefore, it is urgent to improve the quality of bio-oil from digestate pyrolysis.

60 To address the issue mentioned and improve the quality of bio-oil, the catalytic pyrolysis of
61 digestate has been widely concerned in recent years¹⁶. Kim¹⁷ et al. used steel slag as catalyst for
62 digestate pyrolysis in CO₂ atmosphere, they found that the pyrolysis oil in CO₂ atmosphere has
63 lower yield, simpler composition and lower concentration, moreover, the aromaticity of the
64 pyrolysis oil is also reduced due to the restricting dehydrogenation of CO₂. Ghimis¹⁸ et al. found
65 that there are a lot of linear and branched aliphatic hydrocarbons, unsaturated compounds, alcohols,
66 carbonyl compounds and carboxylic acids in the pyrolysis oil with nanostructured MnO₂ as catalyst.
67 Paasikallio¹⁹ et al found that the selectivity of aromatic hydrocarbons can reach 67.6% for digestate
68 catalytic pyrolysis. Digestate is rich in lignin, which contains coumarin alcohol, coniferol and
69 sinapine alcohol^{13,20}. It is a natural source of benzene ring, so digestate has the potential to prepare
70 chemicals containing benzene ring^{21,22}. Therefore, digestate can be considered to treat and utilize by
71 means of catalytic pyrolysis. Molecular sieve catalyst is reported as a good catalyst on converting
72 biomass to aromatic hydrocarbons. Shen²³ et al. studied the catalytic effect of various
73 metal-modified HZSM-5 catalysts on digestate pyrolysis, they found that Fe/HZSM-5 was the best
74 catalyst for high yield of monophenols, which can increase the yield of monophenol in bio oil to

75 79.22% at pyrolysis temperature of 430° C catalytic cracking temperature of 475°C. However, the
76 rarely relative report can't guide which kind of molecular sieve catalyst is suitable for digestate
77 catalytic pyrolysis as well as its catalytic pyrolysis mechanism is not clear. Hence, this study
78 attempts to use 5 types of molecular sieve catalyst to convert digestate into aromatic hydrocarbons
79 and the effects of different types of molecular sieve catalysts on digestate catalytic pyrolysis was
80 analyzed in detailed. . Firstly, the pyrolysis characteristics and thermogravimetric characteristics of
81 digestate were analyzed, and the pyrolysis characteristics of digestate were compared with those of
82 different lignin. Subsequently ,the influence of molecular sieve types on the catalytic pyrolysis
83 products components was explored, and the most suitable molecular sieve catalyst for catalytic
84 pyrolysis of digestate to prepare aromatic hydrocarbons was selected. It is of great significance to
85 the feasibility of digestate catalytic pyrolysis to prepare aromatic hydrocarbon products.

86 **2.Materials and method**

87 **2.1. Raw material**

88 Digestate was selected as the raw material for the experiment. The digestate raw material
89 composed of pig manure, corn silage and sorghum silage from the biogas power plant is reacted by
90 a microbial anaerobic digester and separated by a screw press separator to get the digestate with
91 high moisture content. After 24h air drying, it is placed in an oven at 105°C for continuous drying
92 for 8h. After crushing and screening, 60-100 mesh samples were selected for pyrolysis experiment
93 and catalytic pyrolysis experiment. The experimental raw materials were stored in an oven at a
94 temperature of 50°C before the experiment. The properties of digestate samples in the experiment

95 are shown in **Table 1**. Compared with general biomass like straw and wood, digestate has lower
 96 volatile matter and higher content of lignin^{24, 25}. In addition, the ash content of digestate(12.38 wt%)
 97 is higher than general biomass(1~6 wt%), and the alkaline earth metals in ash may play a catalytic
 98 role in pyrolysis.

99 **Table 1** Properties of digestate (wt.%, dry basis)

Solid Digestate(wt.%)	
Proximate analysis	
Ash	12.38
Volatile Matter	67.07
Fixed Carbon	20.55
Ultimate analysis	
C	45.52
H	5.94
N	1.79
O*	49.75
Compositional analysis	
Cellulose	21.64
Hemicellulose	15.08
Lignin	40.88

100 * - by difference

101 The ZSM-5, SAPO, Beta, MCM and Y zeolite molecular sieve catalysts used in the catalytic
 102 pyrolysis experiment were all purchased from the Catalyst Factory of Nankai University. The
 103 physical and chemical properties of the molecular sieve catalysts are shown in **Table 2**. As is shown
 104 in this table, the silica-alumina ratio of ZSM-5, Beta and MCM is high, reaching 30 or more.
 105 Additionally, the pore size of these catalysts is less than 2nm, which belongs to micropores. Before
 106 the experiment, catalysts were ground with particle size of 60-80 mesh used for screen, and part size
 107 among 60-80 mesh was selected for catalytic pyrolysis. It was pre-calcined at 105°C to remove
 108 impurities and moisture before each trial.

109 **Table 2** Physical and chemical properties of molecular sieve catalysts

molecular sieve catalysts	IZA code	SiO ₂ /Al ₂ O ₃	Dimension of hole	Hole size (Å)	Internal pore volume (Å)
ZSM-5	MFI	30	3	5.1×5.5, 5.3×5.6	6.36

SAPO	CHA	0.56	3	4.3	7.37
Beta	BEA	38	3	6.6×6.7, 5.6×5.6	6.68
MCM	MWW	30	2	4.0×5.5, 4.1×5.1	9.69
Y zeolite	FAU	5.2	3	7.4×7.4	11.24

110 2.2. Thermogravimetric experiment

111 The pyrolysis weight loss process of digestate was analyzed using Labsys 1150
112 thermogravimetric analyzer (TG, Setaram, France). The experimental process is as follows: the dried
113 sample ~10mg was heated up to 900°C from room temperature and the heating rate is 5°C/min. The
114 thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) were performed
115 by using the analyzer software.

116 2.3. Pyrolysis and catalytic pyrolysis experiment

117 Pyrolysis and catalytic pyrolysis experiments of digestate were carried out on a downdraft
118 fixed bed. The pyrolysis reaction system is shown in **Figure 1**, which is mainly composed of an air
119 intake system, a quartz reactor, an electric furnace heating system, a condensation bottle, and a gas
120 drying and purification system. The experimental temperature of pyrolysis is 400-700°C and
121 catalytic pyrolysis temperature is 600°C, and the average heating rate of electric furnace is
122 10°C/min.

123 Specific experimental process is as follows: in each pyrolysis experiment, 1g digestate was
124 added into the basket. For catalytic pyrolysis, in-situ catalytic pyrolysis is adopted, that is, the
125 sample is mixed with the catalyst, in which the digestate and catalyst is both 1g. Before the start of

126 the reaction, the quartz basket is placed in the non-heating zone at the top of the reactor. The flow
127 rate of carrier gas N₂ was 200mL/min, and the system was purged for 30min. After the temperature
128 reaches the set temperature and remains stable. Quartz basket was quickly put into the target
129 temperature pyrolysis reaction zone in the middle of the reactor. The sample is heated rapidly, and
130 the pyrolysis volatiles are taken out of the reactor through carrier gas. The condensable part is
131 condensed in the condenser in the ice-water mixture to form bio-oil, while the non-condensable part
132 is collected by air bag. Finally, after the reaction is over and the reactor is cooled, the solid residue
133 is taken out and weighed and recorded. The total mass of digestate pyrolysis liquid oil is determined
134 by the quality difference of the condensation system before and after the reaction. For pyrolysis
135 experiments of digestate, the mass of char is the mass of solid residue. For catalytic pyrolysis
136 experiments, the quality of char is the difference between the mass of solid residues and the mass of
137 the added catalyst. The mass of non-condensable gas is calculated by subtracting the mass of bio-oil
138 and char from the mass of digestate. The yields of the three products were calculated by dividing
139 their respective mass by the mass of digestate.

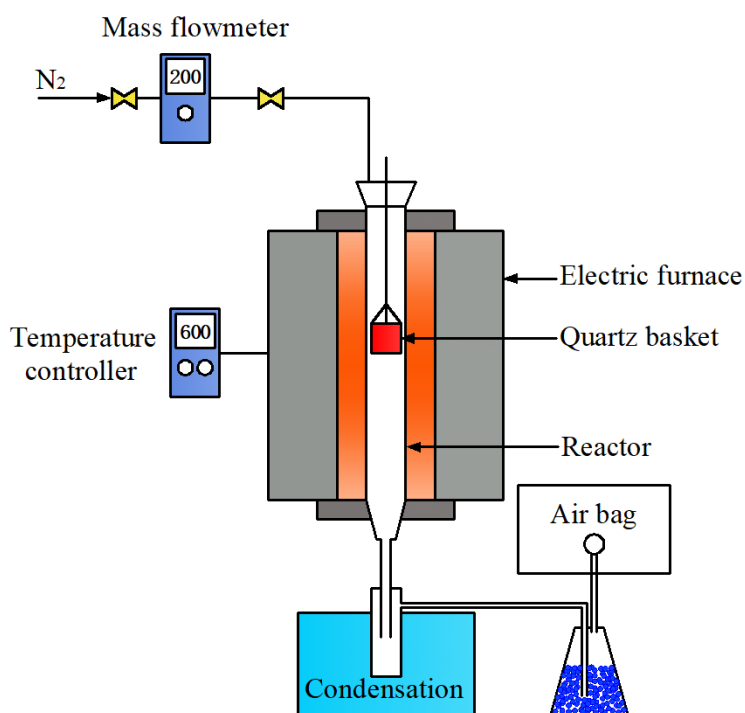


Figure 1 Schematic diagram of downdraft fixed bed pyrolysis reaction system

2.4. Characterization method

Pyrolysis gas component was analyzed using PannaA91 type gas chromatograph (FID-TCD, Changzhou panna Instrument Co., Ltd). The chromatograph with dual channel detector, which is equipped with a thermal conductivity detector (TCD detector) to detect CO₂, H₂, O₂, N₂ and CH₄, while the hydrogen flame ionization detector (FID detector) is used to detect CH₄, C₂H₄, C₂H₆ and other small olefins and alkanes.

The organic component in the pyrolysis liquid products was measured with gas chromatography/mass spectrometry (GC-MS, 7890A/5975C, Agilent). The chromatographic column used for detection was HP-5 weak polar column (30m×0.25mm×0.25μm). Before testing, it

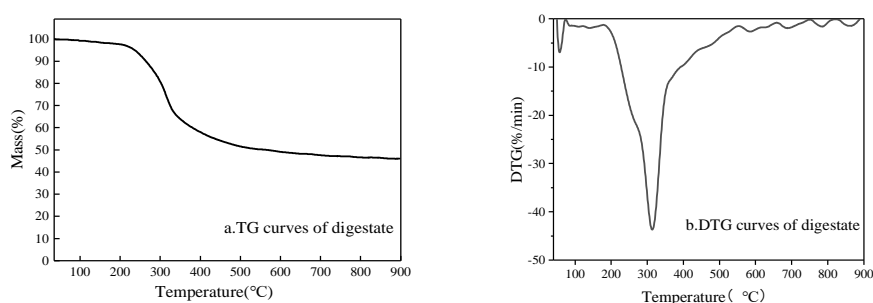
151 is necessary to ensure that the moisture content of liquid product oil is less than 10%.The
152 temperature rise procedure of the column was as follows: the initial temperature of the column was
153 40°C, the temperature was kept for 3min, the temperature rise rate was increased to 150°C at
154 5°C/min, and then the temperature rise rate was increased to 300°C at 10°C/min and kept for
155 5min.The injection temperature of the column was 275°C, the carrier gas (He) flow rate was
156 1.0mL/min, and the split ratio was 20:1.Mass spectrometric detection range, 30-500 (m/z), GC-MS
157 results matched the standard spectral library for NIST2014.

158 **3.Results and discussion**

159 **3.1. Thermogravimetric characteristic analysis of digestate**

160 **Figure 2** shows the TG curve and DTG curve of weight loss characteristics and rate of
161 digestate pyrolysis. Because the dried digestate is still easy to absorb water, the weightlessness
162 behavior of the corresponding raw material at a lower temperature (<200°C) is greatly disturbed, so
163 the thermal weightlessness behavior of the digestate at low temperature is not discussed in detail
164 here. As shown in the figure, the weight loss rate of digestate pyrolysis at 200-400°C is close to
165 36%. The peak value of weight loss rate is between 310-330°C, which is due to the high content of
166 cellulose and lignin in digestate after microbial fermentation. The proportion of cellulose and lignin
167 is 21.64% and 40.88% respectively. Compared with conventional biomass raw materials with
168 similar lignin content ²⁶, the peak range of pyrolysis weight loss of digestate is shifted to low
169 temperature, which may be because the anaerobic fermentation of the internal biogas digester
170 makes the physicochemical properties of the final digestate different from conventional biomass,

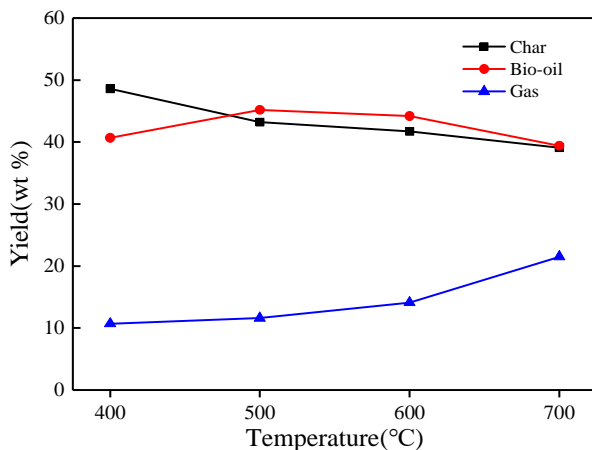
171 and the digestate is degraded to a certain extent in structure. At 400-750°C, the weight loss amount
172 is less, about 10%, which is mainly caused by the slow pyrolysis of lignin. When the final
173 temperature reaches 900°C, the pyrolysis of digestate is finished, and the solid residue of digestate
174 reaches 45%. The thermogravimetric characteristics of digestate were compared with those of lignin
175 from different sources in other papers. The solid residue rates of acid-soluble lignin, alkali lignin
176 and organic solvent extracted lignin after pyrolysis were about 30%, 36% and 35% respectively²⁷.
177 The solid residue rate of digestate after pyrolysis was significantly higher than them. The solid
178 residue rate of enzymatic lignin after pyrolysis is 43%, which is the highest among lignin from
179 different sources²⁷, The solid residue rate of digestate after pyrolysis is close to enzymatic lignin,
180 and the DTG curve of enzymatic lignin is also similar to digestate, with a main peak and a shoulder
181 peak, and the position of the maximum weight loss peak is also close, therefore, digestate could be
182 considered to be closer to enzymatic lignin in pyrolysis characteristics^{27, 28}. The TG curve shows
183 that the thermal weight loss of digestate mainly occurs before 400°C, so in the subsequent pyrolysis
184 experiment, 400-700°C is selected as the pyrolysis temperature.



185
186 **Figure2** (a)TG and (b)DTG curves of digestate

187 **3.2. Pyrolysis product analysis of digestate**

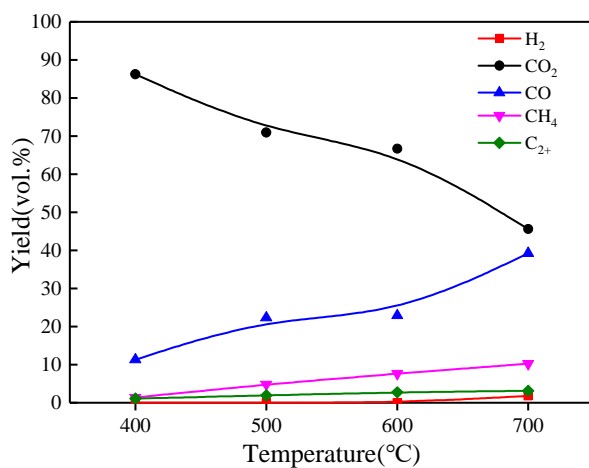
188 The product distribution of digestate pyrolysis at different temperatures is shown in **Figure 3**.
189 As is shown in the figure, the product of digestate pyrolysis is mainly solid char (50wt%) and liquid
190 oil(40%) at 400°C, while gas yield is quite limited. It might be attributed to that the lignin content in
191 digestate is high, and the low temperature condition is not enough to make a large amount of lignin
192 cracking²⁹. With temperature increasing the yield of solid char decreased gradually, and the yield of
193 gas increased, while the yield of liquid bio-oil increased firstly and then decreased, and reached the
194 maximum value (~43wt%) when the temperature was 500-600°C. This is because with the increase
195 of pyrolysis reaction temperature, more organic volatiles are evolved out, and macromolecular
196 substances in volatiles are converted into small molecular gases. However, when the temperature is
197 too high, the degree of secondary reaction is continuously intensified, leading to the decrease of
198 bio-oil yield. Comparing the three-state yield of digestate pyrolysis with lignin from different
199 sources, it is found that at the same pyrolysis temperature, the bio-oil yield and char yield of
200 digestate pyrolysis are higher than those of alkali lignin, dealkaline lignin and prot lignin, while the
201 gas yield is significantly lower than these lignin³⁰. For enzymatic hydrolysis lignin and organic
202 solvent extracted lignin pyrolysis at 500°C, the gas yield is less than 10%, the oil yield is less than
203 25%, and the carbon yield is very high, more than 65%, which is closer to the three-state yield
204 distribution of digestate pyrolysis³¹.



205
206 **Figure 3** Three-state yield distribution of digestate pyrolysis at different temperatures

207 **Figure 4** shows the distribution of gas composition from digestate pyrolysis at different
208 temperatures. The components of pyrolysis gas include CO₂, CO, H₂, CH₄ with some C₂₊. At 400°C,
209 CO₂ and CO are the main components, they accounted for ~85vol.% and ~10vol.% of the total
210 pyrolysis gas, respectively. Since the decomposition of hemicellulose and cellulose occurs mainly at
211 lower temperature, accompanied by a large number of decarbonylation and decarboxylic
212 reactions. As the temperature increases, the content of CO₂ in the pyrolysis gas decreases
213 quickly-straightly, but CO content increases accordingly. When the pyrolysis temperature reaches
214 700°C, the content of CO is equivalent to that of CO₂. This result might be due to the intensification
215 of lignin depolymerization in digestate at higher temperature stage, and the intensification of
216 secondary pyrolysis of volatiles accompanied by temperature rising, so that the generation of CO is
217 dominant at higher temperature³². In addition, the yield of CH₄ increased with the increase of
218 temperature, which was mainly due to the demethylation reaction of the methoxy functional group
219 (-O-CH₃) on lignin at higher temperature³³. For H₂, the content is relatively low because the

220 pyrolysis temperature is low and the volatiles of macromolecules cannot undergo secondary
221 pyrolysis³⁴. A small amount of low carbon olefin C_{2+} is generated in the pyrolysis process,
222 specifically including $C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8$, but the content is very trace and they were
223 not shown here. Comparing the gas release characteristics of digestate pyrolysis with lignin from
224 different sources, the CO_2 produced by enzymatic lignin pyrolysis at $550^\circ C$ is significantly less
225 than digestate, and the CH_4 and H_2 produced are significantly higher than digestate, indicating that
226 the ash or other components in digestate are not conducive to the further pyrolysis of
227 macromolecular saturated hydrocarbons to produce CH_4 and H_2 ³⁵. The pyrolysis of acid soluble
228 lignin at $700^\circ C$ produces more CO_2 and less CO than digestate, and the other gas yields are
229 relatively close, their difference may be due to the influence of more carboxyl groups on acid
230 soluble lignin³⁶.

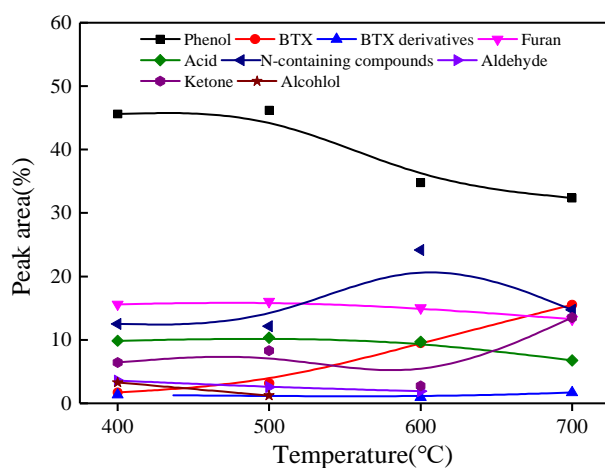


231
232 **Figure 4** Distribution of pyrolysis gas components of digestate at different temperatures

233 The liquid oil composition is shown in **Figure 5**, the main biological material oil component is

234 divided into nine categories, they are phenols, BTX, BTX derivatives, furans, acids,
235 nitrogen-containing compounds, aldehydes, ketones and alcohols. At a lower temperature of 400°C,
236 phenols is the main liquid species with some furans, acids, and nitrogen-containing compounds, etc.,
237 and the content of BTX and their derivatives is very low. A similar situation was found in the
238 experimental results of pyrolysis of lignin by Lin³⁷ et al, the proportion of phenols in the pyrolysis
239 oil of lignin was also the highest, and the proportion of phenols in the pyrolysis oil of milled wood
240 lignin and enzymatic lignin was the closest to that of digestate, both about 45%. With temperature
241 increasing, the contents of BTX increased gradually at the cost of phenols, acids and aldehydes
242 cracking, while no obvious change showed for furans. For nitrogen-containing compounds, the
243 content increased slightly and reached the highest at 600°C, and then the content decreased at higher
244 temperature. The proportion of nitrogen-containing compounds at each pyrolysis temperature is
245 between 12-25%, which is mainly caused by the thermal decomposition of protein contained in
246 digestate³⁸. Among lignin from different sources, most lignin contains almost no nitrogen, and only
247 enzymatic lignin contains a small amount of nitrogen (less than 2%), so there are almost no
248 nitrogen-containing substances in the pyrolysis oil of most lignin, while the pyrolysis oil of
249 enzymatic lignin contains a small amount of nitrogen-containing substances, which is similar to that
250 of digestate³⁵. The reduction of phenols may be due to the high temperature in the lignin
251 depolymerization, intensifying methoxy reaction and secondary reaction, resulting in part of
252 phenols transfer to BTX. In general, the increase of temperature is beneficial to reduce the content
253 of oxygen-containing compounds in the bio-oil and increase the content of BTX in the bio-oil. This
254 is mainly attributed to the promotion of the secondary reaction of volatiles by high temperature. It is

255 also worth noting that although the increase of pyrolysis temperature promoted the formation of
256 BTX, its yield is still limited, less than 20%. Compared with the lignin pyrolysis experiment of
257 Lin³⁷ et al., it is found that the BTX content in the enzymatic lignin pyrolysis oil is close to that of
258 digestate, and the BTX content is significantly higher than that of alkali lignin and acid soluble
259 lignin. It shows that digestate is a raw material similar to enzymatic lignin and has the potential to
260 produce aromatic hydrocarbons by pyrolysis.



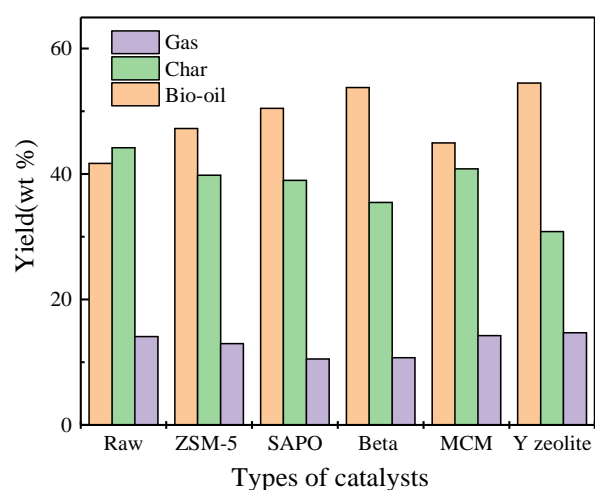
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262 **Figure 5** Composition distribution of pyrolysis bio-oil from digestate at different temperatures

263 3.3. Catalytic pyrolysis characteristics

264 600°C was selected as the temperature of catalytic pyrolysis, because the gas and oil yields of
265 digestate pyrolysis were high at this temperature, and this temperature was suitable for the catalytic
266 reforming of molecular sieve. **Figure 6** shows the product distribution of digestate catalytic
267 pyrolysis with variant catalysts (ZSM-5, SAPO, Beta, MCM and Yzeolite) at 600°C. The solid char

268 and bio-oil yield of the original sample pyrolysis of digestate are higher, both of which are more
269 than 40wt%, while the gas yield is lower, about 14wt%. With molecular sieve catalyst addition, the
270 yield of bio-oil increased, while the yield of gas and char decreased. This is because the transfer of
271 free radicals and the cracking or arrangement of compounds in the process of catalytic pyrolysis
272 promote the yield of pyrolysis oil³⁹. While among various catalysts, Beta and Yzeolite showed the
273 higher liquid yield, it increased to 53.8wt% and 54.5wt% respectively. On the other hand, except
274 MCM and Yzeolite have promoting effects on the pyrolysis gas, the gas yield reduced. As for char,
275 the char yield decreased after the addition of molecular sieve catalyst, especially Beta and Yzeolite,
276 which reduced the char yield from 44.2wt% to 35.5wt% and 30.8wt%, respectively. This may be
277 due to Beta and Yzeolite catalysts promoting the precipitation of volatiles and the formation of
278 more bio-oil, which greatly promoted the secondary pyrolysis of pyrolysis gas and resulted in the
279 increase of condensable substances, while reducing the conversion to char.

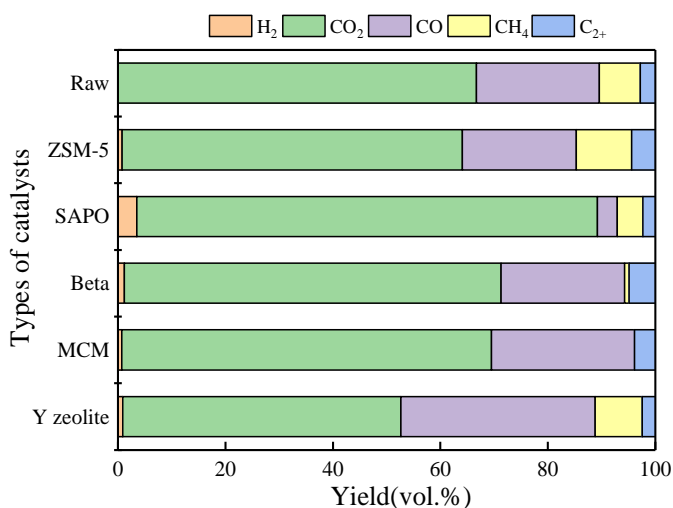


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281 **Figure 6** Products distribution of digestate catalytic pyrolysis under the action of different

282 molecular sieve catalysts

283 **Figure 7** shows the composition distribution of digestate pyrolysis gas under the action of
284 different molecular sieve catalysts. The main components of original sample pyrolysis and catalytic
285 pyrolysis of digestate are CO₂, H₂, CH₄, CO, and a small amount of low carbon hydrocarbons (C₂₊).
286 In addition, a small amount of H₂ appears in catalytic pyrolysis of digestate. CO₂ is one of the
287 important ways of deoxygenation of bio-oil. The promotion or inhibition of CO₂ content by
288 molecular sieve catalyst also affects the quality of bio-oil. The gas distribution results shows that
289 the addition of ZSM-5 and Y zeolite reduces the amount of CO₂ in the pyrolysis gas. For the
290 addition of ZSM-5, the content of CO in the pyrolysis gas decreased, while the content of CH₄ and
291 low carbon hydrocarbon C₂₊ increased, mainly because ZSM-5 can promote the demethylation
292 reaction of digestate pyrolysis and promote the occurrence of secondary crackin⁴⁰. After the addition
293 of Y zeolite, the amount of CO increased significantly, which may be because Y zeolite can promote
294 the decarbonylation reaction of digestate thermolysis, and this is also the most important reaction
295 way that Y zeolite is different from ZSM-5⁴¹. However, the addition of SAPO, Beta and MCM
296 increased the content of CO₂ in the pyrolysis gas, especially the addition of SAPO significantly
297 promoted the content of CO₂, which may be because SAPO promoted the decarboxylation reaction
298 of digestate pyrolysis to a large extent, while the decarbonylation reaction was relatively
299 weakened⁴². The catalysis of MCM and Beta is similar, and relative to the ZSM-5, apart from the
300 CH₄ content were reduced gas composition, quantity of CO₂ and CO, CH₄ content is greatly
301 reduced, these two kinds of catalysts can may also promote decarbonylation and decarboxylic
302 reactions⁴³, promote the secondary cracking of digestate, but inhibits methylation reaction.



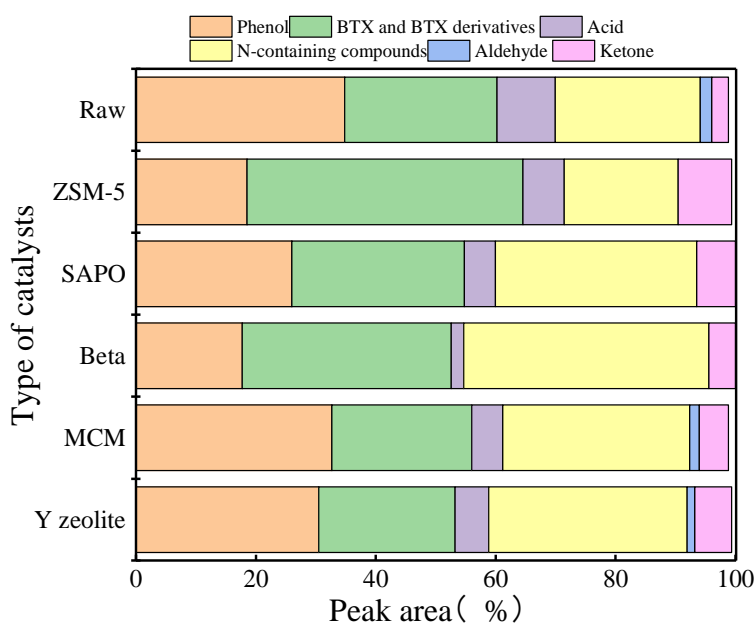
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304 **Figure 7** Catalytic pyrolysis gas composition of digestate under different molecular sieve catalysts

305 As shown in **Figure 8**, the pyrolysis bio-oil from the original sample of digestate is dominated
306 by phenols, nitrogen-containing substances, furans, aromatic compounds and acids. The acids have
307 high oxygen content and are corrosive, which can easily make the bio-oil aging and reduce the
308 quality of bio-oil. Moreover, the high content and complex composition of nitrogen-containing
309 compounds are not conducive to the subsequent utilization of bio-oil, and the nearly 25% BTX and
310 BTX derivatives in bio-oil composition is beneficial to improve the quality of bio-oil. Therefore, it
311 is necessary to reduce the content of acids and nitrogen-containing substances and to direct the
312 composition of bio-oil towards aromatic hydrocarbons. Under the action of catalysts ZSM-5, SAPO,
313 Beta, MCM and Yzeolite, acids, phenols and furans were all effectively inhibited, and the content of
314 aromatic compounds increased significantly. Beta had the most obvious inhibitory effect on acids,
315 and the content of acids decreased from 9.70% to 2.07% . The addition of ZSM-5 has the most
316 obvious effect on promoting the formation of aromatic hydrocarbons and the content of BTX and

317 BTX derivatives increased from 25.45% to 45.99%, while the content of phenolic compounds
318 decreased from 34.79% to 18.5%. Combined with the results of the increase of CH₄ in the pyrolysis
319 gas and C₂₊ content of low carbon hydrocarbon, we can infer that the addition of ZSM-5 may
320 promote the demethylation reaction and secondary cracking of the pyrolysis gas in the catalyst
321 channel⁴⁴. In addition, some phenolic substances may undergo decarbonylation reaction to generate
322 aromatic hydrocarbons. The reduction of furan content indicates that furan in pyrolysis gas may
323 also undergo secondary cracking reaction under the action of ZSM-5 and form BTX by
324 recombination. Beta and ZSM-5 showed similar catalysis for the formation of phenols, BTX and
325 BTX derivatives, while Beta catalyst showed a slightly weaker catalysis for the formation of BTX
326 and BTX derivatives than ZSM-5. In addition, compared with ZSM-5, Zeolite has an obvious
327 promoting effect on furan, but hardly shows an inhibiting effect on phenols, which may be due to
328 the fact that, the pyrolysis gas of digestate tends to deoxidize in the form of CO removal under the
329 action of Y zeolite. SAPO, Beta, MCM and Y zeolite all promoted the formation of
330 nitrogen-containing compounds, leading to the entry of a large number of nitrogen elements into
331 the bio-oil. Therefore, these catalysts are not conducive to the removal of nitrogen elements from
332 condensable substances. This may be because these catalysts have a certain adsorption on
333 nitrogen-containing gas components, and the adsorbed nitrogen-containing gas reacts with
334 monocyclic aromatic hydrocarbon volatiles, resulting in more nitrogen-containing compounds in
335 pyrolysis oil⁴⁵. In particular, the addition of Beta increased the content of nitrogen-containing
336 compounds from 24.17% to 40.91%. Therefore, it is advisable to use Beta catalyst for the
337 production of bio-oil with high nitrogen content, and to extract nitrogen-containing chemicals from

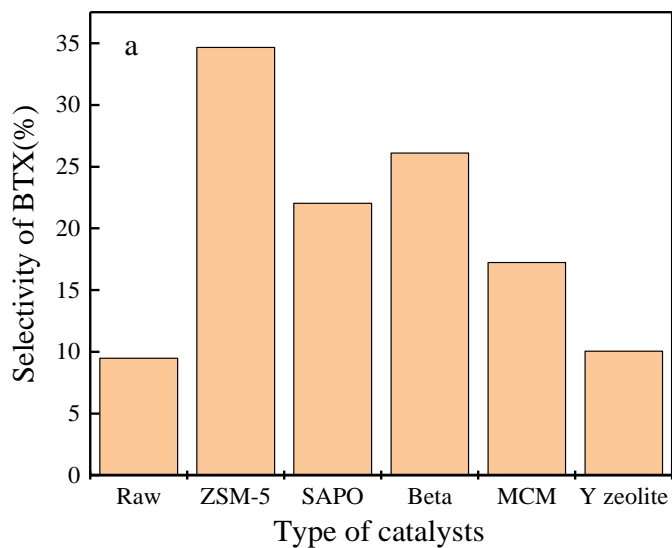
338 it. However, the addition of ZSM-5 could inhibit the production of nitrogen-containing compounds,
339 so it was speculated that ZSM-5 could remove nitrogen in the form of ammonia, which was similar
340 to some predictions of Wei¹³ et al. Under the catalysis of ZSM-5, a series of reactions such as
341 decomposition, dehydration, decarbonylation, decarboxylation and deamination of volatile
342 components have taken place, resulting in a significant reduction of organic nitrogen and organic
343 oxygen compounds, and the phenol that is difficult to crack has also undergone a dehydroxylation
344 reaction at the strong Bronsted acid site of ZSM-5. These results show that ZSM-5 has significant
345 denitrification, deoxidation, cyclization and aromatization^{46, 47}.



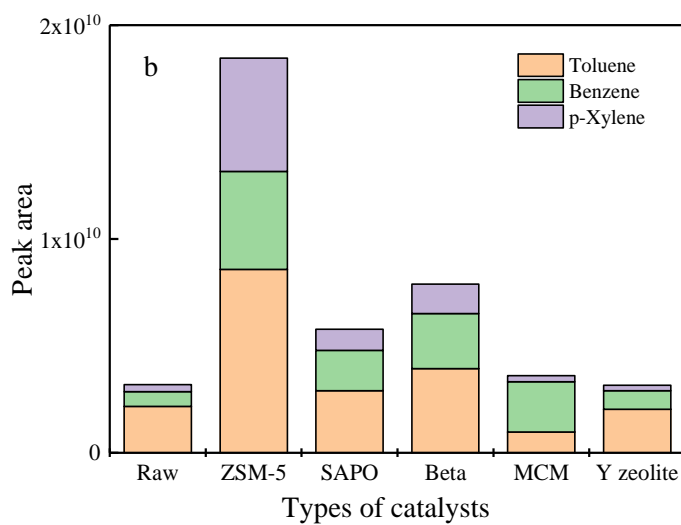
346
347 **Figure 8** Bio-oil composition during catalytic pyrolysis of digestate under different molecular sieve
348 catalysts

349 The selectivity of BTX in digestate catalytic pyrolysis bio-oil is shown in **Figure 9(a)**. The

350 proportion of BTX peak area in bio-oil composition results represents the selectivity of BTX.
351 Compared with no catalyst, the selectivity of BTX was improved after adding catalyst. Among them,
352 ZSM-5 had the most obvious effect on the increasing of BTX selectivity, reaching up to 34.66%
353 from 9.49%. Beta also has a promoting catalysis on the selectivity of BTX, and the worst is Y
354 zeolite. The yield of BTX in digestate catalytic pyrolysis bio-oil is shown in **Figure**
355 **9(b)**. Considering the different working conditions, the raw materials of the experiment and the
356 parameters of the GC-MS test on the bio-oil of each group were the same, so each peak area was
357 used to represent the yield of each component of BTX. According to the BTX yield in the figure,
358 toluene (T) yield was the highest in the pyrolysis of original digestate sample, followed by benzene
359 (B) and P-xylene (X), and the total BTX yield was relatively low. In the pyrolysis oil catalyzed by
360 molecular sieve, the promoting effect of ZSM-5 on B, T and X is very obvious, and the total
361 production of BTX increases significantly, which is more than five times that of the original
362 digestate pyrolysis sample. Compared with ZSM-5, other molecular sieve catalysts have a relatively
363 weak promotion effect on BTX, and the total BTX yield of Beta is relatively high, while Yzeolite
364 and MCM have almost no promotion effect on the BTX yield. In addition, compared with other
365 molecular sieve catalysts, the BTX product distribution of MCM is different, and benzene is the
366 most productive substance in BTX.



367



368

369 **Figure 9** The (a)selectivity and (b)yield of BTX in digestate catalytic pyrolysis bio-oil under the

370 action of different molecular sieve catalysts

371 Overall, under the action of catalysts ZSM-5, SAPO, Beta, MCM and Y zeolite, the acids,

372 phenols and furans in the catalytic pyrolysis of digestate are effectively inhibited, and the content of
373 aromatic hydrocarbons is significantly increased. Among them, for BTX, the addition of ZSM-5 has
374 the most obvious promotion effect. At the same time, the addition of ZSM-5 could inhibit the
375 production of nitrogen-containing compounds. Therefore, in a comprehensive consideration, ZSM-5
376 has more advantages for catalytic pyrolysis of digestate to prepare aromatic hydrocarbons.

377 **4. Conclusion**

378 In this study, the pyrolysis characteristics of digestate raw materials alone were investigated,
379 and on this basis, the characteristics of catalytic pyrolysis of digestate to prepare aromatic
380 hydrocarbons under the action of molecular sieve catalyst were studied. The influence of molecular
381 sieve catalyst types on the catalytic pyrolysis products was investigated. The following conclusions
382 can be drawn:

383 1) TG-DTG experiments show that: at low temperature (200-400°C), the weight loss rate of
384 digestate pyrolysis is close to 36%, and the peak weight loss rate appears at 310-330°C. At high
385 temperature (400-750°C), the weight loss rate of digestate reached 10%. When the digestate
386 pyrolysis is completed, the solid residue of digestate pyrolysis reaches 45%.

387 2) Through the pyrolysis experiment of digestate, it is found that CO₂, CO and CH₄ are the
388 main components of gas products, and phenol is the main component of liquid bio-oil. With the
389 increase of temperature, the content of CO and CH₄ increased, the content of phenols and
390 oxygen-containing compounds such as acids and aldehydes decreased, and the content of BTX
391 increased.

392 3)The pyrolysis experiments of digestate catalyzed by different kinds of molecular sieve
393 catalysts showed that: after catalytic pyrolysis of digestate using molecular sieve as catalyst, acids,
394 phenols and furans in the liquid were effectively inhibited, and the content of aromatic
395 hydrocarbons increased significantly.Among them, the addition of ZSM-5 had the most obvious
396 promotion effect on BTX, which increased BTX selectivity from 9.49% to 34.66%.Meanwhile,
397 ZSM-5 also inhibited the generation of nitrogen-containing compounds.

398

399 Declaration of Competing Interest

400 The authors declare that they have no known competing financial interests or personal relationships
401 that could have appeared to influence the work reported in this paper.

402

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