

1 **Pyrolysis products from industrial waste biomass based on a neural network model**

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12 **Abstract**

13 Pyrolysis of pine sawdust, a typical industrial biomass waste, was studied. The
14 effects of operating temperature, biomass particle size, and carrier gas space velocity
15 on the products of biomass pyrolysis were investigated. A three-layer artificial neural
16 network (ANN) model was developed and trained to simulate and predict the
17 selectivity and yield of gas products. Good agreement was achieved between the
18 experimental and simulated results. The major gas products of biomass pyrolysis are
19 CO, CO₂, H₂, and CH₄. The ANN model showed that the major gas products depended
20 mainly on the temperature, and the total selectivity of CO, CO₂, H₂, and CH₄
21 increased from 2.91% at 300°C to 34.31% at 900°C. The selectivity of main gas
22 products increased with increasing carrier gas flow rate. When the carrier gas flow
23 rate increased from 45 min⁻¹ to 85 min⁻¹, the selectivity of major gas products
24 increased from 29.12% to 34.03%. Within the sample particle size range from 0.1 to
25 1.7 mm, there was no significant difference in the selectivity of major gas products.
26 The pyrolysis temperature also influenced the composition of the tar in the biomass
27 pyrolysis product. In the temperature range investigated, the benzene composition was
28 favored at lower temperatures, such as 400°C, however, the light-weight PAHs were
29 preferably generated at higher temperatures above 600°C.

30 **Key words:** pyrolysis; biomass; tar; artificial neural network (ANN);
31 non-condensable gas

32

33 **1. Introduction**

34 Biomass pyrolysis is a type of thermolysis, thermochemical decomposition of
35 organic material at elevated temperatures in the absence of oxygen, which produces
36 tar, condensable liquid and non-condensable gas products. Biomass pyrolysis process
37 is usually divided into four stages based on a thermal viewpoint [1,2]. In the drying
38 stage in which the temperature is below 100°C, the biomass releases moisture and
39 some bound water. In the initial stage, the biomass temperature is between 100 and
40 200°C. This releases low-molecular-weight gases, such as CO and CO₂, and small
41 amounts of acetic acid. In the intermediate stage, the temperature is between 200 and
42 600°C. Most of the vapor or precursors to bio-oil are produced at this stage. Large
43 molecules of biomass particles decompose into char, condensable gases, and
44 non-condensable gases. The final stage takes place at a temperature between 300 and
45 900°C. The final stage of pyrolysis involves secondary cracking of volatiles into char
46 and non-condensable gases. If they stay in the biomass long enough, large molecule
47 condensable gases will also crack, producing additional char (secondary char) and
48 gases. The condensable gases, if removed quickly from the reaction, condense outside
49 in the downstream reactor as tar or bio-oil. A higher pyrolysis temperature also favors
50 the production of hydrogen, which increases quickly above 600°C [3].

51 Biomass pyrolysis produces non-condensable gases (including H₂, CO, CH₄, and
52 CO₂) tar, and char [4]. Many factors, such as biomass particle diameter, temperature,
53 heating rate, and residence time can influence the production rate and product
54 properties of biomass pyrolysis [5]. Temperature is the most important factor.

55 Biomass releases different products under different temperature profiles [16-19].
56 Several researchers [20-23] have investigated the product selectivity and production
57 rate of biomass pyrolysis at different temperatures, ranging from 300 to 1000°C, in a
58 fluidized bed reactor or revolver. Biomass particle size is also an important factor
59 affecting the pyrolysis reaction rate. Biomass particles with larger diameters have
60 weaker heat transfer capacity, so the internal temperature increases slowly, which
61 affects the selectivity of biomass pyrolysis. Researchers have investigated the
62 relationship between biomass particle size and the selectivity of biomass pyrolysis in
63 fluidized and free-fall reactors [5,24]. The results show that biomass with smaller
64 particle diameters releases more gases, and less tar and char; the fraction of H₂ and
65 CO will increase as the biomass particle diameter becomes even smaller. Cui [25]
66 analyzed biomass pyrolysis via thermogravimetric analysis and a self-designed
67 pressurized thermal gravitational analyzer and concluded that the reaction rate of
68 biomass pyrolysis was higher under higher pressure. Generally, heating rate, flow rate,
69 biomass molecular structure, and reactor pressure influence the composition of
70 products from biomass pyrolysis.

71 Tar is a by-product of biomass pyrolysis, the composition of which is very
72 complex. Currently, more than 300 compounds have been detected in tar; despite this,
73 many compounds remain unknown [26,27]. Tar usually comprises mostly benzene
74 derivatives and polycyclic aromatic hydrocarbons (PAHs) [28-32]. The fractions of
75 six compounds in particular are typically each greater than 5%, including benzene,
76 naphthalene, methylbenzene, ethenylbenzene, phenol, and indene. These compounds

77 are liquids at low temperatures and crack into permanent gases with low molecular
78 weights at high temperatures. These small-molecule gases do not condense into
79 liquids when the reactor temperature falls back to the range within which the original
80 compounds are liquids. Recently, many researchers investigated the reactions of tar at
81 different temperatures. Tar starts to condense below 200°C and starts to react and
82 produce char, pyroligneous acid, additional tar (secondary tar), and gases above
83 200°C. Above 600°C, the secondary tar and pyroligneous acid are evaporated and
84 mixed, producing gases. At a temperature of 500°C, the production rate of tar from
85 biomass pyrolysis is highest. Biomass pyrolysis produces tar through a series of
86 complicated reactions. They depend on many reaction factors, but especially reaction
87 temperature. Tar in the vapor phase cracks into light hydrocarbons, aromatic
88 hydrocarbons, alkenes, hydrocarbons, and PAHs as the reactor temperature increases.

89 Chemical kinetic models are one approach to gain insight into a reaction and
90 provide a better understanding of the effect of the processing parameters. The kinetic
91 models reported by Di Blasi [33] is a typical example that investigated the influence
92 of several variables for wood and biomass pyrolysis, such as reaction temperature,
93 residence time, and pressure. Although a dynamic model provides relatively stable
94 and accurate performance in this reaction, a complicated structure is required,
95 especially for a multiple responses system/multi-stage reaction process which contains
96 many processing parameters and mechanisms.

97 Compared with 'traditional' chemical and physical models, artificial neural
98 networks have the advantages of being able to model complex phenomena rapidly and

99 easily by simply starting with measured values and investigating potentially complex
100 and non-linear relationships, linking various physical values. Additionally, a neural
101 network has versatility as a black box information processor. All fields including
102 neural network applications use the same symbols. Regardless of the form, neurons
103 represent the same ingredient in different neural networks. This commonality makes it
104 possible to share the same neural network theory and algorithms across various areas.
105 Mikulandric et al [34] compared the effects of equilibrium models and neural network
106 model in the biomass gasification process in fixed bed gasifiers. The results derived
107 from different equilibrium modelling approaches (for various operating conditions)
108 cannot be compared or explained in some cases. Results from devised equilibrium
109 models are comparable with results derived from literature only for specific operating
110 points. However, neural network models showed good capability to predict biomass
111 gasification process parameters with reasonable accuracy and speed. As a
112 consequence, the effective utilization of the ANN model was beneficial in
113 understanding the complex relationship between the raw materials and pyrolysis
114 products and even the technical management in the actual pyrolysis process [35].

115 In this study, the distribution of biomass pyrolysis products and the effects of
116 operation conditions on pyrolysis were investigated. We summarized rules on the
117 influences of temperature, biomass particle size, and carrier gas space velocity on
118 biomass pyrolysis products. Moreover, an ANN model was developed and trained to
119 simulate and predict the selectivity and yields of gas products with different operation
120 parameters in the biomass pyrolysis.

121 **2. Materials and Methods**

122 **2.1 Raw material**

123 The typical biomass selected for pyrolysis was pine sawdust (without bark,
124 purchased from Porta Pine, Germany). This biomass was milled, sieved, and classified
125 to obtain fractions of uniform particle size, and then dried for at least 12 h at 105 °C.
126 The particle size of the biomass was classified into six groups: 0.14, 0.17, 0.22, 0.34,
127 0.64, and 1.70 mm. Nitrogen (99.999 vol.%, Beijing Haipu Gas Co. Ltd., China) was
128 used as the carrier gas. Analytical-grade methanol (Beijing Chemical Works, China)
129 was used as the tar absorbent.

130 **2.2 Experimental setup**

131 The configuration of the pyrolysis reactor is shown in Fig. 1. The pyrolysis
132 apparatus consists of a quartz tubular reactor (Length: 1 m and the inner diameter: 50
133 mm). The reactor is heated by a tube furnace (OTF-1200X, Hefei Kejing Material
134 Technology Co. Ltd., China) in an inert N₂ atmosphere. First, 4 g of pine sawdust was
135 introduced into the furnace. The flow rate of carrier gas (N₂) was controlled by a mass
136 flow controller (D08-4E, Beijing Seven Star Electronics Co. Ltd., China). For each
137 experimental run, the reactor was heated to a set temperature (400, 500, 600, 700, or
138 800 °C) at a heating rate of 20 °C min⁻¹ prior to pushing the biomass sample into the
139 heated zone. The reaction time was 30 min. The volatile products passed through two
140 impingers filled with methanol which were cooled in ice-water bath, and the produced
141 tar was remained in the impingers. The remaining aerosol was removed with a filter

142 filled with degreasing cotton. The gas product passed through a wet type gas
143 flowmeter to record the total gas volume. Finally, the gas product was collected in a
144 sampling gas bag (15 L, Dalian Delin Gas Packaging Co. Ltd., China).

145 **2.3 Analytical methods**

146 Produced gases were analyzed by a GC-17A (Shimadzu Corp., Japan) equipped
147 with a thermal conductivity detector (TCD) and a Carboxen-1010 PLOT capillary
148 column (30 m × 0.53-mm I.D., 30- μ m average thicknesses, Supelco Corp., USA). The
149 injection (injection volume of 200 μ L) was performed at 100°C in splitless mode. The
150 oven temperature program was 50°C constantly for 15 min. The temperature of the
151 detector was 200°C. Argon (99.999 vol.%, Beijing Haipu Gas Co. Ltd., China) was
152 used as the carrier gas, at a constant flow of 10 mL/min.

153 TG analysis was carried out with a STA449F3 Jupiter (Netzsch-Gerätebau
154 GmbH, Germany). Approximately 40 mg of pine sawdust were heated in argon at
155 10°C min⁻¹, from ambient to 800°C for pyrolysis.

156 The yield and selectivity of gas product were calculated as follows:

$$157 \quad \text{The yield of gas product (mmol/g)} = \frac{V_o}{24.4 \times 4} \quad (1)$$

$$158 \quad \text{The selectivity of gas product (\%)} = \frac{c_j}{c} \times 100\% \quad (2)$$

$$159 \quad \text{The molar ratio of gas products (mol\%)} = \frac{n_j}{n} \times 100\% \quad (3)$$

160 where v_o is the volume of gas product from pyrolysis of 4 g pine sawdust at room
161 temperature (25°C), c_j is the mass of target gas product (g), c is the mass of pine
162 sawdust used in the biomass pyrolysis (g), n_j is the molar quantity of target gas
163 product (mol), j is different kind of gas products, and n is the molar quantity of total

164 gas products produced in the biomass pyrolysis (mol). All experiments were
165 conducted three times under the same experimental conditions.

166 **2.4 Tar sampling**

167 The products in the pyrolysis process flowed through two impingers filled with
168 100 mL methanol. The solvents in the impingers were passed through an organic filter
169 membrane to remove solid particles and were then diluted with methanol. A
170 3D-fluorescence spectrophotometer (F-7000, Hitachi Corporation, Japan) with a 1 cm
171 light-path length was used to record the 3D-fluorescence spectra of the tar. The scan
172 speed was 12000 nm/min, the PMT voltage was 700 V, and the response time was
173 0.002 s.

174 **2.5 Artificial neural network**

175 An artificial neural network is a layer-parallel information processing structure
176 composed of numerous neurons connected by weighted links, passing signals from
177 one neuron to another. A typical neural network consists of multiple layers, including
178 an input layer, a number of hidden layers, and an output layer. The input layer is a
179 terminal to receive and distribute the input information, while the output layer is the
180 final product of the neural processing. Between the input and output layers are one or
181 more hidden layers, which build up the links between the inputs and outputs. In this
182 paper, a three-layer back propagation (BP) neural network with a logarithm sigmoid
183 function in the hidden layer and a linear function at the output layer was used for the
184 training of the neural network.

185 The experimental data were split into two groups: input set (X) and target output
186 set (T). Three processing parameters, space velocity, reaction temperature, and
187 particle size, were identified as input variables in the model, while the target output
188 variables include selectivity of the four gas products (H₂, CO, CH₄, CO₂). The
189 selectivity for the gas products of the pyrolysis processing can be calculated from the
190 simulated output variables. Additionally, the experimental data were divided randomly
191 into training and test data sets. The training step was used to determine the connection
192 weights between layers, while the test step was used to evaluate the accuracy of the
193 model.

194 **3. Results and Discussion**

195 **3.1 Neural network modeling**

196 **3.1.1 Selection of back-propagation training algorithm**

197 The most widely used neural network architecture is back-propagation (BP),
198 which is a hierarchical design consisting of entirely cross-linked layers. A valid neural
199 network with accompanying proper and fixed weights is achieved when the mean
200 square error (MSE) of the test set reaches a minimum value. In our recent work, we
201 have trained a three-layer feed-forward neural network with different BP algorithms.
202 The Levenberg-Marquardt (LM) training algorithm has shown excellent performance
203 in prediction and function approximation with a minimum MSE value achieved
204 compared with other BP algorithms, consistent with other studies. In this study, the
205 LM algorithm was combined with seven different transfer functions to get the optimal

206 neural network system that could provide a stable and accurate prediction for the
207 biomass pyrolysis process.

208 **3.1.2 Optimization of neuron number**

209 In this work, the LM training algorithm with a logarithmic sigmoid transfer
210 function at the hidden layer and a linear transfer function at the output layer was used
211 for training of the BP neural network (Fig. 2). The optimal number of neurons in the
212 hidden layer is determined based on the minimum value of MSE for the training and
213 test sets. We found the MSE and SED values for four neurons were 0.070389 and
214 0.064, respectively, with four neurons in the hidden layer. Both values decreased
215 significantly, to 0.01 and 0.04, respectively, when seven neurons were used. However,
216 further increasing the number of neuron to 12 did not reduce the MSE or SED
217 significantly. Thus, the optimal neuron number in the hidden layer for the LM-BP
218 structure was determined to be seven.

219 **3.1.3 Testing the neural network model**

220 A test group that included about 15% of the experimental data was used to feed
221 the optimized ANN to evaluate the accuracy of the model. Fig. 3 shows a comparison
222 between the experimental data and those predicted from the LM-BP neural network
223 model. Two lines can be seen in the figure: one is the perfect fit line, $Y = T$. Here, Y is
224 the predicted result and T the experimental, meaning the predicted results were
225 essentially identical to the actual input results.

226 **3.1.4 Sensitivity analysis**

227 The neural net weight matrix and Garson equation were used to determine the
 228 relative importance of the input plasma processing parameters. This equation is based
 229 on the partitioning of connection weights of the optimal ANN model:

$$I_j = \frac{\sum_{m=1}^{m=N_h} \left(\left(|W_{jm}^{ih}| / \sum_{k=1}^{N_i} |W_{km}^{ih}| \right) \times |W_{mn}^{ho}| \right)}{\sum_{k=1}^{k=N_i} \left\{ \sum_{m=1}^{m=N_h} \left(|W_{km}^{ih}| / \sum_{k=1}^{N_i} |W_{km}^{ih}| \right) \times |W_{mn}^{ho}| \right\}} \quad (4)$$

230
 231 where I_j is the relative importance of the j^{th} input variable for the whole process, N_i
 232 and N_h are the number of input and hidden neurons, respectively. W represents the
 233 connection weight. Additionally, the superscripts ‘i,’ ‘h,’ and ‘o’ refer to the input,
 234 hidden, and output layers, respectively, while the subscripts ‘k,’ ‘m,’ and ‘n’ refer to
 235 the input, hidden, and output neurons.

236 Table 1 presents the weights produced by the optimized ANN that were used in
 237 this work. The relative importance of the input parameters was determined by Eq. 1,
 238 as shown in Table 2. In this study, temperature had a significant impact on the reaction
 239 performance of the pyrolysis process in terms of the selectivity of gas product (H_2 ,
 240 CO , CH_4 , and CO_2). Particle size was identified as a second important parameter on
 241 the CO and H_2 selectivity. In contrast, the space velocity contributed least to the
 242 pyrolysis process, because of its lowest importance for all outputs.

243 Table 1. Weight matrices W_1 (weights between input and hidden layer) and W_2
 244 (weights between hidden and output layers).

Neuron	W_1			W_2
	Input variables			Outputs (%)
	Space	Temperature	Particle	Selectivity

	Velocity		Size	H ₂	CO	CH ₄	CO ₂
1	0.539	3.041	-0.841	0.756	1.292	1.257	0.442
2	0.763	10.186	2.694	1.294	0.792	0.753	1.549
3	0.878	2.501	-2.025	-0.539	-0.331	-0.478	-0.037

245

246 Table 2. Relative importance of processing parameters for the optimized ANN model.

Input variable	Importance (%)			
	Selectivity			
	H ₂	CO	CH ₄	CO ₂
Space Velocity	19.18	19.77	19.54	19.50
Temperature	60.85	58.11	57.52	63.51
Particle Size	19.97	22.12	22.94	16.99
Total	100	100	100	100

247

248 3.2 Effect of temperature on pyrolysis products

249 The effect of pyrolysis temperature on gas products is shown in Fig. 4. Under
 250 these operating conditions, the space velocity was 65 min⁻¹, and the biomass particle
 251 size was 0.14-1.70 mm. At the highest temperature in the investigation range (800°C),
 252 the yield of total gas product reached a maximum of about 30.6 mmol/g (RSD =
 253 1.6%), while at 400°C it was 6.8 mmol/g (RSD = 6.9%). The main gas products from
 254 the pyrolysis of biomass are H₂, CO, CH₄, and CO₂.

255 Fig. 5 shows a comparison between the predicted and experimental results for the
 256 selectivities of H₂, CO, CH₄, and CO₂ at different temperatures. The simulated data
 257 obtained from the well-trained neural network model were in fairly good agreement

258 with the experimental data. Temperature showed a significant impact on the pyrolysis
 259 reaction performance. With an increase of temperature from 400°C to 800°C, the
 260 selectivity of H₂ increased from 0.04% to 5.89%, CO from 0.52% to 15.20% and CH₄
 261 from 0.20% to 5.78%, CO₂ from 2.15% to 6.21% (RSD is between 7.6% and 1.3%).
 262 The reactor temperature influences the pyrolysis process, which determines the gas
 263 product distribution. The molar ratio of major gas products in the total gas products
 264 increased from 46.11 mol% to 80.11 mol% with temperature increasing from 400 to
 265 800°C.

266 Higher temperature favors the cracking and reforming of hydrocarbons and thus
 267 increases H₂ and CO formation. With the temperature increase from 400 to 800°C, the
 268 yield of H₂ increased from 0.33 to 17.41 mmol/g and CO from 0.68 to 12.99 mmol/g.
 269 As shown in Table 3, the total ratio of H₂ and CO in the gas products, defined as
 270 syngas, reached 56.71% at 800°C. Over the investigated temperature range, the higher
 271 temperature contributed to higher H₂ and CO selectivity. The H₂/CO molar ratio also
 272 increased from 0.12 to 0.34 mol/mol as the pyrolysis temperature rose from 400 to
 273 800°C.

274 Table 3. Effect of temperature on the total ratio of H₂ and CO and molar ratio of H₂ to
 275 CO in gaseous product from pyrolysis (sample particle size: 0.45–0.90 mm; space
 276 velocity: 65 min⁻¹).

Temperature (°C)	400	500	600	700	800
H ₂ +CO (%) ^a	11.24	16.35	29.63	44.99	56.71
H ₂ /CO (mol/mol) ^b	0.12	0.08	0.16	0.27	0.34

277 ^a The total ratio of H₂ and CO among the total gas products, $(n_{H_2} + n_{CO})/n$.

278 ^b The molar ratio of H₂ to CO in the gas products, n_{H_2}/n_{CO} .

279 The gas product distribution was influenced by the composition of the biomass
280 and the properties of its components. In the pyrolysis process, the gas products
281 originated from the primary pyrolysis and were also products of the secondary
282 decomposition of volatiles. The CO was from unstable carbonyls in the volatiles [36].
283 Because CO originated mainly from the secondary decomposition of volatiles cracked
284 by primary pyrolysis, the selectivity of CO obviously increased with increased
285 temperature. The H₂ resulted mainly from the rearrangement and dehydrogenation of
286 aromatic bonds. As a result, the selectivity of H₂ also obviously increased with
287 increasing temperature from 400 to 800°C.

288 The formation of CO₂ was mainly the result of the primary decomposition of
289 alduronic acid in hemicelluloses at low temperature, about 350°C [37]. When the
290 temperature increased, the carboxyls in the lignin broke up and produced a small
291 quantity of CO₂. For this reason, with temperature increased, the ratio of CO₂ in the
292 gas products decreased but the selectivity increased. The product of CH₄ was formed
293 by the decomposition of methoxyl in lignin. The higher temperature promoted lignin
294 decomposition and the selectivity of CH₄ increased, from 3.82 to 13.10%.

295 The generated tar in biomass pyrolysis was analyzed by the 3-D fluorescence
296 spectrophotometer. When the fluorescence peak of Ex/Em is near the 270/335 nm
297 point (Peak A in Fig. 6), the peak is related to the 1- or 2-ring aromatics in solution:
298 mostly benzene, toluene, and phenol [38]. It can be concluded from Table 4 that with
299 temperature increasing from 400 to 600°C, the peak intensity of the benzene

300 composition from biomass pyrolysis decreased, from 3062 to 1194, and then
 301 maintained a stable lower level when the temperature increased above 600-700°C. In
 302 the temperature range investigated, the benzene composition was favored at lower
 303 temperatures, such as 400°C and it will decompose at higher temperatures. It can be
 304 concluded that higher temperatures promote the formation of gaseous products at the
 305 expense of tar. Moreover, with the temperature increasing above 600°C, there was
 306 another fluorescence peak of Ex/Em near 230/355 nm, which was related to the 2- or
 307 3-ring polycyclic aromatic hydrocarbons (PAHs). The value of peak B increased from
 308 1148 to 1174 with pyrolysis temperature increasing from 600 to 800°C. It can be
 309 concluded that light-weight PAHs were preferably generated at higher temperatures,
 310 above 600°C [39]. Also, at very high temperatures (> 600-700°C),
 311 dehydrogenation/aromatization reactions can lead to formation of polynuclear
 312 aromatic hydrocarbons and, eventually, increase carbonization.

313 Table 4. The intensity of peaks from 3D fluorescence scan on tars of pyrolysis.

Temperature/°C	400	500	600	700	800
Peak A Intensity	3062	2250	1194	1287	1107
Peak B Intensity	No peak	No peak	1148	1653	1774

314

315 **3.3 Effect of carrier gas space velocity on pyrolysis gaseous products**

316 The space velocity of the carrier gas N₂ was set at 45, 65, and 85 min⁻¹. As
 317 shown in Fig. 7, while the space velocity (in standard conditions, the volume of gas
 318 crossing the reactor in unit time) increased from 45 to 85 min⁻¹, the total ratio of major

319 gaseous products, including H₂, CO, CH₄, and CO₂, among the total gas products
320 increased from 85.19 to 89.4 mol%. As seen in Fig. 8, a near-perfect match between
321 the experimental and simulated data at different space velocities was achieved. The
322 selectivity of H₂ increased from 5.19 to 6.10%, CO from 13.36 to 15.86%, and CH₄
323 from 4.81 to 5.72%, whereas CO₂ from 5.76 to 6.34% (RSD was 2.0-7.0%), with the
324 space velocity increase from 45 to 85 min⁻¹. Primary decomposition of biomass
325 material (< 400°C) consists of a degradation process, whereas secondary thermolysis (>
326 400°C) involves aromatization processes [40]. The primary pyrolysis products inside
327 and around the biomass particles in the gas phase will react in secondary pyrolysis.
328 Secondary pyrolysis can produce permanent gases, such as H₂, CH₄, CO and CO₂. In
329 this investigation, increasing the space velocity would remove the primary pyrolysis
330 products attached to the biomass particles faster, which may otherwise hinder the
331 biomass pyrolysis. Thus, secondary pyrolysis reactions would be promoted. As a
332 consequence, more permanent gases was produced.

333 **3.4 Effect of biomass sample particle size on pyrolysis gaseous products**

334 The effect of particle size on the total yield and ratios of gas products are shown
335 in Fig. 9. The total yield of main gas products increased from 30.7 to 32.5
336 mmol/g-biomass with a decrease in particle size (from 1.400-2.000 to 0.150-0.180
337 mm). However, the selectivity of H₂, CO, CH₄, and CO₂ was almost not influenced by
338 the particle size (RSD was between 1.3% and 10%). As a consequence, the reaction
339 mechanism was almost unaffected by particle size. Additionally, the prediction results
340 of the selectivity of CO₂, H₂, CH₄ and CO were in good agreement with the

341 experimental data with different particle sizes in pyrolysis process (shown in Fig. 10),
342 indicating the good potential of the ANN model in simulating the complex pyrolysis
343 process of biomass.

344 Typical TG, DSC and DTG curves for biomass are shown in Fig. 11. When the
345 temperature was lower than 200°C, the DSC curves showed an endothermic peak
346 around 100°C, mainly attributable to dehydration of biomass. In the temperature
347 range of 200-500°C, a DTG peak and sharp decrease in the TG curve are seen. There
348 is an obvious peak around 360°C and then an inconspicuous peak at around 310°C in
349 the DTG curve. The DSC curve also shows an obvious endothermic peak at around
350 360°C. This is mainly relevant to the composition of the biomass. Biomass is typically
351 composed of cellulose, hemicellulose, and lignin [41]. Under ‘ordinary’ heating,
352 cellulose pyrolysis occurs around 250-500°C, hemicellulose pyrolysis at below 350°C,
353 and lignin pyrolysis over the whole temperature rang from ambient to 900°C, but at a
354 slow mass loss rate [42]. The weight loss peaks of hemicellulose and cellulose
355 partially overlap each other. However, the lignin has no sharp weight loss peak.

356 With an increase in particle size from 0.150-0.180 to 1.400-2.000 mm, the TG
357 curves and product gas composition were almost not influenced by particle size. The
358 main reason is that the difference in the particle size was small, from 0.150-0.180 to
359 1.400-2.000 mm. As seen in Fig. 11 (b), the amount of carbon residue increased from
360 20.38 to 21.26 wt.%, with particle size decreasing from 1.400-2.000 to 0.150-0.180
361 mm. The main reason is that the smaller particles can decompose more completely,
362 leave less char and achieve more complete energy conversion.

363 **4. Conclusions**

364 In this work, effects of operating temperature, carrier gas space velocity, and
365 biomass particle size on characteristics of biomass pyrolysis were investigated. A
366 three-layer BP neural network was developed to simulate and predict the complex
367 biomass pyrolysis process. The LM training algorithm combined with a target sigmoid
368 transfer function (logarithmic) in the hidden layer with seven neurons and a linear
369 transfer function at the output layer offered the optimal solution for training the BP
370 neural network. There was fairly good agreement between the experimental results
371 and simulated data for the biomass pyrolysis process. The main gas products of
372 biomass pyrolysis were CO, CO₂, H₂, and CH₄. The yields of the major gas products
373 increased and the composition of the gas products changed as temperature increasing.
374 The tar composition was also influenced by temperature. The benzene composition
375 was favored at lower temperatures, such as 400°C, whereas, the PAHs tended to
376 generate at higher temperature of over 600°C. With the carrier gas space velocity
377 increasing, selectivity of the major products also increased. A large space velocity of
378 carrier gas was beneficial for syngas production. The characteristics of biomass
379 pyrolysis were almost not influenced by the biomass particle size.

380 **5. Acknowledgements**

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383

384 **Figure captions:**

385 Fig. 1. The schematic of the biomass pyrolysis reactor.

386 Fig. 2. Optimized three-layer ANN model with a logarithm sigmoid transfer function
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405 Fig. 11. DTG, DSC (a) and TG (b) curves of biomass for different particle sizes
406 (1.400~2.000 mm; 0.425~0.850 mm and 0.150~0.180 mm) at heating rate of
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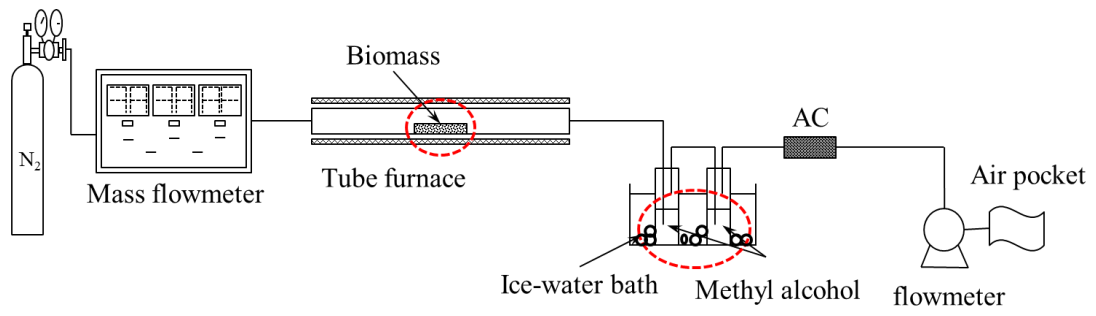
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537 Fig. 1. The schematic of the biomass pyrolysis reactor

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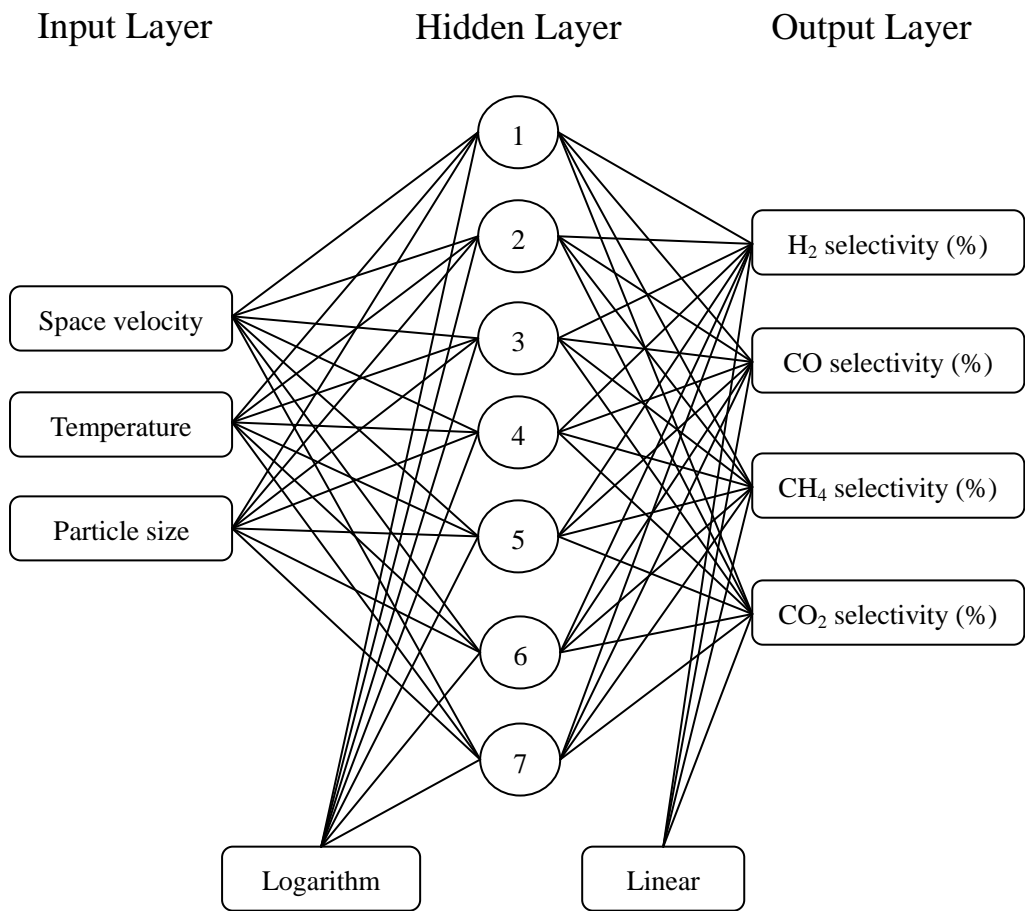
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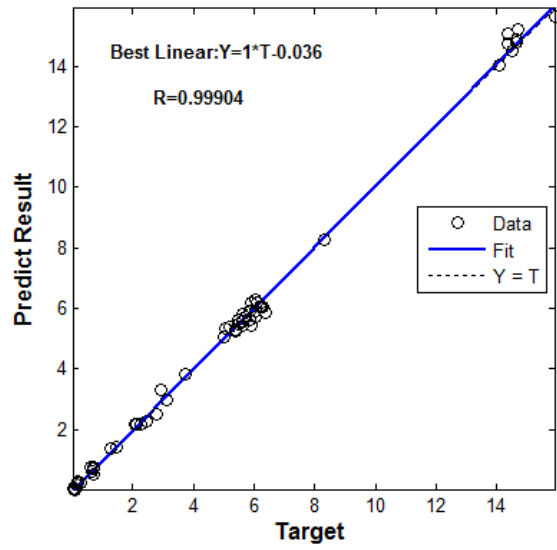
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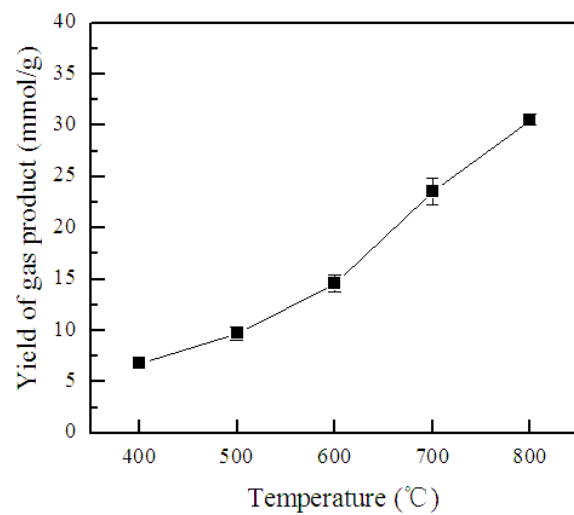
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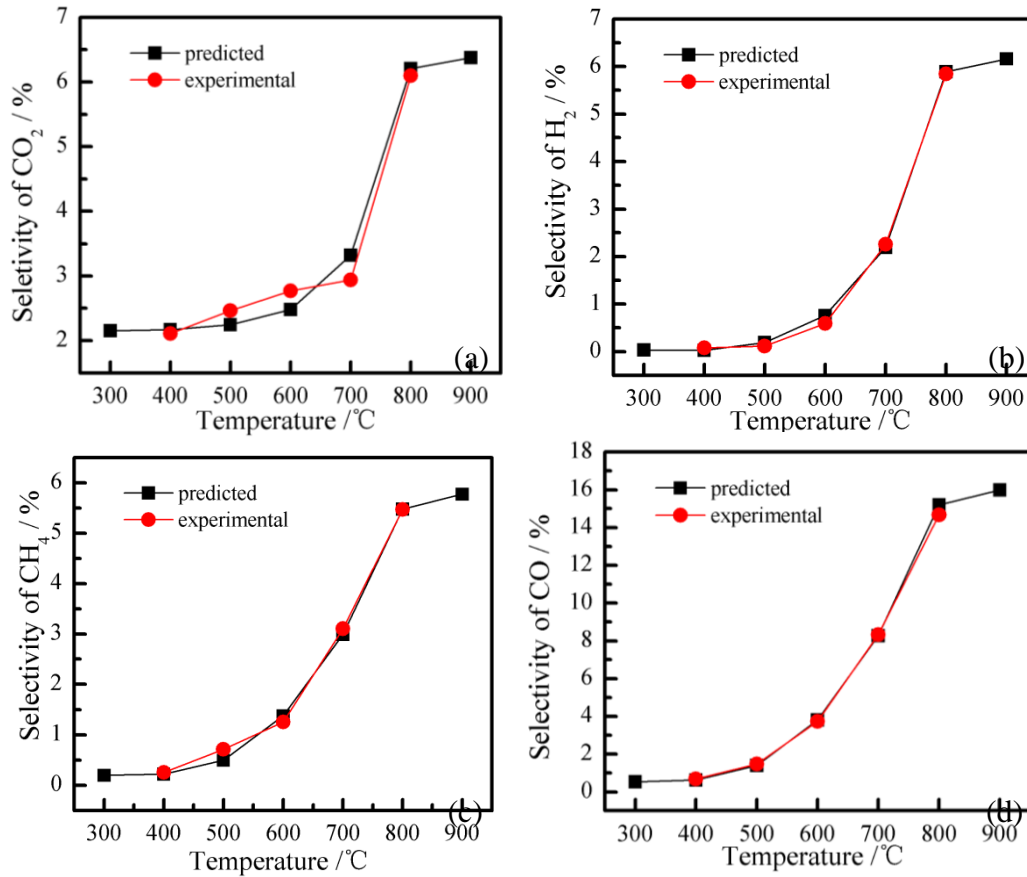
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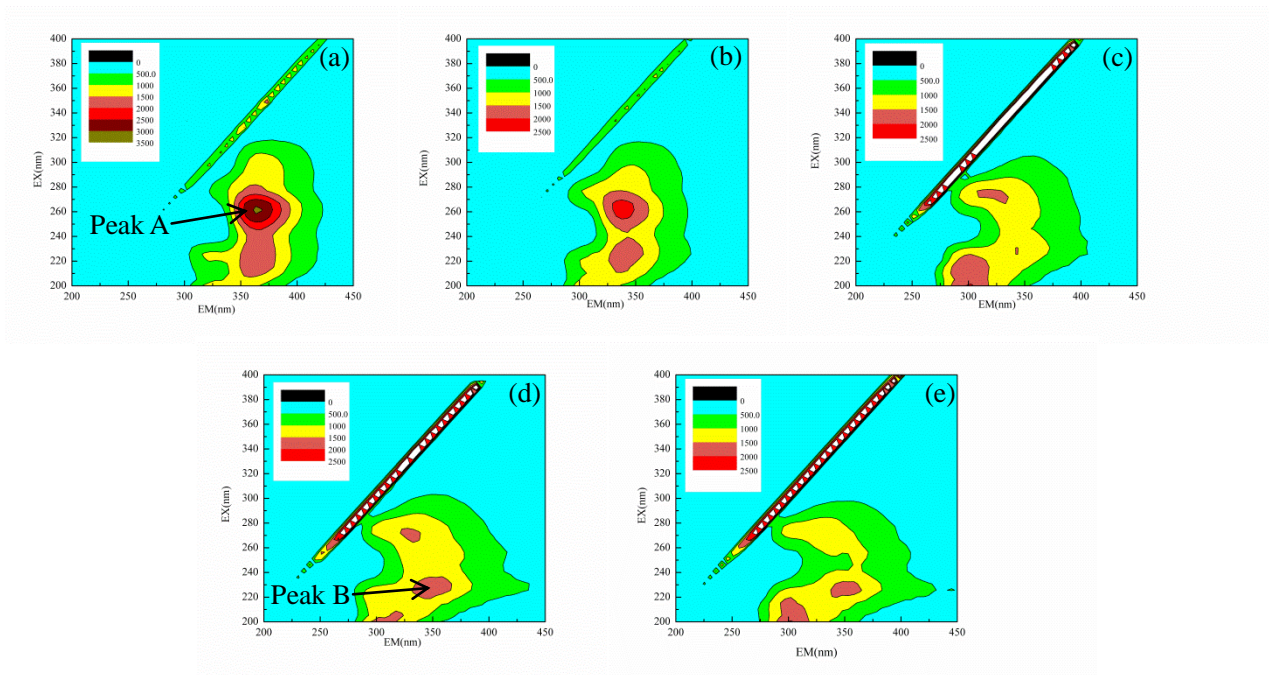
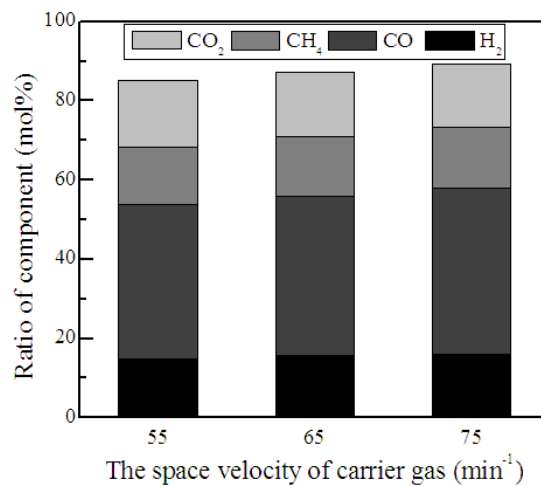


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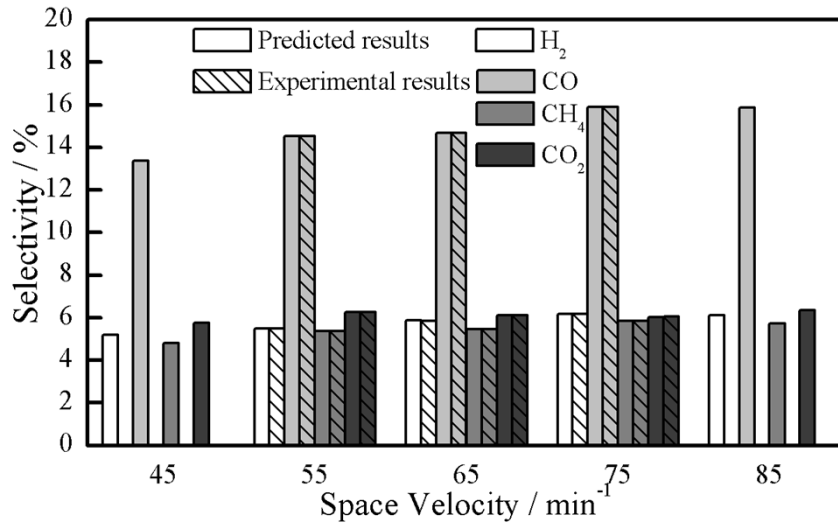
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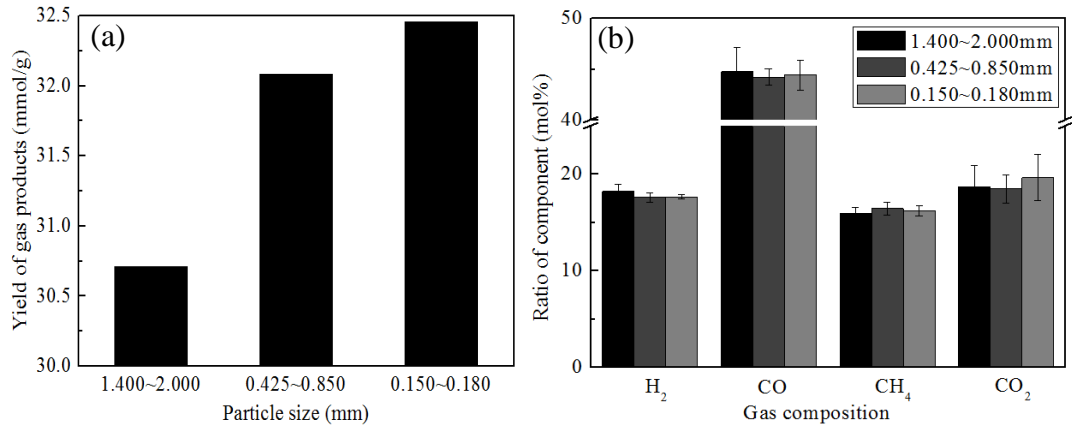
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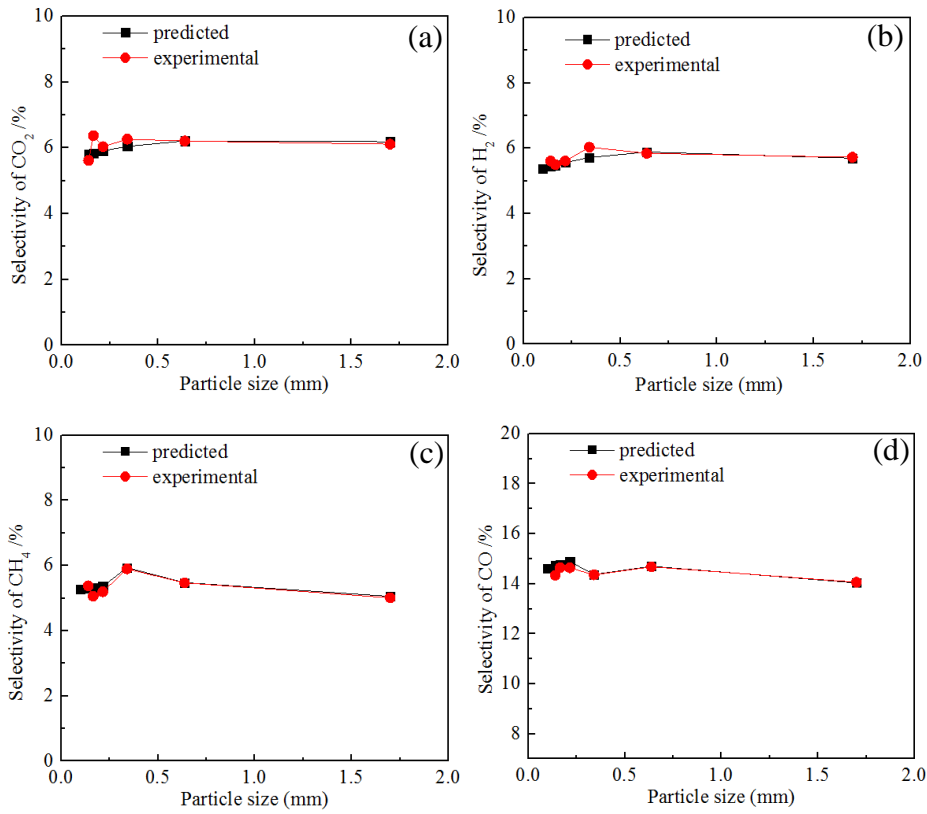
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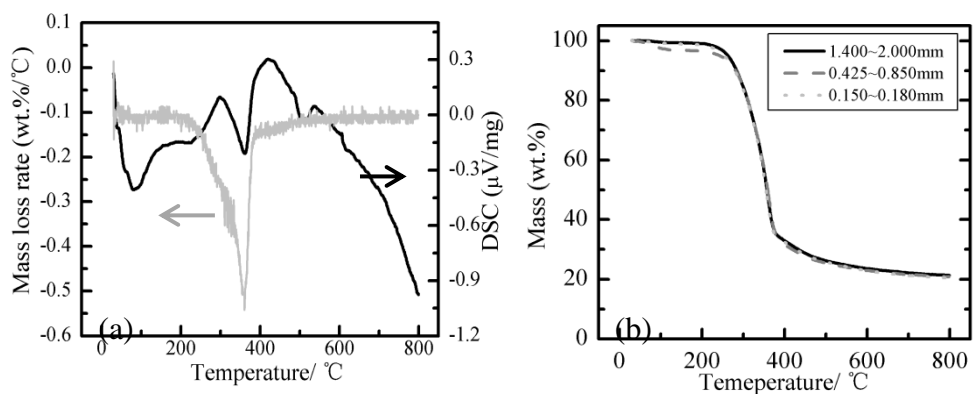
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