

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

Pyrolysis of Rice husk and Corn stalk in Auger Reactor: Part 1. Characterization of Char and Gas at Various Temperatures

(To be submitted to *Energy and Fuels*)

Yang Yu,[†] Yang Yang,[‡] Zhicai Cheng,[†] Paula H. Blanco,[‡] Ronghou Liu[†], A. V.
Bridgwater[‡], and Junmeng Cai,^{*,†}

[†] Biomass Energy Engineering Research Center, Key Laboratory of Urban
Agriculture (South) Ministry of Agriculture, School of Agriculture and Biology,
Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's
Republic of China

[‡] Bioenergy Research Group, European Bioenergy Research Institute (EBRI), Aston
University, Aston Triangle, Birmingham B4 7ET, United Kingdom

Abstract

33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

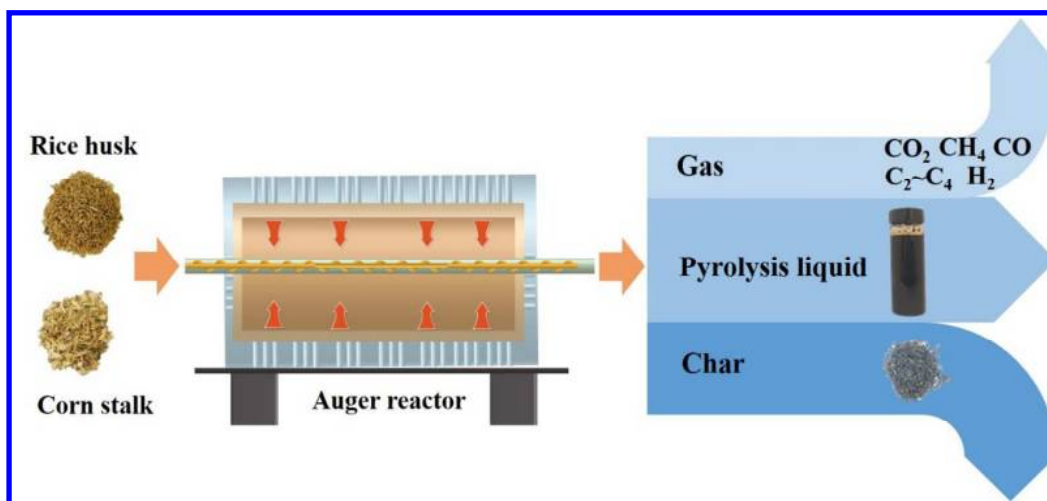
In the series study, rice husk and corn stalk have been pyrolyzed in an auger
pyrolysis reactor at various pyrolysis temperatures of 350, 400, 450, 500, 550 and
600 °C in order to investigate the effect of the pyrolysis temperature on the pyrolysis
performance of the reactor and physicochemical properties of pyrolysis products (this part focus
on the char and gas, the next part focus on the pyrolysis liquid). The results have shown that
the pyrolysis temperature significantly affects the mass yields and properties of the
pyrolysis products. The mass yields of pyrolysis liquid and char are comparable to
those reported for the same feedstocks processed in fluidized bed reactors. With the
increase of the pyrolysis temperature, the pyrolysis liquid yield shows a peak at
500 °C, the char yield decreases while the gas yield increases for both feedstocks. The higher

^{*} **Corresponding author:** Junmeng Cai, Tel.: +86-21-34206624; E-mail:
jmcai@sjtu.edu.cn.

heating value (HHV) and volatile matter content of char increase as the pyrolysis temperature increases from 350 to 600 °C. The gases obtained from the pyrolysis of rice husk and corn stalk mainly contain CO₂, CO, CH₄, H₂ and other light hydrocarbons, the molar fractions of combustible gases increase therefore their HHVs subsequently increase with the increase of the pyrolysis temperature.

Key words: Biomass Pyrolysis; Auger Reactor; Char; Pyrolysis Liquid; Gas

Graphical Abstract



1 Introduction

Nowadays, China is in the period of rapid growth and development and the energy supply cannot meet the demand of energy consumption.^{1,2} Except the import of petroleum from foreign countries, the development of renewable energy including biomass has received more and more attentions. Pyrolysis, the thermal decomposition process occurring in the absence of oxygen, has a great potential in converting biomass into high energy density products: pyrolysis oil, char and pyrolysis gas.³ Pyrolysis is the precursor of combustion and gasification, however pyrolysis has the

1
2
3 advantage of producing a liquid fuel which can be easily stored, transported, and used
4
5 for chemical products as well as heat and power generation.⁴
6

7 The yields and properties of the pyrolysis products vary over several factors
8 including the type of feedstocks, pyrolysis processing conditions, and reactor type.⁵
9 Fast pyrolysis in fluidized bed reactors is a relatively mature technology and it is
10 frequently used in industrial-scale pyrolysis oil production. This process is
11 characterized by very high heating rates ($> 1000 \text{ }^\circ\text{C s}^{-1}$), short pyrolysis vapor
12 residence time ($< 2 \text{ s}$) and rapid condensation rate, thus the process can achieve high
13 pyrolysis liquid yield up to 75 wt.%.⁶ However, this type reactor has limitations such
14 as: (1) large space requirements as reactor vessels with a riser and downer over 10
15 meters high in industry are often required for achieving satisfactory solid fluidization;
16 (2) additional pumping power (thus higher energy costs) is needed to meet the
17 requirement for suspension or circulation of solid fluidizing medium; (3)
18 energy-intensive pre-treatment processes are required because of finely ground
19 feedstock; (4) solid fluidizing medium may be present in solid product resulting in
20 contaminated char product.⁷
21
22
23
24
25
26
27
28
29
30
31
32

33 Different pyrolysis reactor types present different arrangement, are established
34 for different application purposes, and used to process different materials.⁸ Among
35 those configurations, auger reactor pyrolysis is one of the most popular technologies
36 being evaluated nowadays, as does not require large volumes of carrier gases and it
37 can process a wide range of biomass particles.⁹ Due to these advantages, auger
38 reactors were developed and commercialized by Renewable Oil International (RIO,
39 200 kg h^{-1}), and ABRI-TECH Inc. (1 dry ton d^{-1}).¹⁰
40
41
42
43
44
45
46

47 The use of auger reactor for pyrolysis of biomass has been reported in the
48 literature. For example, Puy et al.¹¹ investigated the effect of the temperature, solid
49 residence time, and feedstock flow rate, on the reactor performance and pyrolysis oil
50 properties during the pyrolysis of forest residues in an auger reactor. The results have
51 shown that the greatest yields of pyrolysis liquid and optimum product
52 characterization were obtained at the pyrolysis temperature of $500 \text{ }^\circ\text{C}$, and under a
53
54
55
56
57
58
59
60

1
2
3 solid residence time longer than 2 min. In other work, Thangalazhy-Gopakumar et al.
4
5¹² performed the pyrolysis of pine wood in an auger reactor at different temperatures
6
7 and analyzed the physicochemical properties of pyrolysis oil. The results have shown
8
9 that 475 °C is an appropriate temperature for the production of pyrolysis oil from the
10
11 pyrolysis of pine wood in this particular reaction system. Also the pyrolysis oil
12
13 properties from a continuous auger reactor and a fluidized bed system were compared
14
15 by Ingram et al.,¹³ using wood and bark as feedstocks. The results have shown that
16
17 auger reactor pyrolysis can produce pyrolysis oil comparable to that produced in
18
19 fluidized bed pyrolysis process either in mass yield or chemical composition.
20
21 Bhattacharya et al.¹⁴ studied the co-pyrolysis of pine wood and three plastics at
22
23 different temperatures in a 2 kg h⁻¹ lab scale auger reactor. The obtained pyrolysis
24
25 liquids exhibited higher quality than pine bio-oil. Martínez et al.¹⁵ investigated the
26
27 co-pyrolysis of forestry wastes and waste tyres in a continuous auger reactor and obtained that the
28
29 addition of waste tyres to the biomass blend was beneficial for the quality of the new bio-oils.
30
31 Veses et al.¹⁶ performed the catalytic pyrolysis of forest pine wood in an auger reactor
32
33 using calcium-based catalysts and observed that the addition of low cost calcium
34
35 based catalysts could improve the bio-oil properties.

36
37 The above studies mainly focused on the pyrolysis of woody biomass feedstocks
38
39 in auger reactors and the properties of pyrolysis oil under different circumstances
40
41 including different temperatures, co-pyrolysis with plastics and tyres, and catalytic
42
43 pyrolysis. However, up to now, there are very few researches investigating the effect
44
45 of the pyrolysis temperature and herbaceous biomass on the characteristics of char
46
47 and gas in auger reactors.

48
49 Thus, the main aim of this series papers is to study the effect of the pyrolysis
50
51 temperature on the physicochemical properties of pyrolysis products from the
52
53 pyrolysis of biomass in an auger pyrolysis reactor. This part (Part 1) focuses on char
54
55 and gas, whereas the next part (Part 2) focuses on the study of the pyrolysis liquid.
56
57 The results of this work can be used to check if the thermal energy required for drying
58
59 and pyrolysis reaction can be supplied by gas and char.
60

2 Experimental Section

2.1 Feedstock Preparation

China is the largest agricultural country in the world and is rich in rice husk and corn stalk. According to Ji,¹⁷ there is an annual production of about 40 and 72 million tons of rice husk and corn stalk respectively. Considering this wide availability, both rice husk and corn stalk were chosen as feedstocks for this investigation.

The rice husk and corn stalk samples used in this work were collected from Zhangzhou, Fujian Province and Datong, Shanxi Province in China, respectively. Rice husk sample was processed as received from the farm. The collected corn stalk sample was first ground into about 5 cm particles in a straw crusher with 1250 r min⁻¹ rotating speed. Further size reduction was accomplished by using a cutting mill with a 10 mm screen size. The particle size of the corn stalk sample was reduced to about 1 cm. **Figure 1** shows the corn stalk samples with different sizes and the as-received sample of rice husk. Both samples were dried before the pyrolysis experiments. The samples were spread out on a drying rack for air-drying to a moisture content below 20%. After treatment, the samples were stored at ambient conditions in sealed bags.



Figure 1. Rice husk sample and corn stalk samples with different sizes

The moisture, ash and volatile matter contents of the samples were determined in accordance with the ASTM standards E1756-08,¹⁸ D1755-01,¹⁹ and E872-82,²⁰ respectively.

The ultimate analyses of rice husk and corn stalk were carried out by using a Flash 2000 Organic Elemental Analysis CHON-S Meter (Thermo Fisher Scientific, USA). The oxygen content (dry and ash free basis) was calculated by difference.

The higher heating values (HHVs) of rice husk and corn stalk samples were measured by using an oxygen bomb calorimetry (XRY-1 A+, Shanghai Changji Geological Instrument Co., Ltd, China) in accordance with the ASTM standard D5865-13.²¹

The physicochemical analysis results of both feedstocks are shown in **Table 1**.

Table 1. Proximate and ultimate analysis results of rice husk and corn stalk

	Unit	Rice husk	Corn stalk
<i>Proximate analysis^a</i>			
Moisture	wt. %	16.7	17.6
Ash	wt. %	13.3	8.2
Volatile matter	wt. %	56.0	61.7
Fixed carbon ^b	wt. %	14.0	12.5
<i>Ultimate analysis^c</i>			
C	wt. %	48.78	47.09
H	wt. %	6.59	6.17
N	wt. %	3.73	9.14
S	wt. %	---	0.05
O ^d	wt. %	40.90	37.55
HHV	MJ kg ⁻¹	16.15	15.81

^a wet basis

^b by difference

^c dry ash-free basis

^d by difference

2.2 Auger Pyrolysis System

The pyrolysis experiments were conducted in a 350 g h^{-1} stainless steel bench-scale auger pyrolysis system. This system was designed and constructed at the European Bioenergy Research Institute (EBRI), Aston University, UK. The auger reactor is compact, does not use a heat carrier and operates continuously.

Figure 2 shows the schematic diagram of the auger pyrolysis system. The pyrolysis system consists of the following main components: biomass feeding sub-system, auger reactor sub-system, product recovery sub-system, data acquisition and control sub-system.

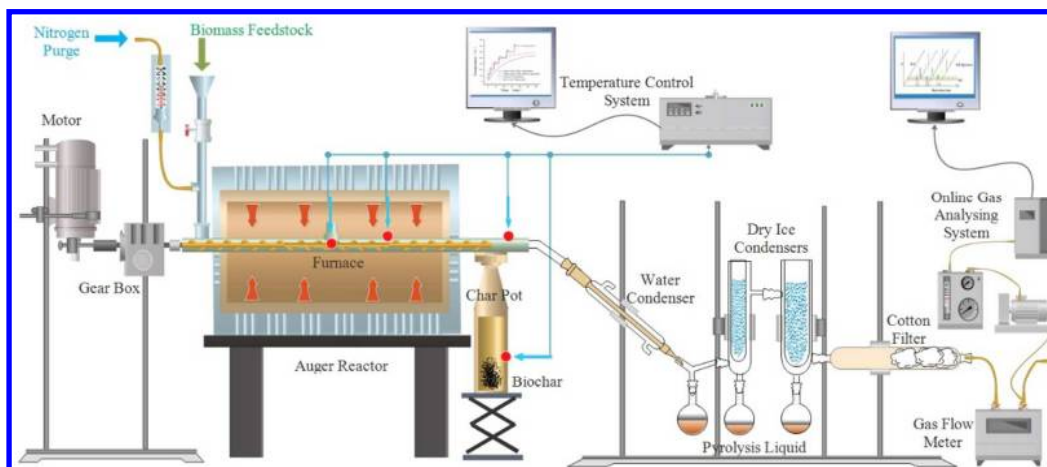


Figure 2. Schematic diagram of auger pyrolysis system

The main component of the biomass feeding sub-system is a simple volumetric screw feeder. The auger reactor system is completely constructed from stainless steel. The reactor kiln is 2.6 cm in diameter and 50 cm in length. A Carbolite VST 12/400 2kW electric furnace is used for providing heat for the pyrolysis reactor. The product recovery sub-system consists of one cool water condenser, two dry ice condensers, and a cotton filter. The data acquisition and control sub-system includes four thermocouples which are arranged at different positions (two of them were placed

1
2
3 inside the auger reactor in order to monitor of the actual pyrolysis temperature, and
4 another two were placed closely outside the wall of screw end and char pot,
5 respectively), online gas chromatography, and gas flow meter.
6
7

8
9 The experiments were performed under six different pyrolysis temperatures (i.e.
10 350, 400, 450, 500, 550 and 600 °C), in order to investigate the effect of temperature
11 on both the product yields and the physicochemical properties of the pyrolysis
12 products (char and gas in Part 1 and pyrolysis liquid in Part 2). For each experiment, a
13 fixed amount of raw material was fed into the auger reactor at a constant feeding rate
14 of 2 g min⁻¹. The reactor was maintained under an inert atmosphere by purging
15 nitrogen before the feedstock is fed into the reactor. The temperature in the reactor
16 was heated to the desired temperature and held for 30 minutes to avoid the
17 temperature gradient inside the reactor. The auger speed applied was 12 rpm, which
18 corresponds to a solid residence time of 60 s. This is longer than the solid residence
19 time in typical fluidized bed reactors.²² However, pyrolysis volatiles move to the
20 condenser within about 5 s. Therefore, the residence time of pyrolysis volatiles in this
21 auger reactor are longer than that in fluidized bed reactors (about 2 s).²³ The samples
22 from the feeding system was then passed to the reactor. The pyrolysis temperature
23 inside the reactor was measured by two thermocouples. The pyrolysis temperature
24 was maintained constant throughout each experiment. All liquids obtained from three
25 condensers were mixed together to measure the total yield of pyrolysis liquid. The
26 char was collected after cooling the reactor to room temperature. The gas produced
27 during pyrolysis was filtered by cotton.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46

47 **2.3 Char analysis**

48 After each pyrolysis experiment, the cooled char was collected and weighted.
49 Then it was placed in a sealed plastic bag for further physicochemical analysis. The
50 collected char samples were dry, and therefore the properties of char samples were
51 presented on a dry basis.
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The ash and volatile matter contents of char was measured in accordance with the ASTM standard D1762 – 84.²⁴ The fixed carbon content of char was calculated by difference.

The ultimate analysis of char was carried out by using a Flash 2000 Organic Elemental Analysis CHON-S Meter (Thermo Fisher Scientific, USA). The oxygen content (dry and ash free basis) was calculated by difference.

The HHV of char was measured in an oxygen bomb calorimeter (XRY-1 A+, Shanghai Changji Geological Instrument Co., Ltd, China) in accordance with the ASTM standard D5865-13.²¹

2.4 Pyrolysis Liquid Yield

All pyrolysis liquid products were collected after each pyrolysis experiment and weighted.

The obtained pyrolysis liquid samples at different pyrolysis temperatures were placed in sealed brown containers and stored at 4 °C for further analysis.

The detailed properties of pyrolysis liquid were presented in Part 2 of this series.

2.5 Gas analysis

The gas released during pyrolysis was analyzed every three minutes by an online gas chromatograph (VARIAN CP-4900, USA). The obtained GC data were processed by means of the software provided by the manufacturer of the online gas chromatography. The chemical composition of gas was obtained by the average of all collected data. The mass yield of gas was calculated by difference considering the yields of pyrolysis liquid and char.

The heating value of gas is contributed by the combustible components (i.e. CO, H₂, CH₄, and some other light hydrocarbons):

$$\text{HHV}_{\text{gas}} = X_{\text{CO}} \cdot \text{HHV}_{\text{CO}} + X_{\text{CH}_4} \cdot \text{HHV}_{\text{CH}_4} + X_{\text{H}_2} \cdot \text{HHV}_{\text{H}_2} + \sum (X_{\text{C}_n\text{H}_m} \cdot \text{HHV}_{\text{C}_n\text{H}_m}) \quad (1)$$

1
2
3 where HHV_{gas} , HHV_{CO} , HHV_{CH_4} , HHV_{H_2} and $HHV_{\text{C}_n\text{H}_m}$ are the heating values
4 of gas, CO, CH₄, H₂, and light hydrocarbon C_nH_m, and X_{CO} , X_{CH_4} , X_{H_2} and
5
6
7
8
9 $X_{\text{C}_n\text{H}_m}$ are the molar fractions of CO, CH₄, H₂, and light hydrocarbon C_nH_m.
10

11 12 13 **3 Results and Discussion**

14
15 The mass yields (on wet feed basis) of pyrolysis products (char, pyrolysis liquid
16 and gas) from the pyrolysis of rice husk and corn stalk at various pyrolysis
17 temperatures are presented in **Figure 3**. From Figure 3 it can be observed that the
18 pyrolysis temperature significantly affects the mass yields of pyrolysis products for
19 both feedstocks. It is also observed that the general char yields from rice husk are
20 higher than those from corn stalk. This is largely due to the fact that there is higher
21 ash content and higher lignin content²⁵ and less volatile matter content in rice husk
22 than in corn stalk. With the increase of the heating temperature, the yield of char
23 decreases (from 46 wt.% at 350 °C to 31 wt.% at 600 °C for rice husk and from 38 wt.%
24 at 350 °C to 27 wt.% at 600 °C for stalk) while the yield of gas increases (from 10 wt.%
25 at 350 °C to 23 wt.% at 600 °C for the pyrolysis of rice husk and from 15 wt.% at
26 350 °C to 26 wt.% at 600 °C for the pyrolysis of corn stalk). The higher temperature
27 can lead to the intensification of secondary reactions in pyrolysis vapors and therefore
28 the production of more gas.²⁶ The yield of pyrolysis liquid shows a peak, 51 wt.% for
29 the pyrolysis of rice husk and 54 wt.% for the pyrolysis of corn stalk, at the pyrolysis
30 temperature of 500 °C. The above results obtained indicate that the auger reactor is
31 able to achieve good results on the yields of pyrolysis liquid and char. For comparison
32 purpose, the mass yields of products obtained from rice husk and corn stalk processed
33 in fluidized bed reactor at 500 °C were presented and taken from the literature.^{27,28}
34 Due to shorter residence time of pyrolysis vapor, fluidized bed reactors produce a
35 little higher pyrolysis liquid yield (54 wt.% for rice husk at 500 °C²⁷ and 61 wt.% for
36 corn stalk at 500 °C²⁸) and a little lower char yield (29 wt.% for rice husk at 500 °C²⁷
37 and 17 wt.% for corn stalk at 500 °C²⁸).
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

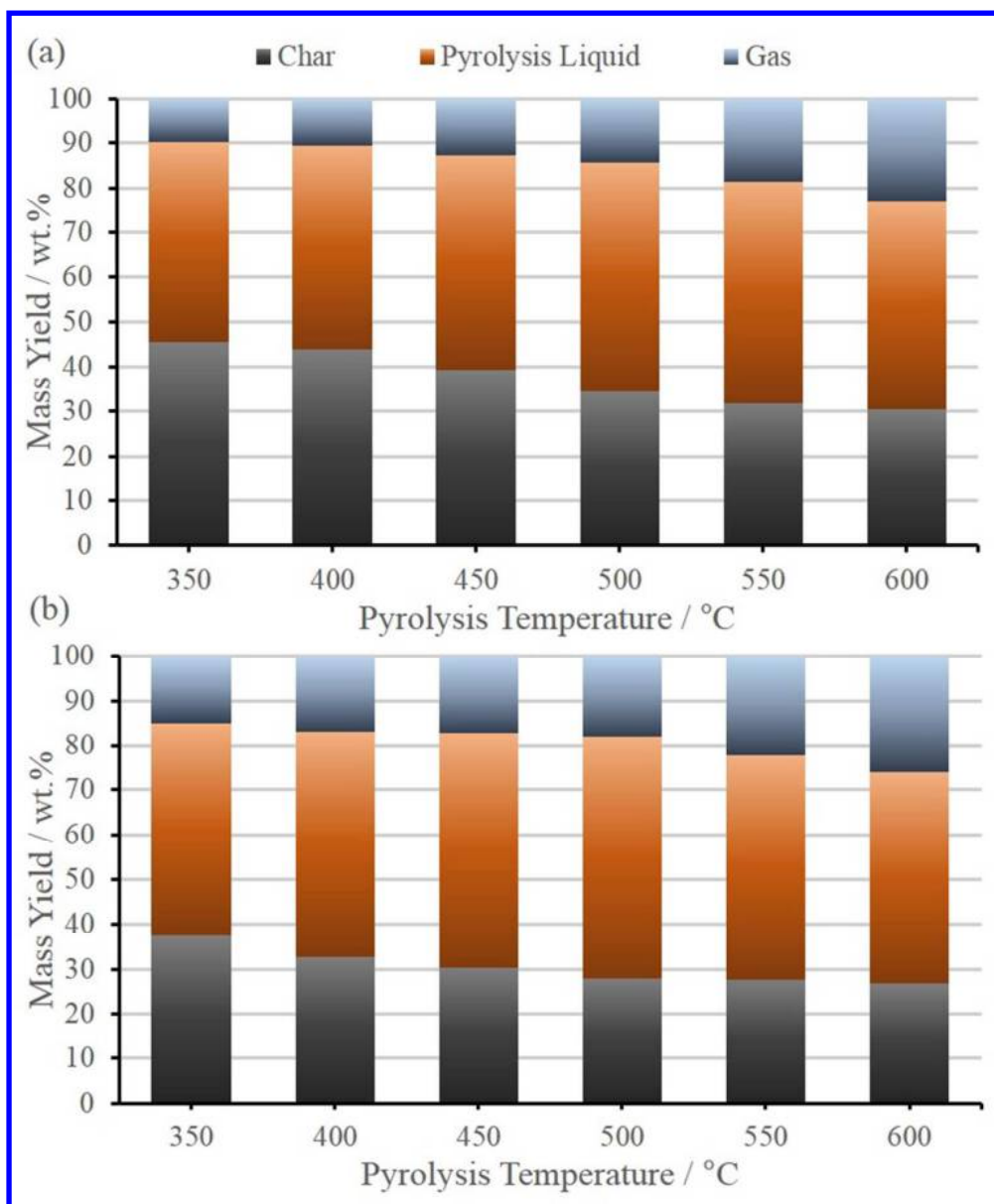


Figure 3. Mass yields of char, pyrolysis liquid and gas from pyrolysis of (a) rice husk (b) corn stalk at various pyrolysis temperatures

Figure 4 shows the proximate analysis results of rice husk and corn stalk and their pyrolysis chars obtained at different pyrolysis temperatures. From Figure 4, it can be observed that (1) the volatile matter content of char is lower than the raw material, (2) the fixed carbon content of char is higher than the raw material, (3) the ash content of char is affected mainly by the raw material, so the ash content of rice husk char is higher than that of corn stalk char, (4) with the increase of pyrolysis temperature (from 350 to 600 °C), the volatile matter content of char decreases (from

33% to 10% for rice husk char, from 37% to 11% for corn stalk char) and the ash content of char increases (from 30% to 44% for rice husk char, from 20% to 33% for corn stalk char) due to the increased thermal degradation rate.

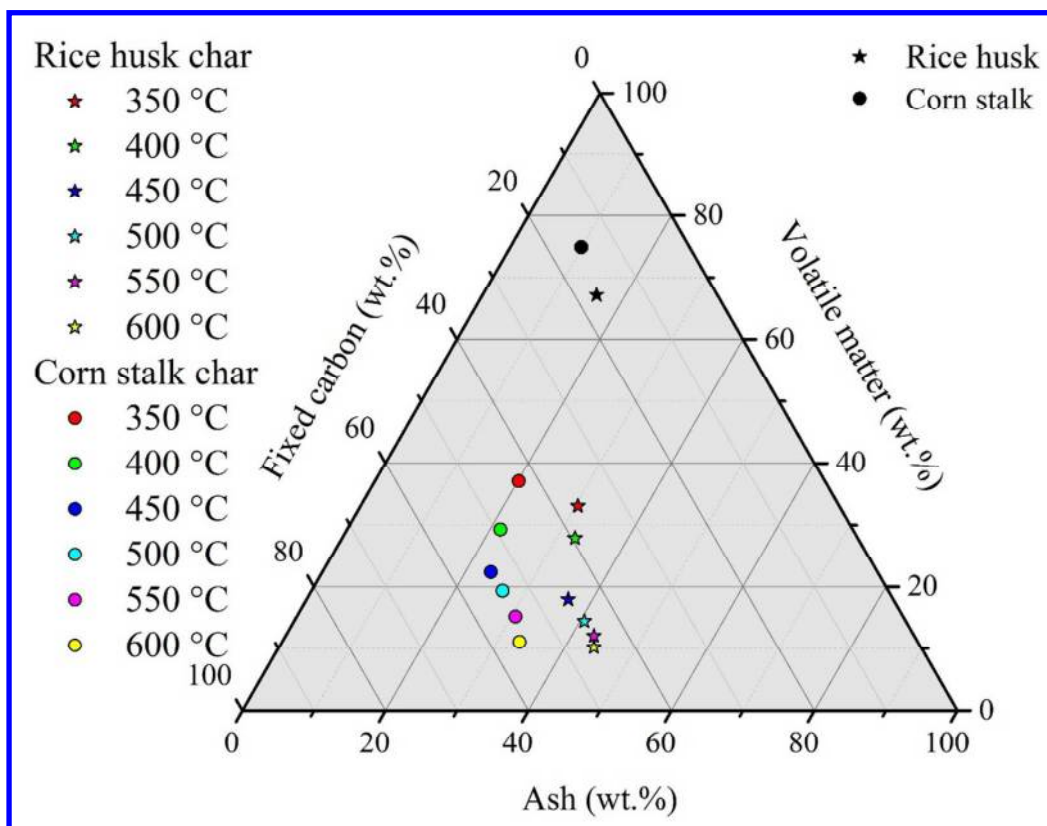


Figure 4. Proximate analysis results of rice husk and corn stalk and their pyrolysis chars at different pyrolysis temperatures (on dry basis)

The atom H:C and O:C ratios of rice husk and corn stalk chars as a function of pyrolysis temperatures are shown in **Figure 5**. From Figure 5, it can be obviously observed that the atom H:C and O:C ratios of char are lower than the raw material, and that both atom H:C and O:C ratios decrease with the increasing of the pyrolysis temperature. The above results indicates that with the increase of the pyrolysis temperature, char loses relatively more oxygen and hydrogen when compared to carbon. This similar result was also reported by Angin.²⁹ This is because the increase in the pyrolysis temperature, intensifies the dehydration and decarboxylation reactions

during the pyrolysis process.³⁰ The decrease in the atom H:C ratio with the increase of the pyrolysis temperature may be also related to the increase in the aromaticity of char, as reported by Xiao et al.³¹

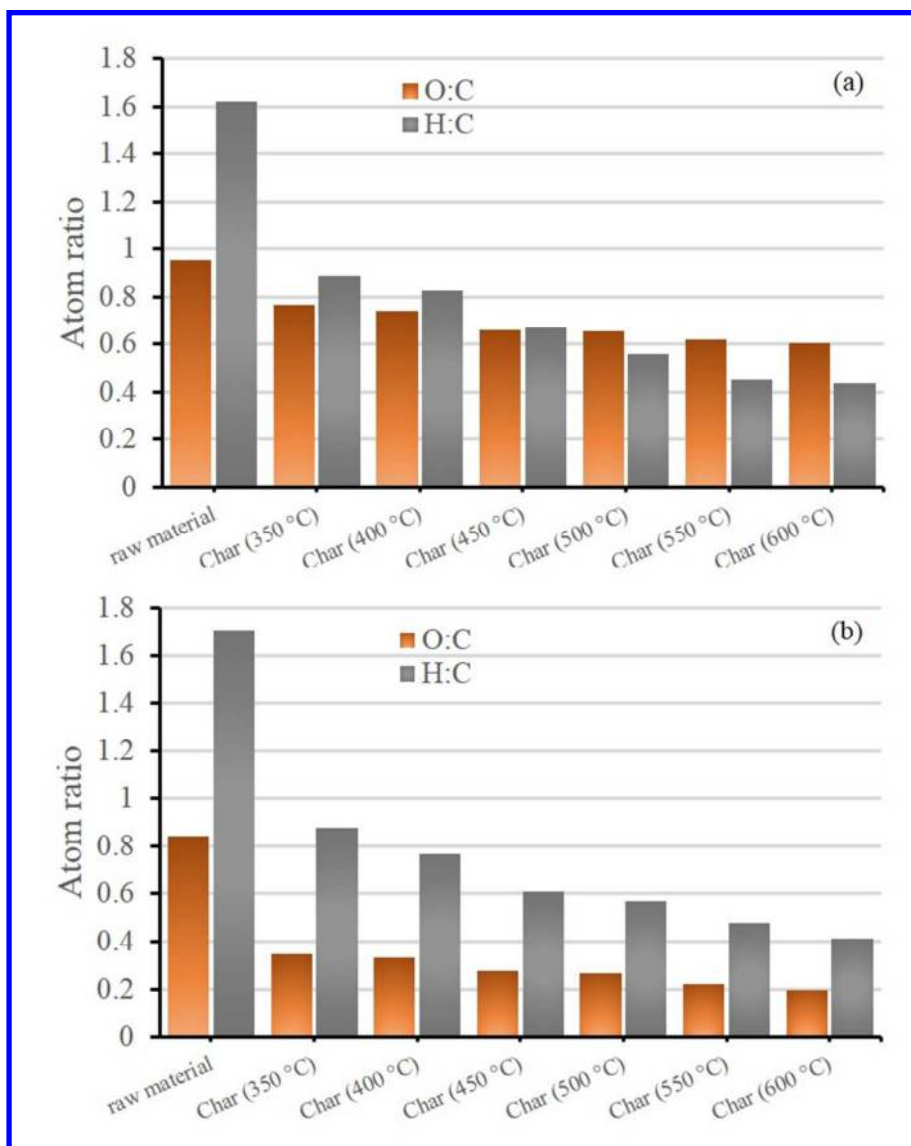


Figure 5. Atom H:C and O:C ratios of chars from pyrolysis of (a) rice husk and (b) corn stalk at various pyrolysis temperatures

Figure 6 shows the HHVs of rice husk and corn stalk as well as those of their chars produced at various pyrolysis temperatures. From Figure 6, it can be observed that (1) the HHV of char is more than that of the raw material, (2) the HHV of corn

stalk char is more than that of rice husk char produced at the same pyrolysis temperature, which may be attributed to the rice husk char contains more ash, (3) with the increase of the pyrolysis temperature from 350 to 600 °C, the HHV of char increases gradually from 17.15 MJ kg⁻¹ to 21.32 MJ kg⁻¹ for rice husk char, and from 19.89 MJ kg⁻¹ to 26.05 MJ kg⁻¹ for corn stalk char.

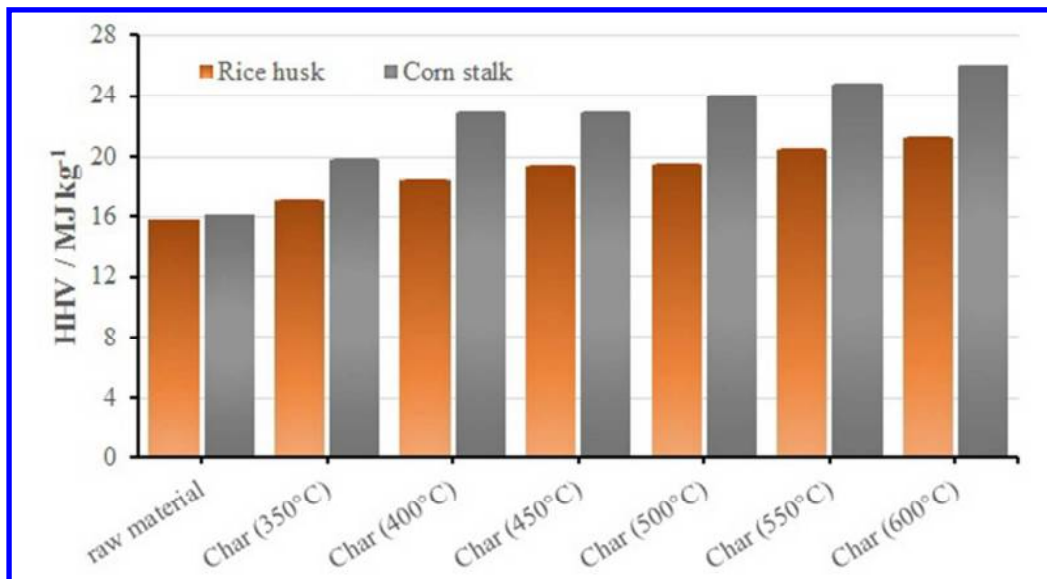


Figure 6. HHVs of chars from pyrolysis of rice husk and corn stalk at various pyrolysis temperatures

The collected online gas chromatography data was processed and the chemical compositions of the gases from the pyrolysis of rice husk and corn stalk were obtained. The results have shown that the gases from the pyrolysis of both feedstocks mainly consist of CO₂, CO, CH₄, H₂ and some other light hydrocarbons (mainly including C₂H₄, C₂H₆, C₃H₆, C₃H₈ and n-C₄H₁₀). The molar fractions of the gas components from the pyrolysis of rice husk and corn stalk at various pyrolysis temperatures are shown in **Figures 7 and Figure 8**, respectively.

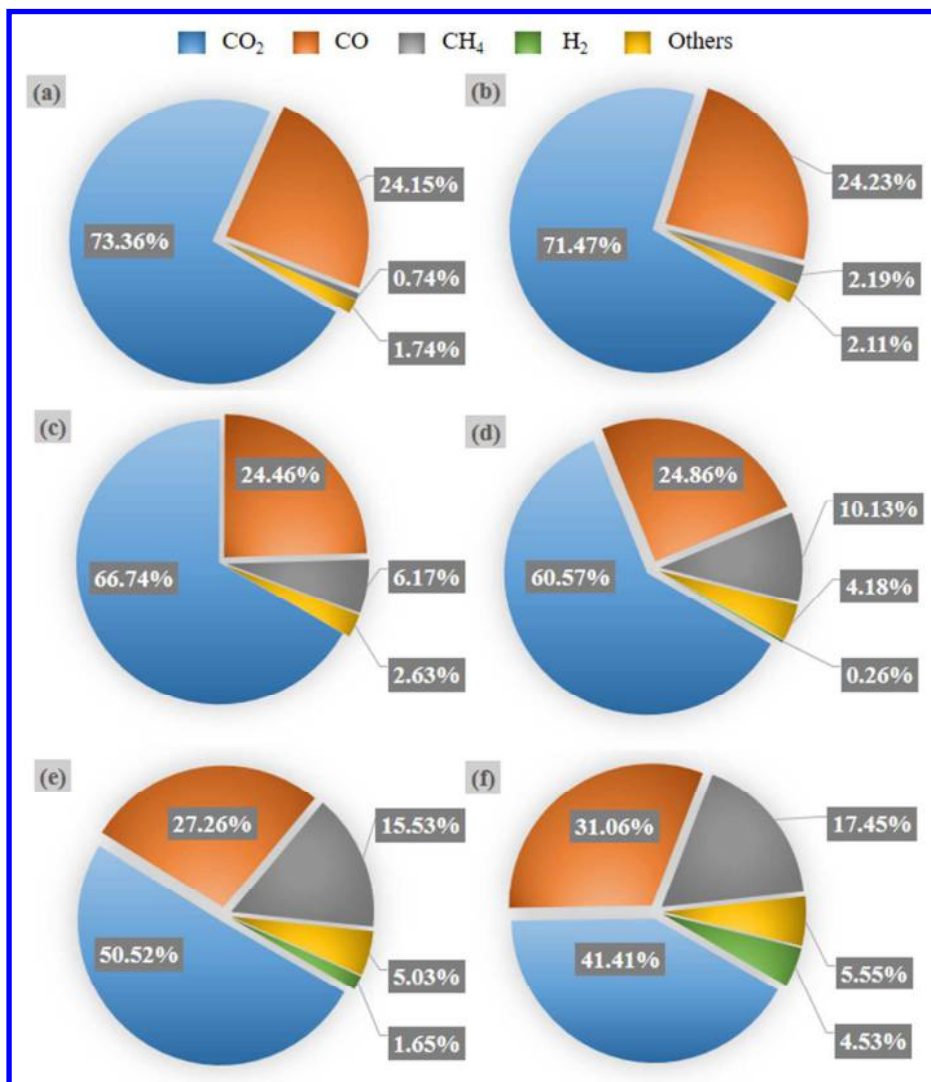


Figure 7. Molar percentages of components of gas from the pyrolysis of rice husk at various temperatures (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C and (f) 600 °C.

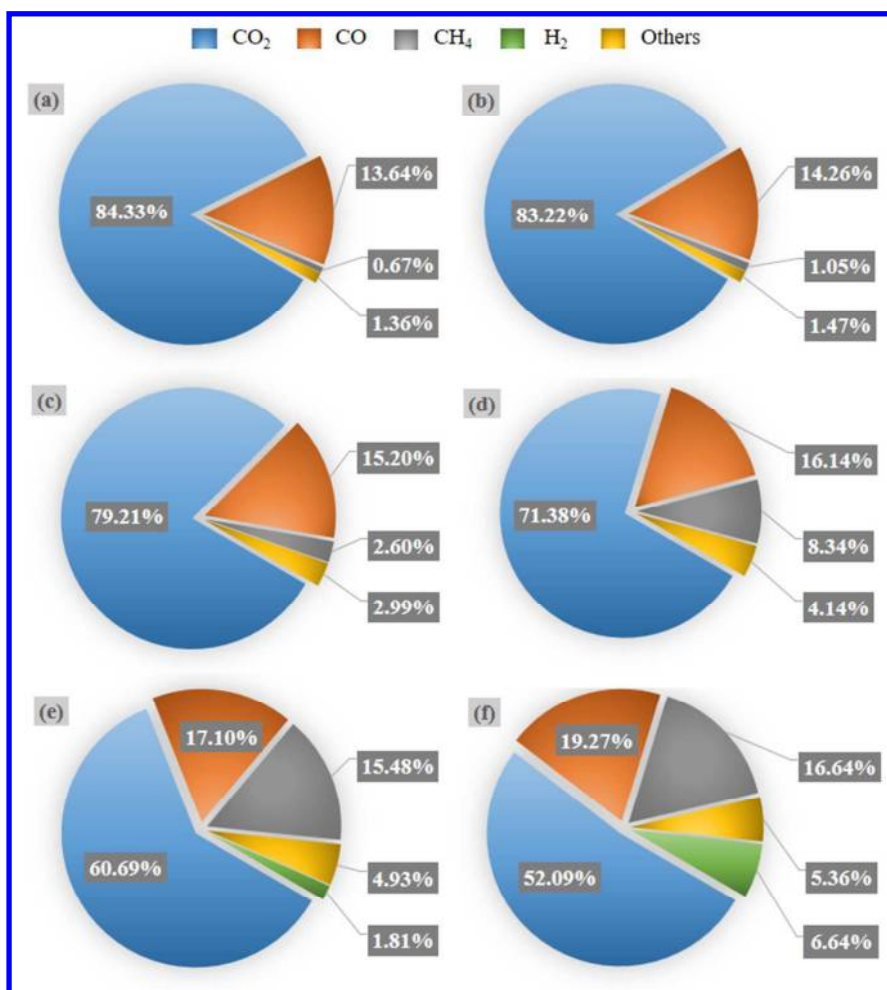


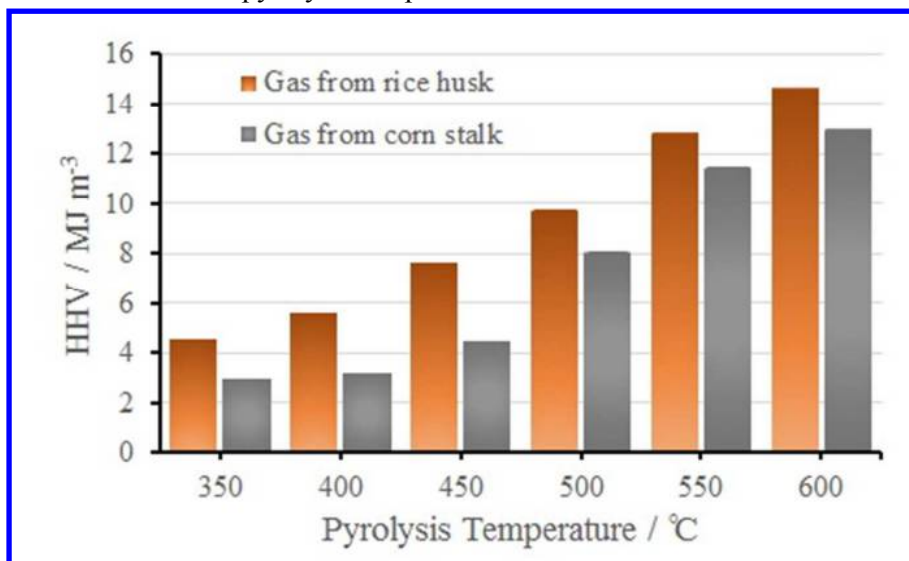
Figure 8. Molar percentages of components of gas from the pyrolysis of corn stalk at various temperatures (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C and (f) 600 °C.

From **Figures 7 and 8**, it can be found that (1) with the increase of the pyrolysis temperature (from 350 to 600 °C), the molar fraction of CO₂ decreases relatively sharply (from 73.4 vol.% to 41.4 vol.% for rice husk gas and from 84.3 vol.% to 52.1 vol.% for corn stalk gas), the molar fraction of CO increases slowly (from 24.2 vol.% to 31.1 vol.% for rice husk gas and from 13.6 vol.% to 19.3 vol.% for corn stalk gas), the molar fraction of CH₄ increase relatively sharply (from 0.7 vol.% to 17.5 vol.% for rice husk gas and from 0.7 vol.% to 16.6 vol.%), (2) H₂ is negligible at low pyrolysis temperatures (< 500 °C for rice husk and < 550 °C for corn stalk) and when the pyrolysis temperature is high enough, the molar fraction of H₂ increases sharply

with the increase of the pyrolysis temperature (from 0.3 vol.% at 500 °C to 4.5 vol.% at 600 °C for rice husk gas and from 1.8 vol.% at 550 °C to 6.6 vol.% at 600 °C for corn stalk gas).

CO₂ is mainly produced from the cracking of partially oxygenated organic compounds (e.g. cellulose and hemicellulose).³² At the auger reactor, the gas residence time is relatively long, the following reactions may occur at high temperatures:³³⁻³⁵ $C + 2H_2O \rightarrow CO_2 + 2H_2$, $C + CO_2 \rightarrow 2CO$, and $3H_2 + CO \rightarrow CH_4 + H_2O$. The releasing of CH₄ and other light hydrocarbons may be due to the reforming and cracking of heavier hydrocarbons in the pyrolysis vapors, which are commonly called as secondary reactions. On the other hand, part of H₂ can also be produced by the cracking of hydrocarbons at higher temperatures, due to the fact that it requires more energy.³⁶

From the above results, it can be concluded that the combustible gas fractions in pyrolysis gas increase gradually with the increase of the pyrolysis temperature. According to Equation (1), the HHVs of gases produced at various temperatures from the pyrolysis of rice husk and corn stalk were calculated and shown in **Figure 9**. From Figure 9 it can be observed that the HHV of the gas increases relatively sharply with the increase of the pyrolysis temperature.



1
2
3 **Figure 9.** HHVs of gases from rice husk and corn stalk at various pyrolysis
4 temperatures
5
6
7
8
9

10 **4 Conclusions**

11
12
13 (1) The pyrolysis of rice husk and corn stalk in an auger pyrolysis reactor have
14 been carried out at six different pyrolysis temperatures (350, 400, 450, 500, 550, and
15 600 °C). The pyrolysis liquid and char yields in the auger reactor are comparable to
16 those reported for the same feedstocks in fluidized bed reactors. The pyrolysis
17 temperature significantly affects the mass yields of the pyrolysis products. Using an
18 auger reactor, rice husk produces more char at the same pyrolysis temperature than
19 corn stalk. With the increase of the pyrolysis temperature (from 350 to 600 °C), the
20 char yield decreases while the gas yield increases. The maximum pyrolysis liquid
21 yield is obtained at the pyrolysis temperature of 500 °C for both feedstocks (51 wt.%
22 of rice husk and 54 wt.% of corn stalk).
23
24
25
26
27
28
29
30
31

32 (2) The proximate analysis results of chars from the pyrolysis rice husk and corn
33 stalk show a decrease in volatile matter and an increase in ash content with the
34 increase of the temperature. Both atom H:C and O:C ratios of char decreases with the
35 increase of the pyrolysis temperature (from 350 to 600 °C) for both feedstocks. The
36 HHV of rice husk char increases from 17.2 MJ kg⁻¹ to 21.3 MJ kg⁻¹ while that of corn
37 stalk char increases from 19.89 MJ kg⁻¹ to 26.05 MJ kg⁻¹ as the pyrolysis temperature
38 increases from 350 to 600 °C.
39
40
41
42
43
44
45

46 (3) The gases from the pyrolysis of rice husk and corn stalk show a similar
47 tendency: the molar fractions of combustible gas including CO, CH₄ and other light
48 hydrocarbons increase gradually while the molar fraction of CO₂ decreases with the
49 increase of the pyrolysis temperature (from 350 to 600 °C). H₂ is detectable at 500 °C
50 and 550 °C for the pyrolysis of rice husk and corn stalk, respectively. When the
51 pyrolysis temperature is high enough, the molar fraction of H₂ increases sharply with
52 the increase of the pyrolysis temperature for the pyrolysis of both feedstocks. The
53
54
55
56
57
58
59
60

1
2
3 HHV of gas increases with the increase of the pyrolysis temperature for both
4 feedstocks.
5
6
7
8
9

10 **Acknowledgements**

11
12
13 Yang Yu, Junmeng Cai, and Zhicai Cheng would like to acknowledge the
14 financial support from the International Research Staff Exchange Scheme (IRSES)
15 ECOFUEL programme (FP7-PEOPLE-2009-IRSES Grant 246772). Yang Yang would
16 like to acknowledge the support from the EPSRC Supergen Bioenergy Challenge
17 “PyroAD” Project (EP/K036793/1). Discussion with Wenfei Cai, Yifeng He,
18 Biaobiao Liu, and Yan Wang, research assistants from School of Agriculture and
19 Biology, Shanghai Jiao Tong University is acknowledged.
20
21
22
23
24
25
26
27
28
29

30 **References**

- 31
32
33 1. Wang, S.; Zhou, D.; Zhou, P.; Wang, Q., CO₂ emissions, energy consumption and
34 economic growth in China: A panel data analysis. *Energy Policy* **2011**, 39, (9),
35 4870-4875.
36
37 2. Ji, L.-Q., A variable asymptote Boltzmann model for modeling and forecasting
38 energy consumption in China. *Energy Sources, Part B: Economics, Planning, and*
39 *Policy* **2016**, 11, (2), 124-129.
40
41 3. Kan, T.; Strezov, V.; Evans, T. J., Lignocellulosic biomass pyrolysis: A review of
42 product properties and effects of pyrolysis parameters. *Renewable and Sustainable*
43 *Energy Reviews* **2016**, 57, 1126-1140.
44
45 4. Czernik, S.; Bridgwater, A., Overview of applications of biomass fast pyrolysis
46 oil. *Energy & Fuels* **2004**, 18, (2), 590-598.
47
48 5. Yaman, S., Pyrolysis of biomass to produce fuels and chemical feedstocks.
49 *Energy Conversion and Management* **2004**, 45, (5), 651-671.
50
51 6. Mohan, D.; Pittman, C. U.; Steele, P. H., Pyrolysis of wood/biomass for bio-oil: a
52
53
54
55
56
57
58
59
60

- critical review. *Energy and Fuels* **2006**, 20, (3), 848-889.
7. Liaw, S.-S.; Wang, Z.; Ndegwa, P.; Frear, C.; Ha, S.; Li, C.-Z.; Garcia-Perez, M., Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas Fir wood. *Journal of Analytical and Applied Pyrolysis* **2012**, 93, 52-62.
8. Bridgwater, A. V.; Meier, D.; Radlein, D., An overview of fast pyrolysis of biomass. *Organic Geochemistry* **1999**, 30, (12), 1479-1493.
9. Bahng, M.-K.; Mukarakate, C.; Robichaud, D. J.; Nimlos, M. R., Current technologies for analysis of biomass thermochemical processing: A review. *Analytica Chimica Acta* **2009**, 651, (2), 117-138.
10. Marshall, A. S. J.; Wu, P. F.; Mun, S. H.; Lalonde, C. In *Commercial application of pyrolysis technology in agriculture*, 2014 Montreal, Quebec Canada July 13–July 16, 2014, 2014; American Society of Agricultural and Biological Engineers: 2014; p 1.
11. Puy, N.; Murillo, R.; Navarro, M. V.; López, J. M.; Rieradevall, J.; Fowler, G.; Aranguren, I.; García, T.; Bartrolí, J.; Mastral, A. M., Valorisation of forestry waste by pyrolysis in an auger reactor. *Waste Management* **2011**, 31, (6), 1339-1349.
12. Thangalazhy-Gopakumar, S.; Adhikari, S.; Ravindran, H.; Gupta, R. B.; Fasina, O.; Tu, M.; Fernando, S. D., Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor. *Bioresource Technology* **2010**, 101, (21), 8389-8395.
13. Ingram, L.; Mohan, D.; Bricka, M.; Steele, P.; Strobel, D.; Crocker, D.; Mitchell, B.; Mohammad, J.; Cantrell, K.; Pittman, C. U., Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils. *Energy & Fuels* **2008**, 22, (1), 614-625.
14. Bhattacharya, P.; Steele, P. H.; Hassan, E. B. M.; Mitchell, B.; Ingram, L.; Pittman Jr, C. U., Wood/plastic copyrolysis in an auger reactor: Chemical and physical analysis of the products. *Fuel* **2009**, 88, (7), 1251-1260.
15. Martínez, J. D.; Veses, A.; Mastral, A. M.; Murillo, R.; Navarro, M. V.; Puy, N.;

- 1
2
3 Artigues, A.; Bartrolí, J.; García, T., Co-pyrolysis of biomass with waste tyres:
4 upgrading of liquid bio-fuel. *Fuel Processing Technology* **2014**, 119, 263-271.
5
6
7 16. Veses, A.; Aznar, M.; Martinez, I.; Martinez, J. D.; Lopez, J. M.; Navarro, M. V.;
8 Callen, M. S.; Murillo, R.; Garcia, T., Catalytic pyrolysis of wood biomass in an auger
9 reactor using calcium-based catalysts. *Bioresour Technol* **2014**, 162, 250-8.
10
11 17. Ji, L.-Q., An assessment of agricultural residue resources for liquid biofuel
12 production in China. *Renewable and Sustainable Energy Reviews* **2015**, 44, 561-575.
13
14 18. ASTM E1756 - 08, Standard Test Method for Determination of Total Solids in
15 Biomass. In ASTM International: West Conshohocken, PA, 2015.
16
17 19. ASTM E17551 - 01, Standard Test Method for Ash in Biomass. In ASTM
18 International: West Conshohocken, PA, 2015.
19
20 20. ASTM E872 - 82, Standard Test Method for Volatile Matter in the Analysis of
21 Particulate Wood Fuels. In ASTM International: West Conshohocken, PA, 2013.
22
23 21. ASTM D5865-13, Standard Test Method for Gross Calorific Value of Coal and
24 Coke. In ASTM International: West Conshohocken, PA, 2013.
25
26 22. Bridgwater, A. V.; Boocock, D. G. B., *Developments in Thermochemical Biomass*
27 *Conversion: Volume 1*. Springer Netherlands: 2013.
28
29 23. Yang, W. C., *Handbook of Fluidization and Fluid-Particle Systems*. Taylor &
30 Francis: 2003.
31
32 24. ASTM D1762 - 84, Standard Test Method for Chemical Analysis of Wood
33 Charcoal. In West Conshohocken, PA: ASTM International, 2013.
34
35 25. Gani, A.; Naruse, I., Effect of cellulose and lignin content on pyrolysis and
36 combustion characteristics for several types of biomass. *Renewable Energy* **2007**, 32,
37 (4), 649-661.
38
39 26. Westerhof, R. J.; Brilman, D. W.; van Swaaij, W. P.; Kersten, S. R., Effect of
40 temperature in fluidized bed fast pyrolysis of biomass: oil quality assessment in test
41 units. *Industrial & Engineering Chemistry Research* **2009**, 49, (3), 1160-1168.
42
43 27. Williams, P. T.; Nugranad, N., Comparison of products from the pyrolysis and
44 catalytic pyrolysis of rice husks. *Energy* **2000**, 25, (6), 493-513.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
28. Mullen, C. A.; Boateng, A. A.; Goldberg, N. M.; Lima, I. M.; Laird, D. A.; Hicks, K. B., Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass and Bioenergy* **2010**, 34, (1), 67-74.
29. Angin, D., Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology* **2013**, 128, 593-597.
30. Jindo, K.; Mizumoto, H.; Sawada, Y.; Sanchez-Monedero, M. A.; Sonoki, T., Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences* **2014**, 11, (23), 6613-6621.
31. Xiao, X.; Chen, Z.; Chen, B., H/C atomic ratio as a smart linkage between pyrolytic temperatures, aromatic clusters and sorption properties of biochars derived from diverse precursory materials. *Scientific Reports* **2016**, 6, 22644.
32. Yang, H.; Yan, R.; Chen, H.; Zheng, C.; Lee, D. H.; Liang, D. T., In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy and Fuels* **2006**, 20, (1), 388-393.
33. Fassinou, W. F.; Van de Steene, L.; Toure, S.; Volle, G.; Girard, P., Pyrolysis of Pinus pinaster in a two-stage gasifier: Influence of processing parameters and thermal cracking of tar. *Fuel Processing Technology* **2009**, 90, (1), 75-90.
34. Morf, P.; Hasler, P.; Nussbaumer, T., Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel* **2002**, 81, (7), 843-853.
35. Domínguez, A.; Fernández, Y.; Fidalgo, B.; Pis, J. J.; Menéndez, J. A., Bio-syngas production with low concentrations of CO₂ and CH₄ from microwave-induced pyrolysis of wet and dried sewage sludge. *Chemosphere* **2008**, 70, (3), 397-403.
36. Bridgwater, A., *Progress in Thermochemical Biomass Conversion*. Wiley: 2008.