Study on the Characteristics of Pyrolysis Gas and Oil from Corn Stalk Pyrolysis

Yang Sun1,2, Sichen Fan1, Tianhua Yang1, Haijun Zhang1, Yongsheng Chen2

1School of Energy and Environment, Shenyang Aerospace University, Liaoning Province key Laboratory of Clean Energy, Shenyang 110136 China
2School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China
*Corresponding author’s e-mail:sunyang@sau.edu.cn

Abstract. In this paper, stem-skins, stem-pith, stem-leaves of corn stalks were separated and pyrolyzed to produce pyrolysis gas and oil on the temperature-controlled slide tube furnace. The gas yield, the gas component and the oil-producing rate of the skins, pith and leaves of corn stalks pyrolysis were studied under the different pyrolysis temperatures and residence time. The results show that the pyrolysis gas yield and the oil production rate were affected significantly by the temperature. With the increase of pyrolysis temperature, the gas yield of the skins, pith and leaves of corn stalks increased, while the oil production rate decreased. The maximum pyrolysis gas yield isthe stem-leaves, the second is the stem-pith, and the stem-skin was the smallest. When the temperature increased from 550 °C to 750 °C, the content of CO and H2 increased with the increase of temperature, while the content of CO2 in pyrolysis gas decreased. The contents of C2H4 and C2H6 did not change obviously, and the total content was about 2%. When the pyrolysis residence time was extended from 10 min to 60 min at 650 °C, the pyrolysis gas production rate of biomass increased gradually. When residence time was 10 min and 60 min, the gas production rate of the stem-skin was 34.32% and 38.92%, respectively. The component of the gaseous product is affected by the residence time, while the effect of oil yield is not significant.

1. Introduction
There is an urgent need to seek clean and renewable energy, due to the shortage of resources and environmental degradation caused by the development and consumption of fossil energy. As a new type of energy, biomass has become a hot spot in the research of the present scholars, due to the advantages of rich total amount, small pollution and continuous and so on.

Pyrolysis is the common means of biomass energy utilization. The biomass pyrolysis is a process of chemical bond breaking of the biomass organic macromolecules under high temperature conditions to produce relatively small molecular gas and tar molecules[1]. The pyrolysis usually occurs at an oxygen-free, temperature of 350-800 °C, and residence time of 0-2 hours. It has been shown that reaction temperature and residence time are important factors affecting biomass pyrolysis. Yang studied the effects of different gasification factors on biomass gasification products characteristics. The results show that the temperature is beneficial to the increase of H2 concentration in gasification gas, but the concentration of CH4 and CO decrease disobviously. The heat value of the gas product is first raised and then decreased during the temperature from 750 °C to 850 °C. In addition, the pyrolysis products were affected by biomass breed and catalyst types [2]. Compared with the
residence time for 10min, the pyrolysis for 30 minutes is more beneficial to generate heavy oil. However, the extended residence time does not accelerate the generation of heavy oil, on the contrary, it will improve the formation of coke and organic acid [3-4]. The higher the temperature, the more complex the composition of heavy oil produced by cellulose pyrolysis, and the lower the yield of biological carbon [5]. Scott found the experiment results that the temperature has an effect on the rapid pyrolysis, at the temperature range of 450-550 °C, the bio-oil yield is the largest, when the temperature exceeds 550 °C, the yield of the bio-oil decrease rapidly, the gas yield is raised, and the solid yield is slightly reduced [6]. Temperature also affects the products compositions and optimum residence time of biomass pyrolysis. With the increase of temperature, the compositions and yields of biomass pyrolysis products increased. At low temperature, there are few kinds of compositions, which is beneficial to the separation and purification of the compositions. Higher than 450 °C, the compositions of biomass pyrolysis products tend to be stable, the yield is only changed, and based on the ideal component, the optimum pyrolysis residence time is shortened at high temperature, but the pyrolysis of biomass is more adequate for a long time low pyrolysis [7-8].

Different products will be produced by pyrolysis the cellulose, hemicellulose and lignin which were main component of agricultural and forestry biomass. The main pyrolysis products of cellulose and hemicellulose were combustible gas, while the main products of lignin pyrolysis are bio-oil and biochar. The three-component pyrolysis theory can be used for the analysis and interpretation of the pyrolysis characteristics of the biomass, and the research shows that the three-component co-pyrolysis has the coupling effect, which can promote the generation of gas and liquid products. The content of the three components of the biomass is different, and influences the distribution and the application of the product. In order to avoid the content error of artificial mixing of three components, meanwhile, the mixing of the cellulose, hemicellulose and lignin can not produce the three-component intertwined effect, and the mixing of three components can not really represent biomass composition. Therefore, different parts of the same biomass are selected as the raw materials in the experiment, the effects of temperature and residence time on the distribution of pyrolysis products were analyzed.

In this paper, the pyrolysis of the skins, pith and leaves of corn stalks were carried out. The effects of temperature and residence time on the pyrolysis of corn straw to oil, gas and gas products were investigated. The aim of the paper is to provide the basic reference data for the comprehensive utilization of the corn stalk.

2. Materials and methods

2.1 Raw materials and chemical reagent

The corn stalk from Shenyang City, Liaoning Province was used for the experiments. Air-dried biomass was artificially separated into the skins, pith and leaves, which were milled with a Retsch SM2000 crusher and then screened. Particle size ranged from 0.83 mm to 1.65 mm. The results of proximate and ultimate analysis of the sample are summarized in Table 1. The content of the cellulose, hemicellulose and lignin of the skins, pith and leaves of corn stalk is measured by the normal-mode cellulose method, as shown in Table 2.

| Table 1 Proximate and ultimate analysis of raw materials |
|---------------------------------------------|
| Proximate analysis W<sub>ad</sub>/% | Ultimate analysis W<sub>ad</sub>/% |
| M<sub>ad</sub> | A<sub>ad</sub> | V<sub>ad</sub> | FC | C | H | O | N | S |
|---|---|---|---|---|---|---|---|---|
| Stem-Skin | 3.39 | 5.96 | 79.96 | 10.69 | 45.31 | 5.83 | 38.55 | 0.97 | 0 |
| Stem-Pith | 3.65 | 2.8 | 91.37 | 2.18 | 45.67 | 6.20 | 40.45 | 1.23 | 0 |
| Stem-Leaf | 3.42 | 5.24 | 81.45 | 9.90 | 44.48 | 6.08 | 39.80 | 0.98 | 0 |

In this experiment, acetone reagent (analytical pure) was used as bio-oil absorbent which was purchased in Shenyang Branch of traditional Chinese Medicine Group.
Table 2 The content of the cellulose, hemicellulose and lignin of cornstalk /%

| Materials      | Cellulose | Hemicellulose | Lignin |
|---------------|-----------|---------------|--------|
| Stem-Skin     | 49.77     | 25.52         | 8.69   |
| Stem-Pith     | 43.65     | 21.46         | 4.91   |
| Stem-Leaf     | 38.49     | 40.41         | 3.40   |

2.2 Experimental facility, methods and gas analysis

As presented in Fig. 1, the experiment was carried out at an atmospheric pressure on a bench-scale slide tube type furnace. The reactor composed of a quartz tube was externally heated by a 3.5 kW electric furnace, the heater reactor can slide from one end to the other. The quartz tube was 2000 mm in height and 50 mm in inner diameter. Three K-type thermocouples were used to measure and control temperature. The furnace wall was covered with a high-temperature insulation blanket.

![Fig 1 Schematic diagram of the experimental set-up used for pyrolysis](image)

1 Nitrogen 2 Slide tube type furnace 3 Hermetically-sealed pyrolysis bottle 4 Pyrolysis oil collection bottle 5 gas bag

A typical experiment run consisted of the following steps. The 5 g raw materials of the corn stalk (the skins, the path and the leaves) are placed in a hermetically-sealed pyrolysis bottles which ones end are sealed, the other end is provided with a pyrolysis products outlet. The air in the pyrolysis bottle is displaced with nitrogen, then put the bottle at one end of the tube furnace without a heater. The pyrolysis bottle is connected to the pyrolysis oil absorption pipe and the gas collecting bag in turn. When the desired temperature was reached, the slide-type tube furnace was slid to one end containing the biomass raw material, and the corn stalk is heated and decomposed. When the temperature of the thermocouple in the reaction bottle reaches the desired temperature, the pyrolysis residence time is started to be counted. At the same time, the liquid and the gas product generated by the pyrolysis were collected, the yield of solid products was measured after pyrolysis residues was cooled.

The produced gas was collected with an aluminum foil gas bag and analyzed offline by gas chromatography (GC). The gas fraction composition, mainly H₂, CO, CH₄, CO₂, and C₂, was identified on a gas chromatograph (model GC-14B, SHIMADZU, Japan) using a thermal conductivity detector (TCD) and double packed columns (TDX-01and GDX-102) with nitrogen and helium as carrier gases. The yield of gas was measured by gravimetric method.

3. Results and discussion

3.1 Effect of temperature on biomass pyrolysis

3.1.1 Effect of temperature on gas yield and bio-oil yield of biomass pyrolysis

Pyrolysis temperature is an important parameter. It influences the reaction rate of the material and simultaneously controls some endothermic or exothermic reversible reactions, therefore, it affects the distribution of the final gas production, improves gas yield conversion, calorific value of pyrolysis gas, and promotes a low tar level in the pyrolysis progress. Studies have shown that, with the increase of the temperature, the yield of the char is gradually reduced, and the non-condensable gas yield is gradually increased, both of which tend to be a certain value, and the yield of the bio-oil has an optimal temperature at the
temperature from 450 to 950 °C. The effect of temperature on gas yield and bio-oil yield of biomass pyrolysis was studied under the conditions of the reaction temperature ranging from 550 °C to 750 °C. The production rate of gas and bio-oil derived from pyrolysis of the stem-skins, stem-pith and stem-leaves of corn stalks is plotted in Fig. 2.

Temperature has a very important effect on pyrolysis gas yield and oil production rate (Fig 2). With increasing temperature, the gas yield of different raw materials such as stem-skin, stem-flesh and stem-leaf increased, while the oil production rate showed a downward trend. The above results are mainly due to the bond breaking reaction of cellulose, hemicellulose and lignin at high temperature to form small molecular hydrocarbons and non-condensable gases. The pyrolysis of three most components of biomass is occurring at different temperatures, e.g. The hemicellulose is at 220 °C -315 °C, the cellulose is at 315°C -400°C, and the lignin is above 400°C. Pyrolysis will produce a large number of volatile substances, with the further increase of temperature, the decomposition reaction increased obviously. The macromolecules generated by the primary pyrolysis reaction will undergo secondary decomposition reaction, condensation reaction, cyclization reaction to form small molecular substances. The higher the temperature, the more intense the secondary reaction, which leads to more gas products, which makes the gas yield increase and makes the bio-oil liquid yield decrease.

As shown in Fig. 2, the gas yield of stem-pith change most obviously in the pyrolysis of the above-mentioned of materials, from 33.82 % wt to 44.54 % wt, which increased by 31.69%. The change of biomass oil yield is not obvious. The gas yield obtained by biomass pyrolysis from large to small is stem-leaves, stem-pith and stem-skins respectively, but the oil production rate was the opposite. The main reason may be that stem-skins contain more cellulose and hemicellulose, and less lignin. This is in good agreement with published literature.

**3.1.2 Effect of temperature on the pyrolysis gas composition.** The effect of temperature on gas composition of biomass pyrolysis was studied under the temperature ranging from 550°C to 750°C. The gas composition is plotted in Fig. 3.

With increasing temperature from 550 °C to 750 °C, H₂ and CH₄ concentration increased from 2.01 and 9.55 vol.% to 17.03 and 14.91 vol.%, respectively, whereas CO and CO₂ decreased from 29.23 and 56.86 vol.% to 25.88 and 39.37 vol.%, no significant changes were detected in the formation of C₂H₆ and C₃H₈ whose concentration was much lower than that of the other permanent gases (Fig. 2a). The changes trend of gas composition derived stem-pith and Stem-leaves pyrolysis are basically the
same (Fig. 2b and Fig. 2c). Similar trends were described in a report by Chen and others [9-10]. It may be because the hemicellulose is the heterogeneous polymers composed of different types of monosaccharides. Cellulose is the macromolecular polysaccharides composed of glucose. High temperature makes hemicellulose and cellulose start to decompose. A large amount of CO and CO$_2$ were formed due to the break of the sugar unit bond. With the increase of temperature, the contents of CH$_4$ and H$_2$ continue to rise. CH$_4$ may come from the demethylation reaction of methyl-containing branches in hemicellulose polymers, or it may be the methyl-containing branches in lignin. When the temperature rises to 550°C, the lignin with rich hydrocarbon-based branched structure decomposed, and CH$_4$ formed greatly, which become the main cause of the increase in the yield of CH$_4$. The effect of temperature on the concentration of CH$_4$ was not noticeable or even a little decline because the increase in the total yield of pyrolysis gases and the yield of H$_2$ and CO increased at high temperature. Carbon dioxide react with coke, which cause the contents of CO$_2$ decrease continuously. The H$_2$ concentration continued to increase with the improvement of temperature, the concentration increased slowly compared to CO$_2$ concentration decline, which mainly due to the dehydrogenation of cellulose, the condensation of aromatic hydrocarbons in lignin and cracking of heavy hydrocarbons. When the temperature further increased, a large number of benzene rings dehydrogenation inside the coke particles formed polycyclic aromatic hydrocarbons, resulting in the generation of H$_2$.

The CO concentration was increased with increasing temperature, which may be because high temperature promotes the breaking of glycosidic bond of cellulose sugar unit to form CO. CO was formed by the breaking of glycoside bonds linked cellulose sugar units under high temperature. The secondary reaction of the semi-coke and dihydroxymethylene group in biomass form a large amount of CO when the temperature is further increased. The contents of C$_2$H$_4$ and C$_2$H$_6$ had no obvious changes with temperature, and the total contents were about 2%.

3.2 Effect of residence time on biomass pyrolysis

3.2.1 Effect of residence time on biomass pyrolysis gas and oil production. The gas yield and oil yield from pyrolysis have a certain relationship with the reaction residence time. The reaction time is too short, the pyrolysis reaction will not be complete. While the reaction time is too long, secondary reactions of thermal decomposition products will be occurred, such as a polymerization reaction or a reduction reaction. In this paper, the relationship between the gas and oil produced by pyrolysis and the reaction residence time was studied under the conditions of the temperature of 650°C, 750°C and materials of stem-skin, stem-pith, and stem-leaf, respectively. The influence of residence time on the gas and oil production rate of biomass pyrolysis is shown in Table 3 and Table 4, respectively.

| Residence time (min) | Gas yield / (wt%) | Bio-oil / (wt%) |
|----------------------|------------------|----------------|
|                      | stem-skin        | stem-pith      | stem-leaf      | stem-skin | stem-pith | stem-leaf | stem-skin | stem-pith | stem-leaf | stem-skin | stem-pith | stem-leaf |
| 10                   | 34.32            | 37.44          | 41.76          | 38.24      | 33.45      | 29.11      |
| 20                   | 36.12            | 39.22          | 44.29          | 37.71      | 33.23      | 28.86      |
| 30                   | 35.45            | 42.52          | 45.22          | 37.66      | 33.12      | 28.21      |
| 60                   | 38.92            | 42.95          | 46.84          | 37.42      | 32.96      | 27.94      |

| Residence time (min) | Gas yield / (wt%) | Bio-oil / (wt%) |
|----------------------|------------------|----------------|
|                      | stem-skin        | stem-pith      | stem-leaf      | stem-skin | stem-pith | stem-leaf | stem-skin | stem-pith | stem-leaf | stem-skin | stem-pith | stem-leaf |
| 10                   | 38.42            | 44.52          | 47.07          | 36.65      | 31.42      | 28.11      |
| 20                   | 38.66            | 44.54          | 47.33          | 36.78      | 31.45      | 28.19      |
| 20                   | 39.20            | 44.69          | 47.69          | 36.91      | 31.38      | 28.08      |
| 60                   | 39.48            | 44.98          | 47.93          | 36.85      | 31.22      | 28.04      |
It can be seen from Tables 3 and Tables 4 that with the extension of residence time from 10 min to 60 min, the gas yield of each biomass material gradually increases, while the change of oil production rate is not obvious. For example, at the temperature of 650°C, the gas yield of stem-skin is 34.32 %, 36.12%, 35.45% and 38.92 % when the residence time is 10 min, 20min, 30 min, and 60 min respectively. This is because, with the extension of the residence time, the pyrolysis reaction is more thorough and more non-condensable pyrolysis gas is generated. It can also be seen in above tables that the reaction of biomass becomes more intense with the increase of temperature, which is conducive to the improvement of gas production rate, but the effect of the residence time on the pyrolysis gas yield is small compared to the temperature effect, meanwhile the results shown that the effect of residence time on pyrolysis products is also related to the temperature.

3.2.2 Effect of residence time on biomass pyrolysis gas composition. In the absence of oxygen, pyrolysis experiments were conducted at 650°C and 750°C to investigate the effect of different residence time on biomass pyrolysis to combustible gas, especially when the residence time varied from 10 min to 60min. The results are shown in Fig. 4.

![Fig 4](image)

**Fig 4** Effect of residence time on biomass pyrolysis gas composition

As shown in Fig. 4, the residence time has a certain effect on the pyrolysis gaseous product. The types of materials effected by residence time are different. As the residence time increased from 10 min to 60 min, the H\(_2\) and CH\(_4\) concentration of Stem-skin pyrolysis gaseous product showed abatement, whereas the content of CO\(_2\) and CO is overall rise trend (Fig 4a). The H\(_2\) and CH\(_4\) concentration of Stem-pith pyrolysis gaseous product was fall first and then rise. The minimum concentration value of H\(_2\) and CH\(_4\) were reached when the residence time was 30 min. whereas the content of CO\(_2\) and CO is first increased and then decreased (Fig 4b). As can be seen from Figs.4c, the residence time is similar to that of the skin and leaf. With the increase of the residence time, the increase of the content of H\(_2\), the CO content is decreased. The different effects of reaction time on the composition of biomass pyrolysis gas may be related to the inconsistency of biomass cellulose and so on composition. The longer the reaction is, the more complete the reaction is, the more the secondary reaction.

4. Conclusions

In this paper, the effects of residence time (reaction time) and temperature on the yield of gas, bio-oil gas and gas components of biomass pyrolysis were investigated. The main results are as follows:

Pyrolysis temperature has an important effect on pyrolysis gas yield, bio-oil yield and gas composition. With the increase of temperature, the gas yield of different parts of corn straw (that is stem-skin, stem-pith, stem-leaf) increased and the oil yield decrease. The gas yield obtained by biomass pyrolysis from large to small was stem-leaf > stem-pith > stem-skins, the gas yield of stem-pith change most obviously in the pyrolysis of the above-mentioned of materials, from 33.82 % wtto 44.54 % wt, which increased by 31.69%. The concentration of CO\(_2\) in pyrolysis gas decreased obviously as the temperature increase. Compared with carbon dioxide, the concentration of hydrogen increases more slowly. Temperature has little effect on methane concentration, the concentration is about 12%, but the absolute mass increases. CO content increased with the increase of temperature, C\(_2\)H\(_4\) and C\(_2\)H\(_6\) did not change obviously, the total content was about 2%.
With the prolongation of residence time, the gas yield of biomass pyrolysis increased gradually, and the change of oil production rate was not obvious. At 650 ℃, the residence time was prolonged from 10 min to 60 min, the gas yield of stem-skin, stem-pith and stem-leaf increased from 34.32% wt, 37.44% wt and 41.76% wt to 38.92% wt, 42.95% wt and 46.84% wt, respectively. The residence time has a certain effect on the concentration of pyrolysis gaseous products, whereas the effect of the residence time on different raw materials was different.

Acknowledgments
The author’s would like to thank the Natural Science Fund of Liaoning Province (2018010810-301) and the National Natural Science Foundation of China (51173160) for financial support on this work.

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