Experimental Study on High Temperature Pyrolysis Characteristics of Biomass Tar in Biomass Gasification-reburning Technology

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Abstract. In order to solve the problem of high-tar content of gasification products in biomass gasification-reburning technology, this thesis proposes an experimental scheme for high temperature thermal cracking of biomass tar, using representative rice hull tar as a sample, and self-designed pyrolysis experiment. On the stage, the reaction temperature of the gasification chamber was measured by a high-temperature thermocouple. At the same time, the biomass tar cracking rate was measured at different temperatures with the thermobalance by appropriately changing pyrolysis temperature, and the Agilent HP5973 GC/MS was employed to analyze the components of pyrolysis products of biomass tar under different temperature conditions. The experimental results show that the total thermal cracking rate of tar increased with the increasing of experimental temperature. In the temperature range of 550°C~655°C, the increasing rate of thermal cracking became slower; when it reached between 655°C and 790°C, the thermal-cracking rate showed a significant growth trend; while entering 790°C~853°C, the growth rate slowed down. The experimental and analytical results reveal the basic laws of high-temperature pyrolysis of biomass tar, and provide a certain technical basis for the industrial production of low-tar and high-quality biomass gas.

1. Introduction

While the global fossil fuel reserves are gradually declining, and the problems of environmental changes or pollution brought by fossil fuels combustion are becoming increasingly prominent, and biomass reburning technology has gradually attracted attention. Biomass mainly refers to agricultural waste such as straw, plant and forestry processing waste, etc. It is a kind of renewable and clean energy. Biomass resource in China is abundant. According to statistics, the annual output of crop straw alone is about 700 million tons, and the annual output of forestry and wood processing waste is about 900 million tons, equivalent to approximately 800 million tons of standard coal [1]. Due to its seasonality, scattered distribution, and low energy density, and high transportation and storage costs, the large-scale application of biomass energy is greatly limited. However, considering the maximization of economic and environmental benefits, the effective use of biomass can alleviate energy tension to a certain extent, and it is still the most popular technology.

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Generally, there are two ways on biomass reburning technology, including direct reburning and reburning with gasification [2]. Direct reburning is realized by the drying and pulverization of biomass as a variety of secondary fuel; reburning with gasification is a way to secondary fuel produced by biomass pyrolysis gasification [3]. The main components of biomass fuel are C, O, low content of N, S, Na, K, etc. It is easy to catch fire because of its high volatile content and low calorific value; its combustion mainly produces CO$_2$, Sox and a little of NO$_x$. While CO$_2$ can be absorbed during plant photosynthesis, biomass burning can achieve zero CO$_2$ emissions from a large cycle. Meanwhile, Na and K can be utilized properly as catalysts to promote the forward reaction progress and promote the efficiency of de-NO; but it can reduce the ash melting point and cause ash to be fouled in heated areas [4].

At present, the high tar content of biomass gasification products is one of the problems that restrict the development of biomass gasification technology. The tar removal of biomass gasification gas is divided into physical method and chemical method. Although tar can be removed effectively with the physical method, it only undergoes a whole of phase change and is not really removed. The tar-containing wastewater must be treated to prevent environmental pollution; and energy contained in tar cannot be utilized, which reduces the gasification efficiency [5]. Chemical methods [6] can be divided into catalytic cracking and pyrolysis. Carlin Myren and other foreign scholars have done a lot of work around tar catalytic cracking. The catalysts are used commonly such as dolomite, silica, and nickel base [7]. In China, Hou Bin [8] et al. in Tsinghua University, Zhou Jingsong [9] et al in Zhejiang University, Lv Pengmei [10] et al. in Guangzhou Energy Institute have done a lot of research in biomass tar catalytic cracking. In terms of high-temperature pyrolysis, YG Pan [11] et al. believe that a certain amount of secondary air is injected under the operating conditions of 830~850°C in the fluidized bed biomass gasification experiment, which is beneficial to eliminating tar in the product gas. For the problem of high biomass tar content, most scholars at home and abroad are devoted to the research of tar catalytic cracking, and there are relatively fewer studies on high temperature pyrolysis of tar. In this thesis, a high temperature secondary pyrolysis experiment is carried out on rice husk tar, and the effects of pyrolysis temperature variation on the pyrolysis ratio of rice hull tar and the composition and content of pyrolysis products are studied. The fixed bed reactor used in this experiment is small in volume, and the gas residence time can be strictly controlled, and the temperature distribution can be adjusted, which is beneficial to increasing the conversion rate and selectivity of chemical reactions, and is beneficial to the high-temperature secondary cracking of tar.

2. Experimental Devices and Methods

2.1 Experimental Materials
Sample: The experimental sample selected from rice husk tar was taken from a farm in Heilongjiang Province. The sample was ventilated and dried at 105°C for 4 hours in a dry box to remove moisture, and sealed and stored in the dark. Its elemental analysis was tested by the commissioned National Coal and Coal Chemical Product Quality Supervision and Inspection Center. The composition analysis results are shown in Table 1.

| Sample          | Water content (%) | Ash content (%) | C$_{ar}$ (%) | H$_{ar}$ (%) | O$_{ar}$ (%) |
|-----------------|-------------------|-----------------|-------------|-------------|-------------|
| Rice husk tar   | 16.50             | 0.06            | 39.8        | 7.3         | 52.9        |

2.2 Experimental bench design
As shown in Figure 1, the self-designed biomass tar high-temperature pyrolysis test-bed is adopted in this experiment, which is mainly composed of gas supply system, combustion system, thermal cracking system, temperature measurement and temperature-control system and gas-cooling system. The main reactor of the thermal cracking system has a total length of 700 mm, and the reaction section
of the bed is a stainless steel tube with an inner diameter of 48 mm, and the length of the reaction section is 600 mm. In order to minimize the heat loss of reactions, the gap between the periphery of the reactor and the protective iron sheet is filled with insulating quartz sand. The manual quantitative one-time feeding is used in the main reactor, and carbon-steel material is used in the upper exhaust pipe, and the other components are made of stainless steel. In order to achieve the purpose on high-temperature secondary pyrolysis of biomass tar, the test a two-stage burner design is adopted, as well as a high-temperature-resistant concrete to insulate the combustion system. The high-temperature flue gas produced by the propane burner provides the heat required for the biomass tar pyrolysis. The uppermost part of the reactor is equipped with a quick-response armored thermocouple to measure the inlet gas temperature, and the reaction temperature is controlled in the range from 400°C to 1300°C. In order to ensure the accuracy of the thermocouple temperature measurement, the working end of the thermocouple should be kept at the center of the reactor, so as to achieve real-time monitoring of the cracking and gasification temperature in the reactor. The gas generated by biomass-tar pyrolysis is condensed by a condenser, and the tap water is used as a condensing medium, and is recycled by a water pump. Non-condensable gas is emptied or sampled for analysis.

2.3 Experimental process
The biomass tar is dosed to the inlet of the pyrolysis reactor and falls to the bottom stainless steel mesh tray. On the one hand the tray acts as a filter during the thermal cracking process, and on the other hand extends the reaction residence time of the tar. During the experiment firstly the combustible gas supplied by the propane cylinder and the air provided by the air compressor is fully burned in the secondary burner, and Laoying3026 Infrared flue gas analyzer is used to monitor the oxygen content in the high temperature flue gas at the tail to ensure that the tar-amount reduction is due to high-temperature pyrolysis instead of combustion; the high-temperature flue gas discharged from the secondary burner enters the thermal-cracking reactor; after the temperature is stabilized, the valve of the bypass line will be opened to make the high-temperature flue gas by the first-stage burner (combustion of propane and air) enter the biomass-tar pyrolysis main-bed (high-temperature flue gas requires a slight excess of fuel to ensure that the biomass tar is pyrolyzed under anoxic conditions); the tar undergoes thermal cracking, and the solid product after thermal cracking remains on the mesh disk, and the gaseous product along with other residues, flows out through the pores of the disk. At the same time, the gaseous products and residues produced by once-cracking are subjected to secondary-cracking by the higher temperature flue gas generated by the secondary burner; and the cracked gas is condensed into liquid through the condenser and collected in the vessel; and the cooled permanent gas flows through the detention barrel and then is vented or collected for sampling analysis. Experiments have confirmed that the tar content in gas after cooling is extremely low and can be ignored. Within the test the system maintained a micro-positive pressure condition to prevent air leakage and ensure the pyrolysis conditions inside the reactor.
3. Experimental contents and results analysis of biomass-tar high-temperature pyrolysis

3.1 Effect of pyrolysis temperature on biomass tar pyrolysis

Biomass-tar pyrolysis is the secondary cracking of biomass tar at higher temperature levels, which is converted into smaller molecular weight gaseous compounds and other products. The temperature required for this method is relatively high, generally reaching 1000~1200°C. The tar is sufficiently decomposed twice at high temperature to make the content extremely low. During the biomass tar pyrolysis, it is heated under an inert atmosphere to cause decomposition of the polymer to produce biomass charcoal, condensable liquid and gaseous products. The pyrolysis conversion reaction of biomass tar is an endothermic reaction. The pyrolysis temperature plays a decisive role in the pyrolysis effect of biomass tar, which not only has a great influence on the pyrolysis ratio of biomass tar, but also directly affects the relevant components of pyrolysis products.

Researchers have added water vapor to reduce tar content and promote tar conversion. The principle is that water vapor reacts with certain components in tar to produce CO, H₂ and CH₄, and reduces the formation of carbon black. The addition of some oxide can be used because the oxide react with some components of the tar, resulting in a tar conversion [12]. In this experiment, the high-temperature flue gas used in the pyrolysis biomass taris provided by propane combustion, and there is no shortage of water vapor, which is also beneficial to the tar content reduction in the tar cracking gas to some extent.

Biomass tar pyrolysis is usually a process of thermal decomposition under an inert atmosphere. It is affected by many aspects, but the reaction temperature plays a decisive role, which directly determines the pyrolysis ratio of biomass tar, that is to say, the degree of biomass tar pyrolysis.

In order to characterize the cleavage effect of biomass tar, this experiment defines the biomass tar pyrolysis ratio as follows:

Pyrolysis ratio of biomass tar represents the percentage of the total mass for the mass of biomass tar pyrolysis during a certain temperature rise, that is:
\[ X_{\text{tar}} = \frac{M_{\text{tar}1} - M_{\text{tar}2}}{M_{\text{tar}1}} \times 100\% = \frac{\Delta m_{\text{tar}}}{M_{\text{tar}1}} \times 100\% \]  

(1)

where \( X_{\text{tar}} \) denotes the pyrolysis ratio of the biomass tar sample (%); \( M_{\text{tar}1} \) and \( M_{\text{tar}2} \) respectively mean the mass of biomass tar before and after cracking (g); \( \Delta m_{\text{tar}} \) is the mass reduction of the biomass tar sample after undergoing a certain temperature-rise process with \( \Delta m_{\text{tar}} = M_{\text{tar}1} - M_{\text{tar}2} \) (g).

Experiments have proved that acetone has good solubility and high solubility for tar. The condenser tube can be washed with acetone. The mass difference before and after the acetone rinsing is the mass of the biomass tar pyrolysis product. And make sure to recover all solvents as much as possible to reduce systematic errors. Thus, the pyrolysis ratio is calculated as shown in Table 2.

| primary/secondary pyrolysis temperature \(^{\circ}\text{C}\) | mass of tar sample before pyrolysis (g) | mass of tar sample after pyrolysis (g) | Pyrolysis mass of tar samples (g) | Pyrolysis ratio of tar samples (%) | Condenser inlet/outlet flue gas temperature \(^{\circ}\text{C}\) |
|-------------------------------------------------|----------------------------------|-----------------------------------|-------------------------------|-----------------------------------|----------------------------------|
| 694/708                                         | 31.746                           | 7.395                             | 24.351                        | 76.71                             | 280/31                           |
| 500/790                                         | 24.397                           | 4.138                             | 20.259                        | 83.04                             | 470/41                           |
| 660/924                                         | 23.985                           | 1.970                             | 22.015                        | 91.79                             | 483/43                           |
| 715/1009                                        | 24.841                           | 1.726                             | 23.115                        | 93.05                             | 541/46                           |
| 715/1100                                        | 27.536                           | 1.537                             | 25.999                        | 94.42                             | 644/50                           |
| 678/1203                                        | 27.272                           | 0.836                             | 26.436                        | 96.93                             | 800/71                           |

Experimental results are analyzed as follows:

1) Figure 2 shows the variation of rice husk tar with pyrolysis temperature under an inert atmosphere. It can be seen that under the pyrolysis condition, \( X_{\text{tar}} \) grows faster than the pyrolysis temperature increasing, within the primary pyrolysis temperature range of 500~715\(^{\circ}\text{C}\) and the secondary pyrolysis temperature range of 708~1203\(^{\circ}\text{C}\), and reaches up to over 96\% at the primary/secondary pyrolysis temperature of 678\(^{\circ}\text{C}/1203\(^{\circ}\text{C}\). The analysis of reasons is that the secondary pyrolysis reaction of the tar in the experimental system is aggravated by the increase of the pyrolysis temperature, and some tar components will be further converted into gaseous light hydrocarbons or liquid products or other small molecules or charcoal etc by demethylation, intramolecular bridges and hydrogen bond cleavage and so on, causing an overall reduction of tar content in the pyrolysis gas. By contrast, it is explained that the proper increase of the temperature level during the tar pyrolysis contributes to the deepening of the pyrolysis reaction of biomass tar, as well as the decrease of the tar content in pyrolysis gas products. Pyrolysis at temperatures above 1200\(^{\circ}\text{C}\) has not been studied due to experimental conditions, but it is foreseeable that the trend of further increase with the increasing of pyrolysis temperature will gradually become flat.
2) In the experimental conditions, $X_{\text{tar}}$ can reach up to 96.93% and increase with the increasing of the pyrolysis temperature. As can be seen from table 2, the pyrolysis ratio of the tar sample increased from 76.71% to 91.79% with the primary pyrolysis temperature approaching 700°C and the secondary pyrolysis temperature increasing from 708°C to 924°C. The pyrolysis ratio of the tar sample after 924°C grows with temperature rise and slows down. This shows that high-temperature secondary pyrolysis has a significant effect on biomass tar pyrolysis, and it is very difficult to attempt to achieve the same pyrolysis ratio variation under high temperature compared with lower temperatures.

3) There must be components which are quite difficult to pyrolyze in the remaining pyrolysis products, so the substances which are continuously increasing as the pyrolysis temperature rise are components which are more difficult to pyrolyze in the GC-MS analysis.

4) When the pyrolysis temperature is in the range of 600~700°C, and the secondary pyrolysis temperature increases, the tail flue discharges rapidly a large amount of non-condensable gas, which reflects the pyrolysis rate is relatively high under the temperature conditions.

5) Considering that some of biomass tar pyrolysis products may be carried by the flue gas into the detention tank to be decelerated and not collected by the condenser, the residue in the detention tank needs to be collected after each experiment. There is mainly water, in addition to a small amount of impurities; the mass of impurities obtained with filter paper, corresponding to the secondary pyrolysis temperatures from high to low, is 0.203g, 0.239g, 0.313g, 0.475g, 0.513g, and 0.561g. Even if the impurities are all pyrolysis products, their mass is much smaller than the total amount, and so it can be ignored.
3.2 GC-MS Analysis of High Temperature Pyrolysis of Biomass Tar

Instrument: American Agilent HP5973GC/MS GC/MS.

Chromatographic conditions: HP-5 trace analysis column is used with the capillary column of 30m ×0.25mm×0.25μm; carrier gas is helium of high purity, and its gas flow is 1.0mL/min, and its nominal initial pressure is 7.89psi, and its average flow rate is 36cm/s, and the split ratio is 5:1; the column temperature (initial temperature) is 55℃, and the equilibrium time is 0.5min and it rises to 300℃ at the rate of 10℃/min and stay 22 minutes; the inlet temperature is 320℃.

Mass spectrometry conditions: ionization source is EI, and electron bombardment energy is 70eV, and mass range m/z is 15-650amu, and scanning time is 3min, and mass scanning mode is SCAN.

These small molecular products are carried into the column by carrier gas (usually ruthenium) for separation, and then enter the mass spectrometry system; the structure identification of the cleavage products is carried out, and finally the pyrolysis components of the biomass tar are analyzed. Analysis of the cleavage products can characterize the pyrolysis of one kind of material.
Figure 7. Total ion chromatogram of tar pyrolysis at the pyrolysis temperature of 715/1100℃.

Figure 8. Total ion chromatogram of tar pyrolysis at the pyrolysis temperature of 678/1203℃.

Figure 3 shows the total ion chromatogram of the pyrolysis of rice husk tar at the pyrolysis temperature of 694°C/708℃. Figures 4, 5, 6, 7 and 8 are respectively the total ion chromatograms of tar pyrolysis at 500°C/790°C, 660°C/924℃, 715°C/1009℃, 715°C/1100℃ and 678°C/1203℃. The main components and relative contents of biomass tar pyrolysis products under different primary/secondary pyrolysis temperature combinations are shown in Tables 3 to 7. Summarily the biomass tar is gradually cracked as the reaction temperature rises, and the types of pyrolysis product gradually increase, and the types of pyrolysis products decrease when it rises to 1300℃. The main products of high-temperature secondary pyrolysis of biomass tar are naphthalene, phenanthrene, anthracene, anthracene, anthracene, dibenzofuran, fluoranthene, biphenyl, biphenylene and its derivatives. And with the increasing of pyrolysis temperature the total contents of main cleavage products of tar showed an increasing trend; the contents of several main components such as lanthanum, phenanthrene, anthracene, fluoranthene and their derivatives increased significantly with the increasing of pyrolysis temperature; the increase amplitudes were 19.540%, 17.792%, 20.389% and 13.518% respectively. The product components whose contents are increasing are mainly aromatic organic compounds and polycyclic aromatic hydrocarbons. The analysis of reasons is that: on the one hand, some components in the tar are converted into aromatic organic compounds or polycyclic aromatic hydrocarbons under high temperature conditions; on the other hand, because the aromatic group has a lower reaction rate than other groups, it is expressed as the content of the aromatic has shown an increasing trend compared with other ethnic groups and its final increase amplitude was higher than the others. This further demonstrates that as the pyrolysis proceeds, the treatment of the tar pyrolysis products will become more and more difficult.

Sample analysis results: After instrumental analysis the total ion chromatograms can be obtained. According to them, the relative contents of main compounds that can be identified are listed below:

Table 3. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 694°C/708℃.

| Serial Number | Residence Time (min) | Name                        | Molecular Formula | Molecular Weight | Relative Content (%) |
|---------------|----------------------|-----------------------------|-------------------|------------------|----------------------|
| 1             | 9.173                | Phenol, 4-ethyl-            | C₈H₁₀O           | 122              | 1.033                |
| 2             | 10.811               | 4-Hydroxy-3-methylacetophenone | C₉H₁₀O₂        | 150              | 1.182                |
| 3             | 11.320               | Phenol, 2-methoxy-4-propyl- | C₁₀H₁₂O₂       | 164              | 1.213                |
| 4             | 11.920               | Naphthalene, 2, 3-dimethyl-  | C₁₂H₁₂        | 156              | 1.374                |
The phenolic materials present at the pyrolysis temperature combination of 694 °C/708 °C is absent at higher temperatures, indicating that the reaction temperature is increased, the secondary pyrolysis of the tar is enhanced, and the intramolecular bridges of tar components are broken. The polycyclic substance is subjected to a ring-opening reaction by heat and is converted into monocyclic substances.

Table 4. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 500 °C/790 °C.
| Serial Number | Residence Time (min) | Name | Molecular Formula | Molecular Weight | Relative Content (%) |
|---------------|----------------------|------|-------------------|------------------|----------------------|
| 1 | 9.400 | Naphthalene | C_{10}H_{8} | 128 | 2.332 |
| 2 | 11.028 | Naphthalene, 2-methyl- | C_{11}H_{10} | 142 | 3.412 |
| 3 | 11.268 | Naphthalene, 1-methyl- | C_{11}H_{10} | 142 | 3.645 |
| 4 | 12.189 | Biphenyl | C_{12}H_{10} | 154 | 1.915 |
| 5 | 12.714 | Naphthalene, 1, 6-dimethyl- | C_{12}H_{12} | 156 | 1.212 |
| 6 | 12.755 | Naphthalene, 2, 6-dimethyl- | C_{12}H_{12} | 156 | 1.365 |
| 7 | 13.107 | Biphenylene 1- | C_{12}H_{6} | 152 | 8.688 |
| 8 | 13.544 | Isopropenynaphthalene | C_{13}H_{12} | 168 | 2.009 |
| 9 | 13.942 | Dibenzo[b]furan | C_{12}H_{8}O | 168 | 4.209 |
| 10 | 14.522 | L-Valine, N-[(9H-fluoren-9-ylmethoxy)carbonyl]- | C_{20}H_{21}NO_{4} | 339 | 1.277 |
| 11 | 14.737 | Fluorene | C_{13}H_{10} | 166 | 6.872 |
| 12 | 14.985 | 1H-Phenalene | C_{13}H_{10} | 166 | 1.735 |
| 13 | 15.178 | Dibenzo[b]furan, 4-methyl- | C_{13}H_{10}O | 182 | 2.181 |
| 14 | 15.338 | 3-(2-Naphthyl) acrylaldehyde | C_{13}H_{10}O | 182 | 1.568 |
| 15 | 16.058 | 9H-Fluorene, 1-methyl- | C_{14}H_{12} | 180 | 1.849 |
| 16 | 16.256 | 1-Heptene, 2-isohexyl-6-methyl- | C_{14}H_{28} | 196 | 4.716 |
| 17 | 16.508 | 1, 1'-Biphenyl, 4-ethenyl- | C_{14}H_{12} | 180 | 1.802 |

Table 5. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 660°C/924°C.
Table 6. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 715°C/1009°C.

| Serial Number | Residence Time (min) | Name                                      | Molecular Formula | Molecular Weight | Relative Content (%) |
|---------------|----------------------|-------------------------------------------|-------------------|------------------|----------------------|
| 1             | 11.038               | Naphthalene, 1-methyl-                    | C_{11}H_{10}       | 142              | 5.989                |
| 2             | 11.274               | Naphthalene, 2-methyl-                    | C_{11}H_{10}       | 142              | 6.996                |
| 3             | 12.198               | Biphenyl                                  | C_{12}H_{10}       | 154              | 4.696                |
| 4             | 13.112               | Biphenylene 1-                           | C_{12}H_{6}        | 152              | 13.042               |
| 5             | 13.551               | Isopropenynaphthalene                     | C_{13}H_{12}       | 168              | 3.751                |
| 6             | 13.949               | Dibenzofuran                              | C_{12}H_{6}O       | 168              | 8.744                |
| 7             | 14.742               | Fluorene                                  | C_{13}H_{10}       | 166              | 12.135               |
| 8             | 15.186               | Dibenzofuran, 4-methyl-                   | C_{13}H_{10}O      | 182              | 2.476                |
| 9             | 16.953               | Phenanthrene                              | C_{14}H_{10}       | 178              | 18.783               |
| 10            | 17.065               | Anthracene                                | C_{14}H_{10}       | 178              | 6.340                |
| 11            | 18.284               | Pentadecanoic acid, 14-methyl-, methylester| C_{15}H_{3}O_{2}   | 339              | 3.908                |
| 12            | 19.755               | Fluoranthene                              | C_{16}H_{10}       | 202              | 6.041                |
| 13            | 14.985               | Pyrene                                    | C_{16}H_{10}       | 202              | 7.098                |

The contents of naphthalene, biphenyl, biphenylene, dibenzofuran and their derivatives have all risen first and fallen later; and the contents of naphthalene and its derivatives reached maximum at the pyrolysis temperature of 500°C/790°C; and the contents of biphenyl, biphenylene and dibenzofuran reached maximum at the combination of pyrolysis temperature of 715°C/1009°C and then decreased rapidly. This is indicated that the high temperature above 1000°C is not conducive to the presence of...
these compounds. The reason for this may be that the substances containing -OH, C=O and C≡O are cracked due to their thermal instability under high temperature conditions; meanwhile, the side rings of these materials are easy to break under high temperature conditions to form other substances, resulting in a sudden content increase of naphthalene, biphenyl, biphenylene, dibenzofuran and its derivatives. Substances existing at lower temperatures such as Pyridine, 4-(2-(pyridyl-4) ethenyl)-, trans-, have N element and heterocyclic compounds containing an element such as N or S are also thermally unstable, so they are liable to be broken when the temperature is further increased.

Table 7. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 715°C/1100°C.

| Serial Number | Residence Time (min) | Name                      | Molecular Formula | Molecular Weight | Relative Content (%) |
|---------------|----------------------|---------------------------|-------------------|------------------|----------------------|
| 1             | 9.409                | Naphthalene               | C10H8             | 128              | 2.465                |
| 2             | 11.032               | Naphthalene, 1-methyl     | C11H10            | 142              | 3.276                |
| 3             | 11.268               | Naphthalene, 2-methyl     | C11H10            | 142              | 2.933                |
| 4             | 12.196               | Naphthalene, 2-ethenyl    | C12H10            | 154              | 1.915                |
| 5             | 12.718               | Naphthalene, 2, 6-dimethyl-| C12H12           | 156              | 2.404                |
| 6             | 12.853               | Biphenyl                  | C12H10            | 154              | 1.161                |
| 7             | 13.108               | Biphenylene               | C12H8             | 152              | 9.391                |
| 8             | 13.552               | 1-Isopropenynaphthalene   | C13H12           | 168              | 1.696                |
| 9             | 13.947               | Dibenzofuran              | C12H6O            | 168              | 5.750                |
| 10            | 14.527               | 1H-Phenalen               | C13H10            | 166              | 1.702                |
| 11            | 14.686               | Fluorene-9-methanol       | C12H12O          | 196              | 1.178                |
| 12            | 14.740               | Fluorene                  | C13H10            | 166              | 15.117               |
| 13            | 15.345               | Dibenzofuran, 4-methyl    | C13H10O          | 182              | 2.502                |
| 14            | 16.261               | 9H-Fluorene, 1-methyl     | C14H12           | 180              | 5.020                |
| 15            | 16.518               | 9H-Fluoren-9-one         | C13H6O           | 180              | 2.749                |
| 16            | 16.949               | Phenanthrene              | C14H10           | 178              | 11.348               |
| 17            | 17.059               | Anthracene                | C14H10           | 178              | 4.058                |
| 18            | 18.287               | Phenanthrene, 1-methyl    | C15H12           | 192              | 4.944                |
| 19            | 18.364               | 4H-Cyclopenta[def]phenanthrene | C15H10    | 190              | 3.393                |
| 20            | 18.877               | 1, 2, 4, 8-Tetramethylbicyclo[6.3.0] undeca-2, 4-diene | C15H24 | 204              | 2.025                |
| 21            | 19.984               | Fluoranthen               | C16H10           | 202              | 6.501                |
| 22            | 20.243               | Pyrene                    | C16H10           | 202              | 2.968                |
| 23            | 21.114               | Pyrene, 1-methyl          | C17H12           | 216              | 1.891                |
| 24            | 21.275               | 11H-Benzo[b]fluorene     | C17H12           | 216              | 1.788                |
| 25            | 23.113               | Triphenylene              | C18H12           | 228              | 1.042                |
Table 8. The relative contents of the distinguishable major compounds of tar pyrolysis products at the primary/secondary pyrolysis temperature of 678°C/1203°C.

| Serial Number | Residence Time (min) | Name                         | Molecular Formula | Molecular Weight | Relative Content (%) |
|---------------|----------------------|------------------------------|-------------------|------------------|----------------------|
| 1             | 13.137               | Acenaphthylene               | C_{12}H_{8}       | 152              | 3.724                |
| 2             | 14.758               | Fluorene                     | C_{13}H_{10}      | 166              | 6.357                |
| 3             | 16.544               | 9H-Fluorene-9-one            | C_{13}H_{6}O      | 180              | 2.478                |
| 4             | 16.954               | Anthracene                   | C_{14}H_{10}      | 178              | 20.881               |
| 5             | 17.067               | Phenanthrene                 | C_{14}H_{12}      | 178              | 7.095                |
| 6             | 18.142               | Anthracene, 1-methyl-        | C_{15}H_{12}      | 192              | 1.092                |
| 7             | 18.204               | Phenanthrene, 2-methyl-4H-   | C_{15}H_{12}      | 192              | 2.035                |
| 8             | 18.368               | Cyclopenta(def)phenanthrene  | C_{15}H_{10}      | 190              | 9.801                |
| 9             | 18.890               | 1, 2, 4, 8-Tetramethylbicyclo[6.3.0]undeca-2, 4-diene | C_{15}H_{24} | 204 | 2.371 |
| 10            | 20.164               | Fluoranthene                 | C_{16}H_{10}      | 202              | 17.519               |
| 11            | 20.247               | Pyrene                       | C_{16}H_{10}      | 202              | 11.108               |
| 12            | 21.129               | Pyrene, 2-methyl-            | C_{17}H_{12}      | 216              | 3.024                |
| 13            | 21.295               | 11H-Benzo[a]fluorene         | C_{17}H_{12}      | 216              | 3.132                |
| 14            | 23.100               | Cyclopenta(cd)pyrene         | C_{18}H_{10}      | 226              | 6.257                |
| 15            | 23.224               | Triphenylene                 | C_{18}H_{12}      | 228              | 3.124                |

4. Conclusions

Pyrolysis products were obtained by high-temperature secondary pyrolysis of biomass tar (represented by rice hull tar) through a self-designed experimental bench, and the pyrolysis ratios of tar at different temperatures were recorded and compared, and simultaneously the relevant indicators are analyzed and the conclusions are as follows:

- The pyrolysis ratio of tar increases with the increase of experimental temperature, and the pyrolysis ratio increases slowly between 550°C and 655°C; the pyrolysis ratio exhibits a large upward trend between 655°C and 790°C and the rising trend slows down between 790°C and 853°C. The above phenomenon indicates that the pyrolysis ratio will increase with the increase of the reaction temperature, but the trend will gradually slow down combined with the measurement results of the thermal balance. Compared with the experimental data of the thermal balance, the tar pyrolysis ratio from the experimental platform has been lower than that of the thermobalance because the amount of tar pyrolysis from the thermobalance is smaller than the bench, and the heat supplied at a certain temperature can be more fully contacted with tar, resulting in a higher pyrolysis ratio.

- The changes of the main components of pyrolysis products represented by naphthalene, anthracene, phenanthrene, 4-ethyl-phenol and n-hexadecanoic acid show that while the reaction temperature is increased, the secondary pyrolysis of tar is enhanced and the breakage of intramolecular bridge bonds are enhanced; the polycyclic substances are converted into monocyclic ones by ring-opening reactions and the increase of the chain-like substances is caused by the ring-opening reactions of a part of the monocyclic substances by heat, and the chain-like radical is converted. In combination with other simple free radicals, such as carboxyl and hydroxyl groups, a chain-like substance is
formed. At the same time, it can be concluded that the phenol derivative and the materials of chain structure have better thermal stability.

- Combined with the GC-MS analysis results of pyrolysis products at reaction temperatures of 423°C, 550°C, 655°C, 790°C and 853°C and the pyrolysis ratio at reaction temperatures, it can be concluded that the pyrolysis ratio varies with the reaction temperature rising and gradually increases due to the reduction of polycyclic aromatic hydrocarbons such as naphthalene, anthracene and phenanthrene.
- Using the American Agilent HP5973GC/MS to analyze pyrolysis products of biomass tar under different pyrolysis temperature combinations, the main components of of biomass tar pyrolysis at different temperatures are naphthalene, phenanthrene, anthracene, pyrene, pyrene, and benzofuran, fluoranthene, biphenyl, biphenylene and their corresponding derivatives. The pyrolysis temperature has a great influence on the pyrolysis products of biomass tar. The yield of solid products gradually decreases with the increase of temperature, and gradually becomes a fixed value; the yield of the gas products decreases with the increase of temperature. The yield of non-condensable pyrolysis gas increases with the increase of reaction temperature.
- At the pyrolysis temperatures of 550°C, 1050°C and 1300°C, the types of pyrolysis components undergo a process of increasing first and then decreasing while the total mass fraction of pyrolysis components shows a process of decreasing from high to low. That is from 85.397% to 83.198%, and finally to 75.483%, a drop of 10%.
- The main pyrolysis products of tar show different changes: the mass fraction of pyrolysis components containing side chains, heterocycles and long chains decreases with temperature rise, while the mass fraction of aromatic organic compounds and polycyclic aromatic hydrocarbons increases with temperature rise; and the total increase is as high as 15.535%.

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