Study on Pyrolysis Characteristics of Rubber Wood Based by TG and Py-GC/MS

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Abstract: In order to explore the formation mechanism of pyrolysis products of rubber wood, the pyrolysis characteristics of rubber wood at different heating rates were investigated by thermogravimetric analyzer (TG), and the pyrolysis behavior and distribution of pyrolysis products of rubber wood at 400, 600 and 800 °C were further analyzed by py-GC/MS. The results showed that with the increase of heating rate, the heat transfer hysteresis of rubber wood pyrolysis occurred. The pyrolysis products of rubber wood mainly include acids, phenols, ketones, aldehydes and aromatic hydrocarbons. At 400 °C, the yields of phenols and aldehydes reach the maximum. At 600 °C, the yields of toluene, ethyl benzene and olefins increase, while the yields of phenols and aldehydes decrease. At 800 °C, the yields of phenols and aldehydes increase slightly. At the same time, the contents of polycyclic aromatic hydrocarbons increase with the increase of temperature, and reach the maximum at this time.

1. Introduction
In recent years, in order to alleviate the pressure of energy shortage, biomass as a renewable energy has been widely used by human beings. Rubber wood is concerned because of its low planting cost, fast growth and short time to become a talent. But it has not been used reasonably so far, resulting in serious waste of resources. Rubber wood contains about 50% cellulose and has the potential to be used as biomass energy[1]. At the same time, rubber wood is used as fuel to bake tobacco leaves and betel nuts. Carcinogenic substances were produced in betel nuts during baking, so it is very important to study the formation mechanism of products during pyrolysis of rubber wood for improving the quality of bio-oil and controlling the generation of carcinogens during pyrolysis[2].

Pyrolysis is one of the important methods for comprehensive utilization of biomass. However, alkanes, aromatic hydrocarbons, phenolic derivatives, aldehydes, etc. are produced during the pyrolysis of rubber wood, and the research on its pyrolysis mechanism is unclear, which seriously restricts its further application. Chen Weixin[3] et al. studied the effect of baking treatment on rubber sawdust, and found that hemicellulose in rubber wood was obviously degraded at 200°C and 250°C, and lignin was also obviously decomposed at 300°C. With the increase of temperature, the content of acid and aldehyde in pyrolysis gas decreased. Xu Xiwei et al.[4] studied the pyrolysis characteristic parameters of Camellia oleifera shells at heating rates of 5, 10, 15, 20 and 25°C/min, and found that the pyrolysis process of Camellia oleifera shells mainly experienced water loss stage, main pyrolysis stage and...
carbonization stage. With the increase of heating rate, the mass loss of samples decreases gradually. In
the main pyrolysis stage, the peak value of the maximum degradation rate shifts to the high temperature
zone with the increase of heating rate.

In this paper, the pyrolysis experiment of rubber wood was carried out on TGA, the pyrolysis
characteristics of rubber wood at different heating rates were studied. Then, the pyrolysis behavior and
the release law of pyrolysis products of rubber wood at different pyrolysis temperatures were studied by
pyrolysis chromatography/mass spectrometry (Py-GC/MS), and the pyrolysis mechanism was analyzed,
which provided theoretical knowledge support for the utilization of rubber wood.

2. experimental materials and methods

2.1. biomass samples
The sample used in this study is rubber sawdust from Hainan Province. Before the experiment, the
samples were cleaned with deionized water, and then placed on a clean cloth for natural air drying for 2
hours, and then placed in a 105°C air drying oven for 12 hours. Before the experiment, the samples were
crushed and ground, and the samples with the particle size of 0.074 mm~0.106mm were taken for the
experiment. Industrial analysis and elemental analysis of samples are shown in Table 1

| Industrial analysis (%) | Elemental analysis (%) |
|-------------------------|------------------------|
| M_ad 8.2 | A_ad 1.4 | V_ad 82.3 | FC_ad 7.9 | C_ad 37.1 | H_ad 6.3 | O_ad 54. | N_ad 1.2 | S_ad 0.5 |

2.2. Experimental Methods
TG test was carried out on netzsch sta449 thermal analyzer (TG). the specific test conditions were as
follows: put the sample (10.00±0.50) mg into a clean crucible, introduce nitrogen with purity of 99.99%
at a flow rate of 50 mL/min, and then put the sample at 5°C/min, 15°C/min and 25°C/min respectively
Py-GC/MS experiments were carried out to study the pyrolysis oil of rubber wood at 400, 600 and 800°C
respectively. In Shimadzu GCMS-GP2010 gas chromatography-mass spectrometry (CDS5000), 0.5mg
sample was put into quartz tube, and both ends were fixed with Shi Ying cotton. The carrier gas of the
thermal cracker is high purity helium with purity of 99.99% (flow rate of 30mL/min). The GC/MS
instrument is equipped with DB-5ms capillary column (30 m × 0.25 mm × 0.25 μm) with split ratio of
1:50. Temperature programmed method is adopted in the column box: the initial temperature is set at 30°C
for 1min, and then the temperature is raised to 150°C at a rate of 3 °C/min for 1 min. MS conditions:
ionization mode EI, electron energy 70 eV, mass scanning range 50~ 600 amu. Using the database to
analyze the mass spectrometry data, the relative content of each compound is represented by the peak
area ratio, and the detected compounds with relative content higher than 0.1% are analyzed.

3. results and discussion

3.1. pyrolysis characteristics of rubber wood under different heating rates
The pyrolysis characteristics of rubber wood at different heating rates are shown in Figure 1. With the
increase of temperature, rubber wood pyrolysis can be divided into three stages: the first stage is drying
stage, and the weight loss rate is about 8% at 30°C-220°C. The DTG curve shows a small weight loss
peak. Due to the evaporation of moisture in rubber wood samples, the weight of rubber wood samples
decreased rapidly.

The second stage is pyrolysis, and the weight loss rate is about 60% at 220°C-470°C. At this stage,
TG curve decreased rapidly, and DTG curve showed shoulder peak. The weight loss rate of rubber wood
increased sharply, and a large number of gas products were produced. In the process of rapid
devolatilization, the decarboxylation reaction occurs because cellulose depolymerizes to form active
cellulose; For example, C-C and C-H in the side chain connected by aromatic structure or naphthalene
structure are broken, which leads to the polymerization and polycondensation of aromatic hydrocarbons, and the bond between (semi) cellulose and lignin (such as O-H, C-O and C=O) is broken, thus generating a large amount of gases (such as H2O, CO and CO2)[5-7].

The third stage is the carbonization stage of rubber wood. After 470°C, the TG curve decreases slowly and the DTG curve gradually stabilizes and tends to zero. In the carbonization stage, it is mainly the pyrolysis of residual lignin and the precipitation of volatile components remaining in charcoal. Because lignin has complex phenylpropane structure and three-dimensional polymer with high thermal stability, the decomposition reaction of lignin is slow and the quality change is weak [8-9].

TG curves of rubber trees have similar trends at different heating rates. With the increase of heating rate, the TG curve moves slightly to the high temperature zone, and the initial temperature and the end temperature of pyrolysis both rise, resulting in thermal hysteresis in pyrolysis reaction. The DTG curve of pyrolysis shows that the maximum weight loss rate increases with the increase of heating rate. In addition, it can be seen from Table 2 that with the increase of heating rate, the volatile matter precipitation index increases obviously. Volatile release index is directly related to the maximum weight loss rate and the average weight loss rate. The half peak width temperature also increases with the increase of temperature. This is because with the increase of heating rate, the reaction rate of rubber wood pyrolysis increases, but there is thermal lag phenomenon in the reaction, and in the same time period, the temperature change accelerates, which leads to the increase of reaction temperature range. It can be seen that the higher the heating rate is, the higher the volatile matter precipitation characteristic index is, and the easier it is to pyrolyze.

### Table 2 Combustion characteristic parameters at different heating rates

| β | T_l | T_2 | W_2 | T_max | ΔT_1/2 | d_max | V_∞ | d_mean | D×10^6 |
|---|-----|-----|-----|-------|--------|-------|-----|--------|--------|
| 5 | 285.2 | 192.5-468.1 | 60.52 | 333.8 | 68.9 | -4.50 | 77.269 | 0.398 | 7.11 |
| 15 | 295.6 | 199.3-465.6 | 59.64 | 348.8 | 76.6 | -11.86 | 80.087 | 1.232 | 50.05 |
| 25 | 296.3 | 203.4-470.2 | 60.02 | 354.9 | 77.8 | -19.64 | 81.544 | 2.146 | 149.60 |
| 35 | 299.7 | 206.0-472.4 | 60.3 | 355.3 | 80.4 | -29.03 | 84.745 | 3.016 | 307.60 |

β is the heating rate (°C/min); T_l is the volatilization temperature (°C); T_2 is the second stage temperature interval (°C); W_2 is the second stage weight loss rate (%); T_max is the peak temperature (°C); ΔT_1/2 is the half peak width temperature (°C); d_max is the maximum weight loss rate (%/min); V_∞ is the final weight loss rate (%); d_mean is the average weight loss rate (%/min); D is the volatile analysis index.

### 3.2. Py-GC/MS analysis of rubber wood

The Py-GC/MS total ion flow diagram of Hevea brasiliensis at different pyrolysis temperatures is shown in Figure 2. The pyrolysis products include acids (1.31%-4.85%), phenols (14.89%-37.81%), ketones (7.69%-12.02%) and esters (1.53%-3.29%).

The pyrolysis reaction of rubber wood mainly includes dehydration, ring fragmentation, ring contraction, ring opening and isomerization, and temperature is one of the important factors affecting...
the distribution of pyrolysis products. When the pyrolysis temperature was 400°C, rubber wood began to pyrolyze, but the pyrolysis was incomplete, and the types of pyrolysis products and relative peak areas were few. With the increase of pyrolysis temperature, (semi) cellulose and lignin are fully cracked, and the types of pyrolysis products increase. This is because biomass pyrolysis is an endothermic process. The higher the reaction temperature, the greater the available energy, and it is easier to break atomic bonds and decompose organic matter [10-11].

Fig 2 Py-GC/MS of Rubber wood at different pyrolysis temperatures

Phenolic compounds in rubber wood pyrolysis products are mainly 3- methylphenol, guaiacol, 2,6-dimethoxyphenol, 4- allyl-2,6-dimethoxyphenol, and a small amount of other phenolic compounds such as 1,2,4- trimethoxyphenol, anti-isoeugenol, 3- methoxycatechol and isovanillin. Fig. 5 shows that the yield of phenolic compounds reaches the maximum at 400°C, especially 2,6- dimethoxyphenol (14.96%), and the relative peak areas of guaiacol, 3- methylphenol and 4- allyl-2,6-dimethoxyphenol are 4.92%, 2.84% and 7.58, respectively. At 600°C, the yield of phenolic compounds was the lowest. Phenolic compounds increased slightly at 800°C. The results showed that at 600°C, the carcinogens such as phenols can be effectively controlled during the pyrolysis of rubber wood.

Aromatic hydrocarbons and naphthenes are produced under all conditions during the pyrolysis of rubber wood, among which aromatic chemicals mainly include toluene, ethylbenzene, naphthalene, 2- methylnapthalene, indene, anthracene, p-xylene, styrene and cyclooctatetraene. As shown in fig 3, with the increase of pyrolysis temperature, the relative peak area of aromatic hydrocarbon products increases, and the yield of aromatic hydrocarbon compounds reaches the maximum at 600°C. When the pyrolysis temperature continues to rise to 800°C, monocyclic aromatic hydrocarbons are polymerized into condensed aromatic hydrocarbons. With the increase of temperature, oxygen-containing compounds are gradually deoxidized and aromatic. Aromatic hydrocarbons are internationally announced carcinogens and important chemical raw materials. Monocyclic aromatic hydrocarbons are widely used in the production of fine chemicals such as dyes, medicines, pesticides, explosives, additives and spices; Fused aromatic hydrocarbons can be used to produce phthalic anhydride, dye intermediates, rubber additives and pesticides [12-13]. When the temperature reaches 600°C, phenolic compounds undergo secondary reaction and crack to produce toluene, ethylbenzene, naphthalene and...
other substances. It shows that at 600°C, the yield of aromatic compounds can be effectively increased and the production of phenolic compounds can be controlled.

Fig 3 Composition of Py-GC/MS at different temperatures

Ketones produced during rubber wood pyrolysis are mainly 4-hydroxy-3-methyl acetophenone, 3,5-dimethoxyacetophenone and 3-methyl-1,2-cyclopentanediione, while aldehydes are mainly furfural and syringaldehyde. At 400°C, the relative peak areas of ketones (12.02%) and aldehydes (12.63%) are significantly higher than other pyrolysis temperatures, which is due to the secondary cracking of cellulose and the ring opening of hemicellulose, resulting in 4-hydroxy-3-methylacetophenone, 2-hydroxyacetaldehyde and other compounds, resulting in an increase in the relative peak areas of ketones and aldehydes [14]. Organic acids and esters produced during pyrolysis are propionic acid, phosphonic acid (p-hydroxyphenyl), diisobutyl phthalate, etc. Acid products are mainly formed by the decomposition of monosaccharide rings (i.e. O-H, C-O-C and carbonyl) at low temperature [15]. It can be seen from Product List 4 that esters are formed near acids and alcohols, indicating that esters are produced by esterification reaction between acids and alcohols.

4. Conclusions
The heating rate has a significant effect on the pyrolysis of rubber wood. With the increase of heating rate, TG curve moves slightly to the high temperature zone, and the initial temperature and the end temperature of pyrolysis both rise. Thermal hysteresis occurs in the pyrolysis reaction, the maximum weight loss rate increases, and heat transfer hysteresis occurs. Analysis of pyrolysis characteristics: With the increase of heating rate, the half-peak width temperature ∆T_{1/2} increases, and the volatile release index increases obviously.

There are acids (1.31%-4.85%), phenols (14.89%-37.81%), ketones (7.69%-12.02%), esters (1.53%-3.29%) and aldehydes (7.48) At 400°C, the relative peak areas of ketones (12.02%), aldehydes (12.63%) and phenols (37.81%) reached the maximum, and the yield of aromatic hydrocarbons reached the maximum at 600°C. When the pyrolysis temperature continues to rise to 800°C, monocyclic aromatic hydrocarbons are polymerized into condensed aromatic hydrocarbons. At 600°C, it can effectively control the production of carcinogens such as phenols during the pyrolysis of rubber wood.

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