# Study on Pyrolysis Behavior of Wood Chips Based on TG-FTIR-MS

Guanghui Zhang[a]; Tiantian Ma[b]; Wenjing Ma[c*]; Lei Huang[d]; Jinxu Jiang[e]; Zhiyuan Liu[f]

Hefei General Machinery Research Institute Co. Ltd, Hefei, China

[a]tjyzgh1988@126.com; [b]13721068050@163.com; [c*]mawenjing1115@163.com*; [d]18361220739@163.com; [e]jjx13146056060@163.com; [f]1229866986@qq.com

**Abstract.** In this paper, the pyrolysis process of wood chips as a typical biomass feedstock was studied. The thermal gravimetric Fourier infrared spectrometry-mass spectrometry (TG-FTIR-MS) combined apparatus and fixed bed pyrolysis apparatus were used for experimental analysis. The results showed that the main pyrolysis temperature range of wood chips was 246-390 ℃, and the maximum weight loss rate was 363 ℃. During the pyrolysis process, the released volatile substances mainly include CO, $CO_2$, $CH_4$, ethers, acids, aldehydes, aromatics and phenols. The results of fixed-bed pyrolysis showed that the three-phase product yields of wood chips pyrolysis at 450-550 ℃ were relatively stable, in which the yield of liquid product was about 50 wt.%, that of coke was about 30 wt.% and that of gas was about 20 wt.%. The content of phenolic substances in pyrolysis oil is the highest, accounting for about 41.4%. This study revealed the evolution law of the escaped substances during the pyrolysis of wood chips, and provided a theoretical basis for the efficient utilization of biomass resources.

**Keywords:** Biomass; Pyrolysis; TG-FTIR-MS; Three-phase product

## 1 Introduction

With the improvement of agricultural production level and the development of rural economy, the output of agricultural waste increases year by year, which brings severe challenges to the rural environment and resource utilization. Agricultural waste is rich in organic matter and nutrients, with potential biomass resource value, and can be widely used as a key raw material for biomass energy and bio-based products. According to the latest data, the world produces about 1 billion tons of agricultural waste every year, and the agricultural sector accounts for about 20% of the total greenhouse gas emissions[1]. Cellulose, hemicellulose, lignin and pectin are the main components of agricultural waste[2]. At present, the world is facing an increasingly serious energy shortage and environmental problems, in order to reduce the use of fossil energy and



W. He et al. (eds.), *Proceedings of the 2024 10th International Conference on Advances in Energy Resources and Environment Engineering (ICAESEE 2024)*, Atlantis Highlights in Engineering 36,
https://doi.org/10.2991/978-94-6463-708-3_34

greenhouse gas emissions, towards the goal of zero solid waste, agricultural waste resource disposal is crucial to the green development of sustainable energy.

Thermal chemical disposal of agricultural waste has the advantages of simple operation, all raw materials can be realized through thermal chemical treatment of resources utilization, at the same time, biomass energy as a renewable energy in the world energy consumption occupies a large proportion, the development and utilization of biomass energy to replace some fossil fuels can alleviate the energy shortage problem to a certain extent. Pyrolysis, gasification and incineration are three common methods in thermochemical disposal[3]. Biomass gasification technology converts biomass with gasification agents such as air and water vapor into syngas such as methane, hydrogen and carbon monoxide by regulating reaction conditions at a high temperature, which can be used to produce hydrocarbon liquid fuel by Fischer-Tropsch synthesis[4]. Biomass direct combustion power generation, heating technology is relatively mature and has been large-scale commercial large-scale application. Biomass is rich in carbon, hydrogen, oxygen and other elements, and the conversion of solid biomass into liquid bio-oil, small molecule gas and biochar by pyrolysis technology is currently a promising biomass utilization method[5]. Compared with biomass raw materials, bio-oil can replace some petroleum fuels and become an important sustainable fuel. It has the advantages of high energy density, convenient storage and transportation, etc., and can be used as engine fuel[6]. Meanwhile, pyrolysis gas and biochar can be burned to supply energy for pyrolysis, power generation or heating processes. Biomass pyrolysis technology applies to a wide range of raw materials, with the advantages of full component utilization and high conversion efficiency, which can convert biomass into chemical products with high added value, reduce the pollution problem of nitrogen oxides and sulfur oxides caused by incineration, and a small amount of heavy metals in biomass can be fixed in biochar to avoid secondary hazards to the environment.

In this paper, a TG-FTIR-MS combined device and a fixed-bed pyrolysis device were used to select wood chips, a typical biomass raw material, for pyrolysis experiment, and the weight loss temperature range of wood chips during pyrolysis was obtained. The release rule of volatile substances was obtained through the combination of infrared and mass spectrometry information. The three-phase product of wood chip pyrolysis was quantitatively analyzed by a fixed bed pyrolysis device.

# 2 Materials and Methods

## 2.1 Experimental Materials

In this paper, wood chips, a typical biomass material, were selected as the research object. Before the experiment, the samples were screened to less than 30 mesh, and the samples were dried in a 105 °C oven for 12 h after screening. The organic element analyzer vario EL cube produced by Elementar of Germany was used to test the elements of raw materials. The content of O element was obtained by subtraction method. The industrial analysis was determined by Muffle furnace, referring to the national standard GB/T 28731-2012. The results of elemental analysis and industrial analysis of different samples are shown in the Table.1. The volatile content of wood chips was 85.1 wt.%, and the ash content was only 0.73 wt.%.

**Table 1.** Elemental and industrial analysis of wood chips

| Elemental analysis, wt.% | | | | | | Industrial analysis, wt.% | | | |
|---|---|---|---|---|---|---|---|---|---|
| C | H | O | N | S | Cl | Moisture | Volatile | Ash | Fixed carbon |
| 49.35 | 6.85 | 41.61 | 1.41 | 0.05 | - | 5.07 | 85.10 | 0.73 | 14.17 |

## 2.2 TG-FTIR-MS

The TG-FTIR-MS device can not only analyze the mass change of raw materials during pyrolysis, but also determine the type of volatilization from raw materials during pyrolysis according to the results of Fourier infrared analysis spectrum and mass spectrometry. According to the wave-number positions of absorption bands in the infrared spectra, the release of different kinds of volatiles and their change trend in the pyrolysis process of organic solid waste can be qualitatively understood. The ion flow diagram of the gas escaping from the sample during pyrolysis can be obtained by mass spectrometry, and the components of the volatiles escaping can be determined. The TG-FTIR-MS test of wood chips was carried out on a synchronous thermal analysis infrared temperament spectrometer (STA8000-Spectrum 3-Clarus690 SQ8C) at a temperature rate of 10 °C·min$^{-1}$ from room temperature to 700 °C in an atmosphere of $N_2$.

## 2.3 Fixed bed Pyrolysis Device

As shown in Fig. 1, the pyrolysis experiment of wood chips was carried out in a fixed bed reactor with a quartz tube diameter of 50 mm and a length of 800 mm. Before each group of pyrolysis experiments, 2 g samples were first put into the ceramic ark and pushed to the middle of the quartz reactor, and then $N_2$ was injected into the quartz reactor to remove the air in the tube. After the air in the reactor was emptied, the reactor was heated up to the target temperature (450 °C, 500 °C, 550 °C) at a temperature rate of 10 °C·min$^{-1}$ and kept warm for 20 min. The $N_2$ flow rate was 100 mL·min$^{-1}$. The tar produced in the pyrolysis process of raw materials is condensed by ice bath method. After condensation, the tar is dissolved in methylene chloride solvent. The gas product is collected by air bag after drying device.

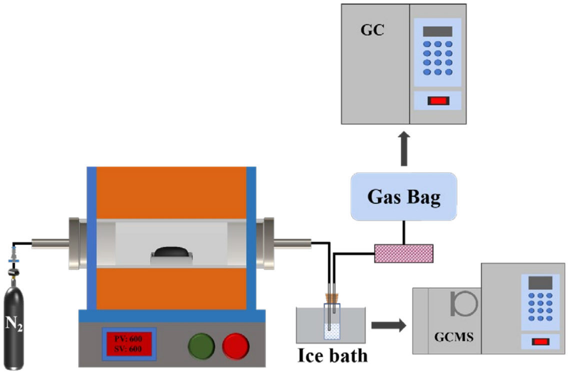



**Fig. 1.** Diagram of fixed bed pyrolysis unit

### 2.4 Analysis Method of Three-Phase Pyrolysis Products

The solid product after pyrolysis is the residual residue after raw material pyrolysis, and its yield is determined by weighing the quality of the samples before and after pyrolysis. The total volume of gas after pyrolysis of raw materials can be calculated by the formula. Through the volume fraction of $N_2$ in the air bag and the volume flow of $N_2$, the total volume of pyrolysis gas and the volumes of different gas phase components can be calculated, so as to obtain the total mass of pyrolysis gas. The yield of liquid oil can be obtained by subtracting the mass of solid residue and gas from the mass of raw material through the principle of material conservation.

$$V_{\text{total}} = \frac{tV_{\text{N2}}}{1000(1-C_{\text{N2}})} \tag{1}$$

Where: Vtotal is the total volume of gas in the bag /L; $V_{N2}$ is the flow rate of carrier gas $N_2$ /mL·min-1 in the experiment; t is gas collection time /min; $C_{N2}$ is the volume fraction of $N_2$ in the total gas /vol.%.

The gas in the bag is measured by a gas chromatograph. The gas chromatograph produced by Shimadzu, model GC-2014, tests the same gas sample more than three times to ensure the accuracy of the results. The pyrolytic tar was determined by gas-liquid chromatography (GC-MS) with model GCMS-QP2010 Ultra and quartz column model Rxi-5Sil MS manufactured by Shimadzu.

## 3 Results and Analysis

### 3.1 Weight Loss Analysis During Pyrolysis

As can be seen from Fig. 2, the pyrolysis process of wood chips can be divided into three stages. The main weight loss stage ranges from 246 °C to 405 °C, and the peak temperature of DTG is 363 °C. In this stage, a large amount of volatiles are released, with the weight loss reaching 67.2%. The secondary reactions such as polycondensation and aromatic cyclization result in the slow reduction of its mass. After 600 °C, the quality of wood chips basically did not change, and the remaining mass was 25.8%.

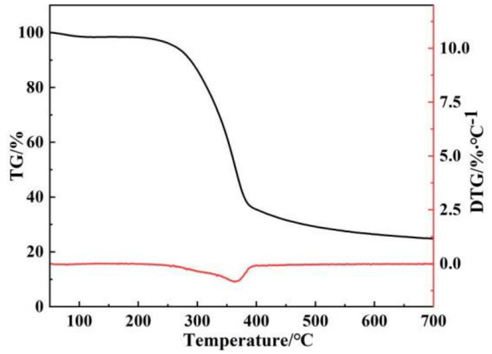
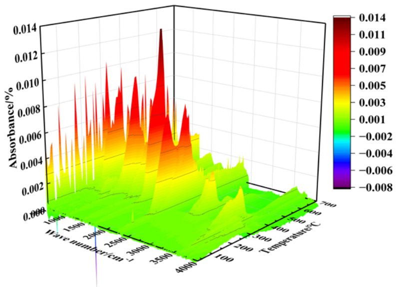


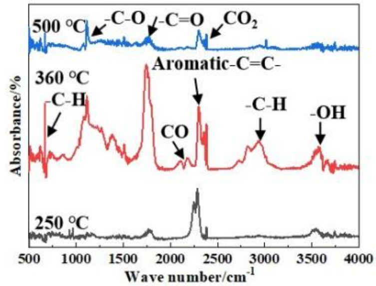

**Fig. 2.** TG and DTG curves of wood chips pyrolysis

### 3.2 FTIR-MS Analysis of Pyrolysis Process

In order to further determine the types of substances released during the pyrolysis of wood chips, the results of FTIR-MS were analyzed. Fig. 3(a) shows the 3D FTIR spectral diagram of volatiles analyzed during the weight loss process of wood chips pyrolysis.




(a)3D FTIR spectrogram




(b)2D FTIR spectra at typical temperatures

**Fig. 3.** 3D FTIR and 2D FTIR spectra of wood chips during pyrolysis

It can be seen from the diagram that the infrared characteristic absorption peak of wood chips pyrolysis products is concentrated between 200 and 500 °C, which is corresponding to the weight loss curve of wood chips pyrolysis in Fig. 2, and there are various absorption peaks. Fig. 3(b) shows the 2D FTIR spectra of volatiles released at different temperatures during pyrolysis. At 360 °C, there are more infrared characteristic absorption peaks and greater intensity, which correspond to the temperature point at the maximum weight loss rate of wood chips, indicating that a large amount of volatiles in raw materials are released at this temperature and the types are relatively complex. According to the types of functional groups corresponding to the absorption peaks of infrared spectra, The main products of wood chips pyrolysis are CO (2000~2200 cm$^{-1}$), $CO_2$ (2300~2400 cm$^{-1}$), $CH_4$ (600~750 cm$^{-1}$), ethers (1080~1150 cm$^{-1}$), acids and aldehydes (1650~1860) cm$^{-1}$), aromatics (2300~2400 cm$^{-1}$) and phenols (3500~3700 cm$^{-1}$)[7].

Cellulose, hemicellulose and lignin are the main components of wood chips[8]: During the heating process, cellulose mainly undergoes two reaction pathways of depolymerization and cleavage of furan rings to form primary pyrolysis products represented by acetaldehyde, glycolaldehyde and acetic acid, while hemicellulose mainly undergoes depolymerization, cleavage of furan rings and substituent shedding to form furfural, ethanol and acetic acid and other substances[8]. Lignin takes guaiacol, eugenol and p-propyl phenol as the basic structural units. After being heated, the chemical bonds between the structural units are dissociated and side chains are broken to form various phenols and various phenolic derivatives. Typical components in the pyrolysis process were detected by mass spectrometer, and the ionic strength of each component changed with temperature, as shown in Fig. 4.

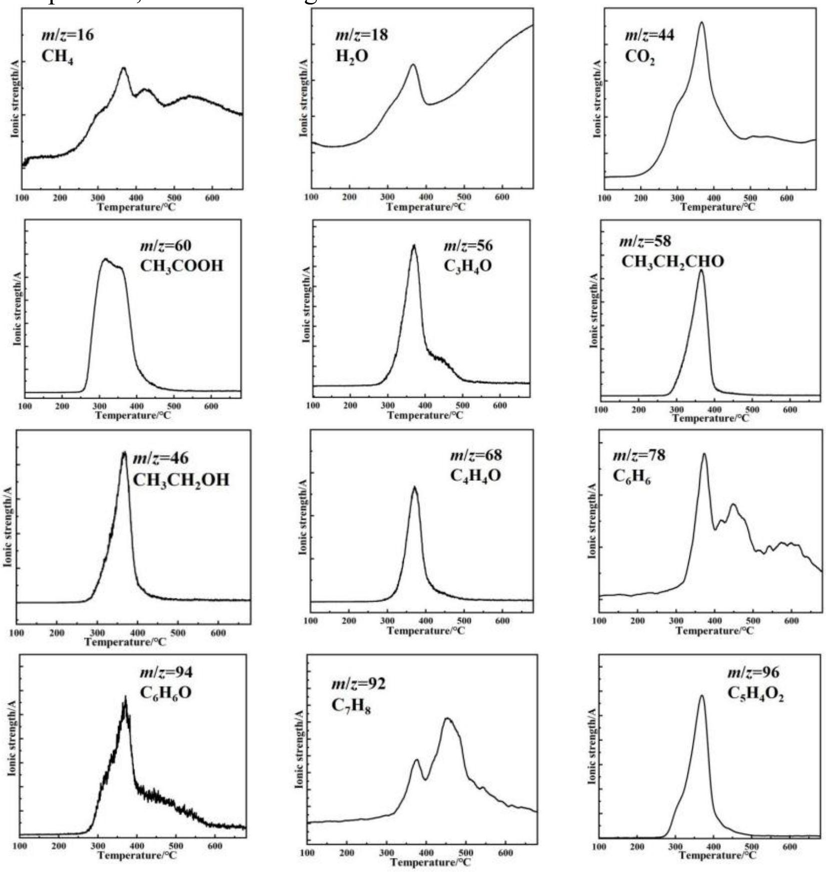
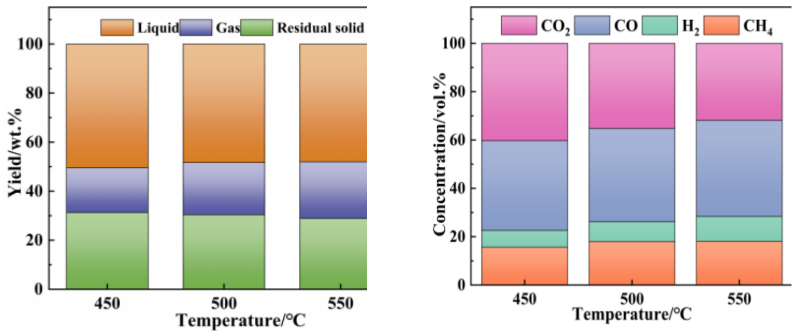



**Fig. 4.** Release curves of typical pyrolysis products of wood chips

The mass-charge ratio m/z=16 and 18 represent $CH_4$ and $H_2O$, respectively, and their characteristic absorption peaks are wider, indicating that $CH_4$ and $H_2O$ are always generated during biomass pyrolysis. At lower temperatures (150-400 °C), $CH_4$ is produced by cleavage of C-C bonds in aliphatic hydrocarbons, while at higher temperatures (400-700 °C), $CH_4$ is produced by cleavage of methoxy ($-OCH_3$) and methylene ($-CH_2-$) groups in lignin[7]. During the depolymerization process of cellulose, dehydration reaction occurs to form dehydrating sugar, releasing a large amount of $H_2O$[9]. With the increase of temperature, part of $H_2O$ will be produced when the pyrolysis products undergo secondary pyrolysis to produce small molecules. Therefore, the generation of $H_2O$ is always accompanied by the pyrolysis process. The main temperature range of $CO_2$ release is 300~400 °C, and its formation is related to the breaking and reforming of -C=O bonds and -COOH bonds formed after the depolymerization of cellulose and hemicellulose[10]. The release temperature of alcohols, aldehydes, ethers and acids is concentrated around 360 °C, at which a large number of volatiles in biomass are released. The mass-charge ratio m/z=78 and m/z=92 represent the aromatic substances benzene and toluene, which have multiple release peaks during the pyrolysis process. This is because the aromatic hydrocarbon substances begin to release at a lower temperature. With the increase of temperature, residual cellulose is secondary cracked, charring and rearrangement reactions occur to produce aromatic hydrocarbons again.

### 3.3 Analysis of Three-Phase Products at Different Pyrolysis Temperatures

In order to determine the product yield of wood chips pyrolysis at different temperatures, a fixed-bed pyrolysis experiment was conducted. According to the TG curve of wood chips in Fig.2, the fixed bed pyrolysis temperature was determined to be 450-550 °C. As can be seen from Fig.5(a), the three-phase product yield of wood chips at 450-550 °C has little change, the liquid product yield is about 50 wt.%, the coke yield is about 30 wt.%, and the gas yield is the lowest, about 20 wt.%. In the Fig.5(b), the pyrolysis gas products of wood chips mainly contain CO, $CO_2$, $CH_4$ and $H_2$, in which CO and $CO_2$ occupy the highest proportion and $H_2$ the lowest proportion. The results of repeated experiments show that the standard deviation of gas concentrations of all components is less than 2 vol.%. With the increase of pyrolysis temperature, the yield of residual solids and pyrolysis oil decreased slightly, but the yield of gas showed the opposite trend, and the higher temperature resulted in the decrease of $CO_2$ concentration. This is because the reaction between cellulose and lignin in wood chips is intensified at high temperature, and more gaseous products are precipitated, especially the methoxy group in lignin is fractured at high temperature to produce more $CH_4$.




(a)Three phase product yield (b) Gas product composition

**Fig. 5.** Three-phase product yield and gas product composition of wood chips at different temperatures

The pyrolysis oil produced by wood chips at 500 °C is selected for composition analysis. The composition of the pyrolysis oil is relatively complex and can be divided into aldehydes, acids, alcohols, phenols, ketones, furans, esters, nitrogenous compounds and hydrocarbons, etc. The relative content of each compound is shown in Fig.6. The proportion of phenolic substances in the liquid oil produced from wood chips is the largest, which is as high as 41.4%, mainly phenol, guaiacol and eugenol. This is because wood chips contain a large amount of lignin, lignin after heat between the structural units of the chemical bond dissociation and side chain break, forming a variety of phenolic derivatives. The decomposition of cellulose and hemicellulose mainly produces alcohols, aldehydes, acids and furans.

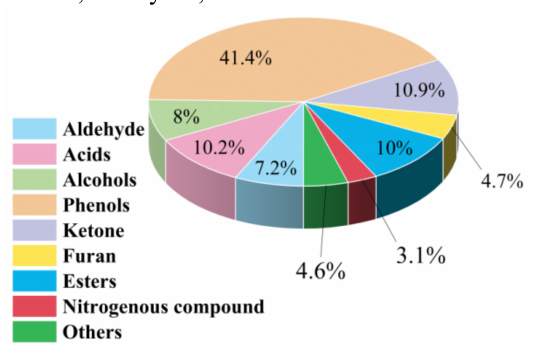



**Fig. 6.** Pyrolysis oil composition of wood chips at 500 °C

## 4 Conclusions

In this paper, the basic pyrolysis characteristics of wood chips were explored. The weight loss characteristics of wood chips during pyrolysis and the release characteristics of pyrolysis products were analyzed by TG-FTIR-MS technology, and the evolution law of substances escaping during pyrolysis was revealed. A fixed-bed pyrolysis device was used to conduct pyrolysis experiments at different temperatures. The yield of pyrolysis products and the composition of gas products were obtained.

The main pyrolysis temperature range of wood chips is 246~390 °C, and the maximum weight loss rate temperature pyrolysis temperature is 363 °C. When the pyrolysis temperature is 500 °C, the proportion of pyrolysis gas in sawdust is 21.3wt. %, in which the proportion of CO and $CO_2$ is the highest, and the proportion of pyrolysis oil is about 48.3wt. %. The types of compounds include aldehydes, acids, alcohols, phenols, ketones, furans, esters and so on. Phenolic substances mainly including phenol, guaiacol and eugenol have the highest content, accounting for about 41.4%. This study not only reveals the detailed process of wood chip pyrolysis, but also provides scientific basis and technical support for the resource utilization of agricultural waste, which is of great significance for promoting the sustainable development of biomass energy.

## References

1. Karić N, Maia AS, Teodorović A, et al. Bio-waste valorisation: Agricultural wastes as biosorbents for removal of (in)organic pollutants in wastewater treatment[J]. Chemical Engineering Journal Advances, 2022, 9: 100239-100255. https://doi.org/10.1016/j.ceja.2021.100239.
2. Babu S, Rathore SS, Singh R, et al. Exploring agricultural waste biomass for energy, food and feed production and pollution mitigation: A review[J]. Bioresource Technology, 2022, 360: 127566-127577. https://doi.org/10.1016/j.biortech.2022.127566.
3. Sherwood J. The significance of biomass in a circular economy[J]. Bioresource Technology, 2020, 300: 122755-122762. https://doi.org/10.1016/j.biortech.2020.122755.
4. Goyal HB, Seal D, Saxena RC. Bio-fuels from thermochemical conversion of renewable resources: A review[J]. Renewable and Sustainable Energy Reviews, 2008, 12(2): 504-517. https://doi.org/10.1016/j.rser.2006.07.014.
5. Nanda S, Berruti F. A technical review of bioenergy and resource recovery from municipal solid waste[J]. Journal of Hazardous Materials, 2021, 403: 123970-123985. https://doi.org/10.1016/j.jhazmat.2020.123970.
6. Qiu BB, Tao XD, Wang JH, et al. Research progress in the preparation of high-quality liquid fuels and chemicals by catalytic pyrolysis of biomass: A review[J]. Energy Conversion and Management, 2022, 261: 115647-115674. https://doi.org/10.1016/j.enconman.2022.115647.
7. Yang J, Chen H, Zhao W, et al. TG-FTIR-MS study of pyrolysis products evolving from peat[J]. Journal of Analytical and Applied Pyrolysis, 2016, 117: 296-309. http://dx.doi.org/10.1016/j.jaap.2015.11.002.
8. Ma W, Rajput G, Pan M, et al. Pyrolysis of typical MSW components by Py-GC/MS and TG-FTIR[J]. Fuel, 2019, 251: 693-708. https://doi.org/10.1016/j.fuel.2019.04.069.
9. Xu Fanfan. Research on fractional pyrolysis and gasification of typical components of municipal solid waste [D]. Qingdao: China University of Petroleum (East China), 2019. https://link.cnki.net/doi/10.27644/d.cnki.gsydu.2019.000947.
10. Qiao Y, Xu F, Xu S, et al. Pyrolysis characteristics and kinetics of typical municipal solid waste components and their mixture: analytical TG-FTIR study[J]. Energy & Fuels, 2018, 32(10): 10801-10812. https://doi.org/10.1021/acs.energyfuels.8b02571.