Thermal properties of biomass tar at rapid heating rates

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Abstract: Gasification of biomass tar by pyrolysis is a valuable source for renewable energy, providing chemicals, a precursor to carbon material and potentially a raw material for liquid fuel. In this research, experimental studies via thermal gravimetric analysis (*TGA*) of biomass tar were implemented at three rapid heating rates (i.e., 10 K/min, 50 K/min, 100 K/min, respectively) in a nitrogen atmosphere. On the basis of analytical methods utilized in thermal dynamics and physical chemistry, the results showed that the thermogravimetric curve (*TG*) of the biomass moved in a high-temperature direction with an increase in the heating rate. The greater the heating rate, the steeper the curve and the lower the resolution, the lag phenomenon of the temperature being more significant. Concurrently, a differential thermal analysis (*DTA*) was one of the methods employed to study the relationship between the temperature difference and the temperature or time of the tested substance and a reference substance. The peak temperature and maximum reaction rate of the differential thermal analysis curve (*DTA*) increased as the heating rate, the volatiles and the molecular residence time of the biomass was shortened at a higher heating rate, thereby potentially inhibiting the generation of carbon and increasing the production and yield of liquid fuel.

Keywords: biomass tar, liquid fuel, rapid heating rate, thermal dynamics, pyrolysis, gasification, renewable energy
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1 Introduction

Energy is a basic material in national economies and also a primary condition for human survival. Biomass is a renewable energy source having advantages of fossil fuel properties such as storage capacity, renewability, transformability, and freedom from pollution[1-3]. Green plants convert solar energy into chemical energy by photosynthesis in their chlorophyll-containing cells and subsequently store this energy in the biomass, where each mole of fixed carbon represents about 470 kJ of energy absorbed[4,5]. The exploitation and utilization of biomass has received much world-wide attention, occupying an important position in energy systems, wherein it is weaker than only coal, oil and natural gas in primary energy, which is considered the world's fourth-largest energy source[6]. Biomass is generally composed of carbon, hydrogen, oxygen, nitrogen and other components of the complex hydrocarbons derived from plant, animal and renewable organic microorganisms[7-9]. At present, biomass conversion technology mainly includes direct combustion, biological conversion and thermo-chemical conversion. In recent years, biomass gasification has developed into a reliable technology, utilizing thermo-chemical treatments, which

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use small amounts of air and oxygen as gasifying agents at elevated temperatures to convert organic matter into combustible gas[10-12]. Through thermochemical transformation, including pyrolysis and gasification, biomass generates gases, liquids and solid fuels which can serve as partial substitutes for fossil fuels. However, tar is an inevitable by-product in the biomass conversion process, the presence of which may cause operating problems such as blockages and corrosions that reduce efficiency in production[13].

Thermo-chemical conversion technology has been the principal focus in the study of biomass conversion. In the process of biomass pyrolysis gasification or char conversion, liquid residue generation occurs. Biomass tar is the fluid residue formed during pyrolysis gasification or coking reaction conversion of biomass in a furnace for combustible gas or straw char, in an environment of a small amount of air or oxygen used as the gasification agent and a temperature above 600℃[14]. In order to achieve liquid fuel conversion of biomass tar and its clean utilization, a clear understanding of its weightlessness and combustion characteristics is particularly important. The biomass pyrolysis process includes a variety of chemical reactions and intermediate states; the reaction mechanism is very complex. Thermogravimetric and differential thermal analysis has been widely used by scientists as an important methodology for studying the process and characteristics of biomass pyrolysis. In addition to the structure of biomass tar, its thermal properties also play a crucial role in its successful control, conversion and further application for preparing carbon materials. Biomass tar decomposition mainly occurs due to cracking, steam reforming, dry reforming and carbon formation reactions[15]. Therefore, the thermal decomposition of biomass tar still has not been fully characterized and understood. Moreover, further systematic study on tar is needed to reveal its complex thermal degradation mechanisms[16].

In this study, experiments on biomass tar at various high heating rates were conducted by using thermogravimetric and differential thermal analysis. The thermal weightlessness characteristics of biomass tar at rapid heating rates were studied in order to provide a scientific reference for developing a technology for the clean conversion of biomass tar to organic material as a basis for further research. Thus, the objective of this research was to study the chemical composition and thermal degradation mechanism of biomass-derived tar in order to better control, separate and utilize this promising biomaterial.

2 Materials and methods

2.1 Samples

The tar used in this study was collected from the pyrolysis gasification residue pool at the Xigou Biomass Fuel Gas Plant in Xihe, Yangcheng County, Shanxi Province, China. The requisite temperature for biomass pyrolysis gasification is 550℃. Before the TGA experiments, the distilled tar was dried in a vacuum oven at 80℃ for 4 hours, and then it was manually ground into small particles below 100 mesh (254 micron). Elemental and industrial analyses of maize straw biomass tar samples were conducted by a Vario MACRO cube v2.0.9 elemental analyzer, a GYFX-8000 industrial analyzer and a ZDHW-5Z automatic calorimeter, all based on China’s national standards: GB476-1991 and GB/T212-2001. The results of the elemental and industrial analyses of the samples are shown in Table 1.

Table 1 Elemental and industrial analysis of the biomass tar samples

Weight /mg	Elemental analysis/wt%				Industrial analysis/wt%			
	N	C	H	S	Moisture	Ash	Volatility	Fixed carbon
38.870	1.392	48.900	7.732	0.232	33.40	0.90	60.02	5.68

2.2 Experimental method

In this research, the thermogravimetric and kinetic characteristics of biomass tar samples were studied under non-isothermal conditions by using a STA 6000 synchronous thermal analyzer manufactured by PerkinElmer, Inc. In accordance with the thermogravimetric analytical method, about 10 mg of the biomass tar sample was placed into a sample plate; then, three heating rates were set by the temperature control unit at 10℃/min, 50℃/min, and 100℃/min, respectively. The carrier gases used in the experiment were high-purity nitrogen and air, respectively, with the gas flow at 60 mL/min, the initial temperature at 30℃, and the terminal temperature at 900℃. The main performance parameters of the thermal analyzer were within a temperature range of 15-1 000℃, a heating rate of 0.1-100℃/min, a sample capacity of 1 500 mg, a balance sensitivity of 0.1 µg, a calorimetric precision accuracy of ±2%, a temperature accuracy of ±0.5%, and a temperature repeatability of ±0.5%.

3 Results and discussion

3.1 Chemical components of samples

The chemical components of the biomass tar samples were determined by gas chromatography-mass spectroscopy (GC-MS), as listed in Table 2.

Table 2 Chemical components of biomass tar by GC-MS analysis

Component	Formula	Molecular weight	Relative contents/%
4-ethyl-phenol	$C_8H_{10}O$	122	9.44
Phenol	C_6H_6O	94	7.49
3-methyl-phenol	C_7H_8O	108	6.38
Naphthalene	$C_{10}H_8$	128	6.14
Acenaphthylene	$C_{12}H_8$	152	5.69
2,3-dihydro-Benzofuran	C_8H_8O	120	5.30
Anthracene	$C_{14}H_{10}$	178	4.61
2-methyl-phenol	C_7H_8O	108	3.51
4-ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	152	3.43
1-methyl-naphthalene	$C_{11}H_{10}$	142	3.26
2-methyl-naphthalene	$C_{11}H_{10}$	142	2.58
2,5-dimethyl-phenol	$C_8H_{10}O$	122	2.26
2-methoxy-4-vinylphenol	$C_9H_{10}O_2$	150	2.24
2,4-dimethyl-phenol	$C_8H_{10}O$	122	2.22
4-ethyl-3-methyl-phenol	$C_9H_{12}O$	136	2.02
1H-phenalene	$C_{13}H_{10}$	166	2.02
Dibenzofuran	$C_{12}H_8O$	168	1.60
2-methoxy-phenol	$C_7H_8O_2$	124	1.59
2,3-Dimethylhydroquinone	$C_8H_{10}O_2$	138	1.58
Biphenyl	$C_{12}H_{10}$	154	1.56
2,6-dimethoxy-phenol	$C_8H_{10}O_3$	154	1.55
1,7-dimethyl-naphthalene	$C_{12}H_{12}$	156	1.53
Fluoranthene	$C_{16}H_{10}$	202	1.45
2,6-dimethoxy-4-(2-propenyl)-phenol	$C_{11}H_{14}O_3$	194	1.43
1,1'-(1,3-butadiyne-1,4-diyl)bis-benzene	$C_{16}H_{10}$	202	1.22
2-ethenyl-naphthalene	$C_{12}H_{10}$	154	1.20
Phenanthrene	$C_{14}H_{10}$	178	1.11
2-ethyl-phenol	$C_8H_{10}O$	122	1.03
Others			14.56

3.2 Gas chromatography–mass spectrometry

The dried tar was dissolved in ethyl acetate having a ratio of tar: solvent = 1 g : 10 mL at room temperature. The solution was centrifuged and the upper liquid fraction collected and diluted to a weight concentration of 0.5% for analysis by gas chromatography-mass spectroscopy (GC-MS) (Table 2). An HP-3800 gas chromatograph equipped with a split/splitless injector and an HP-8410 automatic sampler with splitless injection were used. The injector was maintained at 250℃, and helium having a flow rate of approximately 1.0 mL/min was used as the carrier gas. The GC was equipped with a 30 m (length) × 0.25 mm (inner diameter) Hewlett Packard HP-5MS capillary column with a film of 0.25 mm thickness. The oven temperature program was kept at 40℃ for 3 min, and subsequently heated to 200℃ at 15℃/min, followed by further heating to 280℃ at 1℃/min and held at 280℃ for 5 min. The end of the column was directly introduced into the ion source of an HP 5970 mass selective detector (MSD) in electron ionization (EI) mode. The mass spectrometer conditions were as follows: transfer line, 270℃; ion source, 250℃; and electron energy, 70 eV. The data acquisition was accomplished by HP-UX chemstation software using an HP-UNIX computer and an NBS mass spectra library database. The relative content of each component was determined by dividing the individual peak area by the total peak areas in the chromatogram of the biomass tar.

Table 3 Melting and boiling points of main chemical components in biomass tar

Component	Melting point/℃	Boiling point/℃
4-ethyl-phenol	46	219
Phenol	40.6	181.9
3-methyl-phenol	10.9	202.8
Naphthalene	80.5	217.9
Acenaphthylene	92-93	265-275
2,3-dihydro-Benzofuran	-37	194
Anthracene	218	342
2-methyl-phenol	30-32	191
4-ethyl-2-methoxy-phenol	-30	153
1-methyl-naphthalene	-22	240-243

As listed in Table 2, the main components of biomass tar are 4-ethyl-phenol, Phenol, 3-methyl-phenol, Naphthalene, Acenaphthylene; 2,3-dihydro-Benzofuran; Anthracene; 2-methyl-phenol; 4-ethyl-2-methoxy-phenol; and 1-methyl-naphthalene. The most abundant component is 4-ethyl-phenol at 9.44%, having a melting point of 46℃, and a boiling point of 219℃. Anthracene, (C8H10O) another hydrocarbon component, has a content of up to 4.61%. The chemical and physical properties of the biomass tar have a greater influence on the thermal weight loss characteristics, especially the boiling point of Acenaphthylene, the highest of the components, reaching 265℃. Moreover, the analyzed biomass tar was a complex mixture, the chemical composition of which had a significant influence on the properties thereof and the derived biomaterials.

The respective boiling points of the components are graphed in Figure 1.

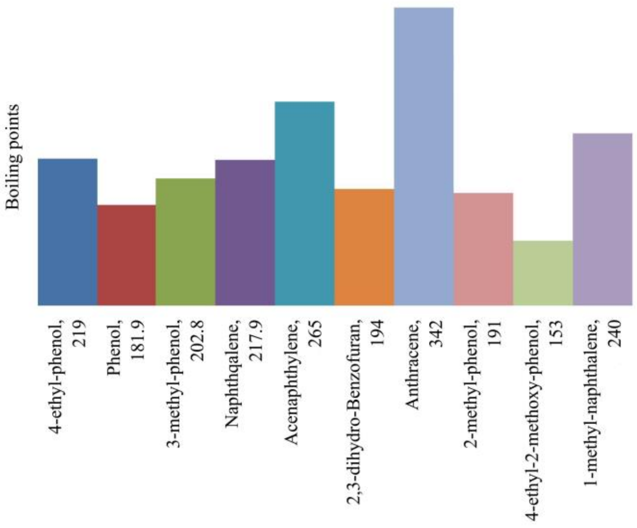


Figure 1 Boiling points of components

Concurrently, the thermal decomposition process of the hydrocarbons was observed within a wide temperature range from 250℃ to 340℃, the respective mass losses being the fastest. Condensation and polymerization also occurred through the loss of side alky groups from the aromatic compounds. The higher the boiling point of the component, the more difficult the gasification. Therefore, the boiling points of the various components in the thermogravimetric experiments should show different gasification trends at rapid heating rates.

3.2 Thermogravimetric analysis

The thermal decomposition process of the tar was characterized by a TA thermogravimetric analyzer (TGA Q50) with a resolution of 0.1 μg. The experiment was implemented in non-isothermal conditions from 30℃ to 800℃ at variable heating rates of 10, 50, and 100 K/min. The sample was ground into powder to avoid the effect of heat transfer during the decomposition process. A weight of 5 mg was selected for thermal analysis in a nitrogen atmosphere at a flow rate of 60 mL/min. At least three samples were run at each heating rate to guarantee the repeatability and reliability of the data obtained. The weight loss curves (TG) and differential thermogravimetric curves (DTG) against the temperature of the samples were recorded for thermal kinetic analysis. In order to avoid the effect of adsorbed water on the decomposition process, all the samples were dried in a vacuum at 80℃ for 48 h.

3.3 Thermogravimetric and differential thermal analysis curves

The thermogravimetric (TG) and differential thermal analysis (*DTA*) curves of biomass tar from corn stover at different heating rates were determined by a synchronous thermal analyzer, as plotted on the graphs in Figure 2.

As indicated in Figure 2a and 2c, the shapes of the TG curves in a nitrogen atmosphere at two different rapid heating rates (10 K/min, 100 K/min, respectively) were very similar, but the starting time for each reaction was different. Figure 2a also indicates that the starting reaction temperature of the thermal weightlessness was about 100℃ when the heating rate was slower. When the pyrolysis reaction temperature reached 350℃, the trend of the change in weight loss was linear with an increase in temperature. Figure 2a shows that the phenomenon of weight loss was very significant at about 150℃ when the heating rate was faster, but the changing trend in weight loss began to decelerate after reaching 400℃; moreover, the change in weight loss was approximately linear with the increase in temperature.

It is significant that the progress of biomass pyrolysis was affected by two different heating rates; moreover, the influence of the heating rate was greater especially in the late reaction process.

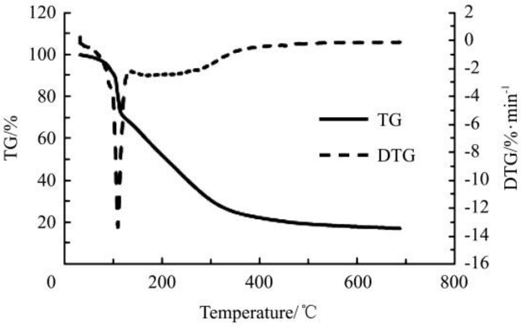
Figure 2 shows that the DTG curve had two peaks: the first, a rush; the second, wider and more obvious as the rate increased. For example, when the heating rate was 50℃/min, the thermal weightlessness process could be divided into four stages:

1) Weightlessness below 100℃, in which drying occurred;

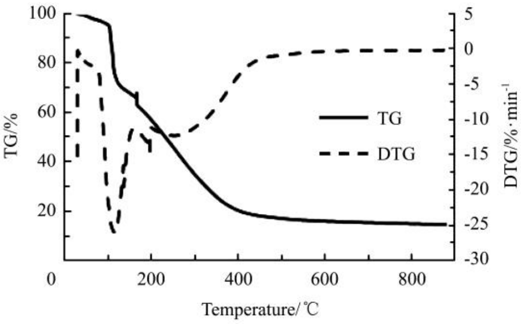
2) Weightlessness between 100℃ and 150℃, a very obvious peak in which burning occurred, producing only water and CO_2, as when the heating rate was less than 10℃/min; in this stage the cracking rate of the differential thermal analysis curve also reached its maximum at 100℃, at which point the weight loss was about 20%;

3) Weightlessness between 150℃ and 400℃, a very wide and flat peak, characterized by volatility and cracking of the main macromolecular compounds;

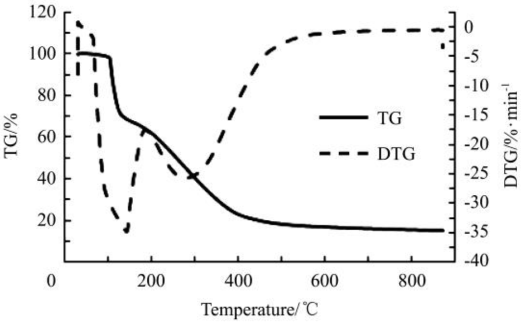
4) Weightlessness between 400℃ and 900℃, closely smooth and straight, in which the cracking rate began to reduce and the weightlessness leveled off.



a. 10 K/min



b. 50 K/min



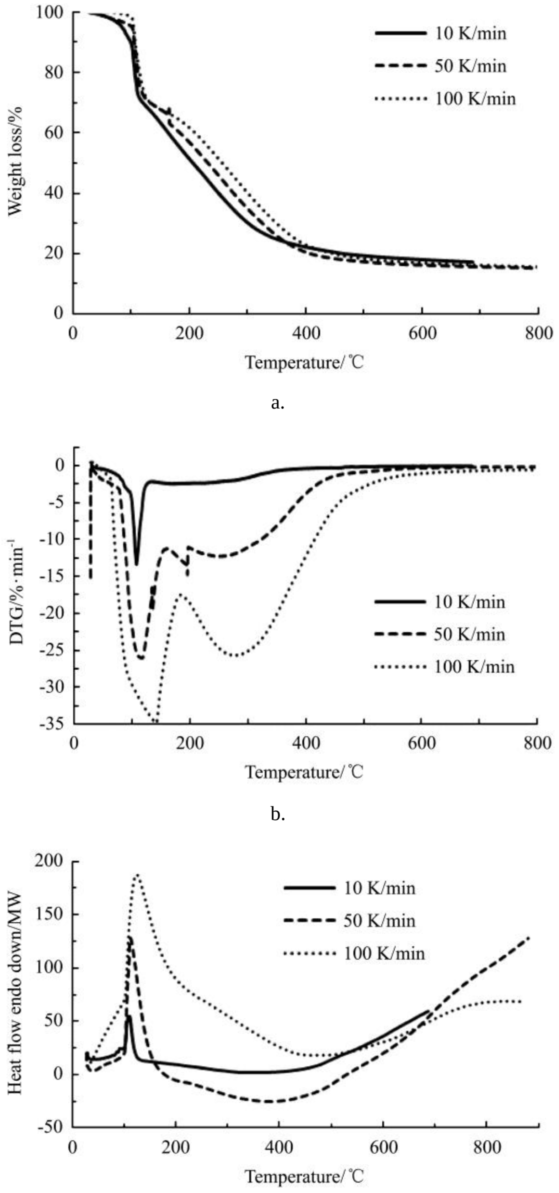
c. 100 K/min

Figure 2 Thermal analysis curves of biomass tar at different heating rates

The solid residue was approximately 20% at a temperature of 900℃. In both the TG and the DTG, the change rule was similar, but the initial cracking temperature was very different. The greater the heating rate, the higher the temperature; whereas, the lower the temperature, the lower the heating rate. In the cracking process, the reaction was exothermic after reaching the pyrolysis temperature.

3.4 Influence of heating rate on thermal weightlessness characteristics

The contrastive analysis of the *TG* and *DTA* curves of biomass tar from corn stover at different heating rates (10℃/min, 50℃/min, 100℃/min, respectively) are plotted in Figure 3.



a.

b.

c.

Figure 3 Contrastive analysis of *TG* and *DTG* curves at different heating rates

As illustrated in Figure 3, the thermal weightlessness process in a nitrogen atmosphere included four main phases: 1) drying, 2) fast release of surface volatility, 3) an interim, and 4) slow release of internal volatility.

In the drying stage, the heating rate had a smaller influence on the evaporation of water. The *TG* curves of the three heating rates were coincidentally within a temperature range between 0℃ and 35℃, and at 100℃ changed with a different heating rate.

Among the DTG curves, the slope and weight loss ratios were the largest of all, namely, when the reaction temperature was within the range of 35-100℃, the process consisted of not only the evaporation of water but also included an initial volatile release. Thus, the greater the heating rate, the more obvious the volatile releases.

In the fast-release stage of surface volatility, the biomass tar first began cracking with the rapid increase in temperature in which the macromolecular consistency was cracked into smaller molecules and generated biomass fuel gas. Therefore, there was an obvious weightlessness in the biomass in the continuous volatile escape of gas from the surface.

The *TG* curves indicate that the weight loss in the biomass tar gradually increased to the maximum, the slopes of the curves being approximately linear. The DTG curves indicate that the temperature at the highest weight-loss rate was about 100℃ when the heating rates were at 10℃/min and 50℃/min, respectively. The temperature at the highest weight-loss rate was about 150℃ when the heating rate was at 100℃/min. The release stage of the surface volatility was a strongly endothermic process because there was an obvious peak in the DTG curves.

The interim stage was one of coexistence characterized by both of a fast release of surface volatility and a slow release of internal volatility. The weight loss in the TG curves began to decrease gradually and parabolically. The weight-loss rate in the *DTG* curves began to decrease approximately linearly from the maximum as the temperature increased. The change in the three *DTG* curves was different: the higher the heating rate, the steeper the slopes.

In the slow-release stage of internal volatility, only a small amount of the volatile matter was released by pyrolysis due to the already completed fast-release process of surface volatility. In the later stage of pyrolysis only coke, ash and a small amount of volatile matter remained in the biomass. Therefore, the release rate of volatile matter was lower as a result of the very small volatile content in this stage. As indicated by the TG curves, the weight loss in the biomass tar was reduced very gently. The end temperature of the pyrolysis was about 690℃ when the heating rate was 10℃/min, and about 800℃ at 50℃/min or 100℃/min. The weight-loss rate was gradually reduced until it became equivalent with that shown in the DTG curves.

4 Conclusions

An experimental study consisting of a thermal gravimetric analysis (*TGA*) of biomass tar at three heating rates (10 K/min, 50 K/min, 100 K/min, respectively) in a nitrogen atmosphere has been completed.

GC-MS techniques were used to characterize the complex structure of the biomass mainly composed of phenols and polycyclic aromatic hydrocarbons, some of which were substituted by ethyl or methoxyl. The main components studied were the phenols and the PAH, which were similar to the tar components in other previously studied biomass resources such as wood and bamboo[17], although the weight proportions of specific chemical compounds are mutually distinguishable.

Table 2 lists the low molecular-weight components of the biomass volatized at the beginning stage of a thermal-chemical conversion process, in which the phenols and polycyclic aromatic hydrocarbons lost their side chains with the increasing temperature and large molecular-weight hydrocarbons formed by the polymerization and condensation reactions. The absorption bands at 1 265 cm^{-1} and 1 036 cm^{-1} were asymmetrical, but symmetrical stretching vibrations of aryl-alkyl ethers were associated with aromatic rings. A number of hydrogen atoms were located on the aromatic rings, indicated by the bands at 830 cm^{-1} and 750 cm^{-1}, attributed to C-H out-of-plane bending vibrations in the rings. In addition, the IR stretching frequency of the carbonyl groups at 1 686 cm^{-1} was lower than that of carbonyl at 1 715 cm^{-1} in ketone, a phenomenon probably caused by the conjugation of carbonyl groups with the aromatic structures and the delocalization of π electrons[18].

The results obtained prompted the following generalizations.

1) The thermal weightlessness process of biomass tar in a nitrogen atmosphere consists of four main phases: drying, fast release of surface volatility, an interim, and slow release of internal volatility.

2) The TG curves of biomass tar move to high temperatures with increases in the heating rate. The greater the heating rate, the steeper the curve and the lower the resolution. The lag phenomena of the respective temperatures are more serious.

3) The peak temperature and maximum reaction rate of *DTA* curves increase with the heating rate.

4) The volatility and molecular residence time of biomass tar are shortened at higher heating rates.

Acknowledgments

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