

Pyrolysis and combustion characteristics of Bio-oil from swine manure

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Abstract Pyrolysis and combustion characteristics of bio-oil derived from swine manure were investigated using thermogravimetry techniques. Thermogravimetric analysis of the bio-oils were carried out in O₂ and N₂ atmosphere under different heating rates (5–20 °C/min) to a maximum temperature of 900 °C. The results indicate that the combustion processes of bio-oil occurred in three stages, namely the water and the lighter compound evaporation, i.e., the release of the volatile compounds, ignition and burning of the heavier compounds (mainly carbon), and finally decomposition of the carbonate compounds. The effect of heating rate was also studied, and higher heating rates were found to facilitate the combustion process. Different reaction kinetic mechanisms were used to treat TG data, and showed that diffusion models are the best fit for describing the combustion of bio-oil in air. The kinetic parameters of the three stages were determined using Coats–Redfern method. The study provided reliable basic data for the burning of bio-oil.

Keywords Bio-oil · TG · Combustion kinetics · Swine manure

Introduction

Since the shortages of petroleum resources dating from the global energy crisis in the 1970s, considerable attention has been focused on the development of alternative fuels. Bio-oil is a liquid fuel produced by the thermochemical conversion (e.g., pyrolysis, hydrothermal liquefaction) of biomass. Due to its vegetation source, bio-oil is a renewable and greenhouse gas neutral fuel when combusted. Considering the great international attention focused on global climate change, these attributes make bio-oil an attractive alternative liquid fuel source for power generation, internal combustion engines, and transport.

Bio-oil is a complex organic mixture with high oxygen content, containing more or less solid carbon particles, and its color is brown to black, having a pungent odor [1]. As substitutes for fossil fuels, bio-oil can produce heat, electricity, and chemicals. However, the most direct application of bio-oil is as boiler fuel oil [2]. Therefore, a deeper study of bio-oil combustion characteristics will contribute to the design, operation, and maintenance of the boilers and improve combustion efficiency and reduce environmental pollution. Combustion is the thermal decomposition of biomass in the presence of excess air or oxygen. Due to the complex nature of bio-oil, the bio-oil combustion is extremely complicated and its combustion behavior and mechanism still not fully understood yet. Few researchers have done research on the combustion characteristics of bio-oil [3–6]. Li et al. [3] studied the combustion characteristics of bio-oil from sewage sludge. Li et al. [4] investigated the biomass tar combustion behavior in coexistence of dolomite and mayenite, and proposed three stages combustion kinetics model.

Animal wastes hold tremendous energy potential and they can be viewed as an underutilized renewable energy

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resource. In recent work, we successfully converted swine manure into bio-oil products in a high-pressure reactor under inert atmosphere [7]. Bio-oils were characterized for physical properties and detailed chemical composition using a combination of chromatographic and spectroscopic techniques [8]. Since the properties of the bio-oil products are dependent on the characteristics of the raw material and the processing conditions, it is necessary to investigate the thermal characteristics of the bio-oils to evaluate the liquefaction process and establish a market for the liquefied oil.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) are a widely used technique to study reaction mechanism and kinetics of solids undergoing thermal decomposition [9–14]. The combined use of differential thermogravimetric (DTG) analysis and DSC data can improve the accuracy of identifying initial and final temperatures corresponding to each transformation step and provides useful information to estimate thermal degradation pseudo-kinetic parameters such as activation energy (E), frequency factor (A), and reaction order(n) [15]. Kinetic research is useful in helping to understand the thermal degradation process, and provided information for designing and controlling a thermal degradation process using biomass.

In this study, the pyrolysis and combustion characteristics of bio-oils derived from swine manure were studied by TG and DSC. Experiments were performed twice for repeatability, and the standard deviation was found to be less than 1% in general. The kinetic constants were obtained considering the thermal degradation of biomass as a system of reactions in series. The effect of heating rate on bio-oil pyrolysis and combustion was also studied.

Experimental

Materials

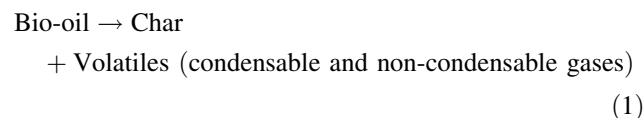
Bio-oil sample was produced from liquefying swine manure using a high-pressure batch reactor. The detail information regarding to the bio-oil production can be found in literature [7]. The properties of bio-oils are presented in Table 1.

Thermogravimetry

Bio-oil samples with an average sample size of 20–30 mg were subjected to TG analysis in nitrogen and air atmosphere using TA Instruments Q600 Simultaneous TGA/DSC (SDT) analyzer where the mass loss, determined TG, and temperature changes (differential thermal analysis, DTA) were recorded simultaneously. Thermogravimetric curves were obtained at three different heating rates (5, 10, 20, and 20 °C/min) between 20 and 900 °C. Purified nitrogen and air at a flow rate of around 60 mL/min was used as the purge gas to provide an inert/oxidative atmosphere for pyrolysis and combustion, respectively.

Kinetic analysis

The combustion kinetics of bio-oil is very complicated. It involved a large number of reactions in series and/or in parallel. However, the oxidation can be described by one-step global model when the sample size is small and with an excess air supply [9, 12, 17], which can be schematized as:



where the reaction rate is a function of the remaining raw material and follows an Arrhenius law dependent on temperature [16].

The solid combustion reaction rates are generally expressed as:

$$d\alpha/dt = kf(\alpha) \quad (2)$$

where the fractional reaction α is defined in the terms of the change in mass of the bio-oil sample:

$$\alpha = (m_0 - m)/(m_0 - m_f) \quad (3)$$

where m_0 , m , and m_f are the initial, actual, and final mass of the sample during an experiment, respectively; $f(\alpha)$ is a function that is characteristic of the way the reaction interface occurs through the sample, which may be represented in the form of an n th order reaction: $f(\alpha) = (1 - \alpha)^n$; and k is the reaction rate constant that obeys the Arrhenius correlation:

$$k = A \exp(-E/RT) \quad (4)$$

Table 1 Properties of bio-oil produced from liquefaction of swine manure

Elemental analysis/wt%				Moisture/wt%	Ash/wt%	PH/water	Heating value/MJ kg ⁻¹	Viscosity 50 °C/cP
C	H	N	O					
72.58	9.76	4.47	13.19	2.37	0.78	5.04	36.05	843

where A is the frequency factor; E is the activation energy, R is the universal gas constant; and T is the absolute temperature. By introducing the Arrhenius correlation, Eq. 2 becomes:

$$dx/dt = A \exp(-E/RT)f(x). \tag{5}$$

For the non-isothermal condition with a heating rate β , Eq. 5 can be rewritten as follows:

$$dx/f(x) = (A/\beta) \exp(-E/RT)dT. \tag{6}$$

Integrating Eq. 6, the following expression can be obtained:

$$g(x) = \int_0^x \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \tag{7}$$

Following Coats and Redfern [16] approximation, the integral form of Eq. 7 is:

$$\ln \left[\frac{g(x)}{T^2} \right] = \ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \tag{8}$$

The general method used in one-step global model for deriving kinetic parameters and for assessing the form of $g(x)$ is by plotting the mass loss data from the TG. A plot of $\ln[g(x)/T^2]$ versus $1/T$ is a straight line having slope E/R . The frequency factor (A) is obtained from the intercept of the line. From the plots, the attempt of different forms of $g(x)$ is plotted, and the expression giving the best regression coefficient is considered to be representative of the sample's reaction order and mechanism.

In this article, a number of forms of the mechanism integral function $g(x)$ were tested with the experimental data, including [17]

- (i) the sigmoid rate model, $g(x) = [-\ln(1 - \alpha)]^{1/m}$, $m = 1, 2, 3$
- (ii) the Geometric models, $g(x) = 1 - (1 - \alpha)^{1/m}$, $m = 2, 3$
- (iii) 1D, 2D and 3D-diffusion models (e.g., 3D: $g(x) = [1 - (1 - \alpha)^{1/3}]^2$)
- (iv) the reaction order model, $g(x) = [1 - (1 - \alpha)^{1-n}]/(1 - n)$ with n the order of reaction ($g(x) = \ln(1 - \alpha)$ when $n = 1$)

Results and discussion

TG Analysis of bio-oils in N₂ and Air

TG curves under inert and oxidative conditions at 20 °C/min are present in Fig. 1. In both conditions, a peak occurred between 50 and 100 °C. The peak was caused by the volatilization of water and the lightest components of

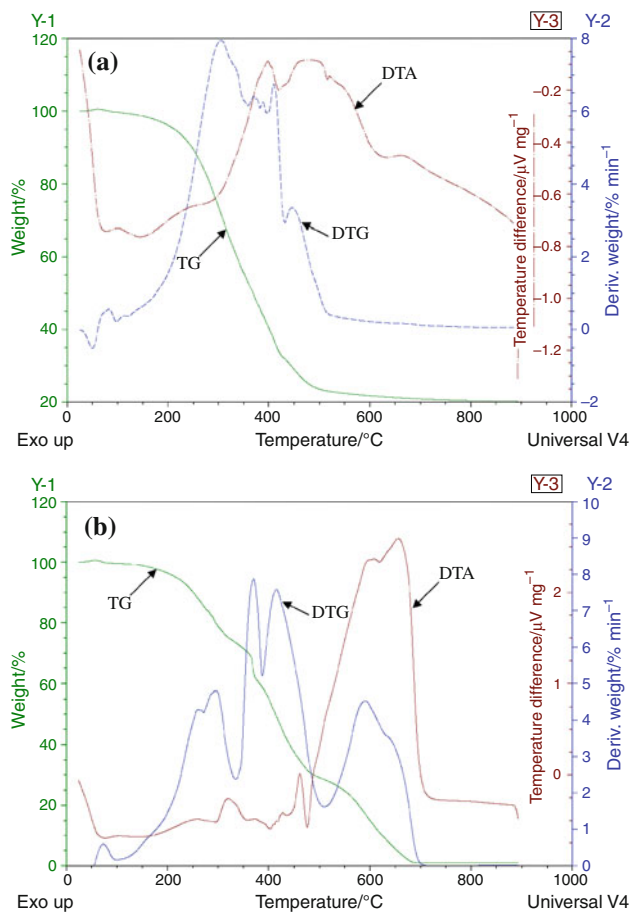


Fig. 1 TG curves under inert and oxidative conditions at 20 °C/min. **a** Under N₂ atmosphere; and **b** under O₂ atmosphere

the oil product [18]. DTA curves indicate that it is an endothermic stage both under inert and oxidative conditions. Mass loss reaches 3 and 4% under inert and oxidative conditions, respectively.

The TG–DTG curve displayed distinct differences after 100 °C. The sample lost most of its weight (90%) between 126 and 526 °C, and a slower rate of further weight loss occurred until 800 °C under a N₂ flow. The weight loss rate reaches its maximum value at 305 °C. This stage is shown as an endothermic process in the DTA curve, which can be attributed to the evaporation of light compounds from the sample. Furthermore, two DTG shoulder peaks emerge at around 368–408 and 447 °C on the right, respectively. The DTA curve displayed two exothermic peaks in this reign, which is probably due to the decomposition reaction of the heavy components in the oil. The residue is 20.47%.

Under oxidative conditions, the DTG curve shows three large overlapping peaks and a flat tail. The first large overlapping peak produces a DTG peak at 296 °C with a weight loss rate of 4.8%/min. The second stage of decomposition is rather rapid. The weight loss rate reaches its maximum at 418 °C with a value about 8%/min suggesting the some

heavy compounds had decomposed. The corresponding DTA curve shows a mild endothermic process before 410 °C, similar to the process in the inert atmosphere, which suggests that organic compounds evaporated in this section. However, it reverses to an exothermic process from 410 to 480 °C. Volatiles oxidation in the gaseous phase might account for this exothermic process [4]. The third large overlapping peak representing combustion reaction of the heavy compounds emerges at 590 °C. It generates a large exothermic peak and only 1.026% residue left.

The combustion of bio-oil from swine manure can be divided into three phases: In the first phase, water and light compounds (e.g., acetone, methanol, and formaldehyde) volatilized and were oxidized, which occurred before 335 °C; in the second phase, the heterogeneous combustion occurred between the heavy compounds and oxygen; in the third stage, the char that was formed during the previous process of evaporating and cracking combusted. The main weight loss occurs in the second region, which corresponds to a mass loss of 44.87%. The volatilization stage of bio-oil from swine manure finishes at 480 °C, which is higher than bio-oil from biomass at 140 °C [3]. This implies that bio-oil from swine manure has better thermal stability.

Heating rate effects on pyrolysis and combustion characteristics

Pyrolysis processes at different heating rates

As shown in Fig. 2, under inert conditions, it was found that the initial weight loss temperature, the maximum weight loss rate, and temperature corresponding to it all rise with increasing of the heating rate. As the heating rate increased from 5 to 20 °C/min, the maximum weight loss rate changes from 2.2 to 7.7%/min, and the corresponding temperature shifted from 260 to 307 °C. Therefore, the release of volatile components is highly affected by heating rate. It can be explained when the heating rate is different, and the speed of heat transference from exterior to interior varies too. At low heating rate, the sample has adequate time to absorb heat, which leads to the bio-oil volatilized at comparatively lower temperature. Another influence of heating rate on pyrolysis is the amount of residue left. Fewer residues left at lower heating rate (5 °C/min). The residue is 16.86% at 5 °C/min and 20.17% at 20 °C/min, respectively.

Combustion processes at different heating rates

Significant changes were found from both TG curves and DTG curves at different heating rates (Fig. 3). The heating rates significantly affect the amount of residue left. The residue is 18.02% at 5 °C/min, comparing to 1.03% at both 10 and 20 °C/min. It has been proposed in many studies

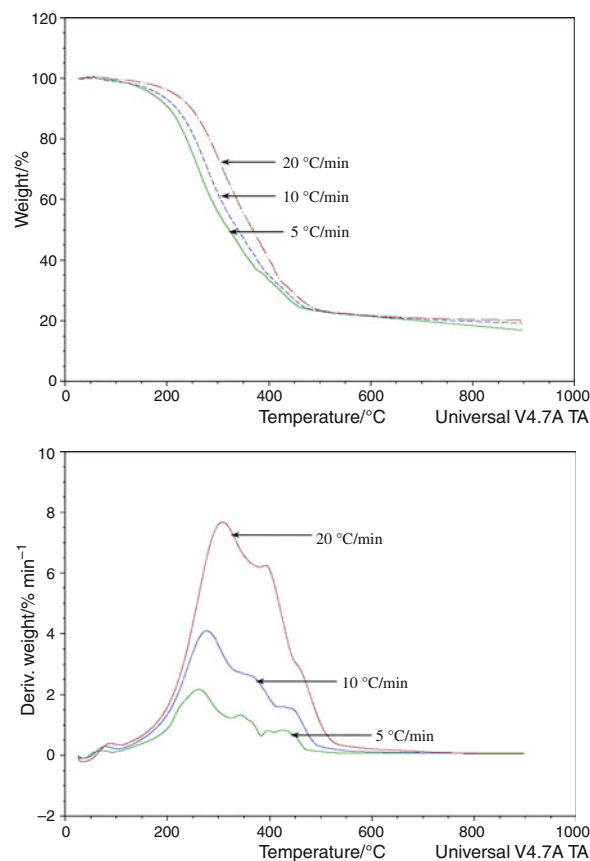


Fig. 2 TG–DTG curves under inert conditions at 5, 10, and 20 °C/min

[19, 20] that the higher heating fluxes in the high heating period decreased the viscosity of the decomposing biomass material, thus enhancing the depolymerization reactions to form higher yields of volatile materials and lower yields of char. As a consequence, it can be assumed that with a heating rate lower than 5 °C/min, the heating fluxes are not sufficient, which could result in an increase in solids yield and decrease in liquids and gases.

Similar to the pyrolysis process in the inert atmosphere, it was found that with the increase of heating rate, the DTG curve was steeper, and the starting and ending temperatures were slightly moved to the high-temperature direction at every step. At 5 °C/min, it took about 90 min from 106 °C to the burnout temperature (545 °C). However, at 20 °C/min (the burnout temperature is 667 °C) it took just 27 min. Therefore, higher heating rates benefit the combustion process by increasing the combustion rates and decreasing the burning duration.

Combustibility characteristic parameters at different heating rates

Several characteristic temperatures are deducted from the TG/DTG curves to evaluate the bio-oil combustion

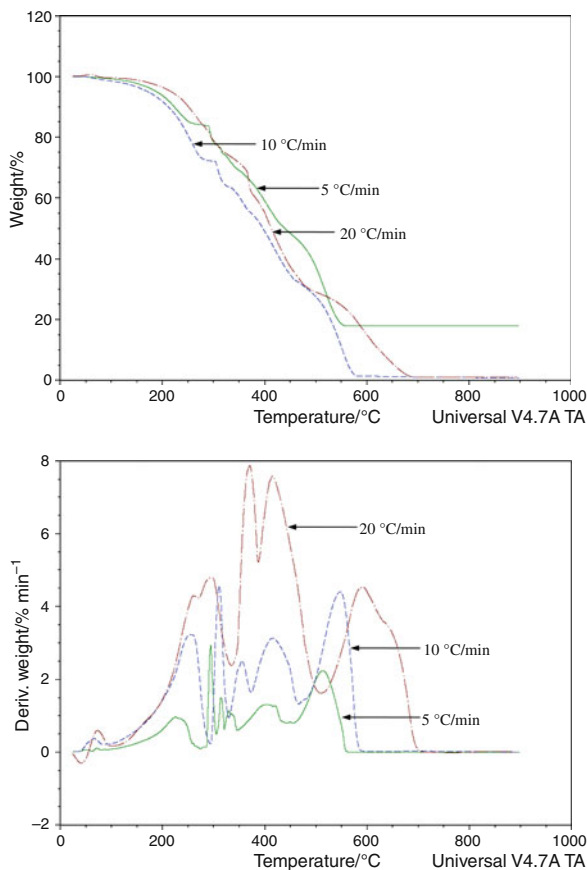


Fig. 3 TG–DTG curves under oxidative conditions at 5, 10, and 20 °C/min

properties, such as the ignition temperature, burnout temperature, and combustibility characteristics index, which were listed in Table 2. These characteristic temperatures reflect the reaction dynamics of the sample during combustion. The combustion of bio-oil is related to ignition, which is not only an important factor for normal operation of burners, but also is a key parameter for new burner designs.

T_i , the ignition temperature, was acquired according to the method described by [21] as follows: A line is drawn across the peak of DTG curve and produces an intersection with the TG curve. Then, a tangent line of the TG curve is drawn through this intersection. At the same time, a horizontal line is drawn based on the initial part of the TG curve. Finally, the tangent line and the horizontal line intersect at a spot, and the corresponding temperature of this spot is ignition temperature. DTG_{max} is the peak of the DTG curve, in other words, the maximum of the weight loss rate during the combustion process. T_{max} is the temperature of greatest combustion rate, which is the corresponding temperature of the DTG_{max} . T_h is the burn out temperature which is defined as the temperature at which conversion (α) of 98% is achieved. The conversion is defined on the basis of the combustible part of the material and described as,

$$\alpha_T = (\omega_0 - \omega_T) / (\omega_0 - \omega_\infty) \times 100\% \tag{9}$$

where, ω_0 and ω_∞ are the masses at the beginning and at the end of the combustion, and ω_T is the mass at temperature T .

Table 2 Combustibility characteristic parameters at different heating rates

$\beta/^\circ\text{C min}^{-1}$	$T_i/^\circ\text{C}$	$T_{max}/^\circ\text{C}$	$T_h/^\circ\text{C}$	$DTG_{max}/\% \text{ min}^{-1}$	$DTG_{mean}/\% \text{ min}^{-1}$	$S/\%^2 \text{ K}^{-3} \text{ min}^{-2} 10^{-8}$
5	267	294	545	2.93	1.42	1.74
10	256	311	570	4.56	2.44	5.74
20	251	369	667	7.85	4.20	12.8

Table 3 Kinetic parameters for combustion reaction of bio-oils

Heating rate $\beta/^\circ\text{C min}^{-1}$	Temperature range/ $^\circ\text{C}$	$E/\text{kJ mol}^{-1}$	A/min^{-1}	Correlation coefficients, R^2	Model
5	25–288	59.01	14.19×10^4	0.969	3D-diffusion
	288–451	33.55	8.1×10^4	0.9954	2D-diffusion
	451–570	38.9	9.3×10^4	0.9775	1D-diffusion
10	25–293	60.15	14.46×10^4	0.9091	3D-diffusion
	293–453	29.73	7.13×10^4	0.9845	2D-diffusion
	453–595	22.55	5.40×10^4	0.9204	1D-diffusion
20	25–335	77.54	18.7×10^4	0.9991	3D-diffusion
	335–512	55.88	13.4×10^4	0.9893	Third order
	512–693	25.15	6.03×10^4	0.9744	2D-diffusion

Combustibility characteristic index S has been widely used by the researcher to characterize combustion properties of solid fuels [21, 22]. S is the integration parameter of ignition and burnout characteristics for bio-oil combustion, and higher values represent better combustion properties. The combustibility characteristic index S is defined as:

$$S = (\text{DTG}_{\max} \times \text{DTG}_{\text{mean}}) / (T_i^2 \times T_h) \quad (10)$$

where $\text{DTG}_{\text{mean}} = (\alpha_{T_h} - \alpha_{T_i}) / ((T_h - T_i) / \beta)$, which is the average rate of the conversion from T_i to T_h and $\beta = 20$ °C/min.

Table 2 reports the combustibility characteristic parameters of the bio-oil at different heating rates. Ignition temperature decreased slightly from 267 to 251 °C as the heating rates increased from 5 to 20 °C/min. Burnout temperature ascended with heating rate, suggesting the combustion process extends to higher temperature. Larger S value obtained at higher heating rate, indicating the combustion properties were improved by increasing the heating rate. These results suggest that the higher heating rates benefit the combustion process of bio-oil from swine manure.

Kinetic analysis

The bio-oil from swine manure has complex components so that a single kinetic model can hardly be used to describe the combustion process. According to the previous analysis, the combustion of the bio-oil from swine manure can be divided into three stages. The kinetic parameters of the three stages at different heating rates are calculated using Coats–Redfern method by considering the combustion of bio-oil as a system of reactions in series.

Four models including more than twelve alpha functions were tested to fit our experimental results. Using the data from TG thermograms (Fig. 3), the values of activation energy and the frequency factor at three temperature regimes for the three bio-oils were computed and reported in Table 3. The individual activation energies for each reaction region were attributed to different reaction mechanisms. In general, the models that best fit the reaction steps were the 1D, 2D, and 3D-diffusion models, except for the second stage of bio-oil from swine manure at 20 °C/min. The best fit for the second stage of bio-oil from swine manure was a third-order reaction model. The linearity (R) of the fitting straight line is all over 0.9, suggesting the combustion process can be well described by the calculation results.

Conclusions

The pyrolysis and combustion characteristics of bio-oils derived from swine manure liquefaction process were

investigated by TG and DSC. The results suggest three stages in the combustion process. In the first stage, the light compounds volatilized and oxidized in the gaseous phase. In the second stage, the heterogeneous combustion occurred between heavy compounds and oxygen. In the third stage, the char that was formed during the previous process of evaporating and cracking combusted. By comparing TG curves and combustibility characteristic parameters, higher heating rates are suggested to facilitate the combustion process. The kinetic parameters of the three stages were determined using the Coats–Redfern method, which considers bio-oil combustion as reactions in series. The calculation shows that the diffusion models are the best fit for describing the combustion of bio-oil in air.

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