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Thermal Decomposition Characteristics and Kinetic Analysis of Chicken Manure in Various Atmospheres

Xiaodong Pu ^{1,2}, Mingdong Wei ³, Xiaopeng Chen ³, Linlin Wang ³ and Liangwei Deng ^{1,2,*}

¹ Biogas Institute of Ministry of Agriculture and Rural Affairs, Chengdu 610041, China; puxiaodong@caas.cn

² Key Laboratory of Development and Application of Rural Renewable Energy, Ministry of Agriculture and Rural Affairs, Chengdu 610041, China

³ School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China; 1704110449@st.gxu.edu.cn (M.W.); lilm@gxu.edu.cn (X.C.); wanglinlin@gxu.edu.cn (L.W.)

* Correspondence: dengliangwei@caas.cn; Tel.: +86-028-85236376

Abstract: Thermal decomposition technology is one of the main ways to treat biomass wastes. By utilizing chicken manure as raw material, thermogravimetric and derivative thermogravimetry (TG and DTG) are carried out on chicken manure at various heating rates (5, 10, 15, and 20 °C/min) under nitrogen and air atmosphere to explore the thermal decomposition characteristics and kinetics. The obtained results indicate that there are great discrepancies between them in these two atmospheres. Chicken manure is pyrolyzed under nitrogen; however, it is first thermally decomposed and then developed for combustion under air. The temperature range of the main peak of thermal decomposition in the air atmosphere is significantly lower than that in the nitrogen atmosphere by about 30 °C. Furthermore, the fluctuation of the DTG curve pertinent to the air atmosphere is commonly greater than that obtained in the nitrogen atmosphere, and the main combustion section usually presents an obvious W-shape peak. The thermal decomposition kinetics of the chicken manure is also determined as random nucleation model F_1 by employing the Malek method, and the mechanism function is derived by $f(\alpha) = 1 - \alpha$. Under nitrogen atmosphere, the activation energy is between 24.18–31.55 kJ·mol^{−1}. Under air atmospheric conditions, the minimum activation energy of the second temperature section is 8.85 kJ·mol^{−1}, and the activation energy of the first section is less than that of the third section. In the presence of both nitrogen and air, the best result for the thermal decomposition of the sample is attained under the action of 10 °C/min heating rate. The corresponding activation energies are 31.55 kJ·mol^{−1} and 95.91 kJ·mol^{−1}, respectively.

Keywords: chicken manure; pyrolysis; kinetic model; activation energy



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1. Introduction

With the accelerated depletion of fossil fuels and their negative impact on the environment, such as energy crisis, greenhouse effect, and environmental pollution, research has grown in the field of alternative energies or renewable sources of energy [1,2]. Biomass wastes can be transformed into energy or biofuel using biochemical and thermochemical processes. Thermochemical processes, such as hydrothermal liquefaction, pyrolysis, gasification, and combustion, apply thermal energy (also potentially combined with chemical catalysts) for the biomass conversion into valuable products of higher energetic value and/or energy [2]. Pyrolysis and combustion are becoming more and more popular nowadays, avoiding fossil fuel exhaustion. Pyrolysis of biomass technology is one of the crucial ways to achieve renewable energy effectively [3,4]. Biomass components can be transformed into gas, oil, and biochar [5]. According to the European Commission Regulation No. 592/2014 of 3 June 2014, chicken manure as a fuel for combustion has interesting applications. Compared with plant biomass, livestock manure is little influenced by the seasons. Large-scale breeding is beneficial to both centralized and energy utilization of manure, and the raw materials can be sufficiently exploited. Among them, the large-scale

breeding of the chicken industry has developed rapidly in China, and thereby, a large amount of chicken manure is produced every year. Chicken manure has the characteristics of high solid content. Thermal decomposition technology can be considered to convert it into high-value biofuel products, which is of great significance for developing new energy and promoting the cause of “carbon peak and neutralization”.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) are the most broadly utilized analytical approaches to analyze the thermal decomposition characteristics of biomass [6]. The common thermal decomposition raw materials are crop straw, rice husk, municipal sludge, and other wastes produced in the process of agricultural and forestry production [7–12]. Torres et al. pointed out that the performance of the bio-waste slow pyrolysis process was integrally evaluated using the exergetic analysis considering the temperature effect, but also energetic, economic, and environmental indicators [2]. The factors affecting biomass thermal decomposition characteristics are very complex, including biomass type, water content, raw material particle size, heating environment, and heating rate, so the reports on biomass pyrolysis kinetic parameters in relevant studies are very scattered [13–18]. Rodriguez et al. reported that thermal decomposition of the lignocellulosic winery wastes at three heating rates, i.e., 5, 10, and 15 °C/min, under a steam/air mixture atmosphere, and showed that the gasification takes place in three visible stage. The distributed activation energy model method (DAEM) was used. The decomposition is not a single reaction stage, it includes the contributions of parallel reaction steps on the global reaction rate [19]. At present, the research on using livestock manure as thermal decomposition raw material is also increasing [10,11]; nevertheless, there are few investigations on the thermal decomposition characteristics of the same chicken manure, and an inclusive study on the thermal decomposition characteristics of chicken manure under various atmospheres has not been reported yet.

The design and operation of a thermochemical conversion system is highly dependent on the thermal decomposition kinetics study of the biomass waste feedstocks. The kinetic parameters are used to predict the dynamics and behavior of biomass pyrolysis, which can be determined by TG-DTG analysis and kinetic analysis methods. The aim of this work was to investigate the thermal decomposition behaviors (pyrolysis and combustion) of the same chicken manure sample using TG-DTG combined technology with different heating rates (i.e., 5, 10, 15, and 20 °C/min) under two atmospheres. The Malek method was used to solve the reaction mechanism, and the frequency factor was used to obtain more accurate activation energy. A comprehensive understanding of the thermal decomposition behavior of chicken manure could provide guidelines for future energy utilization.

2. Materials and Methods

2.1. Materials

Chicken manures are provided by a supplier in Guangxi, China. After sampling, those are placed in the refrigerator in the presence of 4 °C temperature to keep it fresh. During the experimentation phase, about 5 ± 0.1000 g chicken manure is taken into an evaporating dish and then dried in an oven at 105 °C for 24 h. The former research work showed that the particle size of raw materials has a particular influence on the heat transfer in the biomass thermal decomposition process [20]. In order to reduce the difference in particle size, herein, samples with the particle size of 80–100 mesh are selected as analytical raw materials. The dried chicken manure is ground into powder, screened by 80 target standard sieve, put into a sealed bag prepared in advance, put in a dryer, and stored at room temperature. For the sake of lessening the produced error, two parallel subsamples are made for each sample in the test.

2.2. Test Instruments and Methods

The calorific value was determined by shr-15b oxygen bomb calorimeter (Sangli, Nan jing, China). The thermal decomposition characteristics were measured by TG209F3Tarsus (Netzsch, Selbu, Germany). For this purpose, the following instrument parameters were

taken into account: the applicable temperature range: room temperature~1000 °C, heating rate range: 0 °C/min~50 °C/min, cooling time: 20 min (1000 °C to 100 °C), and wide weighing range: up to 2000 mg. Nitrogen and air are utilized as atmosphere, the gas flow rate is 20 mL/min, the pressure is 0.05 MPa, and the initial test temperature is set equal to room temperature. The pyrolysis profile is recorded under the action of four different heating rates (i.e., 5, 10, 15, and 20 °C/min) and in the presence of the atmospheric pressure.

2.3. Kinetic Analysis via Appropriate Models

For the selection of the thermal decomposition mechanism, the obtained thermogravimetric (TG) data from the experimentally observed data can be employed. The common kinetic model functions presented in Table 1 are utilized in the Malek method and their obtained results are compared with the experimental curves. The main objective is to select the appropriate thermal decomposition mechanism of chicken manure, which has been extensively exploited in the research of other thermal decomposition mechanisms [20–24].

Table 1. The common mode functions of the solid state.

Mode	Symbol	$f(\alpha)$	$G(\alpha)$
Nucleation and growth	Nn	$n(1 - \alpha)[- \ln(1 - \alpha)]^{1/(1-n)}$	$[- \ln(1 - \alpha)]^{1/n}$
Phase boundary control reaction	Rn	$n(1 - \alpha)^{(1-1/n)}$	$1 - (1 - \alpha)^{1/n}$
One-diffusion	D ₁	$0.5\alpha^{-1}$	α^2
Two-diffusion	D ₂	$-1/\ln(1 - \alpha)$	$\alpha + (1 - \alpha)\ln(1 - \alpha)$
Three-diffusion	D ₃	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
Four-diffusion	D ₄	$3/2[(1 - \alpha)^{-1/3} - 1]$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$
Random nucleation	F ₁	$(1 - \alpha)$	$- \ln(1 - \alpha)$
Exponential rule	E ₁	α	$\ln \alpha$

The apparent reaction of the chicken manure pyrolysis can be expressed as in the following form:

Chicken manure → Char + Volatiles

The kinetic equation of the pyrolysis process can be given as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $d\alpha/dt$, $k(T)$, and $f(\alpha)$ represent the degradation rate, thermal decomposition rate constant, and reaction model, respectively. The Arrhenius Equation is often employed in a TG-based analysis reaction, which can properly reflect the relationship between reaction rate and temperature:

$$k(T) = Ae^{-E/RT} \quad (2)$$

in which E , A , T , and R in order are, respectively, the activation energy (J/mol), pre-exponential factor (s^{-1}), absolute temperature (K), and universal gas constant (8.314 J/mol.K). Let us state the reaction model by:

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where α denotes the normalized form of the weight loss data of the decomposed sample, n is the reaction order, and the value of α can be evaluated as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (4)$$

where m_0 , mt , and m_∞ are the initial weight of the sample, the weight at time t , and the final weight, respectively. Equation (1) can be rewritten in the following form by incorporating the Arrhenius expression. By assuming a linear heating rate of $\beta = dT/dt$, where β denotes the heating rate, the conversion rate can be converted into a temperature derivative-based relation as follows:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} = \frac{A}{\beta} \cdot e^{-E/RT} \cdot f(\alpha) \quad (5)$$

Rearranging Equation (5) for separation of the variables α and T and then taking the integral:

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (6)$$

where $G(\alpha)$ is the integral form of the kinetic model. Commonly, various models are utilized to solve Equation (6) and obtain the values of kinetic parameters. These methodologies are broadly classified into two major groups: model-free kinetic (iso-conversional methods) and model-fitted kinetic (Coat's Redfern approach) [25].

3. Results and Discussion

3.1. Compositional Characteristics of the Chicken Manure

The industrial analysis and calorific value analysis of the chicken manure are presented in Table 2. The water content is measured on the fresh sample basis, while other analytical values are measured on the dry basis.

Table 2. Industrial analysis and calorific value analysis of the chicken manure.

Industrial Analysis				Calorific Value/(MJ·kg ^{−1})
Moisture/%	Volatile matter/%	Ash/%	Fixed carbon/%	Q _d
49.06	64.87	17.07	18.06	15.58

The data of chicken manure and sawdust measured by other researchers can be compared. Kim and Burra reported that the higher heating value of the wood chips was 19.54 MJ·kg^{−1}, while the higher heating value of dry chicken manure was 13.3 MJ·kg^{−1}, respectively [26,27]. The heating value of this experiment is just between them. Several research works have shown that the chicken litter has calorific values equivalent to low-rank coals such that about 11,600 J/g can be combusted to generate energy [28,29]. The water content of the chicken manure in the present experiment is less than 50%, which is remarkably lower than the reported chicken manure data. For thermochemical treatment of chicken manure, preliminary drying is required to lessen its water content below 30%. This chicken manure sample contains more sawdust, and the water content of the referenced sawdust is less than 8%. This issue indicates that the appropriate addition of sawdust is not only convenient to the clean chicken manure, but also helpful for the reduction of the overall water content of the chicken manure. Sawdust is generally treated as solid waste, but this alone is an excellent biomass resource. Adding sawdust to farms can not only effectively lessen the time and energy consumption required for chicken manure drying and save treatment costs, but also suggest an effective way to recycle sawdust waste and improve resource utilization. The ash content of the chicken manure is about 24–41 times that of the wood chips. The ash of chicken manure contains a large number of metal oxides, which will fuse at high temperatures. The addition of wood chips can adjust the ash content and composition per unit mass, which has a specific reference value in the design of continuous working equipment.

3.2. Thermal Degradation Analysis of the Chicken Manure

3.2.1. Pyrolysis Analysis in the Presence of Nitrogen Atmosphere

Figure 1 presents the TG and DTG curves of the chicken manure pyrolysis in the presence of the nitrogen atmosphere and heating rate of 5 °C/min. The whole weight loss process of both the chicken manure pyrolysis and thermal decomposition experiences five stages: (i) The dehydration and drying stage begins at room temperature and finishes at 115 °C. The mass reduction in this process is considered to be a certain lag in the volatilization of free water by heating. The mass reduction rate is 3.6%, and a small peak is detected in the DTG curve. (ii) The temperature range of the preheating decomposition section is about 115–210 °C, and the chicken manure will decompose slowly in this process.

It is generally considered that the bound water is separated and the quality is slightly lost with the reduction rate of 0.8%. (iii) The main thermal decomposition section is from 210 °C to 430 °C, and about 35% of the obvious mass loss occurs at this stage. The main weight loss peak appears in the DTG curve, which reflects that the biomass in the chicken manure undergoes complex thermochemical reactions. Furthermore, the demonstrated curve has the maximum decomposition rate, which is caused by protein decomposition, wood fiber polymerization, and glycoside bond breaking in the chicken manure [30]. It appeared that mostly cellulose and hemicellulose decomposed during this weight loss. In addition, because the chicken manure in this experiment is mixed with sawdust, and chicken manure and sawdust form a synergistic effect, the temperature of the main thermal decomposition section is reduced. Zeynep reported that temperature range of the main thermal decomposition section is 200–500 °C [31]. (iv) The mass reduction rate of the carbonization stage is 10%, which occurs in the temperature range of 430–630 °C, in which coke conversion reactions occur, such as thermal cracking and dehydrogenation, as well as the decomposition of formed coke and other inorganic substances [32]. (v) The secondary cracking stage occurs when the temperature is placed in the interval 630–725 °C, and an apparent shoulder peak is detectable on the DTG curve. The mass reduction is due to the thermal decomposition of carbon compounds and inorganic components, with a mass reduction rate of about 10.8%. The mass lessens slowly at the temperature interval 725–900 °C, and the final retained mass is 31.1%.

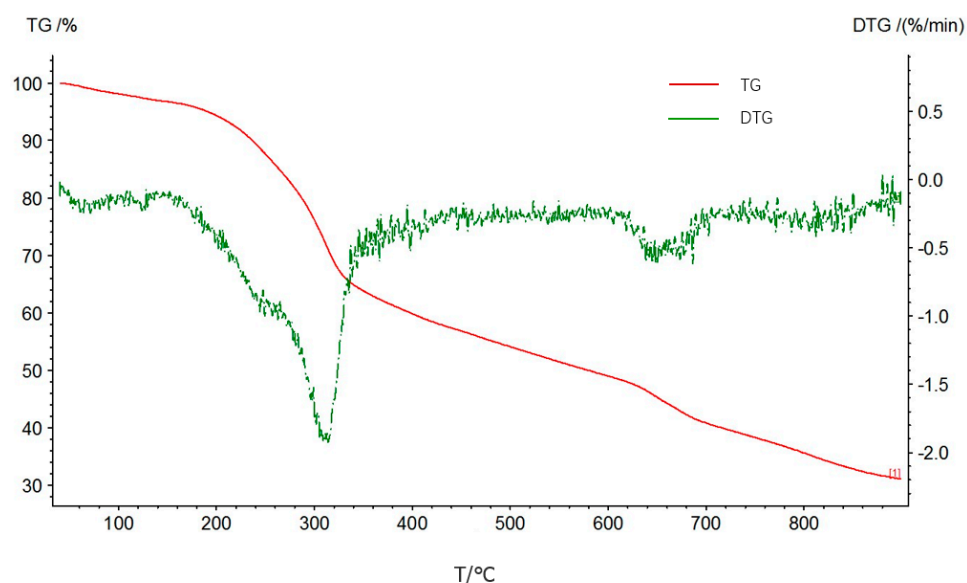


Figure 1. The TG and DTG curves of the chicken manure at a heating rate of 5 °C/min in the presence of nitrogen atmosphere.

3.2.2. Thermal Decomposition Analysis in the Presence of Air Atmosphere

Figure 2 illustrates the TG and DTG curves of the chicken manure burning in the air atmosphere at a heating rate of 5 °C/min. During the process of heating chicken manure from room temperature to 190 °C, it is heated and dehydrated, and oxidative combustion begins at 190 °C, and finally finishes at 680 °C, with the maximum weight loss rate at 275 °C. It is obvious from the DTG curve that there exist three weight loss peaks in the main oxidation combustion section of the chicken manure. Such an issue indicates that the weight loss process of the chicken manure combustion is relatively complex, and the corresponding temperature span is 340 °C, which is 200 °C higher than the range of the thermal decomposition. The main combustion section of the chicken manure can be divided into three stages: (i) For the temperature range of 190–335 °C, the main thermal decomposition of the chicken manure occurs, which is similar to the thermal decomposition

of the chicken manure in the presence of nitrogen atmosphere. A large number of analytes volatilize and there is a certain oxidation reaction in the process. (ii) From 341 °C to 420 °C, a relatively gentle peak appears in the DTG curve. It is considered that the chicken manure is gradually heated, the heat is accumulated, and the thermal decomposition products are continuously oxidized. (iii) From 421 to 530 °C, a large number of accumulated thermal decomposition products undergo violent oxidation reaction and ignition. In the whole process, the chicken manure is first thermally decomposed and then developed for combustion.

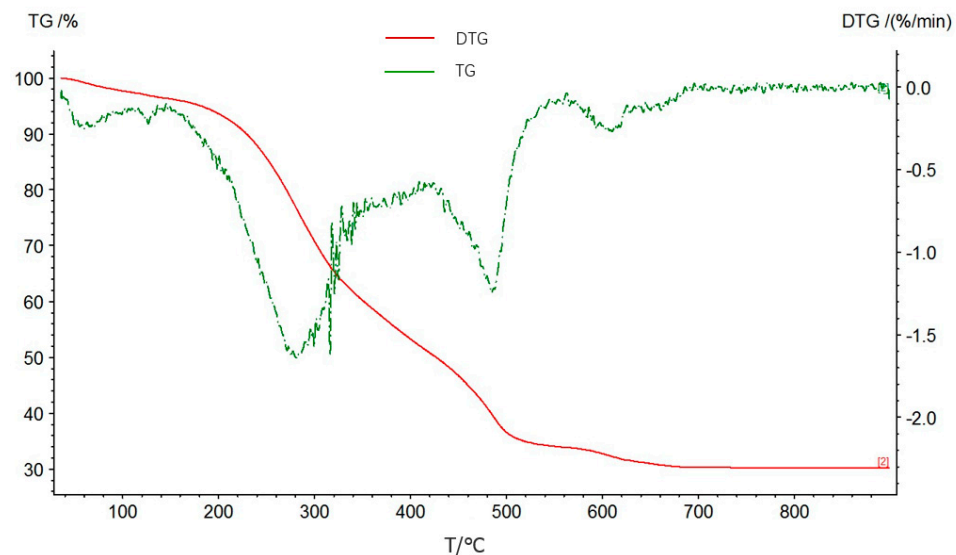


Figure 2. The TG and DTG curves of the chicken manure at a heating rate of 5 °C/min in the presence of air atmosphere.

3.2.3. Effect of Heating Rate on the Thermal Decomposition Characteristics

Figure 3 shows the TG and DTG curves of the chicken manure pyrolysis subjected to nitrogen atmosphere and four levels of the heating rate (i.e., 5, 10, 15, and 20 °C/min). The obtained results reveal that the whole main pyrolysis unit tends to move to the high-temperature zone with the growth of the heating rate, while the secondary pyrolysis unit has an apparent trend. It is obvious from the TG curve that the mass reduction rate of the pyrolysis unit increases with the lessening of the heating rate, and the TG curve deviates slightly from the low-temperature zone to the high-temperature zone. As a general rule, the lower the heating rate in the carbonization stage, the higher the mass reduction rate. This fact also reveals that the longer the residence time of the sample at the same temperature, the more beneficial to decomposition and not beneficial to coke formation. Because the composition of chicken manure is complex, a small fluctuation peak appears at the corresponding temperature of 275 °C on the DTG curve of the main pyrolysis unit, while the highest peak appears at 315 °C. The wavelet dynamic peak is mainly the decomposition of fat, protein, and hemicellulose in the chicken manure, while the highest peak is the decomposition of cellulose, which is more difficult to decompose.

The TG and DTG curves of chicken manure thermal decomposition under different heating rates in the presence of air atmosphere are demonstrated in Figure 4. With the growth of the heating rate, the whole main thermal decomposition oxidation unit has an obvious trend of transferring to the high-temperature zone. At the same temperature, the mass reduction rate lessens with the rise of the heating rate. Except for the ash content corresponding to a 10 °C/min heating rate, faster heating leads to less residual ash.

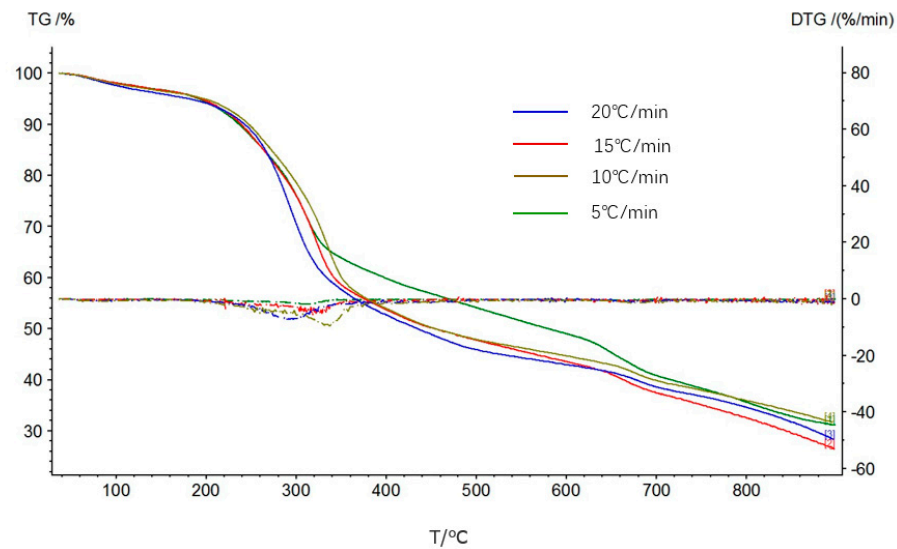


Figure 3. The TG and DTG curves of the chicken manure pyrolysis for different heating rates in the presence of nitrogen atmosphere.

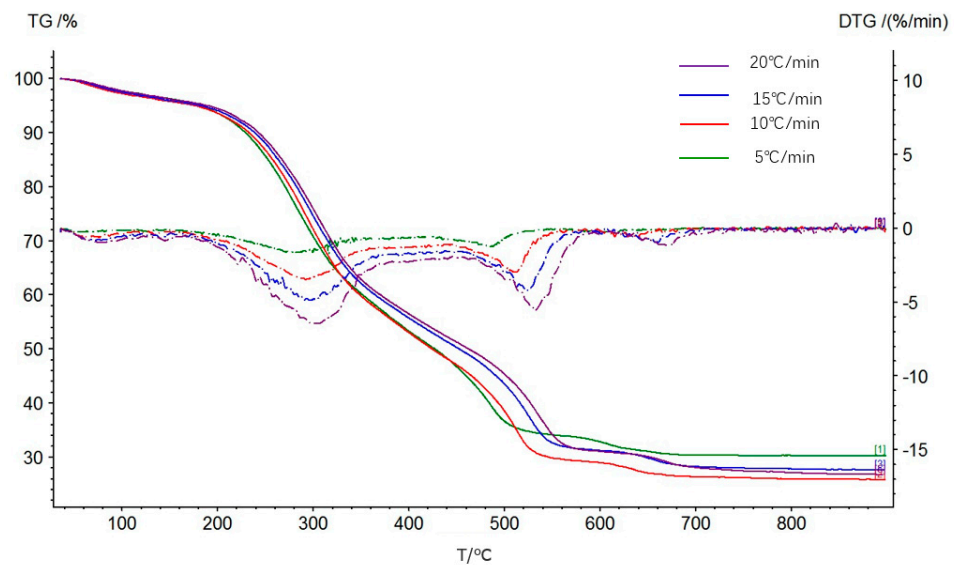


Figure 4. The TG and DTG curves of the chicken manure thermal decomposition for different heating rates in the presence of air atmosphere.

3.2.4. Effects of Different Carrier Gases on the Pyrolysis Characteristics

By comparing Figures 3 and 4, it is realized that the overall evolution trend of the TG and DTG curves of chicken manure in two atmospheres is quite different; however, there exists a slight discrepancy in different heating rate curves under the same atmosphere. A close comparison between the TG-based plotted results in Figure 1 and those in Figure 2 shows that different atmospheres have little effect on the dehydration section. Further, at a heating rate of 5 °C/min, the plots associated with the nitrogen atmosphere lag slightly. The slope and weight loss rates of the TG curve in the main thermal decomposition unit are similar. In the carbonization stage, there are apparent discrepancies in the slope and temperature span of the TG curve between the two atmospheres. Not only thermal decomposition but also oxidation occurs in the air atmosphere; therefore, the weight loss rate is greater in this case. The TG curve of the air atmosphere after secondary thermal decomposition is horizontal, indicating that the chicken manure is completely burned

and incinerated at about 700 °C in the presence of oxygen. Furthermore, the DTG curve fluctuates greatly in the presence of air atmosphere. The temperature range of the main thermal decomposition peak in the air atmosphere is remarkably lower than that in the nitrogen atmosphere by about 30 °C, and the main weight-loss unit presents an obvious W-shape peak. Comparing the obtained results for two atmospheres mentioned above, the amount of residual ash of the samples with a heating rate of 10 °C/min is the least, and the mass reduction rate in the main thermal decomposition stage is also the largest, indicating that the thermal decomposition of the chicken manure is the best at this heating rate.

3.2.5. Confirmation of the Mechanism Function

The macroscopic kinetics of thermal degradation processes is complex because this comprises information about concurrency that leads to occurrence of numerous reaction steps. To disentangle the macroscopic kinetics, the computational methods often assume a one-step degradation process of the biomass as follows. The interval with the conversion rate of 0.1–0.8 is generally selected (i.e., $\alpha = 0.5$ is usually selected) for data fitting. In the present work, the mechanism given in Table 1 is compared with the experimental curve obtained when a heating rate of 5 °C/min in the presence of the nitrogen atmosphere is applied. The overlap rate between the standard curve corresponding to the random nucleation F_1 mechanism and the experimental curve is the highest; therefore, it is chosen as the thermal decomposition mechanism of the chicken manure such that:

$$G(\alpha) = -\ln(1 - \alpha) \quad (7)$$

$$f(\alpha) = 1 - \alpha \quad (8)$$

3.2.6. Calculation of the Thermal Decomposition Kinetic Parameters

Based on the selected mechanism, we can rationally express: $f(\alpha) = 1 - \alpha$. When the heating rate is constant, the secondary reaction in the process of biomass thermal decomposition can be ignored, and the reaction order is $n = 1$. By introducing this to Equation (6), the following equation is obtainable:

$$G(\alpha) = \frac{ART^2}{E\beta} e^{-E/RT} \quad (9)$$

By taking the logarithms of both sides of Equations (3)–(6):

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (10)$$

and an approximate solution to Equation (10) can be easily sought as follows:

$$\ln\left(\frac{-\ln(1 - \alpha)}{T^2}\right) = -\frac{E}{RT} + \ln\frac{AR}{\beta E} \quad (11)$$

Let $y = \ln(-\ln(1 - \alpha))/T^2$ and $x = -1/T$. Equation (11) can also be simplified more as:

$$Y = -\frac{E}{R}x + \ln\frac{AR}{\beta E} \quad (12)$$

The experimental data are processed, the corresponding Y-X diagrams are extracted, and the activation energy E and frequency factor A are calculated according to the slope and intercept of the fitting relation. Take the thermal decomposition of chicken manure in the presence of air at a heating rate of 10 °C/min as an example (see Figure 5).

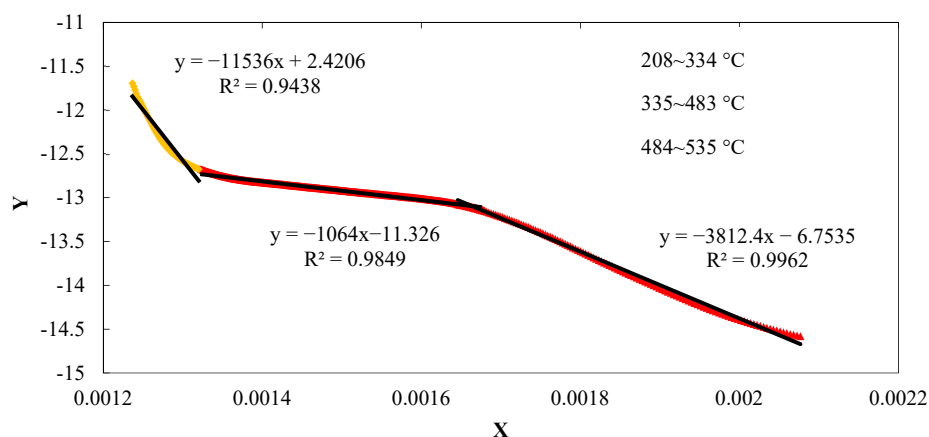


Figure 5. The fitting equation of the chicken manure thermal decomposition subjected to air atmosphere and 10 °C/min heating rate.

According to Figure 5, the thermogravimetric data selected from the temperature interval of 208–535 °C are divided into three branches for fitting. Tables 3 and 4 present the fitting-based results for the exposure of samples to two atmospheres. It can be seen from the given results that the fitting parameter equation has a high correlation coefficient, revealing that the selected mechanism function is consistent with the thermal decomposition reaction of the chicken manure. Based on the fitting equation, the activation energy of the two atmospheres is close under the action of the same heating rate, and there is a little discrepancy between various heating rates. For both atmospheres, the maximum activation energy of the samples is reported for a heating rate of 10 °C/min. These maximum values for the cases of exposure to nitrogen and air atmospheres are 31.55 and 95.91 kJ·mol^{−1}, respectively. TG results showed that both pyrolysis and combustion of pine sawdust presented three weight loss stages, respectively. The apparent activation energy of pyrolysis reaction is 108.18 kJ·mol^{−1} in temperature of 239–394 °C, while with a combustion process this is 128.43 kJ·mol^{−1} in 226–329 °C [33]. The result of this experiment is less than the reported value, which is obviously due to the synergistic effect of the mixture of chicken manure and sawdust. In the same nitrogen atmosphere, the activation energy of chicken manure pyrolysis is much lower than those reported in other investigations [27], which is also lower than the thermal decomposition activation energy of other livestock manure [34–36]. This fact may be attributed to the fact that the chicken manure in this sample comes from small- and medium-sized farms. The chicken manure produced by actual farming is mixed with more sawdust, indicating that the addition of sawdust biomass is beneficial to reducing the thermal decomposition activation energy of chicken manure and promoting the thermal decomposition reaction. In addition, there is no obvious law between different heating rates. There is a specific law in different temperature intervals with the same heating rate of the air atmosphere, that is, the activation energy of the second temperature section is the lowest, and the activation energy of the first section is less than that of the third section. This may be related to the high accumulation of thermal decomposition products in the second temperature section without sufficient oxidation and diffusion. In the third temperature section, cellulose thermal decomposition and oxidation occur, and the corresponding activation energy is higher than that of the protein and half fiber thermal decomposition.

Table 3. The thermal decomposition kinetic parameters of the chicken manure in the presence of nitrogen atmosphere.

β ($^{\circ}\text{C}\cdot\text{min}^{-1}$)	T ($^{\circ}\text{C}$)	Fitted Equation	E ($\text{KJ}\cdot\text{mol}^{-1}$)	A (min^{-1})	R^2
5	191~327	$y = -2908.4x - 13.285$	24.18	0.02	0.9989
10	206~336	$y = -3795.5x - 136.9554$	31.55	36.2	0.9951
15	219~347	$y = -3683.5x - 137.1099$	30.62	45.1	0.9957
20	210~348	$y = -3139.4x - 1312.975$	26.10	0.15	0.9985

Table 4. The thermal decomposition kinetic parameters of the chicken manure in the presence of air atmosphere.

β ($^{\circ}\text{C}\cdot\text{min}^{-1}$)	T ($^{\circ}\text{C}$)	Fitted Equation	E ($\text{KJ}\cdot\text{mol}^{-1}$)	A (min^{-1})	R^2
5	207~337	$y = -3707.3x - 136.8912$	30.81	18.8	0.9913
5	338~437	$y = -969.48x - 1311.481$	8.06	0.5	0.9995
5	438~530	$y = -3721.4x - 137.6544$	30.94	8.8	0.9746
10	208~334	$y = -3812.4x - 136.7535$	31.70	45.5	0.9962
10	335~483	$y = -1064x - 1311.326$	8.85	0.13	0.9849
10	484~535	$y = -11536x + 2.4206$	95.91	1298.1	0.9438
15	200~337	$y = -3624.7x - 137.2471$	30.13	38.7	0.9938
15	238~483	$y = -696.31x - 1312.048$	5.79	0.06	0.9893
15	484~560	$y = -5189.7x - 136.1608$	43.15	164.3	0.9760
20	218~334	$y = -3844.4x - 136.9303$	31.96	75.2	0.9975
20	335~506	$y = -704.02x - 1312.089$	5.85	0.08	0.9604
20	507~567	$y = -5574x - 135.8425$	46.34	323.4	0.9881

4. Conclusions

The results of this study signify the thermochemical characteristics of chicken manure in thermal decomposition processes. The following major results are obtained:

- (1) Because the chicken manure sample in this experiment is taken from the real chicken farm, which is close to the actual production situation, the chicken manure is mixed with sawdust. There are great differences in thermal decomposition under nitrogen and air, and chicken manure and sawdust have a synergistic effect.
- (2) Under the nitrogen atmosphere, according to the results of thermogravimetric analysis, the pyrolysis process of chicken manure in nitrogen atmosphere can be divided into five stages: dehydration, preheating, pyrolysis, carbonization, and secondary pyrolysis. The maximum change of thermal decomposition weight loss rate is 35% in nitrogen atmosphere at 210–430 $^{\circ}\text{C}$. The activation energy is in the range of 24.18–31.55 $\text{kJ}\cdot\text{mol}^{-1}$.
- (3) Under the air atmosphere, thermal decomposition occurs first in the early stage, accompanied by oxidation reaction in the middle, and then combustion. The temperature range of the main thermal decomposition peak in the air atmosphere is remarkably lower than that in the nitrogen atmosphere by about 30 $^{\circ}\text{C}$. The DTG curve in the air atmosphere fluctuates more. There is a certain law in different temperature sections, that is, the activation energy of the second temperature section is the lowest, and the activation energy of the first section is less than that of the third section.
- (4) In the presence of both nitrogen and air atmospheres, the best sample's thermal decomposition is achieved for the case of 10 $^{\circ}\text{C}/\text{min}$ heating rate, and the minimum mass of the residual solid is attained. Furthermore, the corresponding activation energy for the two mentioned above atmospheres is the largest, which in order are 31.55 and 95.91 $\text{kJ}\cdot\text{mol}^{-1}$.
- (5) In order to achieve more high-value products, it is recommended to exploit nitrogen atmosphere, in which the stability of chicken manure is better. For energy-saving and economical purposes, the application of air atmosphere is generally more suitable.

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