Study of Combustion and Dechlorination Characteristic of Garbage and Wood Waste Compound Fuel

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Abstract
The purpose of this work is to find a perfect compound fuel made of domestic garbage and wood waste. In this paper, experimental research on combustion characteristics and thermal reaction dynamic of domestic garbage and wood waste compound fuel were conducted with thermal gravimetric analyser. Moreover, the dechlorination characteristics of the compound fuel were also investigated experimentally. The results show that combustion process of compound fuels can be divided into: drying stage, volatile analysis and combustion stage, polymer combustion stage, fixed carbon combustion stage. In the study of combustion kinetics, the first-order reaction model has a high fitting coefficient, and the whole combustion stage can be simulated by three first-order reaction superposition. Calcium oxide as a chlorine fixation agent, with the increase in the proportion of calcium oxide compound fuel made the efficiency of chlorine increase. The efficiency of chlorine fixation under different pressures was studied. With the increase of pressure, the efficiency of chlorine fixation was improved, but the forming efficiency was higher than a certain range. In conclusion, when the ratio of sawdust and molded garbage is 8:2 has the best combustion performance. The addition ratio of solid to chlorine is Ca:Cl=3:1 and the effect of solid chlorine is the best when the pressure is 15kN.

Key words: compound biomass fuel, combustion characteristic, kinetics, wood waste

1. Introduction

Biomass is the world's fourth largest energy resource after coal, oil and natural gas[1]. It is characterized by a wide range of sources, many species, wide distribution and large output. In many parts of world, biomass becomes an important substitute for fossil fuels[2]. China has very rich biomass resource, that can produce about 700 million tons of crop straw and 100 million tons of agricultural processing waste each year, the total amount of biomass is about 300 million tons of standard coal, it is 4 times about current total energy consumption of China[3,4]. So there is a large amount of biomass can be used. There are four main ways to use biomass: combustion, gasification, liquefaction and pyrolysis, where combustion is the most traditional way and it is widely applied to heat production and power supply projects. Biomass combustion technology accounts for 97% of the world's total biomass utilization[5]. At present, biomass compression molding technology is widely used in combustion. Biomass compression technology uses mechanical compression method to compress raw materials into a certain shape of the larger density of the fuel. These raw materials are agriculture and forestry waste such as sawdust, straw, rice husk, scattered and without a certain shape[6]. Biomass-forming fuels have the following advantages: simple processing, low cost, easy storage and transportation, easy ignition, good combustion performance, high thermal efficiency[7].

Biomass as an important renewable energy source includes not only plants but also organic solid...
waste. Domestic waste refers to the solid waste generated by urban residents in their daily lives. With the development of economy and the acceleration of the urbanization process of China, waste production has increased year by year and the components are becoming more and more complicated. The urban population of China is about 740 million, the average daily production of waste is 1.3 to 1.5 kg per person, resulting in a large number of domestic garbage can’t be completely harmless treatment, in 2014 harmless treatment rate in China is 91.8%. Over the years a large number of living garbage accumulation of more than 500 million square meters of land, most of cities formed a "garbage siege" phenomenon. How to make good use of garbage and wood waste to achieve comprehensive utilization of resources becomes an urgent problem to be solved. It is necessary to find a new method to solve this problem.

As the garbage often contains polyvinyl chloride plastic, salt and other chlorine compounds, rubbish will produce corrosive hydrogen chloride gas at high temperature heat combustion. Hydrogen chloride can soluble in water to form hydrochloric acid easily, so hydrogen chloride emissions to the atmosphere can form acid rain. Hydrogen chloride can also react with iron to produce ferric chloride, in order to avoid corrosion, factories usually lower steam parameters, which resulting in garbage power generation efficiency is only 10% ~ 15%. Due to the chlorine compounds, the combustion process may also produce dioxin, endangering human health. So, it is necessary to reduce the combustion process of hydrogen chloride emissions. The most commonly method to dechlorination is to add chlorination agent in biomass-forming fuels or refuse-derived fuels. The chlorination agent acts both as a chlorine and as a binder. Previous scholars have studied the mechanism of chlorine fixation, the efficiency of chlorine fixation and the best addition ratio of different chlorine fixation agents.

Jinyu Qi et al. studied the effects of reaction temperature on the HCl emission during the incineration process in the range of 700 ~ 900°C, and the effect of the reaction temperature on the HCl emission was studied. The conversion of Cl to HCl is about 83% ~ 92%. And calcium-based dechlorination effect is better than magnesium-based dechlorination agent. Hernandez-Atonal et al. studied the combustion characteristics and pollutant emission characteristics of derived fuels (RDF). The combustion experiments were carried out on three different RDFs. It was found that Ca / (S + 0.5 Cl) had the best effect of chlorine fixation in the range of 1.6-2.2. This conclusion is the same as that of Wang Zhiqi et al. and Wei et al. studied the emission characteristics of sulfur and chlorine in RDF and coal co-combustion. It was found that the effect of sulfur fixation was higher than that of solid chloride, and the ratio of RDF in mixed fuels increased with the concentration of HCl increase. Chang et al. found that the addition of RDF in the calcium hydroxide content of more than 5% after the chlorine effect with the increase in calcium hydroxide is no longer obvious.

Scholars have studied the mechanism of hydrogen chloride generation in biomass and refuse derived fuels. The results show that calcium oxide is a good chlorine fixation agent, but the proportion of calcium oxide is still uncertain and there is a gap in the effect of pressure on the efficiency of chlorine fixation. Therefore, the effect of adding calcium oxide on the efficiency of chlorine fixation under different pressures is studied by high temperature hydrolysis potentiometric titration.

The combustion characteristics of fuels are important indicators of fuel, and the study of combustion characteristics can provide the original information for establishing combustion models, designing combustion equipment, and controlling the combustion process. The combustion characteristics mainly include three parameters: ignition temperature, burnout temperature and comprehensive combustion characteristic index. In order to more fully understand the combustion characteristics of fuel, the most commonly used at home and abroad is the thermal analysis
Scholars have studied the biomass combustion process and kinetics of combustion. Zhou et al. analyzed the thermogravimetric analysis of the mixture of different plastics and coal, and concluded that the decomposition temperature range of the different plastics was different, and the pyrolysis characteristics of the mixture were more complicated than the single component, and it was not a simple superposition relationship. The kinetic analysis uses the first order equation and the simulation results are solved separately according to the different reaction stages. Gil M.V. et al. studied the combustion characteristics of the mixture of pine and coal and carried out kinetic analysis. The combustion of pine is divided into two stages: volatile combustion and coke combustion. The first stage is simulated by the first-order reaction model to obtain the kinetic parameters, and the second stage uses diffusion model. Guo Xiaofen et al. used thermogravimetric analysis (TGA) to study the combustion process and combustion kinetics of Guangzhou refuse-derived fuels. The results show that the combustion of RDF is divided into three weightlessness processes. According to the different weight loss stage, the first-order reaction mechanism is used to solve the kinetic parameters. There are few studies on the combustion characteristics of high calorific value domestic waste and different biomass compound fuels. It is necessary to study the combustion characteristics of mixed fuel of high calorific value waste and biomass, analyzing its kinetics to provide basic data for combustion equipment.

In this paper, experimental research on combustion characteristics and thermal reaction dynamic of domestic garbage and wood waste compound fuel were conducted with thermal gravimetric analyser. Thermal gravimetric analyser was used to investigate the combustion characteristic parameters such as ignition temperature, burnout temperature, and maximum weight loss rate of samples in different ratios. Moreover, the dechlorination characteristics of the compound fuel were also investigated experimentally.

2. Material and methods

2.1 Experimental sample

Wood processing plants often accumulate a large number of residues, which cause financial and energy waste due to lack of long-term effective treatment. In this paper, biomass materials used for the test were sawdust which was taken from a factory in Hebei province. The sawdust raw material was sieved out of under 0.15mm.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Sample composition proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samples</td>
<td>#1</td>
</tr>
<tr>
<td>Sawdust: Laboratory-made garbage</td>
<td>10:0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Proximate and ultimate analysis of materials</th>
</tr>
</thead>
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<tr>
<td>Samples</td>
<td>M_ad</td>
</tr>
<tr>
<td>Sawdust</td>
<td>6.51</td>
</tr>
<tr>
<td>Paper</td>
<td>5.83</td>
</tr>
<tr>
<td>Plastic</td>
<td>0</td>
</tr>
</tbody>
</table>

The laboratory-made modeled domestic garbage was used as material. Ordinary printing paper,
pure polyethylene (PE), polyvinyl chloride (PVC) and polypropylene (PP) mixed at a ratio of 51:32:12:5 as modeled garbage. It was dried in a drying oven at 100°C for two hours. Sawdust and laboratory-made modeled domestic garbage were mixed at the ratio of 10:0, 8:2, 6:4, 4:6, 2:8, 0:10 (Table 1), in order to research the combustion characteristics of mixed biomass fuels, then find a perfect compound fuel made of domestic garbage and wood waste. Elemental and chemical analyses of samples were listed in table 2.

2.2 Experimental instruments

2.2.1 Compression molding equipment

The equipment is mainly composed of digital control valve, pressure pump, pressure sensor and computer and the schematic diagram of it is shown in Fig1. The maximum pressure of this equipment is 300kN. Precision pressure sensor on the top is spoke pressure sensor and precision range is 50kN. Measurement form can be set from computer, value of pressure, pressure rate and holding time can be set in load pressure test mode.

![Compression molding equipment](image)

1. Pressure Sensor 2. Pressure Cylinder 3. Digital controller

2.2.2 Thermal analysis experiment system

In this paper, the STA449F3 Synchronous Thermal Analyzer, which is produced by the German company, is equipped with differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). This equipment combines thermogravimetric analysis and differential thermal analysis, and gets two kinds of signals in one time. Thermal analyzer is composed of balance system, furnace system, temperature control device and recording equipment. One of the most important components is the balance system; it has high requirements for accuracy, reproducibility, seismic performance, reactivity, structural ruggedness and ability to adapt to changes in ambient temperature.

The sample crucible is placed on support frame. Weight change of sample is measured by electronic balance. When the sample changes due to the decomposition or the chemical reaction, signals of the balance output changes, then computer collects the data to obtain the TG curve automatically.

2.2.3 Chlorine content measurement system

In order to measure the chlorine content in samples and the effect of chlorine fixation under different conditions, this paper established a high temperature hydrolysis system (Fig.2). Compound fuel are burned and hydrolyzed in oxygen and water vapor mixed gas stream, the chlorine of sample is
dissolved in water. The chloride ions in absorption bottle 1 and bottle 2 were titrated directly by standard silver nitrate potential method. The chlorine content of solid biomass or garbage was calculated according to the amount of standard silver nitrate titration solution. After calculating the chlorine content in the biomass and the waste, adding a certain amount of fixed chlorine reagent to the compound fuel, then the standard silver nitrate potential method was used to measure chloride released from the combustion of the compound fuel without water vapor, and the effect of different chlorine fixation was calculated.

![Diagram](image)


**Fig.2 High temperature hydrolysis device schematic diagram**

### 2.3 Experimental methods

Differential Scanning Calorimetry (DSC) curve and Derivative Thermo-gravimetric (DTG) curve were performed by NETZSCH Simultaneous Thermal Analyzer STA 409. Samples about (10±0.1)mg were weighted on electronic balance, heat temperature was from 100 to 900°C at heating rates of 10°C/min. The air flow was 20ml/min and 20ml/min of nitrogen as shielding gas.

Guo Xianjun et al.\(^{[24]}\) found that the combustion temperature had the greatest effect on chlorine precipitation in the high temperature hydrolysis experiment system, then combustion atmosphere and residence time followed by combustion temperature. In order to get accurate chlorine content, reduce experimental time and extend service life of equipment, experiments were made to measure chlorine content at 1000°C, 1050°C and 1100°C at staying time 30mins. The chlorine content at the three combustion temperatures was compared to determine appropriate combustion temperature. Then, combustion time was changed for 10min, 20min and 30min at appropriate combustion temperature to determine appropriate time that sample stayed in furnace. After that, we got chlorine content in compound fuel. The chlorine content was measured by potentiometric titration.

Then CaO was added to compound fuel with Ca:2Cl in a ratio of 1: 1; 2: 1, 3: 1 and 4: 1, that means 6mg, 12mg, 18mg and 24mg CaO was added to 1g compound fuel. Well mixed CaO and compound fuel to get new samples, then samples were compressed with 10kN, 15kN, 20kN and 25kN
in Compression molding equipment.

2.4 Definition of combustion characteristic parameters

Ignition temperature\cite{22, 24} represents difficulty of fuel ignition directly. The lower ignition temperature makes fuel easier to ignite. In this paper, TG tangent method is used to determine the ignition temperature. As we can see in Fig.4, the DTG curve is obtained by the differential curve of the TG curve. Find the maximum weight loss rate on DTG curve, make at vertical line, and intersect with the TG curve at point B. At the point B to do tangent, and intersect with TG curve smooth tangent at the point C, and the point C is the ignition temperature.

![Fig.4 TG tangent method sketch](image)

Burned out temperature\cite{22, 24} means after the combustion of the fuel, the TG curve and the DTG curve are not changed. Define the weight loss rate of -1% / min when the corresponding temperature is burnout temperature.

The peak of the DTG curve is the maximum burning rate\cite{22, 24}. The maximum burning rate reflects the severity of the fuel combustion, the greater the maximum burning rate, the greater the burning is.

The higher value of the integrated combustion characteristic index \( S \)\cite{22, 24}, the better the combustion performance of the fuel is. Calculation of \( S \) is

\[
S = \frac{\left(\frac{dX}{dt}\right)_{\text{mean}} \times (dX/dt)_{\text{max}}}{T_i \times T_f},
\]

where \( (dX/dt)_{\text{max}} \) is the maximum burning rate of the combustion process, %·min\(^{-1}\); \( (dX/dt)_{\text{mean}} \) is the average burning rate of the combustion process, %·min\(^{-1}\); \( T_i \) is ignition temperature, K; \( T_f \) is burned out temperature, K.

3. Results and discussion

3.1 Analysis of combustion characteristics

3.1.1 Analysis of combustion procession curve

It is shown in Fig.3, from TG, DTG and DSC curves of each sample, the combustion process of each sample is similar. Three exothermic peaks appear in DSC curve. The distribution represents separation and combustion of volatile matter, the combustion of polymer and the combustion of fixed carbon.

In first stage, with increased temperature, due to volatile matter in samples separated, TG curve of samples were reduced, the DTG curve peaked and the DSC curve changed from endothermic to exothermic. Hydrogen bonds in the intermolecular and intramolecular of cellulose, hemicellulose and
lignin in samples were broken. Due to molecular structure of samples changed, oxidation, dehydrogenation and decarburization of samples took place, and gases with small molecules such as CO, CH\textsubscript{4} and H\textsubscript{2} were formed\textsuperscript{25-27}. At low temperatures, major source of volatiles in plastics is the decomposition of PVC into HCl and chlorinated hydrocarbons\textsuperscript{28}.

The second stage is polymer combustion, this stage is between volatile and fixed carbon combustion and have overlapping parts with the two processes. From Fig.3(b) to Fig.3(f), it is obvious that the polymer combustion lasts long time, and the temperature is 320\textdegree{}C~420\textdegree{}C, which shows a wide exothermic peak in the DSC curve. This phenomenon is due to samples of these figures contain laboratory-made garbage. The last combustion of the polymer ignites the fixed carbon directly. As we can see DTG curves in Fig.3, the maximized weight loss rate occurred in polymer combustion stage.

The third stage is fixed carbon combustion. After volatile decomposition, char remains. Char in the role of polymer combustion began to burn, release a lot of heat. The combustion of fixed carbon occurs between 440\textdegree{}C and 560\textdegree{}C, and a significant exothermic peak is formed in the DSC curves in Fig.3.

3(a) The combustion curves of sawdust

As we can see in Fig.3(a), the DTG curve of sawdust appeared three weight loss peaks, and the maximum weight loss peak appeared in the volatile combustion stage, which indicated that the volatile content of sawdust was high and easy to precipitate. It can be seen from the DSC curve of sample #1 that heat release mainly occurs in the volatile combustion stage, polymer combustion and the fixed carbon combustion. There is no obvious boundary among these three stages. Sawdust is completely combusted at 580\textdegree{}C.
3(b) The combustion curves of sawdust: laboratory-made garbage = 2:8

3(c) The combustion curves of sawdust: laboratory-made garbage = 4:6
3(d) The combustion curves of sawdust: laboratory-made garbage = 6:4

3(e) The combustion curves of sawdust: laboratory-made garbage = 2:8
3.1.2 Analysis of combustion characteristic parameters

From Fig.3(b) to Fig.3(e), the combustion characteristic of compound fuel affect by sawdust and laboratory-made garbage. However it is not a simple liner superimposed by two materials rather than mutual improvement. As the waste content increases, the combustion characteristics are shifted to it. In Fig.3(b), sample #2 contains 80% sawdust and the combustion characteristic more influenced by sawdust. At the same time, influenced by 20% plastic content, the duration of the polymer combustion phase becomes longer and the exothermic is more concentrated. In Fig.3(e), sample #5 contains 80% plastics content, with the impact of plastics combustion characteristic, the oxygen uptake was increased at 200°C. In Fig.3(c) and Fig.3(d), sawdust and garbage ratio of 6: 4 and 4: 6 at low temperature weight loss is more obvious, indicating that the direct synergistic effect of raw materials at this time is more obvious.

From table 3, we can see comprehensive combustion characteristic of each sample. The ignition temperature of the compound fuel decreases as the waste content increases. This is due to plastic component in garbage comes out melting at 130°C, and thermal conductivity is improved as the voids between plastic are reduced. Then the sample internal heating rate increases, volatile more easily precipitates, ignition temperature is advanced. Compared with domestic waste, the compound fuel has a lower ignition temperature and a lower burning out temperature, and the combustion performance is better. The combined combustion characteristics index can reflect the fuel combustion performance.
compound fuel, when the ratio of sawdust and molded garbage is 8:2, the comprehensive combustion characteristic index is the largest, indicating that this ratio of fuel has the best performance. The DSC curve of this sample was integrated in the combustion temperature range to obtain a calorific value over the entire combustion stage is 14490J/g and a heat value is 34621kcal/kg.

Table 3 Comprehensive combustion characteristic index of different raw material proportion

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<tbody>
<tr>
<td></td>
<td>$T_f$</td>
<td>$T_i$</td>
<td>$(dX/dt)_{max}$</td>
<td>$(dX/dt)_{mean}$</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>538</td>
<td>848</td>
<td>7.65</td>
<td>2.88</td>
</tr>
<tr>
<td>#2</td>
<td>535</td>
<td>929</td>
<td>7.42</td>
<td>2.36</td>
</tr>
<tr>
<td>#3</td>
<td>533</td>
<td>933</td>
<td>6.82</td>
<td>2.23</td>
</tr>
<tr>
<td>#4</td>
<td>532</td>
<td>937</td>
<td>6.69</td>
<td>2.28</td>
</tr>
<tr>
<td>#5</td>
<td>531</td>
<td>937</td>
<td>6.56</td>
<td>2.27</td>
</tr>
<tr>
<td>#6</td>
<td>515</td>
<td>951</td>
<td>7.05</td>
<td>2.28</td>
</tr>
</tbody>
</table>

3.2 Kinetics analysis[19-22]

The kinetic analysis of the combustion is mainly to determine the thermal reaction kinetics of the experiment in order to determine the 'kinetic three factors', the mechanism function $f(\alpha)$, the activation energy $E_a$ and the frequency factor $A$, which describe the reaction mechanism[60]. The relationship between reaction rate and concentration is called chemical velocity equation. For a simple reaction, the chemical reaction rate is proportional to the reactant concentrations. For example, a simple chemical reaction as below:

$$aA+bB=\alpha C+\beta D$$

(1)

The chemical reaction rate can be expressed as:

$$w=kC_A^aC_B^b$$

(2)

The power exponent of each reactant concentration term in equation (2) is equal to corresponding previous coefficient in the chemical reaction equation and $n=a+b$ is called reaction order. $k$ is reaction rate, which independent of reactant concentration.

According to relationship of law of mass action, reaction order and reaction rate constant, the isothermal homogeneous reaction kinetics is proposed. The equation is described as[64]:

$$\frac{dc}{dt}=k(T)f(c)$$

(3)

Where, $c$ is product concentration, $t$ is time, $k(T)$ is temperature relation of reaction rate constant, $f(c)$ is mechanism function.

With the development of thermal analysis technology and its extensive application, the development of non-isothermal kinetic equations has been promoted. As the thermal analysis often used constant temperature method, that is, heating rate is a constant, Vallet transformed isothermal homogeneous reaction kinetics equation to non-isothermal reaction kinetics equation.

$$\frac{dc}{dt}=k(T)f(c) \frac{dx}{dt} = \left( \frac{1}{\beta} \right) k(T)f(\alpha)$$

(4)

$$\alpha = \frac{m_i-m_f}{m_i-m_0}$$

(5)

Where, $\beta$ is heating rate, K/min; $\alpha$ is conversion rate, %; $m_0$ is initial mass, mg; $m_f$ is residual mass, mg; $m_i$ is the mass of the sample at a time during the reaction, mg.
Arrhenius argues that the activation energy is determined by the reaction and it is independent of concentration and temperature of the reactants. The value of activation energy (E) has a great effect on the reaction. The smaller the E is, the greater the reaction rate. In the homogeneous reaction (5) is almost applicable to all elementary reactions and most complex reactions. Equation (5) takes to equation 4 obtain the kinetic equation (6) under non-isothermal conditions.

\[
\frac{da}{dT} = \left(\frac{A}{\beta} \right) \exp[-E/(RT)]f(a)
\]  

(6)

The purpose of kinetic research is to find E and A in the above equation that can describe a reaction. Equation 4-6 is subjected to variable separation to obtain Equation (7).

\[
\frac{da}{f(a)} = \left(\frac{A}{\beta} \right) \exp[-E/(RT)]dT
\]  

(7)

In this study, the kinetic analysis of the combustion reaction process of the compound fuel was carried out by the integral method. Define the integral function

\[
F(a) = \int_a^0 \frac{da}{f(a)} = A/\beta \int_{T_0}^T \exp[-E/(RT)]dT
\]  

(8)

Where, \(T_0\) is an initial temperature.

When the temperature is below \(T_0\), reaction does not start, the compound fuel does not occur weightlessness reaction, so the reaction rate at low temperatures is negligible. So equation (8) simplified to equation (9).

\[
F(a) = \int_a^0 \frac{da}{f(a)} = A/\beta \int_{T_0}^T \exp[-E/(RT)]dT
\]  

(9)

In this paper, the Coats-Redfern integral method is used to integrate the above equations. The primitive response function \(f(a) = (1-a)^n\) is given to equation (9) and combined with the Coats-Redfern integral method as follows:

\[
\int_0^a \frac{da}{f(a)} = \frac{A}{\beta} \frac{RT}{E} \left(1-\frac{2RT}{E}\right) \exp \left(-\frac{E}{RT}\right)
\]  

(10)

On both sides of the equation (10) take the logarithm,

\[
\ln \left[ \frac{F(a)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left(1-\frac{2RT}{E}\right) \right] - \frac{E}{RT}
\]  

(11)

Where \(E/RT \gg 1\), \(1-2RT/E=1\), equation (11) approximately equal to equation (12):

\[
\ln \left[ \frac{F(a)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT}
\]  

(12)

Taking \(f(a) = (1-a)^n\) to equation 9 and 12,

\[
n \neq 1, \ln \left[ \frac{n(1-a)^{1-n}}{T^2(1-n)} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT}
\]  

(13)

\[
n = 1, \ln \left[ \frac{\ln(1-a)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT}
\]  

(14)

Making a plot that \(\frac{\ln(1-a)}{T^2}\) or \(\frac{n(1-a)^{1-n}}{T^2(1-n)}\) is y-axis and 1/T is x-axis. The kinetic parameters E and A can be obtained in slope and intercept.

Linear fitting of the equations is performed using different reaction orders. The correlation coefficient is higher and the degree of fitting is better, and then the reaction order of compound fuel is selected. Select four reaction orders \((n=0, 1/2, 1, 2)\) to study the compound fuel (sawdust: mold waste=8:2) at 200℃~340℃ temperature range of fitting calculation. Table 4 shows the fitting
equations and the fitting coefficients. Fig.5 shows the equations for A for different reaction series. Figure 4-1 shows the fitting lines for different reaction orders. From the fitting results of different reaction series, it can be seen that the best reaction order is n=1, the fitting result $R^2$ is 0.9973.

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>Fitting line</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=0</td>
<td>$Y=-0.96858-7586.56x$</td>
<td>0.9814</td>
</tr>
<tr>
<td>n=1/2</td>
<td>$Y=-0.2389-7951.41x$</td>
<td>0.9873</td>
</tr>
<tr>
<td>n=1</td>
<td>$Y=0.5367-8339.74x$</td>
<td>0.9973</td>
</tr>
<tr>
<td>n=2</td>
<td>$Y=2.2267-9187.15x$</td>
<td>0.9920</td>
</tr>
</tbody>
</table>

**Fig.5** The fitting line under different reaction series

When reaction order n=1, the linear fitting of the combustion process is shown in Fig.6. If the whole reaction process is linearly fitted, as shown in Fig.6(a), the fitted linear correlation coefficient is 0.8982, so it is not good to make a fitting result for the whole reaction stage. Fig.6(b) is the fitting result obtained by fitting the solution according to the different stages of combustion process, such as the volatile combustion stage, the polymer combustion stage, the fixed carbon combustion stage. Based on the DTG of the combustion characteristic curve and the inflection point temperature of the DSC curve, the whole combustion process is segmented. The linear correlation coefficient of the segmented fitting is above 0.97, which shows that the result is better than 0.8982. In this paper, the kinetic reaction equation is reduced by Coats-Redfern integral method. The reaction parameters are obtained by using the reaction n = 1 according to the different segmentation of the reaction phase.
According to the combustion test data of different fuels, and the calculation is carried out according to the different reaction stages in the simulation. The results are shown in Table 5.

Table 5 Kinetic parameters of different proportioning

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature/°C</th>
<th>Fitting equation</th>
<th>$E$ (kJ/mol)</th>
<th>$A$ (1/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>230–350</td>
<td>$Y = 0.0713-7999.83x$</td>
<td>66.51</td>
<td>$8.59 \times 10^4$</td>
<td>0.9927</td>
</tr>
<tr>
<td></td>
<td>350–440</td>
<td>$Y = -11.37-987.35x$</td>
<td>8.20</td>
<td>0.113</td>
<td>0.9948</td>
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<tr>
<td></td>
<td>440–550</td>
<td>$Y = -7.25-3970.91x$</td>
<td>33.01</td>
<td>28.2</td>
<td>0.9815</td>
</tr>
<tr>
<td></td>
<td>230–350</td>
<td>$Y = 0.4779-8293.55x$</td>
<td>68.95</td>
<td>$1.33 \times 10^7$</td>
<td>0.9896</td>
</tr>
<tr>
<td>#2</td>
<td>350–440</td>
<td>$Y = -11.11-1175.91x$</td>
<td>9.77</td>
<td>0.1759</td>
<td>0.9839</td>
</tr>
<tr>
<td></td>
<td>440–520</td>
<td>$Y = -8.12-3348.78x$</td>
<td>27.84</td>
<td>9.96</td>
<td>0.9798</td>
</tr>
<tr>
<td>#3</td>
<td>230–300</td>
<td>$Y = 6.49-11560.39x$</td>
<td>96.11</td>
<td>$7.61 \times 10^7$</td>
<td>0.9881</td>
</tr>
</tbody>
</table>
It can be seen from the kinetic parameters that the activation energy of the sawdust is the lowest at the stage of volatilization and combustion, and the activation energy of the high calorific value garbage is the highest, indicating that the volatiles in the sawdust are easier to precipitate than the volatile matter in the rubbish. For the compound fuel, with the increase of the addition amount of sawdust, the activation energy of the volatile combustion decreases. Increasing molecular activity and is beneficial to volatile burning. However, the pre-exponential factor decreases, which is detrimental to the burning of the volatiles. Under the combined effect of activation energy and pre-exponential factor, the volatiles burning rate of the compound fuel is greater than that of the high calorific value garbage, which indicates that the reactivity of adding sawdust to the volatile combustion stage of the fuel is benefit. When the content of sawdust in the compound fuel is 80%, the activation energy of the volatile combustion stage is $68.95 \text{kJ/mol}$ and the pre-exponential factor is $1.33 \times 10^5 \text{min}^{-1}$.

In the fixed carbon combustion stage, the activation energy of the compound fuel of sawdust and high calorific value refuse is lower than that of high calorific value garbage. Moreover, with the increase of sawdust content, the activation energy of coke combustion can be reduced, which is beneficial to ignite the remaining part after burning. The addition of sawdust to high calorific value rubbish is beneficial for improving the reactivity of the high calorific value junk charcoal combustion stage. In conclusion, adding sawdust to high calorific value garbage can reduce the activation energy of fuel and improve the reactivity, which is beneficial to the combustion. The combustibility of compound fuels is superior to that of high calorific value waste.

### 3.3 The Characteristics of Compound Chlorine

#### 3.3.1 Appropriate combustion temperature and combustion time

As we can be seen from Table 6, at condition of 30mins combustion time, compared with the chlorine content at 1050°C or 1100°C, the measured chlorine content at 1000°C error within $\pm 0.05\%$, that meet requirements[31]. Therefore, the combustion temperature of the chlorine content in the compound fuel can be 1000°C.

<table>
<thead>
<tr>
<th>Combustion temperature</th>
<th>1000°C</th>
<th>1050°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine content</td>
<td>0.734%</td>
<td>0.742%</td>
<td>0.732%</td>
</tr>
</tbody>
</table>
It can be seen from Table 7 that the combustion temperature is 1000℃, and the content of chlorine in the compound fuel measured by different burning time is less than 0.05%, which is in accordance with the national standard. Therefore, the measurement conditions of chlorine in the compound fuel are the combustion temperature of 1000℃, the combustion time is 10min. The chlorine content of the compound fuel was measured several times, and then the average value was taken. Finally, the chlorine content was 0.735%.

<table>
<thead>
<tr>
<th>Combustion time</th>
<th>10min</th>
<th>20min</th>
<th>30min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine content</td>
<td>0.731%</td>
<td>0.733%</td>
<td>0.733%</td>
</tr>
</tbody>
</table>

**Table 7 Determination of chlorine in fuels in different combustion time**

3.3.2 **Effect of different pressure on chlorine-fixing efficiency**

The results of the addition of different calcium oxide at different molding pressures are shown in Table 8.

<table>
<thead>
<tr>
<th>Pressure (kN)</th>
<th>Ca:Cl=1:1</th>
<th>Ca:Cl=2:1</th>
<th>Ca:Cl=3:1</th>
<th>Ca:Cl=4:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 kN</td>
<td>50.28%</td>
<td>53.46%</td>
<td>59.96%</td>
<td>62.09%</td>
</tr>
<tr>
<td>15 kN</td>
<td>58.48%</td>
<td>64.69%</td>
<td>68.53%</td>
<td>70.35%</td>
</tr>
<tr>
<td>20 kN</td>
<td>57.25%</td>
<td>63.63%</td>
<td>67.78%</td>
<td>70.06%</td>
</tr>
<tr>
<td>25 kN</td>
<td>57.11%</td>
<td>63.61%</td>
<td>67.37%</td>
<td>69.47%</td>
</tr>
</tbody>
</table>

**Fig.7 Dechlorine efficiency under different conditions**

<table>
<thead>
<tr>
<th>1:1</th>
<th>2:1</th>
<th>3:1</th>
<th>4:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 kN</td>
<td>50.28%</td>
<td>53.46%</td>
<td>59.96%</td>
</tr>
<tr>
<td>15 kN</td>
<td>58.48%</td>
<td>64.69%</td>
<td>68.53%</td>
</tr>
<tr>
<td>20 kN</td>
<td>57.25%</td>
<td>63.63%</td>
<td>67.78%</td>
</tr>
<tr>
<td>25 kN</td>
<td>57.11%</td>
<td>63.61%</td>
<td>67.37%</td>
</tr>
</tbody>
</table>
As we can see in Fig.7 and Table 8, the chlorine fixation efficiency of the compound fuel increases with the increase of the calcium oxide content under the same molding pressure, but it is not significant with the increase of the ratio of calcium to chlorine. When pressure is 15kN, the chlorine fixation efficiency was 68.53% under Ca: Cl was 3:1, chlorination ratio was 70.35% under Ca: Cl was 4:1, so the ratio of Ca to Cl is not an obvious factor. When the molding pressure is over 15kN, the chlorine efficiency is slightly decreased, probably because the molding pressure caused fuel porosity smaller. Since the concentration of water is closely related to the efficiency of calcium oxide removal, the increase of water concentration will inhibit the dechlorination efficiency of calcium oxide. When the fuel porosity becomes small, the product of the reaction of calcium oxide with HCl can’t be discharged in time, resulting reaction blocked and chlorine-fixing efficiency lower[32]. Considering the actual cost of production, the optimum chlorine fixation condition for compound fuels is 3:1 for the ratio of calcium to chlorine, and the molding pressure is 15 kN, and the chlorine fixation efficiency is up to 68%.

**Conclusion**

In this paper, we studied on compound fuels, which mixed by biomass and high calorific value of domestic solid waste. Based on the distribution of municipal solid waste in Beijing, the high calorific value of municipal solid waste was prepared by laboratory. Then, we mixed laboratory-made solid waste and sawdust in different ratio to get compound fuels. The combustion characteristics, combustion kinetics model and the characteristics of the solid chlorine under different conditions were discussed.

Conclusion as below:
1. Combustion process of compound fuels can be divided into: drying stage, volatile analysis and combustion stage, polymer combustion stage, fixed carbon combustion stage.
2. The ignition point of compound fuels decrease with increase of content of the laboratory-made solid waste, and the comprehensive combustion characteristic index increases with the increase of the sawdust content.
3. In the study of combustion kinetics, the first-order reaction model has a high fitting coefficient, and the whole combustion stage can be simulated by three first-order reaction superposition.
4. The effects of combustion temperature and residence time on the chlorine content of the compound fuel were studied. The experimental results showed that the combustion temperature was 1000℃ and the residence time was 10 min. Under this condition, the content of chlorine in the compound fuel could be accurately measured.
5. Calcium oxide as a chlorine fixaion agent, with the increase in the proportion of calcium oxide compound fuel made the efficiency of chlorine increase. The best addition ratio is the calcium to chlorine ratio of 3:1.
6. The efficiency of chlorine fixation under different molding pressures was studied. With the increase of molding pressure, the efficiency of chlorine fixation was improved, but the forming efficiency was higher than a certain range.

**Acknowledgements**

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**Reference**


[18] Yaman S, Cinpolat E, Karatepe N, Kucukbayrak S. Influence of oxidative treatments on the


