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Study on Combustion Characteristics of Glyphosate Waste Liquor

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Abstract. With the continuous development of the economy, the requirements for glyphosate production and environmental protection policies published by the country are becoming stricter. The glyphosate waste liquid has high viscosity and low calorific value, and the conventional waste liquid is difficult to burn. Therefore, how to efficiently treat the glyphosate waste liquid is a problem faced by the current glyphosate production industry. Therefore, the paper analyzes the rheological properties and thermogravimetric analysis of a chemical plant glyphosate waste liquid to understand its viscosity characteristics and incineration characteristics, and provides a strong basis for glyphosate combustion process design, parameter selection and burner selection. It also provides a strong theoretical basis and practical experience for the design of the glyphosate waste liquid treatment process in China.

1 Introduction

Glyphosate is the most widely used herbicide in the world. At present, the annual output of glyphosate in China is about 450,000 tons. Each ton of glyphosate produces about 4 to 5 tons of organic wastewater, while the annual output of glyphosate wastewater in China is about 1.8 to 2.25 million tons. The glyphosate production waste water has a large discharge, high pollution concentration, high toxicity and high salt content. Moreover, the biochemical treatment of glyphosate waste liquid is difficult and costly, so it is not suitable to use biochemical treatment to treat glyphosate waste liquid in the factory. The treatment of this wastewater is one of the problems that plague glyphosate production enterprises.

The chemical name of glyphosate is N-phosphocarboxymethylglycine[1]. The production capacity of a chemical glyphosate is 50,000 tons per year, and the annual production of glyphosate wastewater is about 200,000 tons, that is, about 548 tons of glyphosate wastewater is produced every day. Because the glyphosate waste liquid has a certain calorific value and has the potential to burn, the commonly used method is to concentrate the glyphosate waste liquid and then put it into the combustion machine to burn, and can obtain sodium pyrophosphate and some heat [2-4]. Studying the combustion characteristics and kinetic parameters of waste liquid helps to understand the combustion characteristics of waste liquid and its influence on the design and operation of incinerator [5].

2 Experimental materials and methods

2.1 Experimental materials The two kinds of glyphosate waste liquids provided by a chemical plant are four-effect mother liquor and external mother liquor, and the four-effect mother liquor is made by external mother liquor through oxidation, evaporation and crystallization. The two kinds of waste liquids are shown in Figure1. They are all pale yellow viscous liquids at normal temperature

and are difficult to flow. The color of the four-effect mother liquor is slightly lighter, the density is 1448kg/m^3, and the color of the external mother liquor is slightly deep, and the density is 1538kg/m^3.

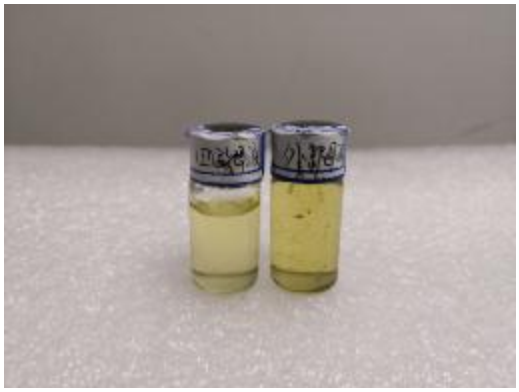

Figure1 Glyphosate waste at room temperature
(left) four-effect mother liquor (right) external mother liquor

As can be seen from the above figure and parameters, the four-effect mother liquor has a purer composition and a heavier density. The external mother liquor has more impurities and a lower density. Table 1 shows the physical properties of the four-effect mother liquor and the external mother liquor.

Table 1 Industrial analysis and calorific value of two glyphosate waste liquids

Sample	Industrial Analysis /%				Low calorific value Qnet.ar(kJ/kg)	High calorific value Qgr.d(kJ/kg)
	Moisture (M)	Ash （A）	Volatile matter （V）	Fixed carbon (FC)		
Four-effect mother liquor	39.98	40.31	18.95	0.76	3210	4740
External mother liquor	50.23	33.43	15.71	0.63	2108	2786

2.2 Experimental methods The rheological properties of waste liquid is one of the important parameters of combustion atomization. Only at the right temperature and the right viscosity, the atomization effect is the best and the combustion is more sufficient, which is also an important basis for burner selection.

We used the NDJ-5S digital viscometer produced by Shanghai Hengping Instrument Factory to measure the viscosity of the two waste liquids at different temperatures. The viscometer has a measuring range of 1 to 1×10^{5}MPa.s and is equipped with a rotor No. 1-4. The speed can be adjusted between 6, 12, 30, 60 rpm, and the measurement accuracy is ±2%. 220V 50Hz AC is used, the viscometer is shown in Figure 2.

Figure 2 NDJ-5S digital viscometer

We separately placed the two samples into the beaker, and uniformly heated them to 20 ° C, 50 ° C, 80 ° C, and 100 °C on an electronic universal electric furnace, and kept the waste liquid in the entire

beaker evenly for a while. Outside the beaker, an insulating cotton is placed and placed under a viscometer for measurement. When the rotor rotates in the liquid, the liquid will produce a viscosity torque acting on the drill, the viscosity is different, and the viscosity moment of the rotor, so the rotor of the corresponding model should be selected for measurement. After a plurality of measurements were averaged, the viscosity values of the two waste liquids were measured.

The combustion characteristics and kinetic parameters of the waste liquid help to understand the combustion characteristics of the waste liquid and its influence on the design and operation of the incinerator [5]. We used the WCT-2C thermogravimetric analyzer produced by Beijing Optical Instrument Factory to perform thermogravimetric analysis on the two waste liquids. The instrument can measure temperature range from room temperature to 1400 ° C, thermogravimetric accuracy of 10 μg, and the sample atmosphere can be oxidized, reduced, inert, and vacuum gas. As shown in Figure 3.

Figure 3 WCT-2C Thermogravimetric Analyzer

We placed an alumina nickname containing 25 mg of sample on two differential thermocouple plates and then lowered the furnace. Set the heating rate to 10 ° C / min, the initial temperature is 60 ° C, the end temperature is 1000 ° C, the experimental atmosphere is air, the air flow is controlled by the flow meter to 70mg / min, and the power is turned on after connecting the inlet and outlet pipes .

3 Analysis of experimental results and experimental conclusions

3.1 Viscosity test results and viscosity temperature characteristics analysis The viscosity test was averaged over multiple measurements to determine the viscosity of the two waste streams. The results are shown in Figures 4 and 5.

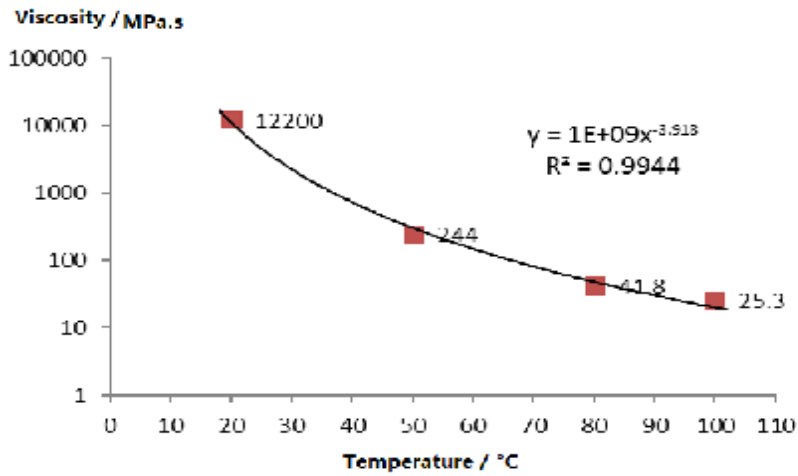

Figure 4 Four-effect mother liquor viscosity temperature curve

The fitting equation of the four-effect mother liquor viscosity temperature curve is

$$Y = 1 * 10^{9 * X^{-3.918}} \quad (1)$$

Y is viscosity / MPa.s
X is temperature / ° C

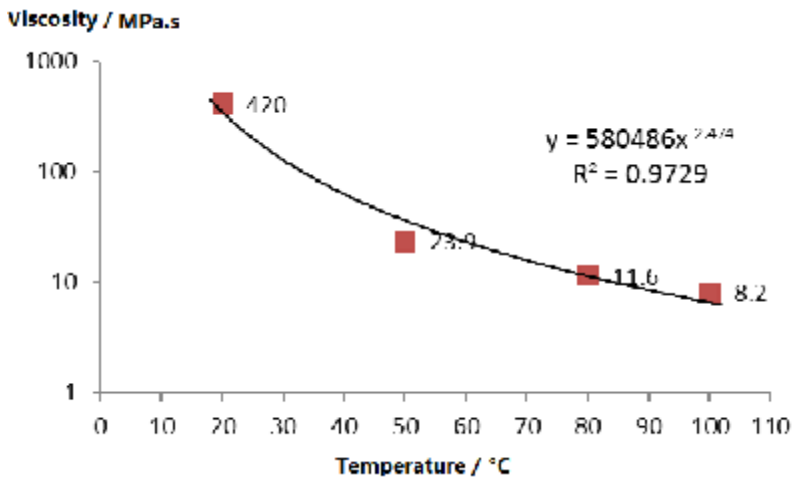

Figure 5 External mother liquor viscosity temperature curve

The external mother liquor viscosity temperature curve fitting equation is

$$Y = 580486X^{-2.474} \quad (2)$$

Y is viscosity / MPa.s
X is temperature / ° C.

From the rheological properties experiment, the viscosity-temperature characteristics of the two waste liquids can be obtained. The viscosity of both waste liquids decreases with increasing temperature. The viscosity is proportional to the atomization effect, and the viscosity directly affects the burner selection and combustion effect. The glyphosate waste liquid combustion is similar to the heavy oil combustion. After studying the glyphosate waste liquid [6,8], combined with the nature of the heavy oil burner, when the viscosity is about 200 MPa.s and the atomization medium pressure is 0.3 MPa, The atomized particles can reach about 25μm, and the effect of the atomizing burner is better [9,10]. Therefore, the two glyphosate waste liquids should be appropriately heated to a viscosity of about 200 mPa.s. Because the moisture content is also one of the important parameters affecting combustion, the four-effect mother liquor is more suitable for the industrial production of sodium pyrophosphate than the two waste liquids. In summary, the four-effect mother liquor of combustion has the best combustion effect when entering the burner at a temperature of 50-55 °C. The external mother liquor that is burned has the best combustion effect when it enters the burner at a temperature of 25 to 30 °C.

3.2 Thermogravimetric results and combustion characteristics analysis Thermogravimetric test results of the two waste liquids are shown in Figure 6.

The combustion characteristics and kinetic parameters of the waste liquid help to understand the combustion characteristics of the waste liquid and its influence on the design and operation of the incinerator [5].

We used the WCT-2C thermogravimetric analyzer produced by Beijing Optical Instrument Factory to perform thermogravimetric analysis on the two waste liquids. The instrument is a thermal

analysis instrument combining a thermogravimetric method and a differential thermal method. The instrument can obtain the thermogravimetric and thermal difference information synchronously by using the same sample in the same measurement. It is better for the TG and DTA curves to help determine whether the thermal effect of the substance is caused by physical processes or chemical processes. It can study the phase transformation, decomposition, compounding, dehydration, adsorption, analysis, solidification, sublimation, evaporation, mass change and other phenomena of substances and differential analysis, composition analysis, thermal parameter analysis, purity determination, reaction kinetics parameter determination and so on. The thermogravimetric analyzer uses 220V 50Hz AC power, the cooling water flow rate is 200L/h, the measurable temperature range is room temperature to 1400°C, the thermogravimetric precision temperature is 10μg, and the sample atmosphere can be oxidized, reduced, inert, and vacuum gas. As shown in Figure 5.

After leveling the balance mainframe, remove the pallets on both sides of the furnace, take off the glass cover, place the aluminum oxide nickname containing 25 mg of sample on the two differential thermocouple plates, and then lower the furnace. The heating rate was set to 10 ° C / min, the initial temperature was 60 ° C, the end temperature was 100 ° C, the experimental atmosphere was air, the flow rate was controlled by a flow meter of 70 mg / min, and the power was turned on after connecting the inlet and outlet pipes.

The experimental results are shown in Figure 6.

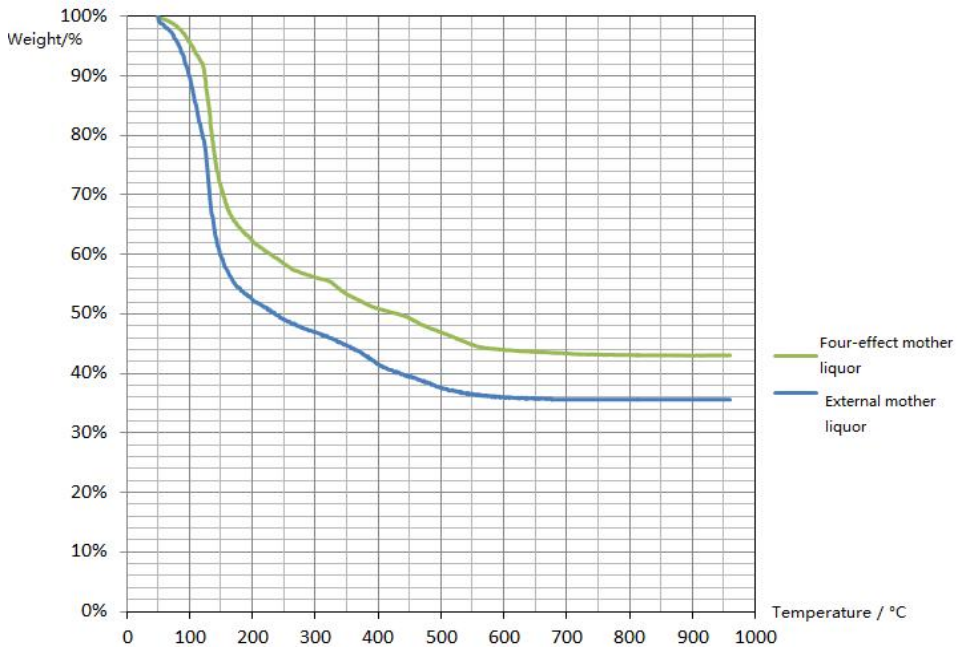

Figure 6 Thermogravimetric analysis results of two waste liquids

It can be seen from the thermogravimetric graph that the two glyphosate waste liquids have undergone evaporation, dehydration and volatilization stages.

The four-effect mother liquor mainly undergoes a dehydration reaction before 160 °C. The weight loss is about 30%, and the waste liquid enters the volatilization analysis, and the reaction phase between the substances is the main reaction stage when the waste liquid is burned, and the temperature ranges from 160 ° C to 600 ° C.

The external mother liquor mainly undergoes a dehydration reaction before 180 °C. The weight loss is about 44%, and the waste liquid enters the volatile analysis, and the reaction phase between the substances is the main reaction stage when the waste liquid is burned, and the temperature ranges from 180 ° C to 600 ° C.

Since the fixed carbon content in the two waste liquids is extremely low, after 600 ° C, the volatile matter in the waste liquid is completely precipitated, and the waste liquid is also burned out. It can be obtained that the shape of the TG curve of the two kinds of waste liquids has a certain similarity, the

temperature regions of the intense combustion are similar, and the basic combustion characteristics of the fuel have similarities.

3.2.1 Ignition characteristics The ignition characteristic is an important combustion characteristic of fuel. The most commonly used TG-DTG method is used to determine the ignition temperature. The temperature corresponding to the intersection of the tangent line and the parallel line at the beginning of the beginning is defined as the ignition temperature.

According to this method, the ignition temperature of the two waste liquids can be calculated from the TG and DTG curves obtained from the experiment, as shown in Table 2.

Table 2 Ignition temperature of two glyphosate waste liquids

Sample	Ignition temperature T/°C
Four-effect mother liquor	196
External mother liquor	201

It can be concluded from Table 2 that the ignition temperature of the four-effect mother liquor is 196 ° C and the ignition temperature of the external mother liquor was 201 °C.

3.2.2 Burnout characteristics The ratio of the weight loss of the waste liquid corresponding to the ignition point on the TG curve to the flammable content of the fuel is defined as the initial burnout rate f1, and the time from the ignition temperature to the ignition temperature is 98% of the combustible mass is defined as the burnout time(τ_0). The ratio of the weight loss of the waste liquid corresponding to the time τ0 to the flammable content of the waste liquid is defined as the total burnout rate f, and the late burnout rate f2=f-f1. The burnout characteristic index expression is as follows.

$$C_b = (f_1 / f_2) / t_0 \tag{3}$$

Among them, f1 reflects the influence of the relative content of volatile matter and the ignition characteristics of combustion, and the larger the f1, the better the flammability. F2 reflects the burning performance of carbon in the fuel, and the larger the f2, the better the burning performance. The burnout characteristic index Cb takes into account the effects of fuel ignition and combustion stability on the burnout. The larger the Cb, the better the burn-up. Table 3 summarizes the burnout characteristic index of the two waste liquids. From the table, it can be seen that the burn-in time of the four-effect mother liquor is 1544s, the burn-up performance is 1.32, the burn-in time of the external mother liquor is 2466s, and the burn-up performance is 0.96.

Table 3 Two types of waste liquid burnout characteristics index

Sample	Burning time τ_0/s	f/%	f_1/%	f_2/%	$C_b/10^{-4}s^{-1}$
Four-effect mother liquor	1554	98	16.67	81.33	1.32
External mother liquor	2	98	18.75	79.25	0.96

It can be obtained that the four-effect mother liquor of the two waste liquids has the lowest ignition temperature, the shorter combustion time and the highest burnout characteristic index, indicating that the burn-up rate is high and the burn-up characteristics are the best. Therefore, the four-effect mother liquor has better ignition characteristics and combustion performance than the external mother liquor.

4 Conclusion

After the analysis of the combustion characteristics of glyphosate waste liquid, we can clearly understand that the glyphosate waste liquid has low calorific value, high viscosity at low temperature,

high water content and high ash content, which will make the combustion of waste liquid unstable. It is easy to be slagging and clogged, and there is also sodium chloride impurity in the burned product sodium pyrophosphate. The above factors make the economic benefits of glyphosate waste liquid incineration to be improved.

Through the experimental study of the glyphosate waste liquid in this paper, the accurate analysis of its characteristics provides an accurate basis for the construction of the glyphosate waste liquid incineration process system, so that the various links in the production system are coordinated and coordinated. It also provides accurate parameters for equipment selection, which makes the selection equipment have the characteristics of reliable performance, overall matching, high efficiency, low consumption and strong operability. The process is flexible, simple, adaptable, easy to operate and manage, low operating costs, and achieve efficient production of the whole system to achieve industrial production.

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