THERMODYNAMIC MODEL AND KINETIC COMPENSATION EFFECT OF OIL SLUDGE PYROLYSIS BASED ON THERMOGRAVIMETRIC ANALYSIS

by

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Oil sludge is an organic solid waste in the petrochemical industry and improper treatment of oil sludge will cause environmental pollution. Pyrolysis is an effective way to realize its resource reuse. In order to understand the pyrolysis behavior and thermodynamic characteristics of oil sludge, four oil sludge samples from storage tanks were used as the research object, and pyrolysis experiments were carried out at heating rates of 5 °C, 10 °C, and 15 °C per minute under a nitrogen atmosphere. The kinetic parameters of pyrolysis of oil sludge are calculated by three equal conversion methods, Friedman method, Flynn-Wall-Ozawa method and Distributed activation energy model, and the most possible thermodynamic models for the main pyrolysis phase were analyzed and discussed by introducing the Malek method. The results show: high heating rate can promote the pyrolysis of oil sludge and in the pyrolysis stage, the apparent activation energy increases with the increase of the conversion rate. The apparent activation energy calculated by the Friedman method method is more reliable. The average apparent activation energies of the four oil sludge are 221.23, 84.71, 94.67, and 116.56 kJ/mol, respectively. The apparent activation energy and the pre-exponential factor are positively correlated, indicating that there is a kinetic compensation effect in the pyrolysis process. The thermodynamic models of the four oil sludge samples are all 3-D diffusion models, but their integral functions are different. The research results can provide theoretical support for the industrialization, harmlessness, and resource utilization of oil sludge pyrolysis.

Key words: oil sludge, thermodynamic model, kinetic compensation effect, thermogravimetric analysis, pyrolysis

Introduction

Oil sludge (OS) refers to the sludge that is mixed with crude-oil, refined oil and other heavy oil in the oil production process such as oil field extraction, oil refining, transportation, use and storage [1]. It has always been regarded as the main pollution in the petroleum and petrochemical industry [2], and is classified as hazardous waste in China [3]. The OS contains radioactive substances, polycyclic aromatic hydrocarbons and heavy metals, which are high-

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ly toxic and carcinogenic. Therefore, if OS is handled improperly, public and environmental health will be seriously threatened [4]. However, since sludge has a high hydrocarbon content, it is a valuable resource for fuel and energy recovery. It has always been the focus to find safe methods for the disposal of sludge and methods for resource utilization of sludge. In China, millions of OS obtained from crude-oil exploitation, transportation, and refining have accounted for a greater percentage (approximately 2%) of the mass of crude-oil [5]. At present, the most common OS disposal methods are widely used in solid waste treatment, but they cannot be effectively applied to OS due to the high ash content and low calorific value of OS [10]. The pyrolysis method can convert OS into light compounds, which not only has a higher energy recovery rate, but also produces less secondary pollution. Therefore, the pyrolysis method is one of the best ways to reduce the harmfulness of OS and realize energy reuse.

Lots of work regarding the research of OS pyrolysis have been done by researchers, mainly focusing on the properties of OS raw materials, the temperature conditions of pyrolysis, and the influence of reaction catalysts on the yield and composition of pyrolysis products. For example, Gong et al. [9] studied the products, distribution and composition of pyrolysis of OS under different pyrolysis temperature, heating method and atmosphere (N_2/CO_2) conditions. It is found that an increase in the heating rate will lead to a decrease in coke and petroleum yield and an increase in gas yield. Atmospheric CO_2 can promote the pyrolysis of OS, resulting in a decrease in coke yield. In addition reaction conditions such as temperature, additives in the pyrolysis process also have an effect on the pyrolysis of OS. Chen et al. [11] showed that the pyrolysis of OS was divided into three-stages: the volatile matter of light organic matter, the thermal decomposition of medium molecular weight matter, the continuous cracking of heavy carbon matter and the formation of solid carbon. As the heating rate increases, the thermogram moves to a higher temperature. Moliner et al. [12] studied the effect of pyrolysis under high temperature and high pressure on the yield and composition of OS pyrolysis products. The study found that the distribution of pyrolysis yield changes significantly with changes in temperature and pressure. The most liquid produced by pyrolysis at 600 °C is mainly composed of alkanes. When the temperature is 650-700 °C, the pyrolysis product is mainly composed of olefin and benzene-toluene-xylene mixture. Lin et al. [13] used rice husk and OS for co-pyrolysis to study the effect of the interaction between rice husk and OS on the pyrolysis process and products. They found that the synergistic effect of OS and rice husk pyrolysis could be enhanced by the minerals and ash in rice husk. The addition of rice husk increased the content of saturated oil and aromatics, and reduced the content of heavy fractions, thereby promoting the recovery of oil from pyrolysis. In addition, the addition of rice husk also promotes the secondary cracking reaction of pyrolysis OS, increases gas production, and generates more H_2 , CO and C_1 - C_2 hydrocarbons. Shie et al. [14] studied the influence of fly ash, zeolite, OS ash and polyvinyl alcohol waste polymer as additives on the pyrolysis of OS, and found that the addition of the above solid waste can increase the yield of pyrolysis recovered oil.

At present, the research on the kinetic characteristics of OS pyrolysis heating process mainly focuses on the pyrolysis mechanism, reaction rate, reaction parameters, and predicted product distribution [15], For example, Punnaruttanakun *et al.* [16] used TGA to study the kinetics and pyrolysis behavior of OS of American Petroleum Institute separator at different heating rates. It is found that hydrogen and acetylene are the main substances in the pyrolysis products. Shao *et al.* [17] used TGA to study the pyrolysis of two OS and found that the pyrolysis mainly occurred at 150-550 °C. The thermodynamic model of pyrolysis was analyzed by C-R integration method, and the apparent activation energy was calculated to be about 30 kJ/mol.

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However, kinetic compensation effects are rarely involved in the thermodynamics of OS pyrolysis. The kinetic compensation effect is an important content in the research of thermodynamics which exists in various systems and reaction processes, so it is clarified that the thermodynamic model of OS pyrolysis and the kinetic compensation effect are essential for a better understanding of the pyrolysis behavior of OS. Therefore, in this paper, the pyrolysis kinetics characteristics of OS through thermogravimetric experiments and the different thermodynamic reaction mechanisms of OS pyrolysis process has been studied. On this basis, the thermodynamic model and kinetic compensation effect of OS pyrolysis are revealed. The research results may help to understand the complex process of OS pyrolysis more deeply, and provide theoretical and technical support for the industrialization, harmlessness and resource utilization of OS pyrolysis.

Experiments and methods

Sample preparation

The samples used in the experiment were taken from the four storage and transportation companies in Zhejiang, and they were numbered OS-A, OS-B, OS-C, and OS-D. The proximate analysis, ultimate analysis and higher heating value (HHV) of OS were shown in tab. 1. The HHV of samples were obtained by eq. (1) based on ultimate analyses [18].

$$HHV = 33.93C + 144.32(H - 0.125O) + 9.3S + 1.494N$$
(1)

where C, H, O, S, and N were their weight percentages, respectively. Equation (1) has also been called Dulong equation. The HHV of OS is much lower than standard coal which indicated that the OS is not suitable for being directly used as a solid fuel [19]. The high ash value indicates that the OS sample has more residues after pyrolysis. The pyrolysis residue can be reused to produce OS ash, and the OS ash can be used as a catalyst to promote pyrolysis. Due to the high water content of some samples, they were first dried to constant weight in a 60 °C incubator for 72 hours, and then hand-grinded in an agate stone bowl, and powder samples with a particle size of less than 300 μ m were screened out and stored in a sealed bag for later use.

	Proximate analyses [wt.%]			HHV	Ultimate analyses [wt.%]					
Samples	Mª	V^{b}	FC ^a	Aª	[MJkg ⁻¹]	С	Н	0	N	S
OS-A	19.91	25.96	8.36	62.16	7.94	15.86	2.29	4.85	0.63	1.26
OS-B	26.57	32.46	11.25	52.33	13.84	25.68	4.25	6.32	0.62	1.35
OS-C	21.15	35.19	9.97	48.87	11.65	21.66	4.21	10.42	1.12	0.97
OS-D	25.39	40.45	6.98	50.86	10.71	21.07	4.13	13.63	0.89	0.59

Table 1. The proximate analyses and ultimate analyses of OS

M - moisture, V - volatile, A - ash, FC - fixed carbon, a - as received, b - dry basis

Experimental equipment and conditions

The SDT Q600 V20.9 Build 20 synchronous thermal analyzer was used for pyrolysis experiment. For each test, about 10 mg of samples were placed in a crucible, and the temperature was increased from room temperature to 800 °C at heating rates of 5, 10, and 15 °C per minute. In order to maintain effective pyrolysis conditions, both the scanning gas and the shielding gas are set to nitrogen, and the flow rate is 40 mL per minute.

Thermodynamic methods

Thermodynamic theory

During the pyrolysis of OS, volatiles, residues and heat are generated. According to the thermodynamic theory, the reaction rate can be expressed by the Arrhenius equation [20]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/(\mathrm{R}T)}f(\alpha) \tag{2}$$

where α is the mass conversion rate of OS pyrolysis, $\alpha = (m_0 - m_t)/(m_0 - m_{\infty})$, m_0 – the mass at the initial moment, m_t – the mass at the moment t, m_{∞} [g] – the mass at the end of the reaction, t [s] – the reaction time, T [°C] – the reaction temperature, A [s⁻¹] – the pre-exponential factor, E [kJmol⁻¹] – the apparent activation energy, R – the molar gas constant, and its value is 8.134 J/molK, and $f(\alpha)$ – the reaction mechanism function.

Under the condition of constant heating rate, the heating rate β :

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

The Coats-Redfern method was used to process eq. (1). Substituting eq. (3) into eq. (2), we can get:

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta} \mathrm{e}^{-E/(\mathrm{R}T)} \mathrm{d}T \tag{4}$$

Equation (4) reflects the relationship between mass consumption and reaction rate.

Determination of activation energy

In TGA, the equal conversion rate method can be used to obtain the apparent activation energy. The equal conversion rate method does not require a specific pyrolysis model $f(\alpha)$, but only a simple conversion of the formula. The following are three common methods for calculating kinetic parameters:

- Friedman method (FR). The FR method [21] is a differential conversion rate method. It is believed that when the conversion rate is the same, $\ln[\beta(d\alpha/dT)]$ at different heating rates has a linear relationship with 1/T, and the slope is -E/R. The apparent activation energy can be obtained at different conversion rates:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln\left[Af(\alpha)\right] - \frac{E}{\mathrm{R}T}$$
(5)

- Flynn-Wall-Ozawa method (FWO). The FWO method [22] is an integral conversion rate method. It is believed that when the conversion rate is the same, $\ln[AE/RG(\alpha)] - 5.331$ is a certain value, and $\ln \beta$ at different heating rates has a linear relationship with 1/T, and the slope it is -1.052E/R. The fitting formula:

$$\ln \beta = \ln \left[\frac{AE}{RG(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT}$$
(6)

 Distributed activation energy model (DAEM). The DAEM method [23] can clearly describe complex chemical reactions, and it has a good ability to determine the kinetic parameters of a series of parallel reactions with different activation energy values:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}$$
(7)

From the intercept and slope in eq. (6), the values of *E* and *A* can be easily obtained.

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Inference method of the thermodynamic model

The sample reaction consists of multiple stages, and each stage has an independent reaction equation. The thermodynamic parameters of each stage are constant, and the total mass loss is equal to the sum of the mass losses in each stage [21]. Malek method [24] was used to infer the dynamic mode from the function $y(\alpha)$:

$$y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{0.5}} = \frac{f(\alpha)G(\alpha)}{f(0.5)G(0.5)}$$
(8)

$$f(\alpha) = \frac{1}{\mathrm{d}G(\alpha)/\mathrm{d}\alpha} \tag{9}$$

where $y(\alpha)$ is the definition function, α – the conversion rate, T [°C] – the temperature corresponding to α , $T_{0.5}$ – the temperature when $\alpha = 0.5$, $f(\alpha)$ and $G(\alpha)$ are the differential of the reaction mechanism function sum and integral form, $d\alpha/dt$ is the reaction rate, $(d\alpha/dt)_{0.5}$ is the reaction rate when $\alpha = 0.5$. When the test value is close to the theoretical value, it can be considered that the corresponding mechanism function can be described as its thermodynamic model. Table 2 describes common thermodynamic models [20].

Table 2. Common thermodynamic modes and integral functions $G(\alpha)$

Function name	Mode	$G(\alpha)$
Parabola principle	1-D diffusion	α^2
Valensi equation	2-D diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$
Jander equation	2-D diffusion	$[1 - (1 - \alpha)^{1/2}]^{1/2}$
Jander equation	3-D diffusion	$[1 - (1 - \alpha)^{1/3}]^2$
Ginstling-Brounshtein equation	3-D diffusion	$1-2\alpha/3-(1-\alpha)^{2/3}$
Zhuralev-Lesokin-Tempelman equation	3-D diffusion	$[(1-\alpha)^{-1/3}-1]^2$
Mample principle	Random nucleation and subsequent growth	$-\ln(1-\alpha)$
Avrami-Erofeev equation	Random nucleation and subsequent growth	$[-ln(1-\alpha)]^{2/5}$
Avrami-Erofeev equation	Random nucleation and subsequent growth	$[-\ln(1-\alpha)]^{1/2}$
Avrami-Erofeev equation	Random nucleation and subsequent growth	$[-\ln(1-\alpha)]^{2/3}$

Results and discussion

Thermogravimetric analysis

The TG curve refers to the relationship curve between the mass and temperature of the measured substance at the program temperature, and describes the mass change of OS during the pyrolysis process. The differential thermogravimetry (DTG) curve is derived from the TG curve and represents the rate of quality change over time. The TG-DTG curves of the four samples at different heating rates are shown in fig. 1.

Overall, the pyrolysis characteristics of the four samples are roughly similar, and the pyrolysis process can be divided into three-stages:

- The first stage is the initial stage of pyrolysis (<100 °C), which is mainly caused by the evaporation of water and the precipitation of low molecular hydrocarbon compounds. The</p>



(a) OS-A, (b) OS-B, (c) OS-C, (d) OS-D

- fluctuation of the DTG curve is mainly caused by this situation. There is a small mass loss peak at this stage, the overall mass is slightly reduced, and the mass loss rate is about 3.5%. - The second stage is the main pyrolysis stage (100-430 °C), and the sample begins to enter a rapid mass loss stage. It can be seen from the DTG curve that there is a maximum mass loss peak for the four samples at this stage, corresponding to 248.45 °C, 216.39 °C, 197.89 °C, and 223.61 °C (taking 10 °C per minute as an example), which means the sample decomposition rate reaches the highest. The mass loss at this stage is mainly caused by the decomposition of large molecular weight organics into small molecular weight organics [25]. The mass loss of the four samples at this stage reached 21%, 31%, 30%, and 33%, respectively. In addition, there is another mass loss peak at this stage, corresponding to 326.21 °C, 333.43 °C, 341.15 °C, and 354.47 °C, respectively. The possible reason is the decomposition of small molecular weight compounds and inorganics also occurred during the pyrolysis process, which leads to two peaks at this stage. Among them, the peaks of the two mass loss peaks of OS-A are not much different, while the peaks of the other three samples are quite different, which indicates that the overall reaction rate of OS-A is faster.
- The third stage is the late stage of pyrolysis (430-800 °C). The produced coke decomposes again. The TG curve shows a slow decline and tends to be flat. When the temperature reached 600 °C, the four samples were completely decomposed, and their mass loss rates reached 29%, 37%, 38%, and 40%, respectively (take 10 °C per minute as an example). This result is also similar to that of Shao *et al.* [17]. They found that pyrolysis mainly occurs at 150-550 °C and decomposes completely after 550 °C.

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With the increase of the heating rate, both TG and DTG curves show a tendency to move toward the high temperature, and the pyrolysis temperature range and the peak-to-peak temperature of the mass loss increase. Thermochemical theory can explain this phenomenon [26]: a high heating rate increases the thermal decomposition rate and the temperature required for sample decomposition. The higher the heating rate, the greater the difference between the two peaks of the DTG curve in the second stage of pyrolysis, which indirectly indicates that the high heating rate is helpful to the pyrolysis of OS. In addition, our work has also shown that the higher the heating rate, the higher the carbon and sulfur content in the residue, and the lower the hydrogen content. This result is similar to the work of Liu *et al.* [15].

Activation energy calculation

In order to calculate the apparent activation energy of OS in storage tanks, according to the pyrolysis data under different heating rates, FR, FWO, and DEAM methods are used to calculate the thermodynamic parameters at equal conversion rates. The apparent activation energies (conversion rate from 0.1-0.9 in intervals of 0.1) of the four samples were calculated based on the FR, FWO, and DEAM method. The average apparent activation energy of the four samples A, B, C, and D calculated by the FR method are 221.23 kJ/mol, 84.71 kJ/mol, 94.67 kJ/mol, and 116.56 kJ/mol. The average apparent activation energy calculated by the FWO method are 215.41 kJ/mol, 79.25 kJ/mol, 89.52 kJ/mol, and 107.25 kJ/mol. The average apparent activation energy calculated by DEAM method are 216.17 kJ/mol, 76.19 kJ/mol, 87.00 kJ/mol, and 108.00 kJ/mol. It can be found that the average apparent activation energy calculated by the three methods is not much different.

Figure 2 shows the relationship between activation energy and conversion rate obtained by FR, FWO, and DAEM methods for four samples. At the beginning, the apparent activation energy of the sample is small. When the conversion rate is from 0.1-0.2, the apparent activation energy decreases. This is because at the beginning of the reaction stage, as the temperature rises, the sample activity is higher. In addition, the sample is easier to decompose due to high mass fraction and large molecular weight. However, in general, the apparent activation energy obtained by the three methods grows with the increase of the conversion rate, which indicates that the pyrolysis reaction becomes more difficult as it progresses. The apparent activation energy of OS-D showed a downward trend after the conversion rate exceeds 0.6, which is possibly caused by the increase of the activity of the sample due to the new reaction. The apparent activation energy also fluctuates with the change of the conversion rate, which indicates that the mechanism function controlling pyrolysis changes during the whole pyrolysis process [27]. The pyrolysis of the sample may be controlled by a multi-step reaction. There may be different thermodynamic models in the pyrolysis process.

In addition, the apparent activation energy obtained by the FR method is slightly higher than that obtained by the FWO method as a whole. This may be due to the following reasons: FR method which is a differential one uses the point value of the overall reaction rate, while FWO method which is an integral one describes the history of the system [28]. It means that the activation energy value obtained by the FWO method involves a systematic error that does not appear in the FR method. Therefore, the FR method is more sensitive than the FWO method, and the activation energy obtained from the FR method is more reliable than the activation energy obtained from the FR method is more reliable than the activation energy obtained from the FR method is more reliable than the activation energy obtained from the FR method is more reliable than the activation energy obtained by the FR method was used in this paper as the kinetic parameters of the four samples.



Thermodynamic model analysis

The heating rate has little effect on the kinetic mode, which is the reason why the multiple heating rate method is used to solve the apparent activation energy problem [30]. Here, a TGA curve obtained at a heating rate of 10 °C per minute is used. From the TGA in section *Thermogravimetric analysis*, it can be seen that the entire process of pyrolysis of OS in the storage tank is divided into three-stages. The second stage is the main pyrolysis stage (100-430 °C), during which mass loss is rapid. Therefore, the thermodynamic model of Phase II was studied by Malek method, and the function mechanism matching curves of the four samples were obtained as shown in figs. 3(a)-3(d).

It can be seen from fig. 3 that in the main pyrolysis stage, the test curve shapes of samples A, C, and D match the theoretical curve of function 4, see tab. 1, while the test curve shape of sample B is close to the theoretical value of function 6. The specific situation is shown in tab. 3. In the main pyrolysis stage, the pyrolysis of samples A, C, and D mainly follows the Jander equation, which is controlled by the 3-D diffusion of the reaction mechanism, and the integral function of the thermodynamic model is $[1 - (1 - \alpha)^{1/3}]^2$. The pyrolysis of sample B mainly follows the Zhuralev-Lesokin-Tempelman equation, which is controlled by the 3-D diffusion of its thermodynamic model is $[(1 - \alpha^{-1/3} - 1)]^2$. It can be seen that although the reaction mechanism of the four samples in the second stage is the same, and they are all controlled by 3-D diffusion, the integral functions of their thermodynamic models are different.





Figure 3. The function mechanism matching curves of the four samples; (a) OS-A, (b) OS-B, (c) OS-C, and (d) OS-D

Sample	Function name	Mode	Integral function
OS-A	Jander equation	3-D diffusion	$[1-(1-\alpha)^{1/3}]^2$
OS-B	Zhuralev-Lesokin-empelman equation	3-D diffusion	$[(1-\alpha)^{-1/3}-1]^2$
OS-C	Jander equation	3-D diffusion	$[1 - (1 - \alpha)^{1/3}]^2$
OS-D	Jander equation	3-D diffusion	$[1 - (1 - \alpha)^{1/3}]^2$

 Table 3. Thermodynamic models of four samples pyrolysis

Kinetic compensation effect

Through the DAEM method, the pre-exponential factor A can be easily obtained, as shown in tab. 4. In combination with tab. 2, it can be seen that the pre-exponential factor, A, value and activation energy, E, value generally increase with the increase of the conversion rate. Therefore, there may be a kinetic compensation effect during the pyrolysis of OS in storage tanks.

Kinetic compensation effect is an important content, which exists in various systems and reaction processes. During the pyrolysis process, the active sites on the surface of the OS will continue to be produced and consumed, thereby generating kinetic compensation. The linear relationship between $\ln A$ and *E* is usually called the dynamic compensation effect, and its mathematical formula can be described:

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$$\ln A = aE + b \tag{10}$$

where *a* and *b* are compensation coefficients.

Table 4. Pre-exponential factors of four kinds of samples

Conversion	OS- A	OS- B	OS- C	OS- D
0.1	$3.87 \cdot 10^{14}$	$1.16 \cdot 10^{6}$	6.38 · 1012	$3.14 \cdot 10^{7}$
0.2	$7.72 \cdot 10^{8}$	$4.37 \cdot 10^{5}$	$1.22 \cdot 10^{12}$	9.30 · 10 ⁵
0.3	$8.04 \cdot 10^{13}$	$4.14 \cdot 10^{5}$	$1.61 \cdot 10^{12}$	6.90 · 10 ⁵
0.4	$3.69 \cdot 10^{20}$	$4.51 \cdot 10^{5}$	$3.42 \cdot 10^{12}$	$1.72 \cdot 10^{6}$
0.5	$2.94 \cdot 10^{25}$	$1.12 \cdot 10^{6}$	$2.06 \cdot 10^{13}$	$1.9 \cdot 10^{8}$
0.6	$5.61 \cdot 10^{25}$	8.03 · 10 ⁷	$1.70 \cdot 10^{16}$	$1.55 \cdot 10^{19}$
0.7	8.90 · 10 ²³	$1.64 \cdot 10^{8}$	$1.93 \cdot 10^{17}$	9.15 · 10 ¹³
0.8	$4.76 \cdot 10^{42}$	$1.26 \cdot 10^{12}$	$3.27 \cdot 10^{17}$	$7.78 \cdot 10^{11}$
0.9	$7.47 \cdot 10^{16}$	$2.10 \cdot 10^{6}$	$1.14 \cdot 10^{16}$	$1.52 \cdot 10^{13}$



Figure 4. The relationship between ln*A* and *E* of the four samples

Equation (10) shows that the effect of changes in apparent activation energy can be partially compensated by the pre-exponential factor. The compensation effect is manifested in that the activation energy can be contained in the exponential term of the rate constant, and can also be contained in the pre-exponential factor. The relationship between $\ln A$ and E of the four samples is shown in fig. 4.

The apparent activation energy of the four samples and the logarithm of the pre-exponential factor show a good linear relationship, which indicates that there is a kinetic compensation effect during the pyrolysis of the sample. The kinetic

compensation effect lines of pyrolysis of different samples can be obtained through the slope and intercept of eq. (10). The reaction kinetics compensation effect equation of OS-A in the range of conversion rate 0.1-0.9 is: $\ln A = 0.17129E + 12.26394$, the correlation coefficient $R^2 = 0.96449$: OS-B reaction kinetic compensation effect equation is: $\ln A = 0.16901E + 3.38655$, correlation coefficient $R^2 = 0.97947$; OS-C reaction kinetic compensation effect equation: $\ln A = 0.15725E + 19.58671$, correlation coefficient $R^2 = 0.96128$; OS-D reaction kinetic compensation effect equation: $\ln A = 0.19641E + 2.34215$, the correlation coefficient $R^2 = 0.96511$.

In addition, the residuals and mean residuals of the kinetic compensation effect fitting curves of the four samples are shown in tab. 5. The residual can provide a certain basis for the rationality of the model and the reliability of the data. It can be found that the mean residual of OS-A is the largest, and the mean residual of OS-B is the smallest. Combined with R^2 , it shows that OS-B has the best fitting effect. Overall, the residual values of the four samples are not large, which further proves the existence of the compensation effect during the pyrolysis process.

OS-A		OS-B		OS-C		OS-D	
lnA	Residual	lnA	Residual	lnA	Residual	lnA	Residual
31.8398	1.7488	12.7001	1.2601	28.3405	1.1429	14.6832	2.5788
26.2124	-5.7476	12.7206	0.2662	28.0992	-0.2691	13.4358	0.3072
34.9520	-2.9342	13.0333	-0.0987	28.5992	-0.4944	13.7943	-0.3494
47.0305	0.3270	13.3738	-0.3548	29.3429	-0.4811	14.9337	-0.5772
56.9495	1.6933	14.2802	-0.3483	30.8478	-0.1919	19.1182	-0.0085
59.7309	-0.4413	17.7739	0.4270	36.5339	0.8364	40.7952	3.3924
58.6655	-3.5202	19.2924	-0.3796	38.5934	1.2094	32.6422	-0.4946
97.5747	0.6936	27.5816	0.2843	40.2395	0.0884	30.4342	-3.0544
30.6718	8.1805	15.6148	-1.0562	38.8140	-1.8406	32.1458	-1.7944
Mean residual	2.8096	Mean residual	0.4972	Mean residual	0.7282	Mean residual	1.3952

Table 5. The residuals and mean residuals of the four sample fits

There are some reasons for the kinetic compensation effect in the thermal analysis kinetics. Koga [31] summarized the causes of the compensation effect from a large number of literatures, and classified them into three categories:

- the physical and chemical properties of the reactants and the reaction process,
- the measurement conditions in the thermal analysis experiment, and
- the calculation and processing methods of experimental data.

Tian *et al.* [32] believed that the kinetic compensation effect was caused by the change of reactant properties in the study of the coal pyrolysis behavior and kinetics.

When the influence of experimental conditions, experimental errors and equipment errors during the experiment are minimized as much as possible, as the reaction progresses during the pyrolysis of OS, the organic matter is continuously cracked, and new active substances will also be generated and participate in the reaction. New active sites are generated, and the active sites continue to appear and consume, resulting in a kinetic compensation effect. In general, there is an obvious compensation effect in the pyrolysis reaction of OS. In addition, the compensation effect equation can be used to obtain the pre-exponential factor while grasping the activation energy distribution of the pyrolysis of OS, and vice versa. The compensation coefficient of the kinetic compensation effect can also characterize the characteristics of the OS pyrolysis reaction itself, which can reduce the influence of experimental factors. This result also further confirms the reliability of the calculated kinetic parameters, can better help determine the mechanism function of pyrolysis, and deepen the theoretical study of OS pyrolysis.

Further analysis revealed that the compensation-lines for the pyrolysis of the four samples are also different, which may be related to the differences in the composition and structure of the active components of the samples and the intermediate products produced during the pyrolysis process. It can be found from fig. 4 that the kinetic compensation-line of OS-A is the longest, followed by OS-D, OS-C, and OS-B, indicating that the larger the active component of the sample, the shorter the kinetic compensation-line of pyrolysis. Therefore, the level of the compensation-line can be used to understand the activity of the OS itself and provide certain theoretical support for its pyrolysis process.

Conclusions

The non-isothermal thermogravimetric method was used to study the pyrolysis characteristics of the OS in four oil storage tanks, and the samples were tested at different heating rates (5 °C per minute, 10 °C per minute, 15 °C per minute). The FR, FWO and DAEM method were used to calculate the kinetic parameters, E and A, of the pyrolysis, and the thermodynamic model of each sample was analyzed by Malek method. The main conclusions are as follows.

- The TG-DTG analysis showed that the dehydration stage in the initial stage of pyrolysis occurred at a temperature below 100 °C. The main pyrolysis stage of OS is between 100-430 °C, which has two main mass loss peaks, and the OS loses weight rapidly. In the late stage of pyrolysis, the temperature range is 430-800 °C, the main reaction is coke decomposition. High heating rate is conducive to the pyrolysis of OS, and the TG-DTG curve tends to move towards high temperature as the rate increases.
- With the conversion rate of 0.1 as the interval, the apparent activation energy at the conversion rate of 0.1-0.9 was calculated by FR, FWO, and DAEM method. The results showed that the apparent activation energy increased with the increase of conversion rate during the main pyrolysis process. The apparent activation energies of the four samples calculated by the three methods are similar. In addition, the change of the pre-exponential factor obtained by the DEAM method is positively correlated with the apparent activation energy, and there is a kinetic compensation effect during the pyrolysis of OS.
- The thermodynamic models of four OS samples pyrolysis were determined by Malek method. In this paper, the reaction mechanism for these four samples in the second stage is the same. The pyrolysis is mainly controlled by the 3-D diffusion model of the reaction mechanism, but the integral function of the thermodynamic model is different.

According to the results of this study, the main pyrolysis stage of OS pyrolysis is 100-430 °C, so low temperature pyrolysis technology is a more suitable pyrolysis method for this type of OS. We will carry on in-depth research on low temperature pyrolysis technology in the next work.

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Nomenclature

A	- ash
Ε	- activation energy, [kJmol ⁻¹]
$f(\alpha)$	- reaction mechanism function
$G(\alpha)$	- integral form of reaction mechanism
	function
HHV	 higher heating value, [MJkg⁻¹]
М	- moisture
m_0	– mass at the initial moment, [g]
m_t	– tmass at the moment t, [g]

- m_{∞} mass at the end of the reaction, [g]
- R molar gas constant, $[8.134 \text{ Jmol}^{-1}\text{K}^{-1}]$
- T temperature, [°C]

 $\begin{array}{l} t & - \text{ time, [s]} \\ V & - \text{ volatile} \\ y(\alpha) & - \text{ definition function} \end{array}$

Greek symbols

 α – mass conversion rate

 β – heating rate, [°C per minute]

Subscripts

- a as received
- b dry basis

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Acronyms

DAEM	distributed estimation on more model
DAEM	- distributed activation energy model
DTG	 differential thermogravimetry
	8 ,

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FC

FR FWO

OS

– fixed carbon– Friedman

- oil sludge

- Flynn-Wall-Ozawa

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