Application of solid waste treatment and resource utilization in tertiary oil recovery in environmental engineering

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ABSTRACT

In this paper, thermogravimetric IR analysis was performed for the pyrolysis and oil-bearing sludge of two solid wastes generated from tertiary oil recovery. The characteristics of combustion, parameters of combustion, synergistic effect of combustion, combustion characteristics of each component, dynamic parameters of combustion and deposition characteristics of gas phase products were studied. It is found that the combustion of residual oil and grease sludge after distillation can be divided into three different combustion stages. The burning property of the residual oil is improved after adding the sludge. In the pyrolysis process, the mixed combustion of residual oil and sludge has an obvious synergistic effect. Under different fuel conditions, there are both promoting and restricting effects between residual oil and oily sludge.

Keywords: Distillation residue, oily sludge, synergistic effect of mixed firing, solid waste, tertiary recovery treatment

1. INTRODUCTION

The residue after three extractions is a solid waste rich in ash. At present, the coking residue produced in the process of petroleum exploitation is more than 10-30t, which seriously restricts the development of the petroleum industry. The residual oil after three times extraction is rich in phenols, sulfides and polycyclic aromatic hydrocarbons, and there are also toxic components such as lead and cadmium, which pose a great threat to ecological safety. The oily sludge in tertiary crude oil is a solid waste containing a lot of oil generated after the distillation of tertiary oil refining, which is semi-solid, semi-solid, with water, dust, and other substances[1]. Oily sludge is rich in various types of oil and gas, in which PAHs have potential genotoxicity to the human body and other ecological environments, and can be transferred underground through the soil layer, and then affect other water environments, causing a series of hazards. Due to the strong stability of oily sludge, it is difficult to degrade and dispose of, if disposed of improperly, it will produce secondary environmental problems. At present, domestic and foreign scholars have proposed a variety of treatment processes, such as solvent extraction, freezing/melting, thermochemical cleaning, ultrasonic treatment, pyrolysis, incineration, and biodegradation. The residual oil and grease sludge of the third refining process all contain organic matter with a certain amount of residual heat, but the existing process adopts the “dumping method”, which not only causes waste heat consumption but also causes air and land pollution[2]. Research on the mixed combustion of residual oil and grease sludge can not only effectively recover the residual heat energy, but also realize the collaborative disposal of the two solid wastes, which has important theoretical and practical significance for promoting the economic and social development of China.

At present, there have been many studies on the disposal of the residual residue of three-cycle oil distillation and oily sludge. Some researchers have determined the residual oil after three times of extractions by thermogravimetric method and studied its reaction performance during pyrolysis[3]. It is found that the end temperature of distillation only has an effect on the low-temperature part, but not on the high-temperature part. The data of TG and differential heat are compared. The results show that the smaller heating speed promotes the combustion of the residue, while the larger heating speed is unfavorable to the ignition and combustion of the residue. Some researchers have carried out mixing tests on the leftovers and dried corn stalks after three times of extraction, and found that the mixed fuel can be divided into three different stages, and the quality of the mixed fuel will also improve with the increase of the fuel ratio. $Na_2SiO_3 \cdot 9H_2$ and OAEO-9 were used to clean oily sludge[4]. It was found that $Na_2SiO_3 \cdot 9H_2O$ had the highest cleaning efficiency, and the oil content after cleaning could reach about 1.6%. Some researchers have used condensate of methanol and LPG for sludge extraction, and experiments have proved that the yield of crude oil is the highest when the ratio is 4:1. This project intends to use thermogravimetric infrared spectroscopy and other means to study the reaction process of the mixed incineration of

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residual oil and sludge, the mixed reaction mechanism of the mixed fuel, the synergistic effect of the mixed fuel, the reaction kinetic characteristics and the formation law. The research results of this paper lay a foundation for the industrial popularization of solid waste from tertiary oil recovery.

2. EXPERIMENTAL DESIGN

The residual oil (RR) and the oily sludge (OS) produced by the same refinery are blended with the residual oil after the three extractions. The mixing ratio and quantity are shown in Table 1 below. The basic characteristic analysis of the dry distillation residue and oily sludge is shown in Table 2.

Table 1. Number and proportion of each sample.

ID	A1	A2	A3	A4	A5	A6
OS: RR	1:01	1:04	2:03	3:02	4:01	1:00

Table 2. Industrial analysis and elemental analysis of dry distillation residue and oily sludge.

Sample	Elemental analysis/%				
	Cad	Had	Oad	Nad	Sad
RR	6.77	7.052	0.417	5.865	0.479
OS	40.57	42.260	6.802	6.083	0.958
Sample	Calorific value/(kJ·kg^{-1})	Industrial analysis/%			
		Mad	Vad	Aad	FCad
RR	3838.29	3998.219	0.979	11.167	89.208
OS	24944.89	25984.260	9.938	53.885	37.281

It can be seen in Table 2 that the residual oil after distillation belongs to low-quality fuel with low volatile content[5]. However, due to its high moisture and high oil content, it is viscous and not conducive to combustion. Adding the residual oil after distillation can not only reduce its viscosity but also increase its contact area with heat and oxygen, thus enhancing its flammability. Therefore, blending the remaining oil and sludge can not only maintain the heat of the mixture but also significantly improve its combustion performance.

3. RESULTS

3.1 Study on combustibility of the sample

Figure 1 shows the mixed combustion characteristics of each sample at 20°C/min. As can be seen from Figure 1, the combustion of the dry distillation residue can be divided into two stages: one is the combustion of the gasification part, and the other is the combustion of the fixed carbon. The release of volatile components of gasification products in the gasification process is converted to about 10%. At this stage, the peak width of the transition rate of the distillation residue becomes smaller, indicating its rapid volatilization decomposition process[6]. In the second stage, the fixed carbon in the residual oil is the main body, and the conversion rate is about 3.65% during this period, and the highest is at 700°C. According to its combustion characteristics, it can be divided into low-quality organic matter combustion, heavy organic matter combustion, and fixed carbon combustion. It can be seen from the TG curve that there is a significant loss of oily sludge when Ti-300°Cand its conversion rate is about 28.24%, which is the main combustion process. In the combustion process of heavy oil at high temperatures, the reaction rate is about 25.14%, and the heavy oil precipitates and burns when it is above 350 degrees. The overall conversion efficiency of the two processes is about 52.41%, indicating that there is a large amount of light and heavy organic matter in the oily sludge. During the combustion of the fixed carbon, the activated carbon in the petroleum sludge is incinerated at a ratio of about 3%.

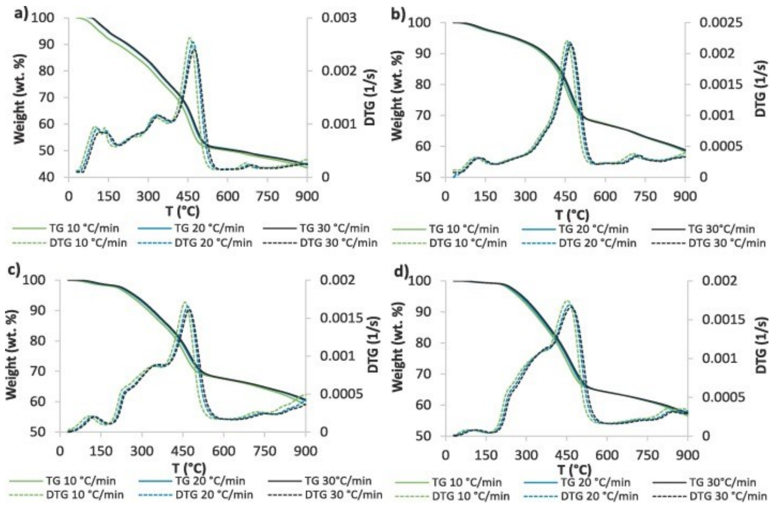

Figure 1. Combustion curves of each sample at 20℃/min.

It can also be seen from Figure 1 that the combustion of the mixed three processes: the combustion of light organic matter in the oily sludge, the co-combustion of volatiles of heavy oil and pyrolysis residues, and the mixed combustion between them. Because the oily sludge contains more combustible components, the conversion rate of the sample will increase significantly when the mixture contains more oil residue[7]. The conversion rate of each phase increases with the increase of oil content in the mixture and increases faster during the first and second combustion. In the three combustion processes, the conversion rate and conversion rate of the four mixed fuels are a little different, indicating that the carbon components and characteristics of the two mixed fuels are basically the same, which is consistent with the industrial research conclusions. When the oil/mud ratio does not exceed 40%, the highest peak conversion rate, while the highest peak conversion rate is when the oil/mud content exceeds 40%.

Figure 2 shows the combustion characteristic curve of sample A4 at various heating speeds. The experimental results show that the overall conversion rate of the system does not change when the heating speed increases, but the heat and mass transfer inside and outside the sample are obviously shifted due to the increase in the heating speed. The three reaction peaks all increase in the sample.

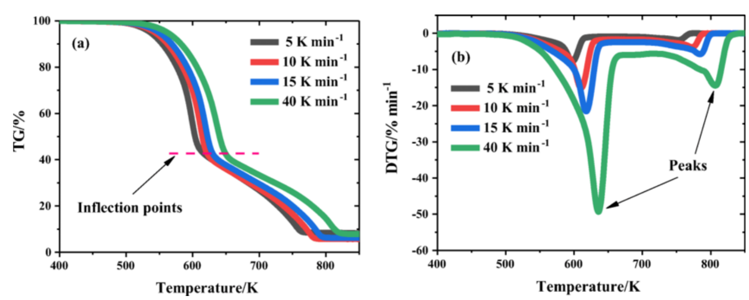

Figure 2. Combustion curves of sample A4 at different heating rates.

3.2 Characteristics of mixed burning of distillation residue and oily sludge

This project intends to study the influence of different combustion characteristic parameters on ignition, stable combustion, combustion characteristics, burnout characteristics, and overall combustion performance through the characterization of different combustion characteristic parameters.

The combustion performance evaluation indexes of each sample are listed in Table 3. The T_i and T_h of the dry distillation residue are 402℃ and 741℃ respectively, while the T_i and T_h of the oily sludge are 214℃ and 698℃ respectively. At 20℃/min, the mixing samples were maintained within 190-210℃, and Th was maintained within 700-720℃. The oil sludge is lower than the dry distillation residue, mainly because the volatile content in the sludge is much higher than that after distillation, and at the same time, in the sludge mixed with it, the volatile content is more likely to precipitate out of the water, thus accelerating the spontaneous combustion of the sludge[8]. Similarly, the T_h of oily sludge is also lower than that of dry distillation residue, mainly because the main component of crude oil is light organic matter, which releases more heat energy in the initial combustion process, thus accelerating the subsequent combustion and accelerating the early burning of the sample. Compared with the sludge, the ignition and combustion temperature of the mixed oil sample are lower than that of the sludge. The main reason is that after high-temperature retorting, the sludge reacts well with the sludge, thus increasing the specific surface area of the sludge. Both T_i and T_h decreased to some extent with the increase of the proportion of oily sludge in the mixed sample. This heavy organic matter in crude oil, which is easier to ignite, and the initial high temperature can better promote the combustion of residues. The T_i and T_h of the sample gradually increase, because the high heating rate causes the combustion lag phenomenon[9]. It can also be seen from Table 3 that the ignition characteristic parameters, stability parameters, mass response characteristic indexes, and total combustion performance indexes of the 6 samples all increase with the increase of oil content. However, the burnout index showed a trend of decreasing first, then increasing, and finally decreasing, which was inconsistent with the oil content, indicating that the higher oil content was unfavorable to the burnout rate of the sample. Although the increase in heating rate will cause an increase in ignition temperature and combustion temperature, it also increases C D_f, indicating that the increase in heating rate enhances the combustion capacity of the sample. Through the analysis of the performance indexes of each fuel, it is found that the performance indexes of sludge are obviously higher than that of residual oil.

Table 3. Evaluation parameters of combustion characteristics of each sample.

Sample	β/(°C·min^{-1})	Ti/°C	Th/°C	C/10^{-6}	Rw/10^{-6}	Df/10^{-2}	Rm/10^{-5}	S/10^{-8}
A1	20	419	772	8.45	7.18	36.35	8.02	1.08
A2	20	219	750	41.10	16.59	32.00	12.50	5.54
A3	20	215	736	62.34	47.57	30.10	21.06	11.84
A4	10	184	720	45.22	32.41	29.70	12.00	4.58
	20	211	733	71.53	53.78	37.21	22.93	15.11
	40	229	761	118.16	91.21	37.97	45.01	46.11
	80	249	783	167.04	135.79	38.93	85.00	122.97
A5	20	206	731	82.10	60.44	39.71	25.93	18.03
A6	20	223	727	105.77	79.98	38.51	36.78	31.76

3.3 Analysis of synergistic effect in the mixed firing process

In order to better analyze the synergistic effect of oily sludge and dry distillation residue in the mixed firing process, DSC experimental curve and calculation curve of the mixed firing process are compared and analyzed based on the same temperature range. The calculation equation of DSC theoretical curve is as follows

$$Q_{\text{cal}} = x_{RR}Q_{RR} + x_{OS}Q_{OS} \tag{1}$$

x_{RR} and x_{OS} are the mass shares of dry distillation residue and oily sludge in the mixed sample, respectively. Q_{RR} is the heat released by the combustion of the dry distillation residue. Q_{OS} is the heat released by burning oily sludge.

Figure 3 shows a comparison of DSC test curves and theoretical analyses for various mixtures. The mixed combustion of residuum and grease is not simply additive but has a synergistic effect. Because the concentration of organic matter in the secondary and secondary combustion products of the two fuels is very different, the two fuels will produce different degrees of mixing in the three combustion processes[10]. The synergistic effect of Phase 3 is smaller than that of Phase 1 and Phase 2 because of the smaller difference in the amount of carbon sequestration in Phase 3 crude oil and distillate. It can be seen from the DSC curve that at this stage, the experimental curves of residual oil and sludge are higher than the theoretical ones, indicating that there is a certain promoting effect between the two fuels. However, in the second step, the test curves of A3, A4, and A5 are all lower than the theoretical ones, indicating that in the second step, the residue after distillation and the sludge are mutually suppressed. However, according to the analysis of combustion characteristics, with the increase of the amount of fuel, its combustion state has also improved, mainly because the two fuels have catalyzed each other to release more heat energy in the previous period of time, thus eliminating the adverse effects of the two fuels when they restrict each other.

Figure 4 shows the ΔQ of the four mixed samples at different heating rates. With the increase of heating rate, ΔQ increases, indicating that from the overall effect, the increase of heating rate is conducive to the mixed burning of dry distillation residue and oily sludge. At the low heating rate, the ΔQ of the four samples is small, and the ΔQ of the sample A5 is even less than 0. The research results show that there is a mutually restrictive relationship between the residue with a high proportion of mud and the oil sludge at a low temperature. When the heating rate is low, the mixed forging effect of treatment group A2 is the best, and when the heating rate is high, the mixed sintering effect is the best.

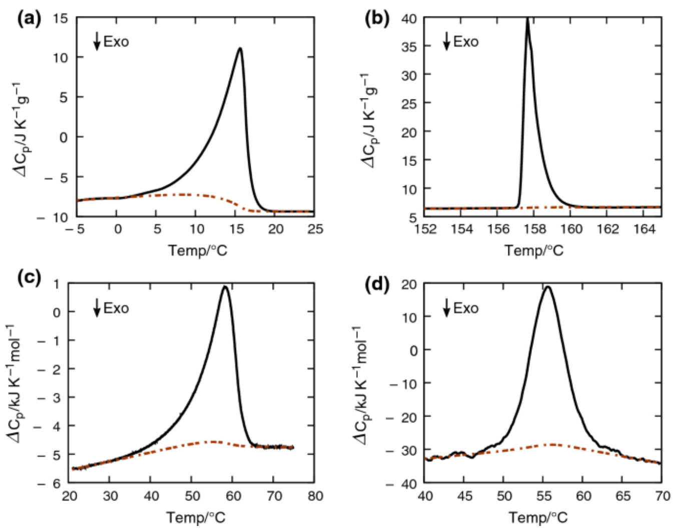

Figure 3. Comparison between experimental curves and calculated curves of mixed DSC samples.

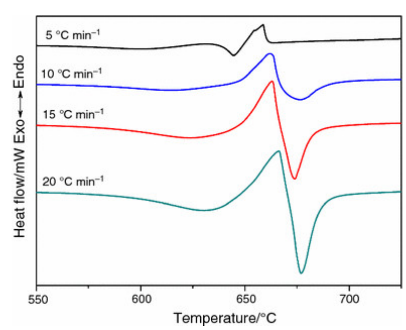

Figure 4. ΔQ of each mixed sample at different heating rates.

3.4 Gaussian peak splitting fitting

Gaussian fitting method can decompose multiple Gaussian peaks into multiple peaks, and each independent sub-reaction can be studied by studying the peak area, peak spacing and overlap degree. The multi-peak fitting function of Origin9.0 is used to fit peaks and achieve multi-peak fitting. A functional equation for Gaussian fitting can be expressed as

$$y = y_0 + \sum_{i=1} \frac{A_i}{w_i\sqrt{\frac{\pi}{2}}} \exp\left[-2\frac{(x-x_{ci})^2}{w_i^2}\right] \tag{2}$$

In equation (2), $i = 1, 2, \cdots; y_0$ is the baseline. A_i is the fitting area. w_i is the fitting peak half-peak width. x_{ci} is the transverse position of the fitting peak. Figure 5 shows the results of fitting the conversion velocity of each sample at 20℃/min with Gaussian peak splitting. In the pyrolysis process, the combustion and conversion rate of pyrolysis products can be divided into three matching Gaussian peaks: volatile component combustion, volatile component combustion and solid component combustion[11-14]. However, under different conditions, the transformation velocity curve of oily sludge shows five Gaussian peaks, namely, gasoline component combustion, diesel component combustion, heavy oil component combustion, ash component combustion, and solid phase combustion.

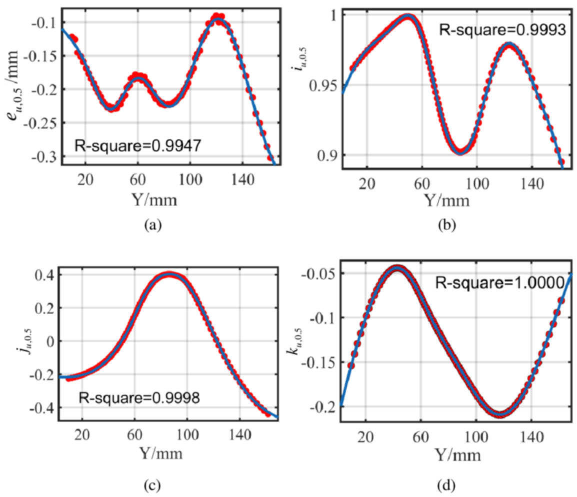

Figure 5. Gaussian peak splitting fitting results.

4. CONCLUSION

The mixed combustion of residual oil and oily sludge can be divided into three stages: mixed combustion, mixed combustion of heavy organic matter and pyrolysis residues, and fixed carbon combustion. The experimental results show that the higher the oil content in the mixture, the higher the conversion rate of the sample. With the increase in heating rate, the mixed combustion performance of the sample is improved, but there is obvious thermal hysteresis during the mixed combustion. The experimental results show that the ignition performance, combustion stability, and combustion state of the sample are improved with the increase of oil content, but the higher mud content is unfavorable to the combustion of the sample. The results show that the combustion performance of sludge is obviously higher than that of residual oil after distillation, and its combustion performance is obviously improved.

REFERENCES

[1] Lu, X., "Management and treatment of waste from tertiary oil recovery experiments," Chemical Engineering and Equipment 1, 114-116 (2023).
[2] Li, D., "Study on treatment and resource utilization of municipal solid waste," Paper making Equipment and Materials 8, 173-175 (2023).
[3] Wang, C., "Effective ways of municipal solid waste treatment and resource utilization," Intelligent Building and Urban Information 10, 100-101 (2021).
[4] Liu, J., Yao, X., Zhai, S., et al., "Technical analysis and prospect of resource utilization of vegetable waste in China," Journal of Agricultural Resources and Environment 37, 94-99 (2020).
[5] Zhang, Z., Xu, C., Shang, R., et al., "Study on the benefit of hydroheat treatment to vegetable waste resource utilization," Modern Chemical Industry 43, 218-221 (2023).
[6] Zheng, Y., Feng, Z., Zhou, K., et al., "Research progress on recycling technology of organic solid waste by enzyme," Journal of Environmental Engineering 11, 1247-1253 (2020).
[7] Chen, J., Qi, W., Jiang, H. L., et al., "Effects of composting of broccoli waste combined with fertilizer reduction

on yield and soil fertility of double cropping rice," Chinese Rice 29, 93-99 (2023).
[8] Wang, X., "Research on resource treatment of solid waste," Industrial Construction 52, 38-44 (2022).
[9] Wang, B., Zhou, X., Wang, M., et al., "Application progress of tertiary oil recovery technology in Zhongyuan Oilfield," Oilfield Chemistry 37, 51-55 (2020).
[10] Oilfield, C. and Li, G., "Advances in main technologies of tertiary enhanced oil recovery in domestic oil fields (Part II)," Oilfield Chemistry 4, 175-181 (2023).
[11] Min, C., Wang, Y., et al., "Research progress on recycling of rural solid waste in China," Journal of Agricultural Resources and Environment 3, 107-112 (2020).
[12] Shakiba, M., Ayatollahi, S. and Riazi, M., "Investigation of oil recovery and CO_2 storage during secondary and tertiary injection of carbonated water in an Iranian carbonate oil reservoir," Journal of Petroleum Science & Engineering, 137, 134-143 (2016). DOI:10.1016/j.petrol.2015.11.020.
[13] Theodorou, K., "Carbon dioxide enhanced oil recovery from the Citronelle Oil Field and carbon sequestration in the Donovan sand, southwest Alabama," (2013).
[14] Christopher, A. O. and Sylvester, O., "Characterization and application of biopolymer producing bacteria for enhanced oil recovery," International Journal of Energy and Environmental Research 10(2), 1-14 (2022).