



Preparation of Porous Coke by Microwave Pyrolysis of Oily Sludge: Optimization Through Response Surface Methodology and TG-FTIR Analysis

WENXUAN LI, XIUPENG MA, XIAOYAN LENG, YINGFEI HOU*

State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum (East China), Qingdao, 266580, China

Abstract: *Oily sludge (OS) is a kind of solid waste with precious oil resources in the petroleum industry. Because OS poses a severe threat to the environment, the treatment of OS has been widely studied. In this work, OS was used to prepare porous sludge coke through microwave pyrolysis and one-step ZnCl₂ activation technique. The response surface methodology was designed to optimize the parameters of the preparation process of porous sludge coke, and the interaction between the parameters was further analyzed. The experimental result showed that the model could fit the experimental results well. The optimal iodine adsorption value of porous sludge coke, 785.23 mg/g, was obtained by using the response surface methodology when the microwave power was 797 W, the ZnCl₂ addition ratio was 0.5, and the pyrolysis time was 25 min. The experimental result showed that the model could fit the experimental results well. The influence of ZnCl₂ on the pyrolysis of OS was investigated through TG-FTIR. The results showed that the presence of ZnCl₂ could prevent the fracture of C-H bond, reduce the rate of carbon source loss caused by the fracture of long-chain hydrocarbons to produce short-chain hydrocarbons in OS, and enrich the carbon source of sludge coke. On the other hand, the molten ZnCl₂ occupied the tiny pores when the oil components in the OS volatilized, which can enrich the pore volume of the sludge coke.*

Keywords: *oily sludge pyrolysis, porous coke, response surface methodology, ZnCl₂ activation, TG-FTIR*

1. Introduction

Oily sludge (OS) refers to the oily solid waste generated in the process of oil exploitation, storage and refining and the treatment of oily wastewater. OS mainly consists of oil, water and sediment, and its oil content is usually between 15 wt% and 50 wt%. In 2016, China government included OS as a toxic and flammable waste in the category of waste mineral oil and waste containing mineral oil. Due to the high oil content of sludge, direct discharge will pose a great threat to the environment. As a stable emulsification system has been formed in the OS, the treatment of OS is difficult, and the treatment cost is high [1]. It is worth nothing that, OS contains large quantities of valuable hydrocarbons. The treatment and utilization of OS through effective methods can not only solve its harm to the environment, but also make full use of valuable hydrocarbons. Therefore, it is crucial to recycle OS effectively [2].

The current treatment methods of OS include incineration treatment, [3] curing treatment, [4] oxidation treatment, [5] biological treatment, [6] separation treatment, [7] and pyrolysis treatment. Among them, incineration and solidification treatments have a significant threat to the environment and have been gradually given up. The oxidation treatment technology has a high cost, and the heavy metal problem cannot be solved. Biological treatment has the disadvantage of taking up land resources for a long time. Other, treatment technologies, such as extraction, ultrasonic separation, and membrane separation are difficult to be operated for large-scale.

At present, the relatively mature technology for OS treatment is pyrolysis technology. The OS was exposed to a high-temperature environment, and the oily hydrocarbon was hydrated and cracked to be

*email: houyf@upc.edu.cn ORCID ID: 0000-0003-4877-4577



separated from the inorganic sediment. It has the advantages of fast processing speed, and recoverable oil can be used and easy to be enlarged. The study on the pyrolysis of OS has become more and more abundant. Lin et al. conducted a pyrolysis study on OS through an iron-carbon catalyst, and the pyrolysis oil conversion efficiency was as high as 95% [8]. Gao et al. studied the fine particles produced by the pyrolysis of OS and solved the problem of pipe blockage during the pyrolysis of sludge [9].

Porous carbon materials have unique advantages such as high specific surface area and adsorption capacity, and have been widely used in various industries, thus triggering extensive research on the preparation of activated carbon. The conversion of OS into valuable materials particularly porous carbon at a low cost has attracted extensive attention. Mojoudi et al. prepared activated carbon with the high specific surface area for phenol adsorption from OS [10]. Wang et al. first separated OS through high-speed centrifugation, and then prepared activated carbon with a high specific surface area of 3292 cm²/g by KOH two-step activation [11]. The activated carbon prepared from OS is proved to be an excellent raw material for the preparation of porous materials. Li et al. prepared supercapacitors electrode materials with an excellent performance by nitrogen doping and KOH activation [12]. OS has a good prospect in the preparation of high-value carbon materials. However, the current preparation method of porous carbon from OS is time-consuming and multi-step, and is operated at high temperature.

In this study, OS was used to prepare porous carbon material, sludge coke, by microwave pyrolysis and one-step zinc chloride activation. The random response surface methodology (RSM) is used to study the experimental process. The random RSM is used to optimize and model the parameters of microwave pyrolysis. The model is symmetrically evaluated and analyzed. Subsequently, TG-FTIR analysis is carried out on the OS, and the influence of zinc chloride on the pyrolysis of OS is investigated.

2. Materials and methods

2.1. Oily sludge analysis

The oil sludge samples used in the experiment came from the bottom of the oil tank in the oil field in eastern China. After sampling, the oil sludge was dried in an oven at 105°C for 24 h. By means of ultrasonic solvent extraction by infrared spectrophotometry, the oil content of OS was measured to be 56.8%. Oil sludge was quantitatively analyzed using the German company Elementar elemental analyzer (Vario ELIII). The test results are shown in Table 1. Automatic Proximate analyzer (JHGF-3) was used for the Proximate analysis of OS. The test results are shown in Table 2.

Table 1. Ultimate analysis of oily sludge sample

Item	C	H	O	N	S
Ultimate analysis(wt.%)	56.43	8.26	5.02	0.41	0.84

Table 2. Proximate analysis of oily sludge sample

Item	Moisture	Volatile	Ash	Fixed carbon
Proximate analysis(wt.%)	0.59	40.07	43.79	5.39

2.2. Experimental procedure

A certain proportion of ZnCl₂ is added into the OS and then the OS is dried completely in the oven. A certain number of samples are put into a tube furnace heated by microwave for pyrolysis, and the whole pyrolysis process is protected by nitrogen. By adjusting the microwave power, microwave action time and different mixing ratio of ZnCl₂, the pyrolysis residue of OS (OS coke) with different properties is obtained. After cooled, the obtained sludge coke is washed with diluted hydrochloric acid to remove ZnO, ZnS, and other substances produced in the pyrolysis process. Then rinse the remaining ZnCl₂ and hydrochloric acid thoroughly with deionized water until it becomes neutral. Finally, the product sludge coke is placed in a 105°C oven for 24 h. The experimental process is shown in Figure 1.

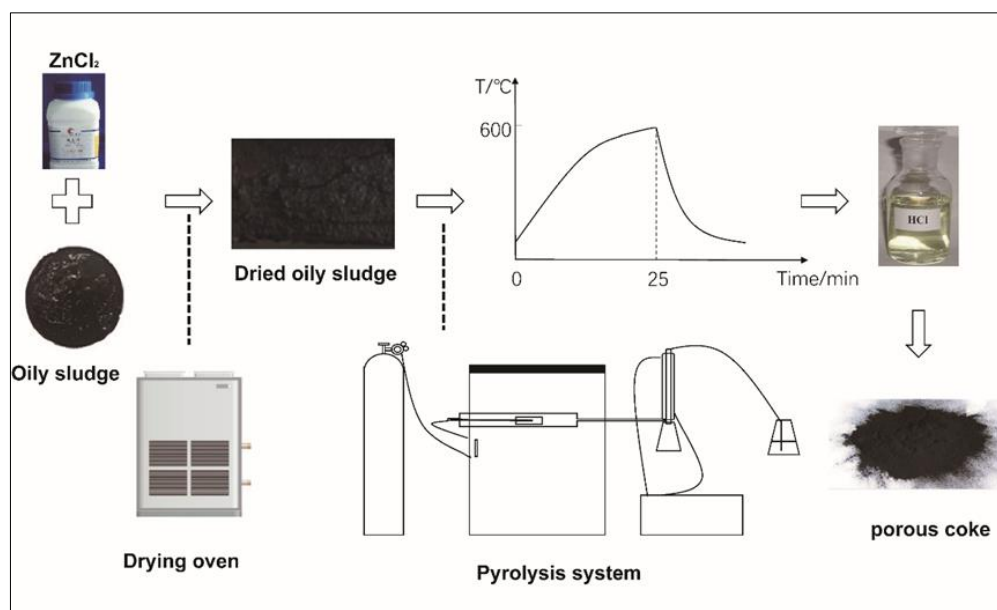


Figure 1. Schematic diagram of experimental process

2.3. Iodine adsorption

The adsorption property of sludge coke is characterized by iodine adsorption value. Iodine adsorption value is the adsorption capacity of porous substances to small molecular impurities. The test steps are as follows. A specific mass of sludge coke is weighed and placed in a conical flask containing a small amount of dilute hydrochloric acid. Then a certain amount of iodine solution of known concentration is poured into the flask. After reached the equilibrium, the adsorbed iodine solution is obtained by filtration and titrated with sodium thiosulfate solution to determine the concentration of the remaining iodine solution. The difference between the concentration of iodine solution before and after the adsorption of sludge coke is the adsorption capacity of sludge coke to iodine.

2.4. Operating parameter design by RSM

RSM is a statistical and mathematical method [13]. In the process of exploring the experimental operating parameters, the RSM is usually used to determine the operating parameters corresponding to the best experimental results and to obtain the experimental fitting model of the response surface. Moreover, the interaction of operating parameters on experimental results can be studied by the three-dimensional surface diagram of RSM. Box-Behnken Design (BBD) is one of the common design methods. Compared with Central Composite Design (CCD), BBD can avoid dangerous extreme experimental operating conditions or impossible experimental operating conditions.

In order to study the effect of experimental operating parameters (microwave power, time and ratio of ZnCl_2) on the adsorption capacity of sludge coke, BBD is used to design and determine the optimal level of each factor and the interaction between each factor. 17 groups of experiments are obtained by using three-factor and three-level BBD. The microwave power level is set as 600W, 700W, and 800W, respectively. The mass ratio of ZnCl_2 to OS is set as 0.5, 1, and 1.5, respectively. The microwave action time is set as 25 min, 35min, and 45min, respectively. In order to reduce the systematic bias caused by external factors, 17 groups of experiments are carried out in random order and averaged three times. In this paper, Design-Expert (8.05b) is used to design the experiment.

2.5. RSM model fitting

The model is fitted and analyzed by using the design-expert platform. Firstly, polynomial fitting is performed. The independent variables are the microwave power, microwave time and the amount of zinc chloride added during the pyrolysis of OS, and the iodine adsorption value of sludge coke is taken as the dependent variable. Furthermore, the predicted value of OS is compared with the actual value, and the



accuracy of the observation model is directly observed. Next, the variance analysis of the model obtained by RSM is carried out. Analysis of variance (ANOVA) is used to determine the statistical analysis model of experimental data, including calculating the parameters such as degree of freedom, correlation coefficient and variance of the model, which can evaluate the fitting degree of the model and the experimental [14].

2.6. Experimental verification and analysis of the model

After the optimal combination of parameters is obtained by random response surface analysis, the predicted value of the model is compared with the experimental value under the optimal operating conditions, and the prediction error is calculated. Consequently, whether the model applies to the microwave pyrolysis process is verified. The interaction between different parameters is analyzed by using the advantages of experimental parameter selection in the process of a random RSM.

2.7. TG-FTIR analysis

The Thermogravimetric analysis (TGA, NETZSCH, STA449F3) is used in conjunction with the Fourier transform infrared spectrometer (FTIR, Bruker, TENSOR II) to analyzed the thermal decomposition behavior and gas release characteristics during sample pyrolysis. One of the samples is OS, and the other is a mixture of OS and ZnCl₂. At first, 5 mg sample is placed on the alumina crucible on the thermal analysis balance. Under the condition of nitrogen with high purity, the samples are experimentally heated to 800°C with a heating rate of 100°C /min. FTIR is used with a resolution of 4 cm⁻¹ and a spectral range of 450 cm⁻¹ to 4000 cm⁻¹. Before loading the sample, a blank test is conducted to eliminate nitrogen error in the spectrum.

3 Results and discussions

3.1. Experiment of oil sludge pyrolysis

The BBD experiment results based on microwave power, time and ZnCl₂ ratio as three independent variables are shown in Table 3. From Table 3, the iodine adsorption value of sludge coke is within the range of 335.289 mg/g ~ 725.018 mg/g. When the power was 700 W, the time was 35 min, and the ratio is 1, the iodine adsorption value is the highest. During the pyrolysis process, the high temperature of the sludge, contributes to the endothermic decomposition of minerals in the sludge. The loss of structural support material inside the mud causes the collapse of the mud structure, resulting in a significant reduction in the specific surface area. When the microwave power and time are both low, the iodine adsorption value of the obtained sludge coke is also low. When the power was 600 W, the time was 25 min, and the ratio was 1, the iodine adsorption value was the lowest. Due to low pyrolysis power and short pyrolysis time, the corresponding internal temperature of the sludge was low. Hence, it is difficult for the heavy oil macromolecules inside the sludge to undergo large-scale carbonization and coking reaction, resulting in a low iodine adsorption value of the product.

Table 3. Experimental parameters design by RSM and experimental results

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	Power, W	Ratio	Time, min	Iodine sorption value, mg/g
14	1	700	1	35	719.313
12	2	700	1.5	45	706.486
10	3	700	1.5	25	523.663
1	4	600	0.5	35	519.856
3	5	600	1.5	35	671.104
4	6	800	1.5	35	647.977
17	7	700	1	35	711.361
2	8	800	0.5	35	669.313
8	9	800	1	45	365.289

9	10	700	0.5	25	664.711
5	11	600	1	25	354.892
15	12	700	1	35	715.018
11	13	700	0.5	45	539.127
7	14	600	1	45	653.12
6	15	800	1	25	670.17
16	16	700	1	35	693.241
13	17	700	1	35	713.286

3.2. Model fitting

The second-order polynomial is used to optimize the microwave conditions of oil sludge. The model showed a highly fit with the experiment results, with an R^2 value of 0.9949. Since different variables had different significance in influencing the results, the number of fitting terms was reduced according to the size of the P-value, and the resulting empirical model equation was simplified as follows:

$$\text{Iodine sorption value} = 713.44 + 31.58A + 6.58B + 6.32C - 43.15AB - 150.78AC + 77.10BC - 90.13A^2 - 108.70C^2 + 25.90A^2B - 24.72AC^2$$

where A is microwave power, where B is pyrolysis time, where C is ZnCl_2 ratio.

The response of the model predicted value and experiment value is shown in Figure 2. The distribution of data points was relatively close to the line, which proves that the experimental value of this model was in good agreement with the predicted value. The residual analysis between the predicted value of the model and the experimental value is shown in Figure 3b and 3c. The residuals were in normal distribution, indicating the validity of the model.

The results of the ANOVA of the model are shown in Table 4. The parameters of ANOVA were not equally important, and P-value is the most critical [15]. As can be seen from Table 3, the p-value of the model fitting was < 0.0001 , and the p-value less than 0.005, indicating that the model can fit the experimental results well. Moreover, the P-value of lack of fit was not significant, which indicates that there was a minimal probability to verify the test default value. The coefficient of variation (C.V.) is relatively low, indicating that the model has high accuracy and reliable predicted values. These data show the reliability of the model which is sufficient to predict the experimental value within the range of experimental variables.

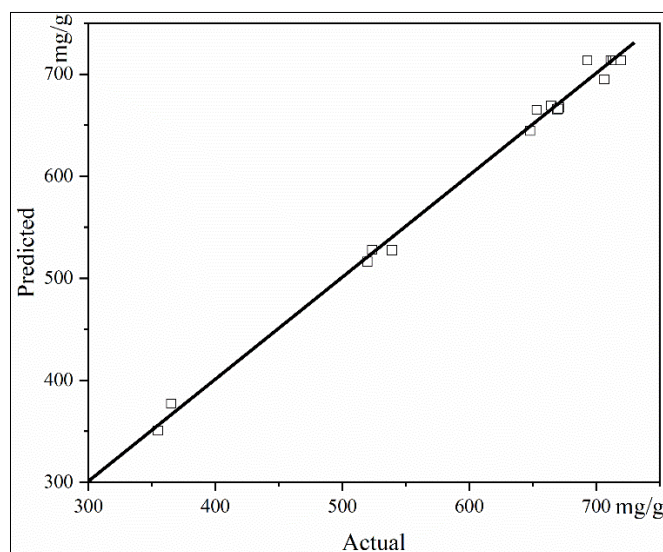


Figure 2. The comparison between the predicted value and the experiment value

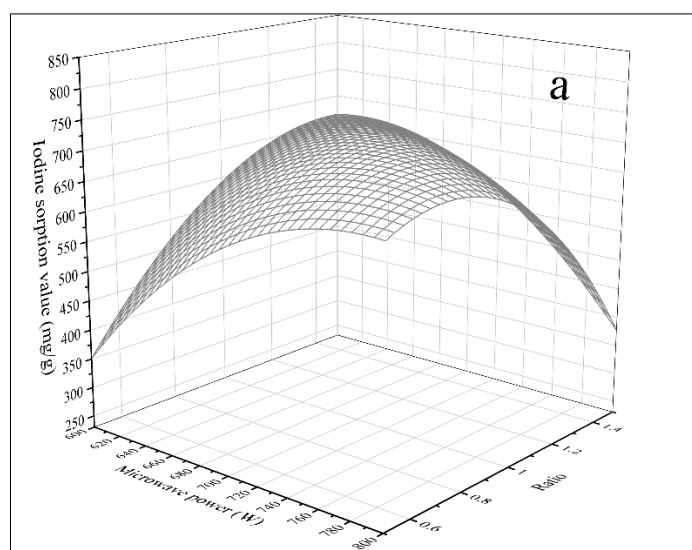
Table 4. Analysis of variance (ANOVA) for the response surface quadratic model of iodine sorption value iodine sorption value

Sources	Mean of square	F-value	P-value	Remark
Model	22010.51	117.04	<0.0001	significant
A	188.33	1.00	0.3356	
B	173.07	0.92	0.3745	
C	319.87	1.70	0.2400	
AB	7446.30	39.59	0.0008	
AC	90935.12	483.53	<0.0001	
BC	23778.74	126.44	<0.0001	
A ²	34298.97	182.38	<0.0001	
C ²	49884.82	265.25	<0.0001	
A ² B	1341.63	7.13	0.0370	
AB ²	1222.23	6.50	0.0435	
Lack of fit	277.76	6.77	0.1285	not significant

C.V. = 2.21, R-Squared = 0.9949, Standard deviation = 3.89, Adequate precision = 135.9

3.3. The interaction of different parameters of the model

Figure 2 is the 3D surface graph studied by RSM, which represents the interaction between parameters and responses [16]. Figure 2a shows the interaction between microwave power and the addition ratio of ZnCl₂. The contour plot shape of the iodine adsorption value was close to a circle, which proves that the interaction between the microwave power and the ratio of adding ZnCl₂ is weak and has little effect in this experiment. Figure 3b shows the interaction relationship between microwave power and microwave time on iodine adsorption value. Moreover, its contour line was elliptic, indicating that it has a strong interaction relationship. It can be seen that when the microwave power and time are at both high value or low value, the iodine adsorption value is low. In the direction of the long axis of the ellipse contour, microwave power and time have a good synergy. Figure 2c shows the interaction between the addition ratio of ZnCl₂ and time. It is shown that when increasing the addition ratio of ZnCl₂, the iodine adsorption value should be increased, the microwave reaction time should be extended. The maximum response value is obtained when ZnCl₂ is greater than 1.2 and the microwave time is between 30 min and 40 min.



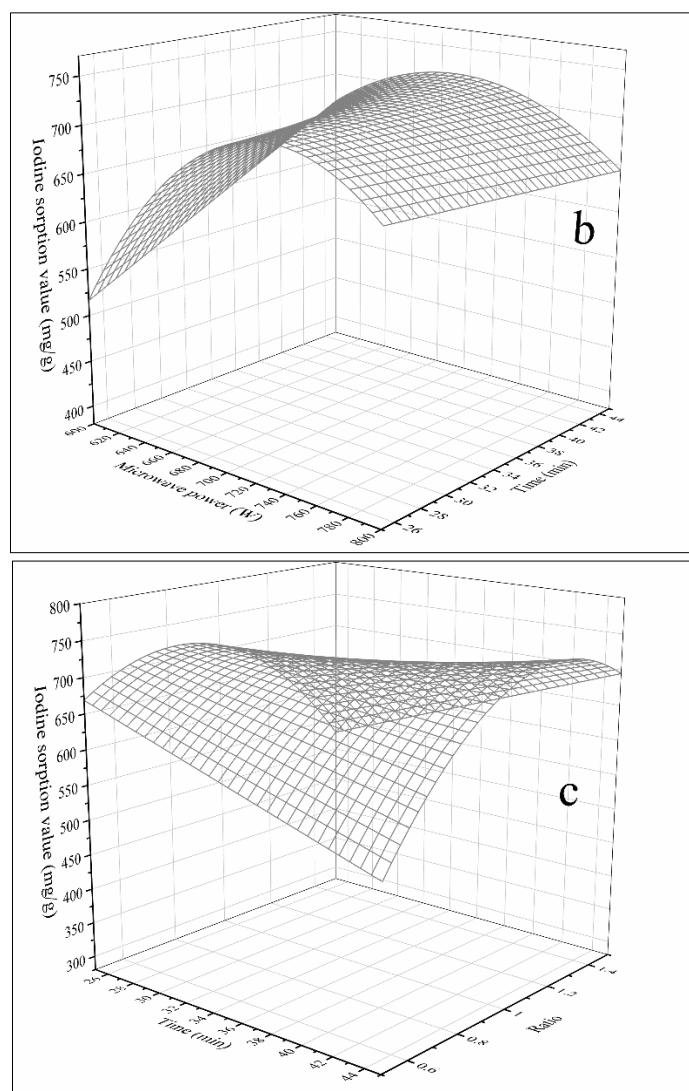


Figure 3. (a) the interaction between microwave power and the addition ratio of $ZnCl_2$
(b) the interaction relationship between microwave power and microwave time
(c) the interaction between the addition ratio of $ZnCl_2$ and time

3.4. Effect of $ZnCl_2$ on the pyrolysis of OS

As can be seen from Figure 4a, the pyrolysis process of OS samples without $ZnCl_2$ can be roughly divided into three stages. They are respectively the initial stage of steady pyrolysis temperature rise from $50^\circ C$ to $250^\circ C$, the rapid weight loss stage from $250^\circ C$ to $550^\circ C$, and the slow weight loss stage after $550^\circ C$.

The first stage ($50^\circ C$ - $250^\circ C$) has less weight loss, which corresponds to the desorption of gas in OS samples and the volatilization of small-molecule hydrocarbons. In the second stage ($250^\circ C$ - $550^\circ C$), the weightlessness ratio reaches 60%. Firstly, a large number of petroleum hydrocarbons are heated and volatilized; secondly, a part of large molecules of hydrocarbons undergo chain breaking, alkylation, and other reactions, which result in the gas escape of small and medium-sized molecules of hydrocarbons [17]. The weight loss in the third stage ($550^\circ C$ - $800^\circ C$) may be related to the thermal decomposition of inorganic minerals in the OS [18, 19].

According to Figure 4b, the pyrolysis process of the OS sample with $ZnCl_2$ can be roughly divided into four stages. They are divided into the first stage of rapid weightlessness from $50^\circ C$ to $250^\circ C$, the second stage of steady weightlessness from $250^\circ C$ to $500^\circ C$, the third stage of rapid weightlessness from $500^\circ C$ - $700^\circ C$, and the fourth stage of slow weightlessness after $700^\circ C$.

It can be seen that the pyrolysis process of OS changed obviously after the addition of ZnCl_2 , which is related to the proportion of ZnCl_2 in OS. During the pyrolysis process, the physical and chemical changes of ZnCl_2 have a strong influence on the TG and DTG curves.

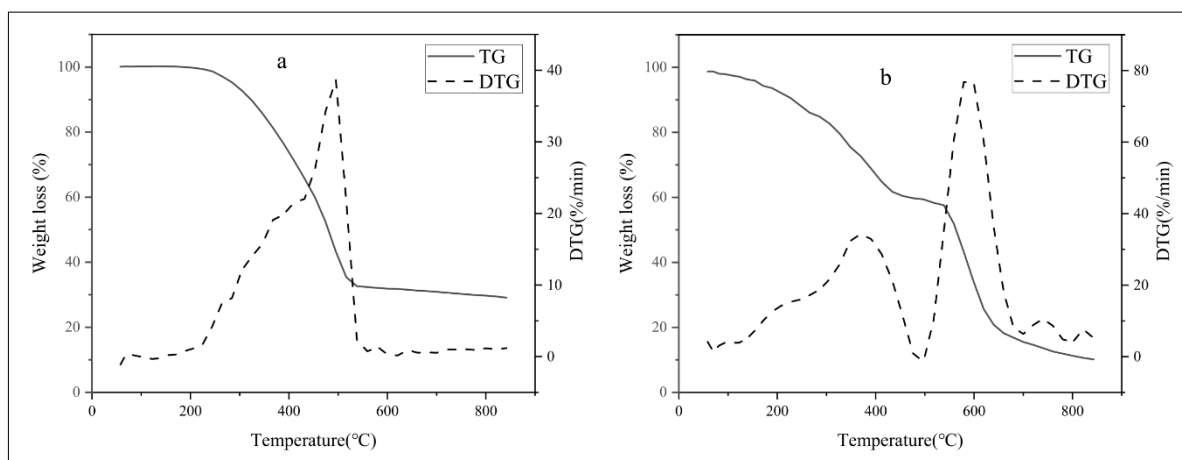
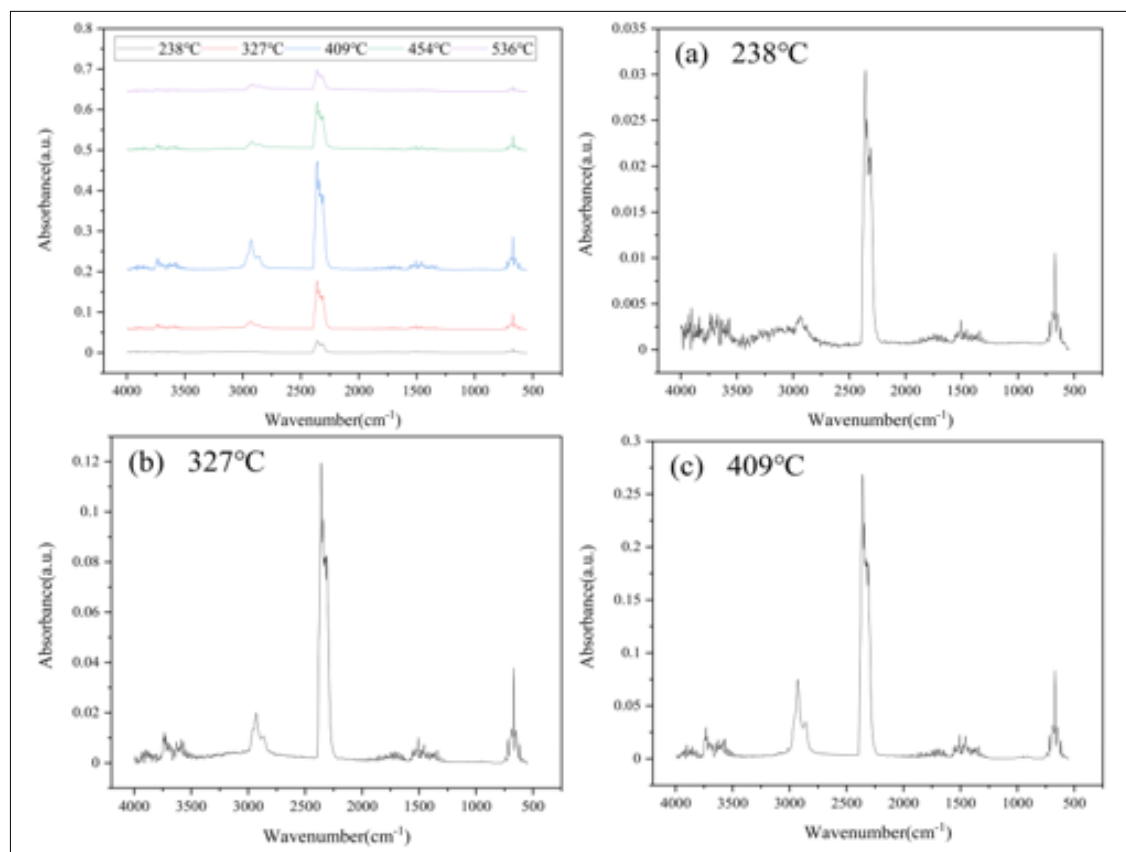


Figure 4. a) TG and DTG curves of oily sludge without ZnCl_2 ,
b) TG and DTG curves of oily sludge with ZnCl_2

3.5. FTIR analysis of microwave pyrolysis



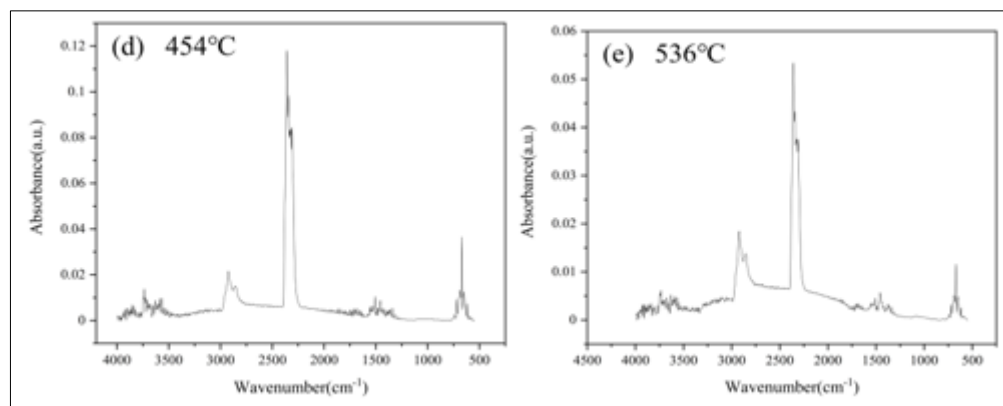


Figure 5. Infrared spectra of the products at different temperatures of oily sludge without ZnCl_2

Table 5. FTIR peaks for gases evolved from oily sludge pyrolysis

Wavenumber (cm^{-1})	Functional group	product	Reference
4000-3500	O-H	H_2O	20
1990-1300	H-O-H		
2400-2240 and 667	C=C	CO_2	21
3115-2675	C-H	hydrocarbon gas	22
1600-1420	C=C	Olefin and arene	21

The gas produced in the pyrolysis process is analyzed qualitatively and quantitatively by FTIR. The infrared spectra of sludge pyrolysis without adding ZnCl_2 is shown in Figure 5. The peaks at 2400 cm^{-1} - 2240 cm^{-1} and 669 cm^{-1} indicate the presence of CO_2 [21]. In the whole pyrolysis process, the largest amount of gas produced is CO_2 , and the amount of CO_2 escaping follows the rule of increasing first and then decreasing [23]. In the infrared spectrogram of the first stage (238°C), there are wide peaks of 4000 cm^{-1} - 3500 cm^{-1} and 1900 cm^{-1} - 1300 cm^{-1} , [20] indicating the presence of H_2O . A wide peak at 3000 cm^{-1} - 2880 cm^{-1} is presumed to be a C-H absorption peak [22]. The C-H absorption peak is mainly hydrocarbon gas escape. With the increase of temperature, the C-H absorption peak first becomes strong and then weak. In the rapid pyrolysis stage (327°C , 409°C), there are wide peaks of 1600 cm^{-1} - 1420 cm^{-1} in the spectrogram corresponding to the absorption vibration peak of the C=C stretching vibration, which is supposed to be olefin gas volatilization [21].

The thermogravimetric diagram of the pyrolysis of OS and the infrared spectra of the escaping gas were analyzed. In the first stage (50°C - 250°C), weight loss is relatively slow, and the amount of gas escaping is small. The escaping gases are mainly CO_2 and H_2O and a minimal amount of hydrocarbons. The reason is mainly the physical desorption of the gas in the OS and the volatilization of the bound water in the OS and the volatilization of the low boiling point hydrocarbons, respectively. In the second stage (250°C - 550°C), the OS sample rapidly loses weight, and a large number of gas escapes, mainly CO_2 and a lot of hydrocarbon gas, and a small amount of water. There were slim C-H absorptions peaks and C=C stretching vibration peaks on the infrared spectra at 327 and 409°C , indicating that more light oil components (alkanes and alkenes) were volatilized by heat [9]. After further heating, a small amount of hydrocarbon gas still escaped, which is speculated to be the product of the pyrolysis broken chain of heavy oil macromolecules. The rapid weightlessness in the heating process of the second stage is mainly divided into two parts. One is due to the rapid loss of mass caused by thermal volatilization of light oil components in the sludge. The other is that the long chain of heavy oil components in OS is broken due to the continuous increase of temperature. In this process, the components of light oil volatilized by heat, and the mass loss of the sample was rapid. In the TG-FTIR analysis, the rate of temperature rise is $100^\circ\text{C}/\text{min}$, so the weight loss from the volatilization of light oil and the weight loss from the broken chain of heavy oil are combined into the same phase on the thermogravimetric chart. In the third stage, the quality

loss slows down. The minerals in the OS are slowly decomposed by heat, and the resulting CO_2 escapes [18].

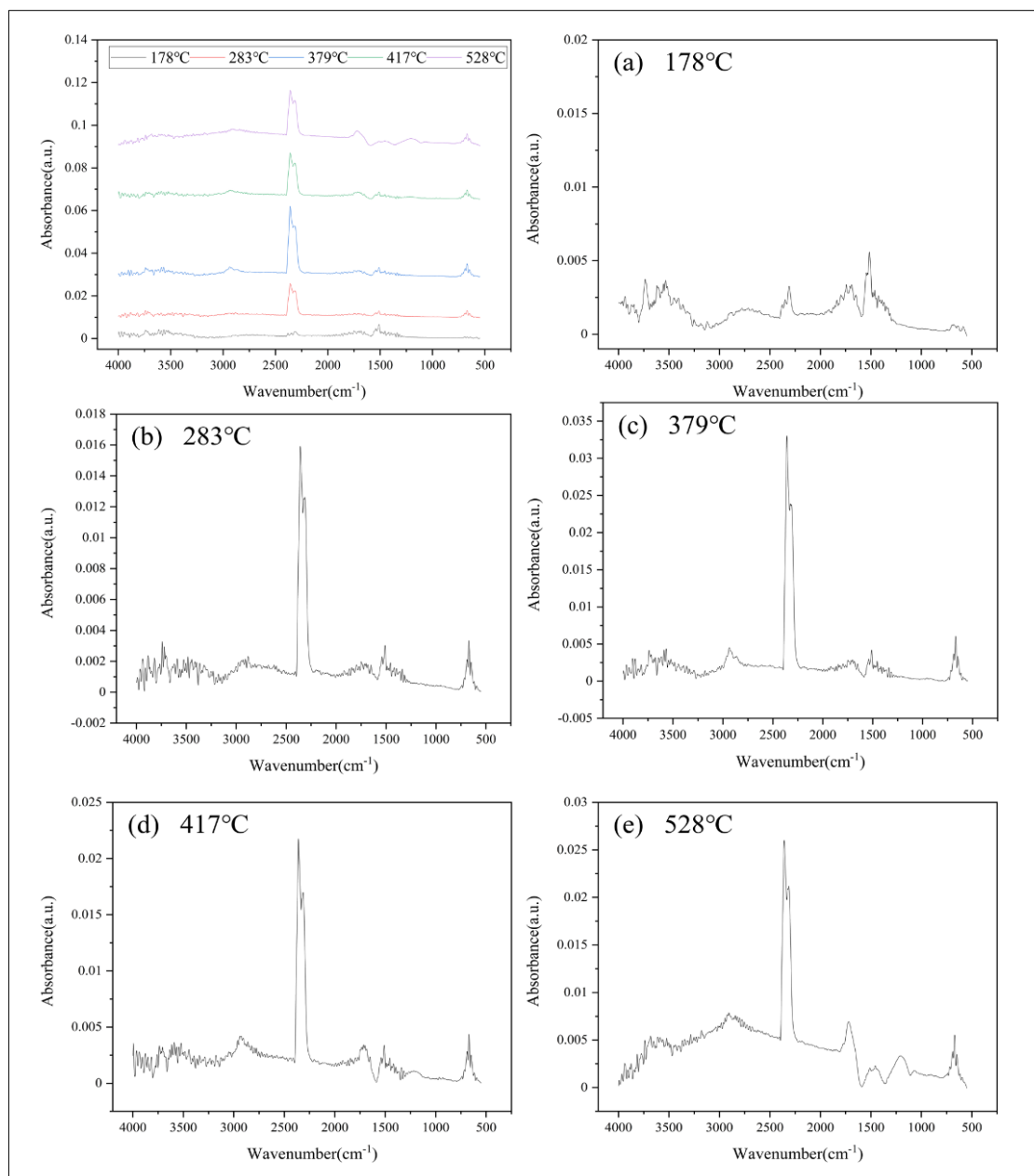


Figure 6. Infrared spectra of the products at different temperature points of oily sludge with ZnCl_2

The Infrared spectra obtained by pyrolysis OS with ZnCl_2 is shown in Figure 6. Figure 6a shows that the escaping gases at 178°C are mainly water vapor and other gases adsorbed in the sample. Therefore, the weightlessness in the first stage is only the evaporation of residual water in the sludge and the desorption of a small amount of physically adsorbed gas. In the subsequent infrared spectra, a large amount of CO_2 and gas containing the C-H bond continued to escape. Gas escape in the second stage was similar to that of OS without ZnCl_2 . The difference was that the amount of gas escaping changes more gently.

The effect of ZnCl_2 on pyrolysis was analyzed by combining the thermogravimetric diagram of the pyrolysis of OS and the infrared spectrogram of the escaping gas. The mass loss in the first stage (50°C - 250°C) is mainly water evaporation. It was speculated that the main reason was that a large amount of ZnCl_2 was added to the OS. ZnCl_2 and water are easy to form acid, adhere to the surface of the sludge



particles [24]. Hence, the water in the acid can not be completely removed in 110°C oven. The second stage (250 -500°C) corresponds to the rapid weight-loss stage of the OS samples without ZnCl₂, but the loss of the OS samples with ZnCl₂ was much slow. The first reason was that compared with the oil sludge without ZnCl₂, the oil sludge content of this sample is 50%, and the weight loss percentage was less at this stage. Secondly, at 283°C (Figure 6b), there was no C-H stretching vibration peak, which proves that there was no hydrocarbon escaping at this time. At 379°C (Figure 6c), the C-H stretching vibration peak of the hydrocarbon was much weaker than that of the OS sample without ZnCl₂. It is speculated that ZnCl₂ can inhibit the volatilization of light oil in OS during pyrolysis. In the process, ZnCl₂ gradually changes from a solid-state to a molten state. The pores inside the sludge were blocked, and it was difficult for the light oil components to escape through the molten ZnCl₂. In the third stage (500-700°C), the fastest mass loss occurred, but no strong peak appeared on the infrared spectrum. The temperature at this stage was close to the boiling point of ZnCl₂, and mass loss at this stage is about 45%. ZnCl₂ could not be detected on the infrared spectrum, and no stiff peak appeared on the infrared spectrum, and the mass loss was rapid. Therefore, it is speculated that this stage was caused by the rapid volatilization of ZnCl₂. The slow mass loss in the fourth stage is due to the pyrolysis of minerals in the OS and the by-products produced by ZnCl₂ in the process of sludge pyrolysis.

In general, the mass loss of OS is slowed down by the addition of ZnCl₂. During the pyrolysis process of OS with ZnCl₂, the volatilization rate of light oil molecules in OS decreased. As a result, after the pyrolysis temperature rises, there are more carbon sources in the oil sludge for the condensation of long-chain carbon to form sludge coke. On the other hand, due to the addition of ZnCl₂, ZnCl₂ occupies the tiny pores of gas volatilization in the OS. After the pyrolysis, the ZnCl₂ occupying the pore was washed off after rinsing with diluted hydrochloric acid and deionized water. Therefore, abundant pores are left in the OS, which significantly increases the pore volume of the sludge coke after the pyrolysis of the OS.

4. Conclusions

The porous sludge coke prepared by microwave-assisted rapid pyrolysis and one-step activation of ZnCl₂ from OS has excellent adsorption performance, and this method has a good prospect.

RSM well fit the experiment of preparing adsorbent material from oily sludge and successfully prepared sludge coke with iodine adsorption value of 785.23mg/g.

ZnCl₂ has a significant impact on the pyrolysis process of oily sludge, which can slow down the volatilization of light oil components, effectively prevent the fracture of C-H bond in the sludge, and occupy the tiny channels in the sludge so that the sludge coke formed has a high adsorption capacity.

Acknowledgments: The authors gratefully acknowledge the financial supports from the State Key Laboratory of Petroleum Pollution Control (no. PPC2018002) and National Science and Technology Major Projects (no. 2016ZX050040003). They also thank the State Key Laboratory of Heavy Oil in China University of Petroleum (East China).

References

1. CHENG, S., TAKAHASHI, F., GAO, N., YOSHIKAWA, K., LI, A., Evaluation of Oil Sludge Ash as a Solid Heat Carrier in the Pyrolysis Process of Oil Sludge for Oil Production. *Energ. Fuel.*, **30** (7), 2016, 5970-5979.
2. QING, Y., YEFEI, W., WEI, Z., FULIN, Z., The Application of Oily Sludge in Chinese Oilfield. *Petrol Sci Technol.*, **28** (2), 2010, 190-197.
3. HU, G., LI, J., ZENG, G., Recent development in the treatment of oily sludge from petroleum industry: A review. *J. Hazard Mater.*, **261**, 2013, 470-490.
4. ZHANG, Z., ZHANG, Y., et al. Solidification of oily sludge. *Petroleum Science and Technology*.
5. JING, G.L., LUAN, M.M., HAN, C.J., CHEN, T.T., Pretreatment of oily sludge by wet air oxidation. *J. Energy Inst.*, **165**(WR3), 2012, 151-155.



6. LIU, Y., LIU, Y., LIU, Z., ZHANG, A., Strengthening effects of ammonia nitrogen on the harmless biological treatment of oily sludge. *Chem. Ecol.*, **35** (1), 2019, 20-35.
7. TENG, Q., LIN, H., ZENG, M., XIE, Y., ZHANG, D., Study on two-step process of petroleum substances recovery from oily sludge. *IOP Conference Series: Earth and Environmental Science*. 208, 2018, 12003.
8. LIN, B., HUANG, Q., YANG, Y., CHI, Y., Preparation of Fe-char catalyst from tank cleaning oily sludge for the catalytic cracking of oily sludge. *J. Anal. Appl. Pyrol.*, **139**, 2019, 308-318.
9. GAO, N., WANG, X., QUAN, C., WU, C., Study of oily sludge pyrolysis combined with fine particle removal using a ceramic membrane in a fixed-bed reactor. *Chem. Eng. Process.*, **128**, 2018, 276-281.
10. MOJOUDI, N., MIRGHAFARI, N., SOLEIMANI, M., SHARIATMADARI, H., BELVER, C., BEDIA, J., Phenol adsorption on high microporous activated carbons prepared from oily sludge: equilibrium, kinetic and thermodynamic studies. *Sci. Rep-UK.*, **9** (1), 2019.
11. WANG, J., LIU, T., HUANG, Q., MA, Z., CHI, Y., YAN, J., Production and characterization of high-quality activated carbon from oily sludge. *Fuel Process. Technol.*, **162**, 2017, 13-19.
12. LI, X., LIU, K., LIU, Z., WANG, Z., LI, B., ZHANG, D., Hierarchical porous carbon from hazardous waste oily sludge for all-solid-state flexible supercapacitor. *Electrochim Acta.*, **240**, 2017, 43-52.
13. BASHIRI, M., SAMAEI, F., Heuristic and metaheuristic structure of response surface methodology in process optimization. *IEEE.*, 2011, 1495-1499.
14. ARROYO, Y., SANZ-TEJEDOR, M.A., SAN, J.J., GARCÍA-ESCUADERO, L.A., Statistical Study of Combustion Characteristics and Optimal Operation Factor Determination in an Emulsion Burner Fueled with Vegetable Oils. *Energ. Fuel.*, **33** (11), 2019, 10989-10998.
15. EDWARDS, D.J., MEE, R.W., Fractional Box-Behnken Designs for One-Step Response Surface Methodology. *J. Qual. Technol.*, **43** (4), 2011, 288-306.
16. LEE, Y.R., TIAN, M., ROW, K.H., Optimized Synthesis Conditions of Ionic Liquid-Silica Using Response Surface Methodology. *Asian J. Chem.*, **26** (18), 2014, 6189-6193.
17. GAO, N., WANG, X., QUAN, C., WU, C., Study of oily sludge pyrolysis combined with fine particle removal using a ceramic membrane in a fixed-bed reactor. *Chem. Eng. Process.*, **128**, 2018, 276-281.
18. LIN, B., HUANG, Q., ALI, M., WANG, F., CHI, Y., YAN, J., Continuous catalytic pyrolysis of oily sludge using U-shape reactor for producing saturates-enriched light oil. *P. Combust. Inst.*, **37** (3), 2019, 3101-3108.
19. ZHANG, B., ZHANG, L., YANG, Z., HE, Z., An experiment study of biomass steam gasification over NiO/Dolomite for hydrogen-rich gas production. *Int. J. Hydrogen Energ.*, **42** (1), 2017, 76-85.
20. SMAL, I.M., YU, Q., VENEMAN, R., FRÄNZEL-LUITEN, B., BRILMAN, D.W.F., TG-FTIR Measurement of CO₂-H₂O co-adsorption for CO₂ air capture sorbent screening. *Energy Procedia*. **63**, 2014, 6834-6841.
21. OUDGHIRI, F., ALLALI, N., QUIROGA, J.M., RODRÍGUEZ-BARROSO, M.R., TG-FTIR analysis on pyrolysis and combustion of marine sediment. *Infrared Physics & Technology*, **78**, 2016, 268-274.
22. TANG, Y., MA, X., WANG, Z., WU, Z., YU, Q., A study of the thermal degradation of six typical municipal waste components in CO₂ and N₂ atmospheres using TGA-FTIR. *Electrochim Acta.*, **657**, 2017, 12-19.
23. CHANG, C., SHIE, J., LIN, J., WU, C., LEE, D., CHANG, C., Major Products Obtained from the Pyrolysis of Oil Sludge. *Engr. Fuel.*, **14** (6), 2000, 1176-1183.
24. HE, X., GAO, Y., SANG, S., LEI, N., Phase Equilibria of the Ternary Systems ZnCl₂-MgCl₂-H₂O and ZnCl₂-PbCl₂-H₂O at 323 K. *Journal of Chemical & Engineering Data*. **64** (2), 2019, 471-476

Manuscript received: 14.01.2022